Hydrothermal Synthesis of Zinc Oxide Nanowire Arrays For Photovoltaic Applications

by

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ABSTRACT

Zinc oxide (ZnO) nanowires with excellent crystal quality can be grown vertically aligned from a substrate using hydrothermal synthesis, a low-cost, scalable process that is compatible with many semiconductor processing techniques. However, precise control over nanowire array dimensions such as nanowire spacing, diameter, length, and alignment, which is important for optoelectronic device applications, has proven elusive due to lack of understanding regarding fundamental aqueous growth mechanisms at the nanoscale.

Here, we utilize electron-beam lithography to template ZnO seed layers, demonstrating that seed layer engineering via judicious choice of seed deposition conditions and annealing can yield well-aligned nanowire arrays with single nanowire spatial precision on a variety of device relevant substrates.

Subsequently, we use bottom-up patterning techniques and investigate the competition between diffusive transport and surface reaction in hydrothermal growth to achieve control over nanowire spacing and enhanced nanowire array uniformity over length scales suitable for photovoltaic (PV) device fabrication. By analyzing the role of temperature, concentration, and areal seed density on the balance between diffusion vs. reaction rates at the solution-nanowire interface, we show that the $c$-facet grows via the direct incorporation mechanism. With this knowledge, we use additives to shift the nanowire growth system into a reaction-limited regime, making nanowire growth rate independent of the patterned template. As a consequence, we achieve ZnO nanowire array uniformity that is critical for device applications.
Finally, we incorporate precisely tailored nanowire arrays into PbS quantum dot PV devices. We explore the device parameter space – both experimentally and computationally – by varying nanowire length and active layer thickness, which allows us to investigate the effect of nanowire arrays on fundamental optical and electronic phenomena in nanostructured PV devices. We demonstrate enhanced charge collection in a 200 nm nanowire/470 nm active layer thickness device architecture. Our investigations suggest that interfacial recombination is an additional loss mechanism in nanowire devices, which we combat using atomic layer deposited TiO₂ surface passivation, further enhancing device performance. Our fundamental findings focusing on the growth of precisely controlled hydrothermal ZnO nanowire arrays can be readily extended to other optoelectronic devices and other hydrothermally synthesized materials systems.

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To Silvija,
For your patience, wisdom, and understanding

To the Gradečak group, past and present,
For sharing success and failure, tears and laughter, and for unstinting support

To Shiahn
For always helping, never judging

To Olivia,
For our conversations

To Yinjin
For warmth, generosity, and friendship

To Sharon,
For sweetness, calm, and love

To Pa, Ma and Jun,
For unconditional love and support from around the world
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CHAPTER 1

Introduction
1.1 Engineering at the nanoscale

Nanotechnology has been, and continues to be, a key driving force in many revolutionary technologies that continue to change the world today. Our increasing dexterity in manipulating matter at the nanoscale has enabled advances in fields such as computing [1], lighting [2,3], energy [4], medicine [5,6], and many others [7]. The promise of engineering at the nanoscale lies in using morphology to tailor the optical, electrical, and mechanical properties of a material to access enhanced and novel capabilities. This is because many phenomena have operative length scales of $10 - 1000$ nm: quantum confinement is engineered relative to the typical Bohr radius of $\sim 10$ nm [8]; transistor gate lengths and gate thicknesses follow carrier diffusion lengths of $\sim 10 - 100$ nm [1]; grain sizes of $\sim 10$ nm are ideal for strengthening of metal alloys using the Hall-Petch mechanism [9]; solar cells are $100 - 1000$ nm thick in order to maximize optical absorption given by the Beer-Lambert Law [10].

Nanostructured devices function because the critical parts of their architecture have been engineered to have dimensions of $1 - 100$ nm [11]. Nanostructures can be classified into the number of dimensions which are nanoscaled [12]: zero-dimensional nanostructures include nanoparticles and nanospheres, nanowires, nanorods, and nanotubes are 1-dimensional, while 2-dimensional nanostructures include thin films and single-atom thick structures like graphene. Each of these nanostructures possesses quantum-confined analogues (quantum dots, quantum wires, and quantum wells respectively) if the relevant dimensions are sub-Bohr radius.

Due to their size, several unique challenges exist when incorporating nanostructures into devices. First, material quality has to be maintained during their synthesis. Nanostructures are
susceptible to poorer surface quality compared to the bulk material; this arises from increased concentrations of surface and point defects due to their high surface area to volume ratio [3, 8, 13–16]. Defect management schemes such as using surface passivation layers [17], ligands [15] and post-annealing [14] have been employed, but producing high-quality material remains a challenge. Second, the final nanostructured morphology needs to be precisely controlled: parameters such as size, spacing and orientation must be carefully tuned to ensure optimum device operation [14, 18]. Regardless of whether the morphology is achieved by top-down patterning or bottom-up growth techniques, nanostructure dimensions need to be precise and uniform. Finally, fabrication techniques need to be scalable and compatible with other processing steps and materials. While high-temperature vacuum deposition processes can yield high quality material over large areas, these harsh processes may not be compatible with substrates, especially flexible substrates that have lower processing temperatures [19]. In summary, a device-suitable fabrication technique needs to yield nanostructures with precisely controlled size, spacing and orientation with large-area uniformity, be compatible with prior processing steps and materials, and have minimal sacrifice in material quality compared to the bulk.

In this chapter, we begin by introducing concepts in solution phase nanocrystal growth as part of a greater framework of crystal growth in general, highlighting promises and challenges for nanostructure synthesis from aqueous medium. We then discuss optical and electronic properties of ZnO as a semiconductor and segue into hydrothermal synthesis of seeded ZnO nanostructures for various electronic device applications, which is the focus of Chapters 3 and 4.
of this work. Finally, we briefly cover operating concepts of photovoltaic devices as a prelude to the final chapter of this thesis.

1.2 Solution phase crystal growth

Crystallization from a supersaturated solution is arguably the most basic form of crystal growth. Solution phase nanocrystal growth is technically no different from the elementary school science demonstration where a seed crystal is lowered into a supersaturated solution, producing acicular crystals over the course of hours or days. The concept demonstrated is that when the ionic product of the solution exceeds the solubility product, nucleation and growth takes place on the seed facets, causing the most energetic facets to elongate. Since the solubility product is a function of temperature, supersaturation is achieved by either lowering the solution temperature, or by increasing the concentration of its constituent ions. Nevertheless, many steps remain between ions in solution and ions locked into crystal lattice positions; at the nanoscale, the step that controls the process, \textit{i.e.} the rate-limiting step, is crucial since it dictates the overall growth rate. Furthermore, there are multiple rate-limiting steps operating on different crystal facets and it is critical that the \textit{relative rates} are well-controlled to produce the desired nanocrystal morphology. It is therefore pertinent at this juncture that we consider the processes taking place between solution and crystal.

The dry processing analogues to solution phase growth are the vapor-solid (VS) mechanism in chemical vapor deposition (CVD), molecular beam epitaxy (MBE), or sputtering, if plasma assisted \cite{20,21}. In contrast to foreign seed particle assisted growth techniques (\textit{e.g.} vapor-liquid-solid (VLS) growth), each of the above involves atomic species impinging directly
onto the crystal surface, carried by solution, carrier gas, or simply through vacuum. These techniques differ in the type of species impinging on the crystal surface, as well as the energy of the species, shown in Figure 1-1. In MBE and sputtering, the atoms arrive singly at the surface with high energy [21], which is a result of a long mean free path and few collisions with gas atoms along the way. Therefore, adatoms have long surface diffusion lengths $L_D$ compared to nanocrystal facet dimensions. This affects nucleation and growth since adatoms can easily be incorporated into crystal facets adjacent to the facets on which they were initially adsorbed. In CVD, the atomic species are produced by cracking at high temperature, typically in the vicinity of the substrate, and approach the substrate carried by an inert gas [22]. While the species is still fairly energetic due to the high temperature, its energy is lower than that for MBE and sputtering, and therefore the adatom surface diffusion length is comparable to nanocrystal dimensions [20,22]. This results in a rich diversity of growth regimes that are temperature and flux dependent.

Figure 1-1. Cross-section of nanowires grown on a substrate showing effect of different adatom diffusion length $L_D$: for short $L_D$, effective adatom flux is restricted to the capture area of the facet, but for long $L_D$ adatoms can be incorporated into facets different from the facet on which they initially adsorbed.
In solution phase nanocrystal growth, the carrier medium is liquid. Therefore, the maximum temperature at which growth can be carried out is the solvent boiling point for a particular pressure; pressure vessels are required if growth at elevated temperatures is desired. Working at comparatively lower temperatures than vapor phase growth, coupled with the viscous medium, means that species arrive at the crystal surface with significantly lower energy [23,24]. Adatom surface diffusion length is shorter than the nanocrystal dimension, and therefore adjacent facets can be considered effectively independent, with each facet supplied only with the flux that it captures on its surface area [25]. The species arriving at the facet is also different. In solvents, there is significant interaction between the species and the surrounding medium, so the species will impinge on the crystal facet surrounded by one or more shells of solvent molecules [26]. In aqueous medium this is known as the hydration shell and highly charged ions like $\text{Al}^{3+}$ may have up to forty layers of water molecules around it, on top of water molecules already coordinated to the ion. Coordination and hydration shell thickness are also affected by pH, which presents further opportunities for growth control [27].

The nature of the crystal surface is an important factor in how the facet responds to the growth conditions. Crystal surfaces are two-dimensional defects consisting of dangling bonds. The surface energy is a measure of dangling bond density and nanocrystals will seek to minimize the total surface energy by increasing the area of low energy facets and reducing that of high energy facets [28]. This is because high energy facets have a greater dangling bond density and therefore preferentially adsorb and incorporate adatoms. Their higher growth rate causes them to grow themselves out of existence, leaving lower energy facets. The equilibrium morphology of a crystal at a particular set of conditions is known as the Wulff shape. Propagation of a crystal face
along its surface normal takes place when adatoms are incorporated into lattice positions. The rate of propagation depends heavily on the defect density of the crystal surface and the three main growth mechanisms are *normal growth*, *2D layer-by-layer*, and *dislocation growth* [20].

(a) Direct incorporation  
(b) Layer-by-layer  
(c) Dislocation

Figure 1-2. Equilibrium surface structure of Kossel crystals for the (a) direct incorporation, (b) layer-by-layer, and (c) dislocation mechanisms.

Crystal faces are rarely atomically flat – although a perfectly flat surface has the lowest dangling bond density, at temperatures above absolute zero configurational entropy will cause some degree of surface roughening [20]. On an atomically rough crystal surface, crystal positions are no longer equivalent – the energy landscape now has positions on the crystal surface that have higher dangling bond density than others. These positions are energetically favorable for adatoms to reside in and are known as *steps* or *kinks* (Figure 1-2) depending on whether they are one- or zero-dimensional, respectively [29]. While crystal positions along steps have extra dangling bonds compared to the flat surface, it is kinks that have the highest energy. Therefore, the kink density (or distance between kinks) is an important parameter because it determines the propensity of a crystal face for incorporating adatoms, which is directly related to its growth rate. When the kink density of the surface is very high, *i.e.* there is substantial surface roughening, impinging adatoms incorporate directly into crystal positions; this is known as the *normal growth mechanism* or the *direct incorporation growth mechanism* (Figure 1-2a).
Apart from equilibrium surface roughness, growing surfaces can also generate steps through 2D island nucleation (Figure 1-2b). 2D islands are defined as single atom thick features on the crystal surface that consist of aggregations of two or more adatoms bonded to each other. In the birth-death model of 2D island nucleation, adatoms on the crystal surface are continually moving laterally on the surface, forming and breaking bonds with each other [30]. At high enough atomic flux, there exists a certain equilibrium density of 2D islands on the crystal surface, with an accompanying step density. Following nucleation of a 2D island, adatoms can add to kink sites on the island step edges, causing the island to propagate outwards laterally [21]. Eventually, the island covers the entire crystal face and new islands nucleate again. The 2D island nucleation and growth mechanism is responsible for many features seen on crystal surfaces including mounds [31,32], volcanoes, and wedding cakes [33]. These features result from differences in the relative rates of nucleation and growth – slow step growth rates coupled with high nucleation rates cause new 2D islands to nucleate on prior islands before they can fully cover the crystal surface, resulting in growth of 3D mounds [34]. In general, these 3D features are undesirable because they can introduce internal interfaces in the crystal that diminish crystal quality. Therefore, it is important to choose growth conditions to remain in a regime where a growing 2D island completely covers the crystal face before the following island nucleates – this regime is called layer-by-layer (LBL).

Crystal surface defects are important for growth since they are energetically favorable locations for adatoms to incorporate into the surface. Apart from steps and kinks that are already present on the surface, screw dislocations can also introduce steps that help the crystal surface
incorporate adatoms. This is the basis of Burton-Cabrera-Frank (BCF) theory [29,35] and is also known as the dislocation growth mechanism (Figure 1-2c). In this theory, screw dislocations terminating at the crystal surface must end in a step. The step will contain kinks and will therefore propagate along the crystal surface at a particular step growth rate. As the step moves forward, it exposes the crystal surface thereby germinating another step. The end result is that the crystal face grows normally in a spiral mound, which is characteristic of the dislocation growth mechanism.

The three mechanisms outlined above are functions of temperature, supersaturation, and the nature of the crystal facet. Notably, each mechanism has a unique relationship with supersaturation due to the way the crystal surface interacts with the solution. Therefore, observing the way facet growth rate varies with changes in supersaturation can give us information about which mechanism is dominant under a particular set of growth conditions. It is important to remember that different mechanisms become dominant as supersaturation changes, and that different facet types on the same crystal may have different dominant mechanisms at the same supersaturation. This is particularly important for nanocrystal growth because the relative facet growth rates determine the final morphology. Therefore, precise knowledge of growth regimes in the context of crystal surface properties is required for controlling nanocrystal morphology.
1.3 **Zinc oxide: Material properties**

![Figure 1-3. (a) Wulff shape of ZnO. (b) Wurtzite crystal structure showing zinc and oxygen positions.](image)

ZnO is an earth-abundant wide bandgap (3.37 eV) semiconductor with the wurtzite crystal structure [36]. The Wulff shape is a hexagonal prism with *c*-facet (0001) and *m*-facet (11\(\bar{2}0\)) faces (Figure 1-3a). Alternating layers of zinc and oxygen atoms are stacked along the *c*-facet normal, giving rise to the dipole moment that results in piezoelectric behavior (Figure 1-3b). This dipole moment means that ZnO crystals are either Zn- or O- polar along the *c*-axis [37]. It is important to note that the crystal polarity is different from the *c*-facet termination, which can also be either zinc or oxygen – this distinction becomes important when studying growth mechanisms [30]. Unlike the *c*-facet, the *m*-facet is neutral as it contains equal numbers of zinc and oxygen atoms. Large single crystals of ZnO (up to inches in diameter) are readily grown from chemical bath deposition and have found use in optical applications due to their high index and birefringent optical effects [38]. The exciton binding energy of 60 meV results in an observed optical bandgap of 3.31 eV, and thus ZnO crystals are transparent in the visible spectrum – it is a direct bandgap absorber with an absorption edge of 375 nm [36]. Photoluminescence of ZnO shows a sharp peak at ~ 380 nm attributed to near-band edge...
emission, as well as broad defect peaks at ~ 550 nm and 620 nm (Figure 1-4), attributed to oxygen vacancies and zinc interstitials respectively [39–41]. The ratio of defect emission peak to near band edge emission peak intensity is typically used as an indication of crystal quality.

![Photoluminescence spectra of ZnO nanowire arrays as grown (high defect concentration, red) and after annealing at 400 °C (low defect concentration, black) showing near band edge (NBE) peak and defect peaks from oxygen vacancies and zinc interstitials. Spectra normalized to NBE peak intensity.](image)

The electronic properties of ZnO vary widely with processing conditions. As-synthesized ZnO is intrinsically n-type with typical carrier concentrations of $10^{16} - 10^{18}$ cm$^{-3}$; this is attributed to the presence of hydrogen interstitials, which are the only point defects that are present in high enough concentrations and have an activation energy commensurate with the observed doping concentration [36]. The n-type doping concentration can be modulated by changing the growth conditions or by post-annealing in forming atmosphere, both of which change the hydrogen interstitial concentration. ZnO has a high n-type bulk mobility of 300 cm$^2$V$^{-1}$s$^{-1}$. Controllable and stable p-type doping has proven elusive in ZnO. Substitutional p-
type doping schemes either aim to replace zinc with group III elements such as aluminum [42,43] or gallium [44], or to replace oxygen with group I metals such as potassium [45] or lithium [46], but it is difficult to achieve sufficiently high concentrations of dopants to compensate the intrinsic n-type doping. The minority carrier mobility is around $1 - 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

### 1.4 Synthesis of bulk and nanostructured ZnO

ZnO crystals can be synthesized by both wet and dry techniques. Dry techniques for coating ZnO films include CVD, and MBE. ZnO has a small lattice mismatch with GaN and sapphire [36], and high quality single crystal epitaxial films can be obtained on these substrates. Polycrystalline films are deposited on substrates like silicon and glass. In these techniques, the key parameter is the amount and species of oxygen used because it controls the degree of n-type doping in the films, thus affecting its conductivity [47]. Changes in the deposition conditions can switch the system from thin film to nanostructure growth: nanowires [31,48], nanowalls [49,50], nanobelts [51], and nano-tetrapods [52] have been demonstrated via CVD. Nanostructures and thin films deposited by CVD have generally high crystal quality as investigated using photoluminescence and x-ray diffraction (XRD) analysis [50].

![ZnO nanostructures](image)

Figure 1-5. ZnO nanostructures with various dimensionality: (a) nanoparticles [53], (b) nanowire array, (c) nanowalls [54] and (d) polycrystalline thin film [55].
Large ZnO crystals used as substrates for commercial purposes are most commonly grown using the hydrothermal method, which is both simpler and more cost-effective than vapor deposition or melt growth [38]. Although zinc is amphoteric, ZnO (and Zn(OH)₂, a possible reaction intermediate) are insoluble at pH between 4 – 11, and therefore crystallization will take place in supersaturated solution in this range [27,56]. A diverse range of ZnO nanostructures have been synthesized using the hydrothermal method (Figure 1-5). Apart from the usual parameters of temperature and concentration available for tuning the growth, other parameters including solvent type [57,58], counterion [57,58], and presence of additives [27,59,60] have made possible the synthesis of nanowalls [54], nanowires [53], nanorods [61,62], nanotubes [61], nanoparticles [63], hollow spheres [64], and even star-shaped nanoprisms [65]. Hydrothermally synthesized nanostructures typically have higher oxygen vacancy concentrations, which manifest themselves in photoluminescence spectra with high defect peak intensity at 550 nm [50]. This is due to the poorer surface quality which could arise from adsorbed solvent molecules or nonstoichiometric surface chemistry [16,40], but the defect intensity greatly decreases following annealing above 300 °C, which drives out impurities [66].

1.5 Hydrothermal synthesis of ZnO nanowires

Figure 1-6. Hydrothermal synthesis process steps beginning with seed layer deposition via sol-gel spincoating. Subsequent annealing converts zinc acetate into ZnO nanoparticles, which are then immersed into growth solution at 60 – 90 °C to hydrothermally synthesize nanowires.
Vertically aligned ZnO nanowire arrays with high crystal quality can be grown on a multitude of device-relevant substrates at benign temperature and pH conditions from aqueous solutions [19,53]. This makes hydrothermal synthesis a very promising method for producing ZnO nanostructures since alternative methods such as CVD and MBE require temperatures in excess of substrate tolerances and also use metal seed particles that act as recombination centers [48]. In contrast, ZnO nanowires are grown from ZnO nanoparticle seeds, which can be deposited on substrates as a thin film from spincoated sol-gel suspensions [19,67] or by sputtering [68,69] (Figure 1-6). The sol-gel seeding technique is low temperature (> 150 °C), highly scalable, processed in ambient atmosphere, substrate-independent, and introduces no material foreign to the ZnO system. Upon immersion of the ZnO polycrystalline thin film into a supersaturated aqueous solution of Zn²⁺ at elevated temperature (60 – 90 °C), preferential growth of ZnO c-planes takes place, producing a dense array of vertically oriented ZnO nanowires on the substrate [70]. Several implications of this process are immediately apparent:

1. **Nanowires do not have** an epitaxial relationship with the substrate.

   In general, seeding processes are substrate-independent [55,71] *i.e.* they can be carried out on single crystal, polycrystalline, or amorphous substrates with similar results. The sol-gel spincoating process produces nanoparticle films that are tens of nanometers thick. Naturally, these c-facet terminated nanoparticles (of about 5 nm in diameter) do not share an epitaxial relationship with the substrate, having random orientations within the film [59]. While polycrystalline ZnO thin films deposited by sputtering or vapor deposition tend to have c-plane texturing normal to the substrate [69], it is understood that the
orientation is a result of deposition conditions rather than epitaxial bonding with the underlying substrate.

2. Position and orientation of nanowires is directly dependent on the seeds. The nanowire/nanorod morphology is a result of the $c$-facet growth rate greatly exceeding the $m$-facet growth rate under a certain set of growth conditions. Since nanowires grow directly from ZnO grains in the seed layer, seed position is analogous to nanowire position, and the initial seed orientation determines the angle of the nanowire relative to the substrate [55,69]. This provides opportunities for patterning the seed layer to dictate where nanowires grow on the substrate, which is advantageous for device fabrication [72]. Therefore, the seeding process is critical in controlling the final nanowire array morphology.

3. Nanowire growth occurs because the vertical ($c$-plane) growth rate exceeds the lateral ($m$-plane) growth rate. Dimensions can therefore be controlled by solution-growth parameters. Crystal growth theory states that the facet with the highest surface energy will have the highest growth rate, and will therefore grow until it no longer exists and is replaced by lower energy facets. The nanowire morphology obtained in hydrothermal synthesis results from the higher energy $c$-facet growing faster than the $m$-facets, causing an elongated crystal to form [70,73]. However, the relative growth rates are functions of temperature, supersaturation, solvent, and the presence of other species during synthesis.
Therefore, it is possible to use these growth parameters to tune the final aspect ratio of the nanocrystal.

1.6 ZnO nanowire devices

Figure 1-7. Various morphologies of ZnO nanowires incorporated into devices: (a) dye-sensitized solar cell [74] (b) PbS quantum dot solar cell [75] (c) piezoelectric energy harvester [76] (d) field-emitter [27].

The compatibility of ZnO nanowire array hydrothermal synthesis with device fabrication techniques has led to ZnO nanowires being incorporated into several types of devices that leverage its optical, electronic and mechanical properties. Zinc oxide nanocrystals with crystal quality good enough for optical applications can be synthesized by both vapor phase and hydrothermal methods. Optically pumped lasing has been observed in hydrothermally grown ZnO nanorods [77] and electrically pumped lasing in ZnO nanowires deposited with MBE and CVD [78]; it is critical to produce smooth nanorod facets that can act as Fabry-Perot cavities in order to display lasing at low thresholds. Tapered ZnO nanowires have also been used as field
emitters [27] (Figure 1-7d). By controlling the tip radius using sidewall additives, sharp tipped nanowires grown using hydrothermal synthesis displayed electrically stimulated field emission, which may be useful in lighting and display applications.

ZnO nanowires have also been used as mechanical energy harvesting devices, which use their piezoelectric behavior to transduce vibrations into electrical energy [76,79,80] (Figure 1-7c). Vertically aligned nanowire arrays are embedded in a polymer like poly-methylmethacrylate (PMMA), and electrical contacts are made to the nanowire tips. The nanowires oscillate in response to applied vibration, generating power through the piezoelectric effect. In these devices, nanowire aspect ratio is a key parameter for maximizing the output voltage since bending of the nanowires causes the potential difference to build up across their cross-sections [76]. Furthermore, the output current depends on the nanowire density. Therefore, the performance of these piezoelectric energy harvesters is particularly dependent on nanowire array morphology. These devices could be used to scavenge vibrational energy from automobile engines, air-conditioning units, or turbines to power miniaturized electronic devices.

ZnO nanoparticle films are widely used in photovoltaic devices as hole-blocking layers in hybrid polymer-ZnO nanoparticle devices [81,82], and as the n-type semiconductor in PbS quantum dot devices [83,84] and perovskite devices [85]. The nanoparticles are easily synthesized from precipitation in alcoholic solution and are spincoated onto the substrate to form a thin film. The active layers are then deposited on top of the ZnO nanoparticle film. Incorporating nanowires into the device fabrication is simply carried out by immersing the nanoparticle film into growth solution, which generates a dense array of nanowires [86,87]. The
active layers are then deposited in the same way, embedding nanowires into the device (Figures 1-7a and 1-7b). Nanowires have been shown to provide high n-type conductivity pathways to enhance charge extraction. However, although hydrothermal synthesis of ZnO nanowires from the nanoparticle film may seem trivial, control over the nanowire array morphology is limited to using growth time to vary the nanowire length. Therefore, there are opportunities to further enhance device performance by tailoring other array parameters such as nanowire diameter and areal density.

1.7 Fundamentals of photovoltaic devices

In semiconductors, the photovoltaic effect refers to generation of electrons and holes by absorption of photons that are more energetic than the optical bandgap of the material [88]. Depending on the material, one or more electron-hole pairs can be generated from the absorption of an incident photon [89]. Following excitation, these excess carriers thermalize back to the band edges and are free to drift, diffuse, and eventually recombine. The equilibrium excess carrier concentration (over the intrinsic carrier concentration) for a certain photon flux is given by the recombination rate $R$ subtracted from optical generation rate $G_{opt}$.

Photovoltaic devices work by extracting excess carriers into an external circuit where they transfer their electrical energy to a load. For this to happen, excess carriers need to be conveyed to the physical edges of the device before they can recombine and lose their energy as heat and light. This is accomplished by using either a Schottky junction or p-n junction to collect carriers with their electric field [90]. In materials with high exciton binding energies (greater than $kT$, which is 25.8 meV at 300 K) the electric field also serves to dissociate excitons into
electron-hole pairs that can then be collected [91]. While some photovoltaic devices utilize Schottky junctions, the vast majority of photovoltaic devices are made of p-n homo- or heterojunctions. The $J-V$ curve for a p-n junction under illumination is shown in Figure 1-8a.

Several key metrics are used to compare photovoltaics to each other [92]. The device power conversion efficiency (PCE) is the most important. PCE is measured by illuminating the device using standardized solar spectra and measuring the power generated by the device. For terrestrial applications, the standard spectrum is known as AM 1.5G, which mimics the sun's power spectrum at ground level. The maximum power is obtained at the operating voltage and current $V_{\text{max}}$ and $J_{\text{max}}$ respectively, given by the shaded area under the $J-V$ curve. There are three other important metrics of photovoltaic device quality. In the absence of an external circuit, charge builds up on either side of the p-n junction, generating a potential difference called open-circuit voltage ($V_{\text{oc}}$). Alternatively, connecting the device to an external circuit with no load

![Figure 1-8. (a) $J-V$ curve for a typical p-n junction photovoltaic device. (b) equivalent circuit of photovoltaic device.](image-url)
causes current to flow, which is known as short-circuit current ($J_{sc}$). These are the points where the $J$-$V$ curve crosses the voltage and current axes, respectively.

$V_{oc}$ and $J_{sc}$ are important parameters because they reflect key properties of the active layer, namely the bandgap and the absorption-extraction product [92]. For a p-n junction, the maximum $V_{oc}$ is given by the difference in the quasi-Fermi level between the p- and n-type regions, which is in turn limited by the bandgap. Conceptually, this is the energy carried by each electron-hole pair. Since the single junction Shockley-Queisser limit occurs at a bandgap of 1.34 eV [93], choosing a material that has equal or close to this bandgap is important for achieving high PCE. Materials with tunable bandgaps such as quantum dots are thus highly desirable since they can be synthesized to have bandgaps of exactly 1.34 eV. On the other hand, $J_{sc}$ represents the maximum current that can be collected from the device under normal operating conditions (forward bias). Under short circuit conditions, the built-in electric field is at its maximum extent. Since carrier collection via drift is almost 100% efficient, almost all carriers in the quasi-neutral region will be extracted [94]. Extraction of carriers outside of the quasi-neutral region takes place by diffusion and deteriorates as device thickness increases. $J_{sc}$ is the maximum possible current because as the device is forward-biased, the depletion width decreases and more carriers have to be extracted by the less-efficient diffusion process. The product of $V_{oc}$ and $J_{sc}$ is thus the theoretical maximum power that could be extracted by a particular active layer, that is, the power if every carrier with energy equal to the bandgap was extracted.
Figure 1-9. Band structure for a ZnO (n-type) and PbS QD (p-type) junction at zero bias and when biased at $V_{max}$. The extent of the electric field $E$ is indicated by the arrow length. The corresponding collection efficiency by drift and diffusion are shown inside and outside the depletion region.

At the maximum power point, the bands are almost flat and therefore the bulk of carrier collection occurs via diffusion. It is therefore important that the active layer has a high minority carrier diffusion length, since minority carrier collection is the limiting factor to $J_{max}$. The ratio of the maximum observed power to the product of $J_{sc}$ and $V_{oc}$ is the fill factor (FF). This is best understood by considering the equivalent circuit for a photovoltaic device, shown in Figure 1-8b [90]. The series and shunt resistance in a photovoltaic device are approximate representations of processes taking place in the device. Series resistance is the internal resistance to flow of charge to the external circuit. It results from resistance of the active layers, junction, and contact resistance. Minimizing series resistance is desirable since it will increase current extracted from the device. Shunt resistance reflects how alternate pathways for charge can reduce the efficiency of the device. High shunt resistance is desirable since it means that current flows exclusively through the active layers and no shorting pathways exist in the device. Low shunt resistance and high series resistance cause the fill factor to decrease, so it is important to ensure that the active layer has a high conductivity with no shorting pathways for achieving maximum PCE.
1.8 Thesis overview

In this thesis, we demonstrate control over ZnO nanowire array dimensions including nanowire spacing, diameter and length, and orientation using the seeded hydrothermal synthesis technique. These arrays are incorporated into PbS colloidal QD photovoltaic devices to elucidate the effect of nanostructured electrodes on device operation and identify the morphology that maximizes device efficiency.

Chapter 2 provides an in-depth review of hydrothermal synthesis of ZnO nanowires and solution phase transport and growth mechanisms of ZnO crystal surfaces. We also review progress in PbS QD solar cells, focusing on incorporation of nanostructures into these devices.

Chapter 3 demonstrates control of ZnO nanowire spacing using electron-beam lithography (EBL), a top-down lithographic approach. We use EBL-patterned PMMA masks on spincoated and sputtered ZnO seed layers to investigate the effect of substrate choice, annealing, and deposition technique on final nanowire array morphology. EBL is capable of producing arrays with precisely controlled morphology and is therefore useful for small-scale (millimeter scale areas) investigation of device properties, but not for fabrication of entire photovoltaic devices.

In Chapter 4, we show that dynamic-deposition spincoating, a highly scalable bottom-up technique, can be used to control nanowire areal density over an order of magnitude, which gives us the capability to fabricate devices with varying nanowire spacing. In conjunction with nanowire density control, we apply diffusion/reaction-limited analysis to separate the effect of
diffusive transport from \(c\)-plane surface reaction rate to define guidelines for precise and independent control of nanowire length and diameter. We show that operating in rate-limiting growth regimes yields spatially independent growth rates, thus producing device-suitable nanowire arrays with uniform lengths across the substrate.

In Chapter 5, we fabricate ZnO nanowire-PbS QD photovoltaic devices with precisely controlled nanowire lengths and device thicknesses to investigate the effect of nanowire morphology on charge extraction. We observe a strong effect of nanowire length on \(J_{sc}\) which peaks at a nanowire length of 200 nm. By carrying out external quantum efficiency (EQE) measurements, diffuse reflectance measurements, and optical simulation, we identify interfacial recombination at the ZnO-PbS interface as a key loss mechanism. We use atomic layer deposition of TiO\(_2\) to surface passivate the nanowire arrays, achieving enhanced current collection and thus power conversion efficiency in these devices.
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CHAPTER 2

Background
2.1 The influence of seed layer on ZnO nanowire morphology

As the first step of the ZnO nanowire growth process, seeding is of paramount importance in producing arrays with well controlled morphology. Seed nanocrystals are directly responsible for controlling nanowire placement and alignment which, indirectly, affect other array properties like nanowire diameter and length. From the fabrication standpoint, the seeding process is alternately robust and delicate in different aspects, and therefore having knowledge of the most critical parameters will save time and effort in processing. Furthermore, there are various techniques for generating and patterning ZnO nanocrystals on the substrate, each having unique advantages and disadvantages given the particular process requirements. In this section we will review progress in seeding and patterning of ZnO seeds for device applications and outline outstanding challenges.

Figure 2-1. Overview of various ZnO seed deposition techniques and morphologies. Cross-section schematics and associated top-down scanning electron microscope (SEM) images of ZnO seed layers deposited under various conditions on Si substrates. Schematics are not to scale.
The two most common seeding techniques are sol-gel spincoating and RF sputtering (Figure 2-1). Other techniques for self-seeding include pulsed laser deposition [1] and molecular beam epitaxy [2]; foreign seed particles like aluminum [3] and gold [4] have also been used. In contrast to other techniques, sol-gel spincoating and sputtering yield good crystal quality under relatively benign processing conditions. These two methods can be further sub-divided into the continuous and discrete seed layer deposition methods, where adjacent seed crystals are in contact or separated, respectively. Understanding this distinction is important because discrete and continuous seed layers behave differently in terms of the way vertical nanowire orientation is achieved. Initial demonstrations of seeded ZnO nanowire growth used sol-gel spincoating of a colloidal suspension of zinc acetate in ethanol to generate a thin layer of discrete ZnO seeds (Figure 2-1a) [5]. Vertical alignment of the seeds was achieved with a high temperature annealing step of between 200 – 350 °C, even though the phase transformation from zinc acetate (ZnAc) to ZnO takes place at 175 °C. The high temperature anneal was necessary to effect rearrangement within the seeds that resulted in the c-axis aligned normal to the substrate.

![Diagram](image)

Figure 2-2. Summary of the various hypotheses for ZnO seed grain texturing with c-axis aligned normal to the substrate. Proposed equilibrium structures of ZnO seeds are shown on a cross-sectional view of the substrate. Colors represent different seed facets.
The mechanism behind alignment of ZnO seeds with the c-axis normal to the substrate is currently not fully understood. This alignment has been demonstrated on silicon (100) and (111) [6], indium tin oxide (ITO) [5] and Kapton polymer [7], which shows that it is a non-epitaxial process since these substrates are single-crystal, polycrystalline, and amorphous, respectively. The continuous variation of nanowire orientation with annealing time and temperature suggests that it is kinetically limited [8]. However, it remains unclear why the seed realignment results in the c-facet facing upwards although the c-facet is the high energy facet (it would be expected that the system reduces its total surface energy by minimizing the c-facet area). There have been three proposed explanations for the seed realignment, outlined in Figure 2-2. The first, and most widely accepted explanation, is that the c-facet is stabilized by impurities, thus reducing its surface energy (Figure 2-2a) [5]. This is plausible because the sol-gel process involves organic ligands and solvents, and it would therefore not be unexpected to find organic residue that could stabilize the c-facet on the seed surfaces. Another explanation is that as discrete seed layers consist of ZnO nanocrystals that are only tens of atomic layers thick, ZnO does not have the wurtzite crystal structure, instead arranging itself in a layered, graphite-like crystal structure that is stable (Figure 2-2b) [5]. The stability of graphitic layers of ZnO nanocrystals has been shown theoretically, and experimentally on Pt surfaces [9], but not on Si, ITO, or glass. Thicker layers of ZnO undergo rearrangement into nanorods when annealed at high temperature for extended periods of time, so it is plausible that thin layers of ZnO are thermodynamically stable [10]. Finally, it is also possible that the c-facet is not atomically smooth, but has a certain characteristic roughness that compensates for the high c-facet energy by exposing other lower energy facets (Figure 2-2c), but this has similarly not been investigated in practice [5]. Regardless of the exact mechanism, well-aligned nanowire arrays can be grown using a high
temperature seed layer anneal. However, using annealing to align ZnO seeds is less effective on substrates like ITO and plastics, which cannot tolerate the high temperature: annealing at lower temperatures means tolerating some degree of sacrifice in nanowire alignment. Another alignment mechanism for aligning nanowires is thus necessary for nanowire arrays to be incorporated into device fabrication processes.

The two nanowire array parameters directly controlled by seeding are nanowire density (i.e. placement of nanowires) and nanowire orientation. As demonstrated by Tian et. al. [11] and Huang et. al. [8], these parameters are not independent. Nanowire orientation is a function of nanowire density – nanowire arrays become more vertically aligned as nanowire density increases. This is due to a physical effect termed mutual impingement (Figure 2-3). Mutual impingement works by hindering off-axis nanowires from growing when they encounter neighboring off-axis nanowires. At high nanowire densities, there are enough off-axis nanowires such that only nanowires perpendicular to the substrate continue growing. This causes the array vertical alignment, quantified by the order parameter, to increase with growth time as off-axis nanowires coalesce and cease to grow upwards from the substrate. We introduce here a method for obtaining and quantifying the distribution of nanowire off-normal tilt angles. The order parameter $S$ quantifies the relative alignment of an ensemble with respect to a vector (called the director) which, in the case of directed growth from a substrate, is the substrate normal. $S$ is given by:

$$ S = \frac{3}{2} (\cos^2 \varphi) - \frac{1}{2} \quad (1) $$
where $\phi$ is the angle between an individual nanowire growth axis and the substrate normal (Figure 2-3). $S$ ranges from 1, which implies perfect ensemble alignment with the director, to -0.5, which means perfect alignment perpendicular to the director.

Figure 2-3. Nanowire array cross-section showing mutual impingement and deviation of nanowire growth axis from the substrate normal quantified by the angle $\phi$.

The effect of mutual impingement is most obvious in seed layers where the seeds are dense and are *randomly aligned* with the substrate. While this may seem counterintuitive, XRD studies have shown that from a randomly oriented polycrystalline film, the effect of mutual impingement is strong enough that within several tens of nanometers of growth only vertically aligned nanowires survive and continue growing [11]. Since the likelihood of off-axis nanowires encountering another off-axis nanowire depends on the nanowire density, this mechanism works best when nanowire density is very high ($> 10^{10}$ cm$^{-2}$). It also follows that annealing, which reduces the seed density by causing coalescence of seeds through grain growth, is detrimental to nanowire alignment for randomly aligned seed layers [12]. This is precisely the behavior observed in continuous spincoated seed layers (Figure 2-1b), which consist of multiple layers of seeds around 5 – 10 nm in diameter stacked on top of each other. Dense nanowire arrays grown from these seed layers show good alignment through the mutual impingement effect; the alignment deteriorates in response to annealing or seed layer patterning [13], both of which
decrease the nanowire density. It has therefore been difficult to achieve good alignment with usual lithographic patterning since off-axis nanowires are obtained in regions where nanowire density decreases, such as at the pattern edges.

![Cross-section SEM images of nanowire arrays grown from increasing thickness of sputtered ZnO seed on Si substrates, with corresponding $S$ indicated.](image)

Figure 2-4. Nanowire alignment in arrays grown from sputtered seed layers. (a) – (d) Cross-section SEM images of nanowire arrays grown from increasing thickness of sputtered ZnO seed on Si substrates, with corresponding $S$ indicated. (e) Order parameter vs. sputtered seed layer thickness.

The opposite effect is observed in sputtered seed layers [14]. As shown in Figure 2-4a – d, thin layers of sputtered ZnO (< 10 nm) display poor nanowire alignment, while well-aligned nanowires grow from the columnar grains in sputtered films that are greater than 20 nm in thickness. Incidentally, the preferred off-axis orientation of nanowires grown from discrete sputtered seeds, which unlike sol-gel spincoated discrete seeds are free of residue, lends credence to the theory that the c-facet of spincoated seeds is stabilized by leftover organics from the solvent. Furthermore, annealing discrete sputtered seeds has no effect on nanowire alignment, showing that sputtered seeds assume an equilibrium structure upon being deposited on the surface. Annealing continuous sputtered ZnO films causes grain growth, as well as a small
improvement in nanowire alignment [15]. As expected, nanowire alignment is already excellent on unannealed films [16] and, because it does not rely on mutual impingement, does not deteriorate with annealing. Continuous sputtered films are thus suitable for lithographic patterning since alignment is almost independent of density. Nanowire arrays grown from dense sputtered films have lower nanowire areal densities than those grown from dense spincoated films because the grain sizes produced in sputtering are much larger than those produced by spincoating. This is again likely due to c-facet stabilization by organic impurities left over from sol-gel processing.

Figure 2-5. Examples of patterned ZnO nanowire arrays obtained by (a) nanosphere lithography adapted from [17], (b) electron beam lithography adapted from [18], (c) nanoimprint lithography adapted from [19] and (d) photolithography adapted from [20].

Seed layer patterning has had mixed effectiveness at controlling nanowire placement. Lithographic techniques, summarized in Figure 2-5, include nanosphere lithography [17], electron beam lithography (EBL) [21,22], interference lithography [23], nanoimprint lithography [19], and traditional photolithography [20]. The effectiveness of the technique depends on the desired array morphology: photolithography is suitable for patterning dense nanowire arrays with
micron-scale critical dimensions, but controlling the spacing between individual nanowires requires a lithographic technique capable of producing hole patterns with sub-10 nm diameter and ~100 nm pitch. The ability to vary inter-nanowire distance in the 100 – 1000 nm lengthscale is important for using nanowires to manipulate interaction between optical and electronic phenomena in nanostructured devices. When patterned mask holes are too large, multiple seeds are exposed to growth solution, causing more than one nanowire to grow per hole and thereby negating the pattern spacing [13]. Furthermore, nanowire orientation deteriorates as nanowires are spaced further apart on certain types of seed layers, so appropriate choice of seed layer deposition technique is critical. The capability to place single, vertically oriented nanowires at specific positions is key to using nanowires to control device electronic and optical behavior, but this has proven difficult to achieve over the large areas required for photovoltaic applications.

When the nanocrystalline ZnO seeds on the substrate are immersed in aqueous solution, interaction with the solvent causes them to either dissolve or grow. Which of these processes takes place depends on the concentration of Zn$^{2+}$ and OH$^-$ ions, as well as the seed dimensions themselves. The chemical reactions expected at the seed/solution interface are:

$$Zn^{2+} (aq) + 2OH^- (aq) \rightleftharpoons Zn(OH)_2 (s)$$

$$Zn(OH)_2 (s) \rightleftharpoons ZnO (c) + H_2O (l)$$

where crystallization of ZnO happens via a reaction intermediate Zn(OH)$_2$ [24]. Crystal growth will take place when the ionic product exceeds the solubility product $K_{sp}$.
\[ [\text{Zn}^{2+}] [\text{OH}^-]^2 > K_{sp} = k_c \exp \frac{\Delta G_c}{kT} \]  

(2)

where \( k_c \) is the rate constant of crystallization, \( \Delta G_c \) is the Gibbs free energy of crystallization, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. However, growth of seeds is mutually dependent: mean-field theory states that due to the Gibbs-Thomson effect, larger seeds will grow at the expense of smaller seeds because they have a lower curvature and thus lower interfacial energy, facilitating incorporation of ions into the surface [25]. ZnO nanowire arrays grown from seed layers with a narrow grain size distribution have greater uniformity across the substrate since all seeds are equally likely to grow or dissolve [26].

2.2 Solution phase chemical equilibria

The nature of aqueous ions impinging upon the ZnO crystal surface depends heavily on the chemistry of the growth solution. ZnO nanowire growth has been shown to be highly sensitive to temperature [27], zinc concentration [7,28], pH [20,27,29,30], type of counterion [28,31], type of buffer solution [20,32], and the presence of impurities [27]. Since these factors are interrelated, it has been difficult to isolate their individual effects on nanowire growth. Careful selection of growth chemistry to maintain homeostatic conditions is thus necessary to investigate growth mechanisms of ZnO crystal facets.
Figure 2-6. Speciation plots for aqueous solutions of 10 mM and 20 mM zinc ions in equimolar hexamethylene tetramine (HMTA) buffer.

Zinc ions in solution are highly labile and thus display a rich diversity of complexation reactions in their interaction with water molecules [33]. They also interact with ammonia, which is usually present in solution due to a common buffer chemistry used in nanowire growth, which relies on hexamethylenetetramine (HMTA) decomposition to maintain a pH of 5.5. The following reactions are all present in the typical buffered solution chemistry:

\[
H^+ + OH^- \rightleftharpoons H_2O \\
NH_4^+ + OH^- \rightleftharpoons NH_3(aq) + H_2O \\
Zn^{2+} + OH^- \rightleftharpoons ZnOH^+ \\
Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_2(aq) \\
Zn^{2+} + 3OH^- \rightleftharpoons Zn(OH)_3^- \\
Zn^{2+} + 4OH^- \rightleftharpoons Zn(OH)_4^{2+} \\
Zn^{2+} + NH_3 \rightleftharpoons Zn(NH_3)^{2+} \\
Zn^{2+} + 2NH_3 \rightleftharpoons Zn(NH_3)_2^{2+}
\]
Each of these reactions has a certain reaction constant and therefore the relative concentration of each zinc complex is a function of temperature, pH, and zinc concentration. Under a specific combination of conditions, one or more species could be dominant. Due to their size to charge ratio, each species has a different hydrodynamic radius and thus a different aqueous diffusion length. We can thus expect that the observed crystal growth rate will be a function of the dominant zinc species via differences in diffusive transport to the growing crystal surface. Changes in species concentration, or speciation, can be modeled as a function of pH and temperature if the individual reaction equilibrium constants are known. The speciation plots for zinc concentrations of 10 mM and 20 mM are shown in Figure 2-6a and Figure 2-6b, respectively. The simulations show that Zn$^{2+}$ is dominant in acidic solution from pH 0 to pH 7; in basic solutions a multitude of complexes exist in varying concentrations. It is therefore imperative that studies of growth mechanisms take place in acidic solution since it is very difficult to separate the effects of different complexes on diffusive transport in crystal growth. Apart from the different diffusion rates, it is also unclear if complexation can affect the adsorption/desorption equilibrium on the crystal surface, so ensuring that Zn[($\text{H}_2\text{O}$)$_6$]$^{2+}$ is the only complex in solution would greatly simplify such investigations.
Maintaining homeostatic concentration, temperature and pH has proven to be challenging in practice. The most common method of growing ZnO nanowires is bulk growth, wherein the substrate is suspended in the growth solution and kept at the growth temperature for the required duration [4]. The ease of this method as well as its ability to produce excellent nanowire arrays have, rather unfortunately, been counterproductive to investigating growth mechanisms simply because bulk growth does not ensure that growth conditions are constant with time [34]. It has been shown that the zinc concentration, even in the presence of a buffer, will vary over an order of magnitude over typical growth times of about an hour due to consumption of zinc ions. The system will therefore pass through multiple speciation regimes, which means that the dominant species could change during the course of growth [35]. Furthermore, despite the presence of the buffer, the pH can change as well. Any conclusions that such investigations make with respect to growth mechanism are thus suspect since the system is not homeostatic.

2.3 Crystal growth mechanisms

General crystal growth mechanisms were described in Chapter 1. These mechanisms are valid for all types of crystal growth including crystallization from the melt, vapor phase, or solution phase; the growth medium mainly affects the adatom flux to the crystal growth interface. We now focus on the specific case of ZnO crystal growth from the solution phase, i.e. building up a ZnO crystal from complexed zinc ions in aqueous solution, and its growth rate dependence on temperature and supersaturation. Knowing how aqueous zinc ions become locked into ZnO crystal positions is important for growth control because the growth mechanism dictates how the growth rate changes with macroscopic parameters. We can then tune these parameters to achieve the desired morphology. This knowledge will inform process design that
produces nanostructures with sufficient morphological precision for a particular device architecture.

Identifying the operative growth mechanism on a crystal facet has typically been performed using two methods. First, the surface morphology may provide some indication of which mechanism is at work. Layer-by-layer (LBL) and dislocation growth are the most distinctive, since the presence of 2D islands and dislocations, respectively, are indicative of these growth mechanisms [36]. Morin et. al. used transmission electron microscopy (TEM) to directly observe screw dislocations in the ZnO nanowire core [37], showing that nanowires grow by the dislocation mechanism when ‘seeded’ by GaN threading dislocations. Under other growth
conditions, the LBL mechanism has been hypothesized based on observation of features such as mounds [38], volcanoes [1,39] and pyramids [40,41]. These features result from a mismatch between the 2D island step growth rate and the 2D island nucleation rate [42]. Figure 2-7 details how some of these features may form. When the 2D island nucleation rate is greater than the step growth rate, a 2D island does not fully cover the crystal surface before the subsequent 2D island nucleates on top of it causing the build-up of layers into 3D structures (Figure 2-7c). The 3D structures are further emphasized by poor inter-layer diffusion due to the Ehrlich-Schwoebel barrier and the Zeno effect. The Ehrlich-Schwoebel barrier refers to the peak in bond energy at the step edge that forms a potential barrier for adatoms diffusing from upper to lower islands. Since adatom capture depends on the island area, this causes upper islands to grow laterally at the expense of the lower islands [43]. Eventually, a 3D pyramid is formed. The Zeno effect refers to a phenomenon where adjacent islands shadow each other from atomic flux from the solution, forming deep valleys between pyramids into which it is difficult for adatoms to diffuse [44]. After multiple layers have been deposited, this process causes characteristic mountain-valley morphology to build up on the crystal surface. The 3D features are generally undesirable as they introduce defective internal surfaces that reduce the crystal quality. Therefore, it is desirable to stay in a growth regime where 2D LBL growth is dominant, with each layer fully covering the surface before the next layer nucleates (Figure 2-7a and b).

Another way of identifying the crystal facet growth mechanism is by observing the facet growth rate as a function of supersaturation [45,46]. Each growth mechanism has a different relationship with supersaturation, which provides a unique way of identifying it. The most rigorous methods rely both on observing characteristic surface features and on growth rate-
supersaturation studies to definitively identify the growth mechanism [4]. The relationship between facet growth rate $R$ and concentration for the three main growth mechanisms are [42]:

Normal growth

$$R_{\text{normal}} = a v \left( \frac{a}{\delta} \right)^2 e^{-\left( \frac{\Delta U}{kT} \right)} v_{\text{atom}} (C - C_0)$$  \hspace{1cm} (3)

Layer-by-layer

$$R_{\text{LBL}} \propto C \left( \ln \left( \frac{C}{C_0} \right) \right)^{\frac{1}{2}} e^{-\frac{A}{\ln(C/C_0)}} l^2$$  \hspace{1cm} (4)

Dislocation

$$R_{\text{dislocation}} = C \frac{\sigma^2}{\sigma_c \ln \left( \frac{d}{\alpha a} \right)}$$  \hspace{1cm} (5)

where $a$ is the lattice parameter, $v$ is the characteristic atomic vibrational frequency, $\delta$ is the kink spacing, $\Delta U$ is the energy of crystallization, $v_{\text{atom}}$ is the aqueous ion hydrodynamic radius, $C$ is the aqueous concentration, $C_0$ is the equilibrium concentration, $A$ is a constant that takes into account 2D nucleation parameters, $L$ is the nanocrystal side length, $\sigma$ is the supersaturation, $\sigma_c$ is the characteristic supersaturation, and $d$ is the stagnant layer thickness.

Growth via direct incorporation, or normal growth, has a linear relationship with concentration (Eqn 3). This is because adatoms fall directly into kinks on the surface, given the high surface roughness of the crystal facet. When the kink density is very high (kink spacing on the order of several atomic diameters) the facet growth rate then depends linearly on the atomic flux impinging on the surface that, in the case of solution phase growth, is linear with concentration. It is therefore easy to control the facet growth rate with concentration since the relationship is linear. Large crystals of ZnO grown using hydrothermal synthesis are known to grow via direct incorporation on the c-facet [47]. Unlike the direct incorporation growth mechanism, the dislocation mechanism has a parabolic relationship with supersaturation (Eqn 5).
This is because dislocations provide surface defects in which adatoms can incorporate, and the 2D island nucleation is therefore not required [36], but the step still needs to propagate laterally to cover the surface. The parabolic relationship results from the rate at which a dislocation spiral propagates upwards around the dislocation core, generating new layers in a helical fashion. Finally, the LBL mechanism has a superlinear relationship with supersaturation, which reflects the convolution of the 2D island nucleation rate as well as the step growth rate (Eqn 4). This relationship only holds for 2D LBL, that is, each layer fully covers the surface before the next layer nucleates. When 3D LBL takes place, the relationship is even more complicated and is not suited to such growth rate-supersaturation investigations.

In practice, therefore, identification of crystal growth mechanisms involves immersing an initial seed crystal in a solution of known, constant supersaturation for a certain duration. The changes in dimensions of the crystal are then measured to determine the growth rate. Further high resolution surface characterization like scanning tunneling microscopy (STM) that resolves features such as dislocations and 2D islands can also be used to strengthen the case in favor of a particular mechanism [44].

One final factor needs to be considered if quantitative results are desired. The derived relationships between facet growth rate and supersaturation typically take the supersaturation as that directly adjacent to the crystal-solution interface. However, it is impossible to measure this concentration directly – the concentration measured by titration or atomic-emission spectroscopy (AES) comes from aliquots drawn from solution in the vicinity of the crystal. Unlike in vapor phase deposition, the much higher viscosity of water means that a concentration gradient exists
between the bulk solution and the solution at the growth interface. Transport of reactant between the bulk solution and the interface can take place by flow (due to stirring or convection currents) or by diffusion [48–50]. Since reactant transport and incorporation are serial events, either can be rate-limiting steps for crystal growth. The interplay between reactant transport and surface reaction rate is especially important in selective area growth (SAG) of patterned ZnO seed layers, since operating in rate-limiting regimes promises uniform growth independent of pattern fill-factor. The pertinent points of the diffusion/reaction growth model are covered in the subsequent analysis.

The diffusion/reaction-limited growth model is typically used to model catalytic activity in reaction vessels, wherein the Thiele modulus gives a measure of reactant diffusion to catalytic sites vs. surface reaction rate at these sites [51,52]. It was adapted by Boercker et al. [48] to describe nanowire growth; a brief overview of its derivation is given in Figure 2-8, which aims
to show how diffusion flux and crystallization rate are incorporated in this nanowire growth model. Fick’s second law is used to model diffusion of Zn$^{2+}$ growth units in the fluid. Zinc flux to the surface, $J_{zn}$, is given as:

$$J_{zn} = -D \frac{dC_{zn}}{dz}$$

(6)

where $D$ is the Zn$^{2+}$ aqueous diffusion coefficient ($2.91 \times 10^{-9}$ m$^2$s$^{-1}$)$^4$, $C_{zn}$ is the Zn$^{2+}$ concentration (m$^{-3}$) and $z$ is the coordinate normal to the substrate (m).

The reaction rate of dehydration of [Zn(H$\text{H}_2\text{O})_6$]$^{2+}$ to ZnO (ZnO crystallization) at the surface, for a reaction of $n^{th}$ order, is given by:

$$r_{surf} = k_n C_0^n S$$

(7)

where $r_{surf}$ is the surface reaction rate (m$^{-2}$s$^{-1}$), $k_n$ is the $n^{th}$ order reaction rate constant (m$^{-n}$s$^{-n}$), $C_0$ is the concentration at $z = 0$ (m$^{-3}$) and $n$ is the exponent equal to the reaction order. Here, $S$ is the c-plane area ratio (equal to nanowire density (m$^{-2}$) multiplied by mean nanowire top-face area (m$^2$)).

Since Zn$^{2+}$ flux to the surface is equal to incorporation into the nanowire, we perform mass balance at the nanowire growth front: $J_{zn} = r_{surf}$. We further assume steady state diffusion and first-order kinetics to obtain:
where \( \delta \) is the stagnant layer thickness (m). Depletion of Zn\(^{2+} \) in bulk synthesis typically follows exponential decay kinetics, which is indicative of first-order kinetics in ZnO nanowire growth. Since we can measure \( C_\infty \), we solve Equation (S4) for \( C_0 \) and define the Thiele modulus \( \phi \):

\[
C_0 = \frac{C_\infty}{\phi + 1}, \quad \phi \equiv \frac{k_1 S \delta}{D}
\]

We relate this back to the nanowire growth rate by taking into account that the surface reaction rate, the rate at which \([\text{Zn(H}_2\text{O)}_6]^{2+}\) dehydrates to ZnO, is equivalent to the c-plane growth rate:

\[
\tau_{surf} = R_{c-plane} \rho S = J_{zn}
\]

where \( \rho \) is the ZnO molar density \((4.20 \times 10^{28} \text{ m}^{-3})^6\). After rearranging:

\[
R_{c-plane} = \frac{J_{zn}}{\rho S} = \frac{k_1 C_\infty}{\rho(\phi + 1)} = \frac{k_1 C_\infty D}{\rho D + \rho \delta k_1 S}
\]

we are able to obtain the relationship between c-plane growth rate \( R_{c-plane} \) and external parameters Zn\(^{2+} \) concentration \( C_\infty \) and c-plane area ratio \( S \). Therefore, by observing \( R_{c-plane} \) as a function of \( S \), we can obtain an idea of whether the nanowire growth under a particular set of conditions is reaction- or diffusion-limited via the Thiele modulus \( \phi \). When \( \phi \) is greater than 1,
the surface reaction is fast and therefore nanowire growth is dominated by the rate of reactant diffusion to the nanowire growth front. When $\phi$ is less than one, surface reaction is slow and therefore nanowire growth is reaction-limited.

The ability to predict how nanowire growth rate changes with concentration, surface reaction rate, and total $c$-facet area forms the backbone of nanowire growth control, which is the subject of Chapter 4 of this thesis. This set of relationships between key growth parameters and nanowire growth rate allows us to obtain the desired morphology \textit{via} informed process design, instead of by trial and error. For example, designing nanowire growth processes to operate in reaction-limited regimes ($\phi < 1$) promises uniform growth rates independent of seed layer pattern density, which is important when incorporating nanowires into a specific device architecture. Furthermore, separating the effects of diffusion vs. reaction on the observed nanowire growth rate also yields insight into fundamental processes taking place at the nanowire growth interface such as reaction intermediates and the effect of surface adsorbents on adatom incorporation.
2.4 Growth control using additives

![Image of ZnO nanostructures with morphology controlled using additives.](image)

Figure 2-9. ZnO nanostructures with morphology controlled using additives. (a) Sidewall adsorbent PEI produces long nanowire arrays used in dye-sensitized solar cells. Adapted from [53]. (b) Citrate top-facet adsorbent produces stacked, biomimetic nanoplates. Adapted from [54]. (c) Aluminum sidewall adsorbent produces sharp-tipped nanowires for field emitters. Adapted from [27]. (d) Cadmium top-facet adsorbent produces nanoplates. Adapted from [27].

ZnO crystallization has been shown to be very sensitive to solution purity. Metal ions and organic molecules at the parts-per-billion to parts-per-trillion concentration can profoundly affect the nanostructured morphology. The widely applicable Kubota-Mullins model has successfully described observed changes in step growth rate by understanding that such additives (or impurities, if undesired) effect changes in the growth rate by surface adsorption, blocking adatoms from reaching kink sites [55]. The surface concentrations of these additives typically follow Langmuir adsorption kinetics [56,57] and consequently the facet growth rates can be tuned by changing the bulk additive concentration. Since each facet has a different polarity and attracts different ions in solution depending on the ion charge density [27], different additives adsorb to the c- and m-facets of the crystal, providing opportunities for growth control. The first additives investigated were citrate and polyethyleneimine, which reduced the growth rates on the c- and m-facets, respectively. Tian et. al. used variation in citrate concentration to produce...
biomimetic ZnO nanostructures [54], while Greene et. al. used polyethylenimine to grow high aspect ratio nanowire arrays for dye-sensitized solar cell applications [53]. Joo et. al. [27] showed that metal ions with a +3 oxidation state in solution, including Al\(^{3+}\) and Ga\(^{3+}\), adhere to the negatively charged lateral facet, producing long, tapered nanowires. In contrast, ions with a +2 oxidation state like Mg\(^{2+}\) adhere to the positively charged top facet, producing nanoplates. Careful selection of additives can produce nanostructures with aspect ratios ranging from less than one (nanoplates) to greater than one hundred (nanowires), shown in Figure 2-9a – d.

Surface sensitivity to foreign metal ions and polyelectrolytes is both bane and boon to ZnO nanowire growth. On one hand, solution purity is critical for run-to-run consistency since the concentration of metal ions at which nanowire growth rates can be altered (~ hundreds of pM) is low enough to be virtually undetectable even by the most sensitive techniques. Great care must thus be taken in solution preparation and cleaning of glassware to avoid introducing minute amounts of impurities since a large range of common metal ions is effective in altering ZnO nanowire growth. On the other hand, a rich diversity of nanostructural shapes and sizes can be obtained because of the strong effect of additives on surface reaction rate. Being able to use minute concentrations of metal ion additives means that facet growth rates can be tuned without affecting zinc speciation in the system (as mentioned in Section 2.2), and also that both c- and m-plane adsorbents can be used simultaneously, providing even more control over the aspect ratio. We show in Chapter 4 of this thesis precisely how additives alter \(k_f\) (surface reaction rate constant) to transform a particular nanowire growth process from diffusion-limited to reaction-limited with the aim of increasing nanowire length uniformity across a patterned substrate.
2.5 Nanostructured optoelectronic devices

Nanostructured semiconductor materials are of particular interest in optoelectronic device applications because of their ability to modulate optical and electronic processes at length scales of 10 nm to 1 μm. A myriad of processes are operative at these length scales, including optical absorption [58,59], electronic mobility [60,61], quantum confinement [62], and luminescence [27]. Therefore, semiconductor nanostructures with dimensions that can be modulated at these length scales [63] offer us many opportunities to manipulate these phenomena, with the ultimate goal of improving overall device performance.

Nanostructured semiconductors can be paired with other dissimilar semiconductor materials to yield hybrid semiconductor devices [64–66]. The pairing is effectively a composite material – one that leverages the best properties of each individual material to alleviate any shortcomings of the other – in which the desired properties are not mechanical, but rather optical and electronic. Nanostructured semiconductors are particularly useful in enhancing the performance of optoelectronic devices because materials that possess both good optical and electronic properties are rare. For instance, light emitting diodes (LEDs) require a direct bandgap at the desired emission energy, coupled with high electronic mobility. However, it has been challenging to produce high-quality semiconductor material that fulfills these two requirements – silicon has an indirect bandgap [67], indium-doped gallium nitride suffers from high defect concentration at increased doping concentrations [68], and organic emitters are hindered by poor lifetime and low electronic mobility [69,70].

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Photovoltaics (PV) are another type of optoelectronic device in which incorporation of nanostructured semiconductors has enhanced device performance [64]. The active layer, which consists of material that is highly absorptive in the near-IR and visible spectrum, should ideally have high hole and electron mobilities in order for charge to be extracted efficiently. In particular, the active layer needs to be thick enough to absorb as much incident light as possible; carrier diffusion length often falls short of this minimum thickness, resulting in poor charge extraction that limits device efficiency [58]. This trade-off between optical absorption and charge extraction is known as the generation-extraction compromise. With this in mind, it is materials that possess the desired optical properties but sub-optimal electronic mobilities that have benefitted most from incorporation of nanostructured semiconductor materials, in the form of nanoparticles, nanorods, and nanowires [65]. Nanostructured electrodes transcend the generation-extraction compromise by forming high mobility pathways that greatly increase the efficiency of charge extraction [71], allowing the active layer thickness to be increased for better optical absorption.

Quantum dot (QD) photovoltaics utilize semiconductor nanocrystals with sub-Bohr radius dimensionality as their active layer [72]. Due to quantum confinement in three dimensions, the optical bandgap of a QD film is dependent on the nanocrystal size and can therefore be easily tuned to 1.34 eV, the single junction Shockley-Queisser limit [73]. In particular, PbS QDs can be synthesized with excellent size control in a scalable one-pot process; appropriate choice of ligands confers long-term stability to the PbS QDs in solution. To form the active layer of a QD PV device, the QD solution is spincoated in successive layers of about 10 – 30 nm per spincoating step. After each step, solution-phase ligand exchange is carried out – this
process exchanges the existing ligands used for QD synthesis for different ligands that passivate the QD surface, resulting in improved electronic properties. Recent studies have shown that key material properties such as bandgap, carrier mobility, and dielectric constant are a function of ligand choice [74-76], and therefore this step is critical for obtaining efficient devices.

Figure 2-10. Inverted architecture for (a) planar and (b) nanowire array QD PV device cross-section showing AM 1.5G illumination through glass substrate. (c) Energy band diagram showing key processes (1) optical absorption (2) electron-hole pair generation and (3) collection to electrodes via drift and diffusion.

The typical inverted device architecture for planar vs. nanowire array QD PV devices is shown in Figure 2-10. Beginning with transparent conductive electrodes – indium tin oxide (ITO), fluorine tin oxide (FTO), and graphene have been used – patterned on glass, the n-type ZnO layer is deposited either by spincoating or sputtering. Nanowire arrays are then synthesized hydrothermally from the ZnO seed layer, with variation in growth solution concentration and
growth time used to tune nanowire array dimensions. Sequential deposition of QD layers is then used to lay down the active layer over these vertically aligned nanowire arrays; total active layer thickness depends on the number of layers deposited. While it is important that the active layer fully covers the nanowires to prevent short circuiting the device via nanowires contacting the Au back electrode, active layers that are too thick suffer from poor charge transport. The active layer thickness must therefore be precisely matched to the nanowire array dimensions.

Figure 2-11. Simulated QD device cross-section optical generation profile (top) for illumination from the left. The electron and hole diffusion lengths are indicated, measured from the cathode and anode respectively. (Bottom) Proportion of incident power absorbed and optical generation rate $G_{op}$ vs. QD device thickness.

ZnO nanowire arrays enhance charge collection because QD PV devices are susceptible to the generation-extraction compromise: an 700 nm thick QD film absorbs 85% of incident
light, but this already exceeds both the electron and hole diffusion lengths of about 100 nm and 300 nm respectively, thus sacrificing carrier collection [77] (Figure 2-11). Therefore, incorporating ZnO nanowire arrays has had significant benefit: ZnO nanowires improve charge extraction by providing high n-type mobility pathways for electrons generated deep in the device, thereby enhancing performance by increasing short-circuit current ($J_{sc}$) [78].

Despite the success of ZnO nanowire/PbS QD devices, there are several outstanding questions concerning the role played by ZnO nanowires in the active layer. First, although ZnO nanowire electrodes enhance $J_{sc}$ over planar ZnO nanoparticle electrodes, the optimal device geometry to maximize $J_{sc}$ remains unclear. Second, ZnO nanowire QD devices typically show lower open circuit voltage ($V_{oc}$) than planar ZnO devices. Reduced $V_{oc}$ can result from multiple sources such as shunting, interfacial recombination, or trap-mediated recombination [77]; which of these dominates in ZnO nanowire QD devices is still unknown. Finally, optical effects of ZnO nanowires in QD PV devices have not been investigated. While it has been hypothesized that increased scattering at the nanowire-QD interface can increase the optical pathlength, resulting in potentially higher $J_{sc}$, whether this effect is significant remains in question. Investigating this phenomenon using ZnO nanowire arrays with varying lengths in PbS QD PV is the subject of Chapter 5 of this thesis.
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CHAPTER 3

Electron-Beam Lithography Patterned ZnO Nanowire Arrays

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Abstract

Hydrothermally synthesized zinc oxide nanowire arrays have been used as nanostructured acceptors in emerging photovoltaic (PV) devices. The nanoscale dimensions of such arrays allow for enhanced charge extraction from PV active layers, but the device performance critically depends on the nanowire array pitch and alignment. In this study, we templated hydrothermally-grown ZnO nanowire arrays via high-resolution electron-beam-lithography defined masks, achieving the dual requirements of high-resolution patterning at a pitch of several hundred nanometers while maintaining hole sizes small enough to control nanowire array morphology. We investigated several process conditions, including the effect of annealing sputtered and spincoated ZnO seed layers on nanowire growth, to optimize array property metrics – branching from individual template holes and off-normal alignment. We found that decreasing template hole size decreases branching prevalence but also reduces alignment. Annealing seed layers
improves alignment, and sputtered seed layers yield nanowire arrays superior to spincoated seed layers. We show that these effects arise from variation in the size of the template holes relative to the ZnO grain size in the seed layer. The quantitative control of branching and alignment of the nanowire array that is achieved in this study will open new paths toward engineering more efficient electrodes to increase photocurrent in nanostructured PVs. This control is also applicable to inorganic nanowire growth in general, nanomechanical generators, nanowire transistors, and surface-energy engineering.
3.1 Overview

Top-down patterning of ZnO seed layers is a simple and effective way of controlling nanowire spacing. As covered in the Background (Chapter 2), a plethora of lithographic techniques have successfully produced patterned ZnO nanowire arrays with critical dimensions from the micron to tens of nanometers scale. This is because most polymer-based resists are compatible with the low temperature, neutral pH hydrothermal growth process and thus more robust metal or inorganic oxide masks are not required, which greatly simplifies the patterning process and reduces the chance of contamination by additional deposition and etching steps. Both positive and negative tone resists have been used to pattern ZnO seed layers: the former use mask openings to expose only the patterned parts of the seed layer to growth solution, while negative resists shield the seed layer from an etchant and are subsequently removed before hydrothermal growth. The achievable precision of patterned nanowire array dimensions thus depends to a great extent on the characteristics of the seed layer that, as mentioned before, are in turn dependent on deposition and processing conditions [2–6]. The seed layer grain size and orientation with respect to the substrate vary greatly depending on the type of deposition used, annealing time and temperature, and type of substrate used. This provides opportunities for exercising a great deal of control over array morphology and it is therefore important to understand the role played by seed layer morphology in patterned growth.

Patterned nanowire arrays display two types of imperfections. Branching refers to the growth of multiple nanowires from a single template hole, which is deleterious because it diminishes the efficacy of a template already tuned to the desired nanowire spacing. Nanowires can also grow with orientations tilted away from the substrate normal. The nanowire orientation
is quantified by its angle with respect to the substrate; growing nanowires oriented normal to the substrate is also important in keeping the nanowire spacing uniform throughout the film thickness and for reducing defects in materials deposited within the nanowire array. Taken together, good orientation and low percentage of branching are required to grow single nanowires at the precise positions for optimizing device performance. However, although ZnO seed layer processing has a profound effect on nanowire morphology, quantitative studies are lacking. Few studies have attempted to quantify nanowire orientation and to relate its variation to seed layer processing and lithographic patterning. In general, previous reports have observed high quality ZnO nanowire array growth on sputtered seed layers [7–9], but array quality is inconsistent for nanowires grown on spincoated seed layers [10,11].

Controlling the spacing between nanowires as a function of film thickness is particularly important for the case of nanostructured photovoltaic devices. ZnO nanowires have been incorporated into quantum dot photovoltaic devices (QD PV) to provide high mobility n-type pathways to extract electrons (the minority carrier) that are optically generated deep in the device [12–14]. Nanowires enhance charge extraction efficiency from dead zones in the PV device, thus allowing active layers to be made thicker with the intention of increasing the fraction of insolated power absorbed [15]. The nanostructured architecture accomplishes this by allowing optical generation to take place vertically while charge collection occurs laterally, giving rise to the term generation-collection orthogonalization. The nanowires used in such devices have to possess a high degree of vertical orientation since their spacing corresponds to twice the minority carrier diffusion length. In particular, for MPA-treated PbS QDs, current density will be maximized at a nanowire array pitch of 276 nm [16]. More generally, since the electron diffusion length in PbS
QD films varies between 100 – 200 nm depending on ligand, controlling nanowire spacing between 200 – 400 nm would be useful for optimizing QD PV power conversion efficiency [17]. ZnO nanowire templating therefore needs to achieve: (1) sufficiently small template-hole diameter for single nanowire growth and (2) high resolution pitch control for controlling device optical and electronic processes in the 200 – 400 nm range. However, no previous studies on ZnO nanowire templating have been able to achieve both of the requirements simultaneously.

In this study, we focus on controlling the branching and alignment of ZnO nanowire arrays fabricated by electron-beam lithography (EBL) and hydrothermal synthesis at the length scales that are relevant for nanowire-based QD PV devices. We specifically focus on the following process parameters: substrate, seed layer deposition and annealing, and template hole size. Templated nanowire arrays were grown on silicon, indium tin oxide-coated glass (ITO/glass) and poly(ethylene naphthalate) (PEN) substrates, and we found that substrate type contributes minimally to nanowire array quality. Arrays grown on sputtered seed layers show superior alignment compared to those grown on spincoated seed layers, while both show similar degrees of branching. However, annealing of spincoated seed layers improves nanowire array alignment. Control via template hole diameter is particularly dependent on the method for seed layer deposition – while a decrease in hole diameter decreases branching, smaller holes result in poorer alignment for spincoated seed layers but have no effect on sputtered seed layers. We suggest that array control can be achieved with engineered template hole size relative to seed layer grain size, and explain our results based on this hypothesis.
3.2 Experimental methods

The EBL-templated hydrothermal growth process used in this work is shown in Figure 3-1. ZnO nanowire arrays were grown with hydrothermal synthesis after using EBL to define templates on both sputtered and spincoated seed layers. The nanowire arrays were then inspected with either scanning electron microscopy (SEM) or helium ion beam microscopy (HIM), and images were analyzed to extract branching and alignment metrics.

3.2.1 Templated growth

As shown in Figure 3-1a, ZnO seed layers were first deposited on Si (111), ITO/glass, and PEN substrates by spincoating or sputtering. We chose Si substrates for their low surface roughness as a suitable baseline for high quality nanowire growth. ITO/glass is a common conducting substrate used for PV device electrodes. We chose PEN substrate to represent a possible flexible PV substrate; its high thermal resistance makes it compatible with the 175 °C seed layer annealing step. Spincoated layers were deposited from a solution of 0.3 M zinc acetate monoethanolamine (1:1) in 2-methoxyethanol at 4000 rpm, 2000 rpm s⁻¹ ramp, for 60 s and annealed at 175 °C for 10 min; this process was repeated to produce a ZnO thickness of ~30 nm. RF-sputtered ZnO films were deposited by using an AJA Orion 5 at 100 W, 3 mT Ar for 24 min for a thickness of ~180 nm. Seed layers were then annealed on a hotplate at 400 °C in ambient atmosphere for 2 h (Figure 3-1b).
Figure 3-1. EBL fabrication process for templated hydrothermal ZnO growth. (a) ZnO seed layer deposition either by spincoating from solution (top) or sputtering (bottom), (b) a subset of samples were annealed at 400 °C for 2 h, while others were not annealed and used as a control, (c) PMMA resist was spincoated and (d) templating holes were defined by EBL. (e) Nanowires grew through the template holes in the hydrothermal growth solution, and (f) oxygen plasma etching was applied to remove the remaining PMMA and expose the bases of the nanowires. Colors: gray is the substrate, red is ZnO, and black is the PMMA resist.
Poly(methyl methacrylate) electron-beam resist (4% dilution, 950PMMA A MicroChem) was spincoated (shown in Figure 3-1c) at 4000 rpm for 60 s, followed by a post-bake at 85°C for 2 min (below the PMMA glass transition temperature, for solvent evaporation), and measured to be ~100 nm thick via ellipsometry. As shown in Figure 3-1d, a Raith 150 electron-beam lithography tool was used to write a 15 × 15 square array of circles at a pitch of 276 nm (~300 pA, 30 keV, 6 mm working distance). The electron-beam dose for each exposure varied from 100 to 40,000 μC cm⁻². After the lithography step, samples were developed at 24 °C in a solution of 3:1 isopropanol (IPA):methyl isobutylketone (MIBK) for 1 min, rinsed with IPA for 1 min, and blown dry with nitrogen. As PMMA is a positive tone resist at the delivered dose, the development solution dissolved the areas exposed by the electron beam to leave behind holes in the PMMA film, exposing the underlying ZnO seed layer.

Depicted in Figure 3-1e, hydrothermal growth of ZnO nanowires was performed by suspending patterned substrates face down in an aqueous growth solution (MilliQ 18 MΩ) consisting of 25 mM zinc nitrate, 25 mM hexamethylene tetramine and 5 mM polyethyleneimine (all from Sigma-Aldrich) at 90 °C for 100 min. Oxygen plasma etching was then used to remove the PMMA mask, leaving lithographically-defined nanowire arrays (Figure 3-1f).

A Zeiss Orion HIM operating at 35 kV and a working distance of 10 mm was used to image the resulting nanowire arrays (both top down and at 45° tilt) and pre-growth PMMA template hole arrays and seed layers. A Veeco Nanoscope IV atomic force microscope (AFM) was used for imaging of the ZnO seed layers in tapping mode with a standard Si tip.
3.2.2 Image analysis

Three morphological parameters were measured from micrographs to characterize the effects of process variables. First, prior to nanowire growth, we measured the diameter of templating holes as the controlled experimental variable. The measurement was performed using a Matlab procedure from top-down micrographs of the resulting template hole arrays. For a given template array, the lithographic dose delivered to each hole location was designed to be the same. Hole diameters were averaged over each individual array to obtain the template hole diameter metric as the controlled variable.

Second, the degree of branching was determined by counting the number of branched nanowires from top-down micrographs. Figure 3-2a depicts branching, where an individual templating hole results in multiple emerging nanowires. Here, we use the term nonbranched to describe a template hole that results in a single nanowire. Conversely, we use the term branched to describe a template hole that results in two or more nanowires. For each array of nanowires, the prevalence of nonbranching was calculated as the number of nonbranched divided by the sum

![Figure 3-2](image_url)

Figure 3-2. Analysis of micrographs for nanowire branching and alignment. (a) Micrographs of nanowires which typify branched (left) and nonbranched (right) arrays. (b) Micrographs of nanowires which typify high (left) and low (right) order parameter $S$. All micrographs are at the same scale.
of branched and nonbranched holes. Holes without nanowires were excluded and this issue is discussed as nanowire array yield.

Figure 3-3. Measured angles $\alpha$ for actual nanowire tilt angle $\theta$ were transformed to the substrate normal plane angles $\phi$ in order to obtain values for calculation of the Herman's order parameter $S$.

Lastly, we measured the alignment of the nanowires and calculated the order parameter as a quantitative metric. The Herman's order parameter $S = \frac{3}{2} \langle \cos^2 \phi \rangle - \frac{1}{2}$, where $\phi$ is the deviation angle between the nanowire and the substrate normal, is a widely used measure of the preferential alignment [18–20]. As shown in Figure 3-2b, $\phi$ was obtained from SEM micrographs of nanowire arrays taken at 45° tilt. A geometric transformation (Figure 3-3) was necessary to convert the measured value $\alpha$ to the in-plane value $\phi$. $\phi$ is an estimate for $\theta$, the nanowire misalignment angle. We make the assumption that $\theta$ is rotationally symmetric about the substrate normal, allowing us to project $\theta$ onto the x-z plane to obtain $\phi$, which gives us an angular distribution for calculation of the order parameter. This is a valid assumption given that
the larger number of seed grains in both sputtered and spincoated seed layers gives rise to random seed orientation in the x-y plane, an observation borne out by previously reported XRD studies of ZnO seed layers. In order to obtain $\phi$ from the angle $\alpha$, which is measured from SEM images collected at 45° tilt, the geometric transform given by the following equation was performed:

$$\varphi = \tan^{-1} \left( \frac{\tan \alpha}{\cos 45^\circ} \right)$$

where $\alpha$ and $\varphi$ are the projections of actual angle $\theta$ onto the 45° and x-z planes respectively.

Ten arrays of 225 holes each were patterned and grown for each combination of substrates and processing conditions, giving us a large sample size of ~ 2000 nanowires per experiment. For each array, $S$ was calculated by averaging values for all nanowires in the array and it ranges between values of 1 for alignment normal to the substrate and -0.5 for alignment parallel with the substrate surface.

### 3.3 Results and discussion

#### 3.3.1 Templated ZnO nanowire arrays on silicon, ITO and PEN

As shown in Figure 3-4, we achieved growth of templated unbranched ZnO nanowire arrays with good alignment for all substrates, annealing conditions, coating processes, and a range of template hole diameters. Figure 3-4b – i show examples of nanowire arrays grown on Si and ITO/glass. Nanowire diameter is constricted at the base due to PMMA template confinement; unconstrained lateral growth takes place when the nanowire emerges above the template causing larger diameters. Qualitatively, rigid substrates (Si and ITO/glass) result in less
branched, more aligned nanowire arrays than flexible PEN substrates. The nanowires grown on Si and ITO/glass are comparable to those achieved using high-resolution templating of hydrothermally-grown ZnO nanowires on Si, GaAs, GaN, and sapphire [3,4,21–23]. Nanowire alignment is marginally more orthogonal on Si as compared to ITO/glass substrates. Figure 3-4a shows that high resolution templated growth on flexible PEN substrates can be achieved, despite the non-conductive nature (and therefore challenging EBL patterning process) of PEN. Nevertheless, the reliability of the fabrication process for PEN substrates is lower than that for Si and ITO/glass. We attribute lower reliability to thermal degradation of the substrate, mechanical bending of the substrate from thin film stress, difficulty in carrying out EBL on a non-conducting surface, and possibly, reduced adhesion energy between the ZnO nanowires and the substrate.

![Image of helium ion micrographs of 276-nm pitch templated nanowire arrays obtained at 45° tilt.](image)

Figure 3-4. Helium ion micrographs of 276-nm pitch templated nanowire arrays obtained at 45° tilt. All micrographs were chosen as the best example (most aligned and least branched) from each experimental process combination of substrate, seed layer deposition, and annealing. Note that template hole diameters are not identical for each image. Nanowire growth from an annealed seed layer on PEN was not tested. All scale bars are identical.
Good ZnO crystal quality was confirmed using photoluminescence (Figure 3-5) – only strong near-band edge emission at 380 nm is seen, and there is an absence of broad defect peaks at ~ 550 nm and 620 nm, attributed to oxygen vacancies and zinc interstitials respectively [24–26].

![Photoluminescence spectrum for ZnO arrays grown with PEI. PL intensities normalized to near band edge (NBE) peak at 380 nm.](image)

Figure 3-5. Photoluminescence spectrum for ZnO arrays grown with PEI. PL intensities normalized to near band edge (NBE) peak at 380 nm.

### 3.3.2 Effect of changing template hole size on nanowire yield

Figure 3-6 shows the measured nanowire yield versus template hole diameter for the eight experimental conditions tested in this study. The nanowire yield for each array is given as a percentage of the 225 patterned holes from which nanowires grew. For all substrates and conditions, the nanowire yield increased as template hole diameter increased. We postulate two possible reasons for this behavior. The first reason is simply that as holes became smaller, the possibility that the lithographic process produced fully open holes decreases. When template
holes are very small, precision in electron dosage and resist development needs to be high in order to result in maximum number of opened template holes. Therefore, as hole size decreases, the likelihood that holes are opened, exposing the seed layer to growth solution, decreases as well. Second, seed orientation may play a part in decreasing nanowire yield. Because seeds are randomly orientated with respect to the substrate, they may be hindered by the thickness of the resist if they are sufficiently tilted away from the substrate normal. This is supported by the fact that the yield was higher on Si substrates vs. ITO substrates (due to lower surface roughness), for sputtered vs. spincoated seed layers (due to more highly textured seeds with c-axis pointing normal to the substrate), and for annealed vs. unannealed seed layers (also due to seed layer texturing after the annealing process).

Figure 3-6. Nanowire yield vs. template hole diameter for (a) ITO and (b) Si substrates under different seed layer processing conditions.
3.3.3 Effect of changing template hole size on branching

![Graphs showing the effect of changing template hole size on branching](image)

Figure 3-7. Percentage of non-branched nanowires and alignment vs. template hole diameter. (a) and (b) Percentage of non-branched nanowires as a function of template hole diameter for spincoated and sputtered seed layers respectively. Percentage data points are plotted for each templating hole array of each respective measured templating hole diameter falling in the specific bin. (c) and (d) Plots of the order parameter $S$ as a function of template hole diameter for spincoated and sputtered substrates respectively. Each data point is the average $S$ for all of the
Branching is detrimental to PV charge collection because having multiple nanowires emerge from a single template hole negates the precise placement of individual nanowires engineered in the template. Additionally, branched and misaligned wire growth can reduce the QD volume in the film and generate voids in the film due to poor QD infiltration during the QD deposition process. Therefore, understanding and controlling nanowire branching and alignment is critical for future development of nanowire-based QD PV devices.

Figures 3-7a and b show the frequency of non-branching nanowires versus the measured template hole size. We varied the template hole diameter between 50 and 100 nm, a length scale challenging for many lithographic techniques. For clarity, spincoated (Figure 3-7a and c) and sputtered (Figure 3-7b and d) seed layers are separated, and templating hole diameters are binned in 10-nm intervals. In general, the frequency of branching can be controlled over the whole range of 0 - 100% and we define >90% non-branched as an optimized array. Branching trends are similar for both sputtered and spincoated seed layers. A range of template hole sizes results in arrays that have low enough branching to be acceptable for device fabrication, but we always observe a decrease in branching as hole size decreases. Arrays on spincoated and sputtered seed layers behave differently when annealed – branching increases after annealing for spincoated seed layers (Figure 3-7a), whereas the opposite is true for sputtered seed layers (Figure 3-7b). We attribute this effect to two effects: mutual impingement and template confinement. These will be elaborated on subsequently.
3.3.4 Effect of changing template hole size on alignment

Figures 3-7c and d display plots of order parameter, $S$, versus the measured template hole size. We observed two different trends depending on the nature of the seed layer: for spincoated seed layers (Figure 3-7c) the order parameter ranges from 0.5 to 0.9, whereas for sputtered seed layers (Figure 3-7d) the variation is much smaller, ranging from 0.65 to 0.98. For spincoated samples, nanowire alignment improves with increasing hole diameter, whereas there is little variation in alignment with changing hole diameter for sputtered samples.

3.3.5 Effect of annealing and template hole size on morphology

In addition to the strong effect that the size of the template hole has on array characteristics, annealing generally results in better nanowire alignment, although annealing increases branching in spincoated seed layers. Figure 3-7c shows that annealing spincoated seed layers results in more aligned nanowires. Figure 3-7d shows that annealing the sputtered seed layer on ITO/glass substrates only slightly affects alignment, which can be attributed to the already excellent alignment of the unannealed sputtered seed layer [7].

The results show that template hole size and annealing have a strong impact on branching and alignment. Branching has been shown to be affected by growth temperature [3] and concentration [27], seed alignment [4], seed density [8], seed nucleation and growth [28], and template hole size [29]. We suggest that the size of ZnO grains in the seed layer is the underlying factor that leads to the observed influence of template hole size and annealing on nanowire growth. As the template holes are expected to be larger than the ZnO grains in the seed layer, the number of exposed ZnO grains, and therefore the prevalence of branching, is a function of the
respective sizes of the template hole and exposed ZnO grains. A precise measurement of ZnO grain sizes in the seed layer is thus necessary.

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<td>Annealed</td>
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Figure 3-8. HIM and AFM micrographs of ZnO seed layers on Si before hydrothermal growth. Grayscale and colored images are HIM and AFM micrographs, respectively. Thermal annealing (bottom row), as opposed to no annealing (top row), increases the grain diameter. The diameters were measured from HIMs as (mean ± standard deviation) (a) 7.5±2.0, (b) 39.6±23.3, (c) 21.7±8.9, and (d) 51.2±16.1 nm. All scale bars and vertical AFM scales are identical.

Figure 3-8 shows that seed layer grain size increases after annealing for both sputter-coating (from 39.6 ± 23.3 to 51.2 ± 16.1 nm) and spincoating (7.5 ± 2.0 to 21.7 ± 8.9 nm). Template hole diameters typically range from 40 – 120 nm, which is larger than the grain diameters and thus multiple grains are exposed to the hydrothermal growth solution. Therefore, nanowire branching is reduced as the template hole diameter decreases because fewer ZnO grains are exposed to the growth solution. Annealing reduces overall branching for sputtered seed layers by increasing the ZnO grain size, though this does not apply to spincoated seed layers because the ZnO grains are much smaller than in sputtered seed layers. To explain increased
branching for spincoated seed layers after annealing, we discuss the twofold effect of annealing in increasing grain size and enhancing seed layer alignment below.

Isolating the factors that explain the observed trends in alignment is more challenging because alignment is affected not only by the number of exposed grains, but also by seed layer texturing. In seeded growth, nanowires grow directly from the c-planes of individual ZnO grains in the seed layer, and therefore the texture of grains in the seed layer significantly alters the final nanowire alignment. ZnO films used as seed layers are typically annealed to improve their c-plane texturing with respect to the substrate [30,31], which is in agreement with our results where annealing generally improves nanowire alignment.

Figure 3-9. Density effects on impingement. Two HIM micrographs showing that branching leads to better alignment through nanowire crowding.

Furthermore, the prevalence of branching also changes nanowire density, which can affect alignment. Misaligned nanowires tend to impinge mutually and/or grow into the PMMA template sidewalls, preventing further growth and leaving only nanowires growing normal to the substrate [11]. We observe this effect in Figure 3-9, which shows two nanowire arrays grown on sputtered seed layer with different densities achieved by annealing sample (a) and not annealing...
The annealed sample shows the lower nanowire density as expected due to grain growth in the seed layer causing fewer seeds exposed per template hole. Although we expect better alignment in the annealed sample, nanowires are more misaligned in this sample due to the effect of nanowire density. We observe that alignment is a function of template hole diameter in samples with substantial nanowire branching and poor seed layer texturing, such as in spincoated seed layers (Figure 3-7c). As annealing improves grain alignment in highly misoriented spincoated seed layers, fewer nanowires impinge into PMMA sidewalls, causing branching to increase as more nanowires are able to grow vertically. This relationship suggests that the dependence of the order parameter on template hole diameter and branching are actually mutually related, especially for spincoated seed layers where the grain sizes, whether annealed or unannealed, are much smaller than the template hole diameters. On the other hand, the effect of nanowire density on order parameter is less pronounced in sputtered samples where seed layer texturing has already been enhanced (Figure 3-7d) and we therefore suggest nanowire density is too low for mutual impingement to have an effect. Finally, annealing also has the added effect of increasing the grain size and decreasing the nanowire density, which is in turn detrimental to nanowire alignment [32]; this could explain the marginally poorer alignment in annealed sputtered seed layers on ITO compared to unannealed seed layers (Figure 3-7d).

3.4 Conclusion

In conclusion, we show that lithographic masks can be used for high-resolution templated hydrothermal growth of ZnO nanowires and that the tested process parameters (substrate type, seed layer deposition, annealing, and template hole size) can control branching and nanowire alignment. We found that a well aligned ZnO nanowire array suitable for use in PV devices
could be templated on an ITO/glass substrate on an annealed spincoated seed layer. This is the first example of EBL-templating of ZnO nanowires at high-resolution pitches suited to QD-based PV devices. Future research can pair larger ZnO seed layer grains with transparent or flexible substrates and take advantage of parallel lithographic approaches such as nano-imprint lithography [33], self-assembled microspheres [34] or low-cost optical interference lithography [35]. Beyond ZnO nanowire QD PVs, this work is widely applicable in other fields, such as nanomechanical energy generators, surface-energy engineering, nanowire transistors, and templated growth of other inorganic nanowires [36–39].
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CHAPTER 4

Dimension Tailored ZnO Nanowire Arrays

This chapter is adapted with permission from Ref [1]:

Abstract

Hydrothermally-synthesized ZnO nanowire arrays are critical components in a range of nanostructured semiconductor devices. The device performance is governed by relevant nanowire morphological parameters that cannot be fully controlled during bulk hydrothermal synthesis due to its transient nature. Here, we maintain homeostatic zinc concentration, pH, and temperature by employing continuous flow synthesis and demonstrate independent tailoring of nanowire array dimensions including areal density, length, and diameter on device-relevant lengthscales. By applying diffusion/reaction-limited analysis, we separate the effect of local diffusive transport from the c-plane surface reaction rate and identify direct incorporation as the c-plane growth mechanism. Our analysis defines guidelines for precise and independent control of the nanowire length and diameter by operating in rate-limiting regimes. We validate its utility by using surface adsorbents that limit reaction rate to obtain spatially uniform vertical growth rates across a patterned substrate.
4.1 Overview

Process scalability is particularly pertinent to photovoltaic device applications because large device areas are required to maximize insolation capture. For this reason, electron-beam lithography (EBL), with which we demonstrated precisely spaced aligned ZnO nanowire arrays in Chapter 3, is less viable as a photovoltaic processing technique. EBL is a serial process, meaning that patterning time increases linearly with device area thereby greatly reducing throughput at commercial scales. The strength of EBL lies in its deterministic nature such that template holes can be placed at the pre-defined locations and with sizes on the order of 50 nm. While this makes EBL excellent for investigation of device properties up to the millimeter scale, even laboratory scale photovoltaic devices have dimensions of at least several millimeters, making EBL prohibitive in terms of processing time and cost (Figure 4-1). As discussed in Chapter 3, template features should ideally be smaller than 70 nm to achieve > 90% unbranched nanowires. We therefore extended our analysis to control nanowire spacing and seed size using spincoating: a bottom-up technique that does not provide deterministic positioning of the nanowires, but is both scalable and time efficient.

![Figure 4-1. Top-view schematic of typical laboratory scale photovoltaic device patterned ITO electrode on glass illustrating difference in patterning time for spincoated seed layers vs. EBL](image)

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While sol-gel spincoating of continuous ZnO seed layers has successfully produced well-aligned, dense nanowire arrays, sparse seed layers (where seeds are not mutually contacting) have been less frequently investigated on device-relevant substrates because of their comparatively poorer alignment. This is because the mutual impingement effect that produces well-aligned nanowire arrays on dense seed layers is comparatively weak in low areal density nanowire arrays grown from sparse seed layers. Sparse seeds thus rely on a high-temperature annealing step to align seed crystals with their c-axis normal to the substrate, but substrates such as ITO and polymers are not amenable to temperatures above ~ 200 °C. Furthermore, poor uniformity such as streaks and concentric circles arising from the spincoating process are particularly obvious on sparse seed layers. Nevertheless, spincoating remains attractive for photovoltaic applications for its simplicity, robustness, and time-efficiency; the engineering challenges highlighted above could be overcome by careful optimization of the process.

We now turn our attention to the hydrothermal growth process. Hydrothermal synthesis has recently emerged as a scalable alternative to vapor-phase techniques [2] for producing vertically-aligned ZnO nanowire arrays [3,4] with excellent crystal quality at the wafer scale [5–8] and on a range of substrates, under relatively benign temperature and pH conditions. Growth [5,9–12] and seeding conditions [6,8,13] have been used to achieve limited variation of nanowire length, diameter, and areal density. However, future applications will require simultaneous tailoring of multiple device-dependent critical dimensions, while selected area growth (SAG) of ZnO nanowire arrays [14–17] reinforces the need for uniform growth rates over an entire substrate despite varying pattern fill factor [18,19]. The growth rate in regions with varying nanowire areal densities can vary significantly because of the reactant diffusion [20] that,
coincidentally, varies on similar lengthscales (100 nm – 1 μm) as those required for mediating light and charge interaction.

ZnO nanowire arrays are currently optimized via a time-consuming empirical approach, often termed “cook-and-look”, where the desired nanowire morphology is obtained through an iterative growth-characterization loop during bulk synthesis [21]. To transform the nanowire growth into a more deterministic process, it is critical to identify both the dominant growth mechanisms and the effect of diffusive transport vs. reaction. In particular, identifying the c-plane growth mechanism is important for controlling the nanowire growth rate [11], impurity interaction [22,23], and dopant incorporation [24]. We covered in Section 2.3 determination of solution-phase crystal growth mechanisms by observing the facet growth rate-supersaturation relationship [25–28] or special surface features [9,20,29–31]. Applying this approach to ZnO requires constant Zn²⁺ and OH⁻ concentrations, but typical bulk synthesis [5,7,21] – where a solution containing fixed amounts of reactants is sealed and heated – is unsuitable because reactant supersaturation decreases during growth due to consumption. Despite efforts to account for variation of reactant supersaturation during growth [6,27,32], identifying the growth mechanism has been challenging [11,21,29,30], mostly due to diverse Zn²⁺ speciation [11,29,33]. In contrast, continuous flow (CF) synthesis maintains homeostatic reactant supersaturation [26,34], which makes it ideal for rigorous investigation, and ultimately control, of the nanowire growth mechanisms.

Even if the global reactant concentration is kept constant, the local environment of individual nanowires has to be considered because the reactant concentration may vary spatially
in the vicinity of different nanowires [12]. The effect of diffusive reactant transport on morphology has often been invoked, albeit qualitatively [5,20,32,35]. Boercker et al. [36] showed that nanowire length varied as the inverse square root of nanowire density when operating in a diffusion-limited growth regime, and Lee et al. [12] observed Gibbs-Thomson effects in nanowire arrays with non-uniform diameters. It is thus necessary to make a distinction between the nanowire growth behavior observed in sparse vs. dense nanowire arrays (i.e. arrays grown using discrete seeds vs. mutually contacting seeds, respectively), since reactant transport to nanowire growth planes may obscure the actual growth rate variation with respect to the reactant concentration measured in the bulk solution.

In this study, we approach dimensional tailoring of ZnO nanowire arrays by first formulating a method to separate the effects of diffusive transport and reaction rate on observed nanowire growth rate. We used dynamic deposition spincoating as a robust, scalable method to vary nanowire areal density, achieving large area uniformity while maintaining excellent vertical alignment. In contrast to previous studies, we show that c-plane growth rate depends on the total area ratio of c-plane exposed to solution, which is particularly pertinent to nanowire growth on sparse or patterned seed layers. We applied a diffusion/reaction-limited analytical model to separate the effects of diffusion and reaction, helping us to identify the direct incorporation growth mechanism relevant for ZnO nanowire c-planes. The diffusion/reaction-limited model further yields a set of design guidelines for obtaining uniform nanowire growth rates by choosing synthesis conditions that are stable and rate-limiting. We demonstrate that surface adsorbent-limited growth using citrate ions gives homogeneous c-plane growth rates irrespective of the nanowire spacing (i.e. areal density), which we precisely define using electron-beam lithography.
These design guidelines account for the interplay between transport and reaction, and will greatly facilitate bottom-up design of solution-phase processes for low-dimension metal oxide nanocrystal growth.

4.2 Experimental methods

4.2.1 Seeding

Si (100) or (111) substrates were cleaned for seeding with (1) DI rinse, (2) 10 min sonication in acetone, (3) 10 min in boiling IPA (4) 10 min in piranha solution (5) DI rinse, and dried with N₂. Spincoated seed layers were deposited from a sol-gel solution consisting of 1:1 zinc acetate (99.999%) to monoethanolamine in 2-methoxyethanol (all chemicals from Sigma-Aldrich). Dense seed layers were deposited with a 0.3 M seed solution at 4000 rotations per minute (rpm) and annealed at 150 °C in air; this process was done twice to yield a ~30 nm thick seed layer. To obtain sparse seed layers, dynamic deposition was used: 50 µL of a 0.01 M seed solution was dispensed onto the substrate once it had reached the targeted spin speed. The substrate was then annealed at 400 °C in air. Sputtered seed layers were RF deposited on an AJA Orion 5 at 3 mTorr, 12 sccm Ar, 100 W.

4.2.2 Continuous flow vs. bulk hydrothermal synthesis

We constructed a continuous flow (CF) growth reactor capable of constantly replenishing growth solution in a chemical bath (Figure 4-2a) in order to achieve homeostatic conditions compared to bulk synthesis (Figure 4-2b). Substrates were suspended in a chamber with a
reaction volume of 125 cm$^3$. To achieve homeostatic conditions, dedicated peristaltic pumps and Teflon tubing were used to prevent the feed solutions from being contaminated by contact with any external parts of the setup. Feed solutions were prepared with MilliQ deionized water (18.2 MΩ.cm), zinc nitrate hexahydrate ($\geq$99.0%, Sigma-Aldrich) and hexamethylene tetramine (HMTA, $\geq$99.5%, Sigma-Aldrich). HMTA was used as the hydroxide source for its excellent pH stability [9,37] between 4 – 5. Individual pump rate was $\sim$ 4 cm$^3$ min$^{-1}$. For a reaction volume of 125 cm$^3$, complete exchange of growth solution took place approximately every 16 min.

![Diagram](image)

Figure 4-2. CF synthesis. (a) A schematic of the CF reactor showing heated zinc nitrate and HMTA source solutions, separate peristaltic pump lines, vertically suspended substrate, micropipette aliquot removal for Zn$^{2+}$ concentration measurement and thermocouple position. (b) Growth solution Zn$^{2+}$ concentration and temperature vs. time. The Zn$^{2+}$ concentration, measured by inductively coupled plasma – atomic emission spectroscopy (ICP-AES), and temperature are plotted for a 160 min period with initial 40 min stabilization and 120 min growth time. Shaded and unshaded symbols represent CF and bulk synthesis measurements respectively.
One of the novelties of our setup lies in using the hydraulic gradient generated by pump inflow to drain the growth solution, instead of relying on an eluent pump, as is the case for other CF reactors. (As it is challenging to precisely measure and control pump rate, inlet and outlet pumps are frequently imbalanced, causing fluctuations in the reaction volume [34]) Fluctuations in reaction volume are detrimental to the stability of the reaction environment. In our reactor setup, the inlet and outlet flows are equal and therefore the reaction volume is stable. Furthermore, the mouth of the outlet line is positioned in the center of the reaction vessel, and therefore the chemical composition of the inlet and outlet flows can also be assumed to be equal. The solution was stirred at 180 rounds/min with an 8 mm magnetic stirbar.

These design considerations allowed us to achieve an error in Zn$^{2+}$ concentration of $< 0.5$ mM and an error in temperature of $< 1$ °C over the course of the typical growth (Figure 4-2b). There were also no substantial flow effects as nanowire growth was uniform over the full $\frac{1}{2}$" square substrate. Up to three substrates can be grown at the same time and substrates can be inserted or removed at any time during the growth.

Bulk synthesis was carried out at a 1:1 zinc nitrate to HMTA ratio at 2.5 mM, with 20 mg in 3 ml of polyethyleneimine added. Zn$^{2+}$ concentration was measured by taking filtered aliquots that were characterized with inductive coupled plasma-atomic emission spectroscopy (ICP-AES), on a HORIBA Jobim Yvon ICP-AES with zinc standard samples ($1000 \pm 1$ ppm, Sigma-Aldrich) at the 202.551 nm peak. Seeded substrates underwent a 1 min O$_2$ plasma clean and were immersed after the growth solution had equilibrated for 40 min. After growth, the substrate was removed, rinsed with DI water, and blown dry with N$_2$. Imaging was performed on an FEI Helios
scanning electron microscope (SEM) on both top-down and cleaved cross-sectional nanowire arrays. Electron-beam lithography was carried out on an Elionix ELS-F125 system at 125 kV accelerating voltage, 0.2 pA current, and 0.16 – 0.8 μs nm⁻² dwell time.

### 4.2.3 Image analysis

![Image](image.png)

Figure 4-3. Measurement of nanowire array metrics (a) Measured nanowire array height vs. distance from a substrate edge. (b) Labelled nanowires from a top-down SEM image, for calculating non-dimensional c-plane area ratio defined in the main text.

To reduce selection bias, nanowire properties were measured at different positions on the substrate. Nanowire array height was measured from cross-section SEM images. Images were taken every 500 μm along the cleaved substrate, giving us 15 to 20 data points across the ½” substrate (Figure 4-3a). In general, nanowire array height was uniform across the substrate with a standard error of less than 10%. Several samples showed an edge effect (increased nanowire height at the substrate edges) which we attribute to accumulation of seed solution during spincoating. For these samples, data points within 1 mm of the substrate edge were neglected.
Nanowire density was measured by taking SEM images at 50000× magnification at three different positions on the surface. Nanowires were labeled, counted, and their diameter measured using ImageJ (Figure 4-3b). The diameters of > 100 nanowires were measured at each position on the surface giving a total sample size of > 300 nanowires for each sample. The c-facet area was calculated by assuming hexagonal cross sections for the nanowires and calculating the mean nanowire c-facet area from the mean diameter measurements. The mean nanowire c-facet area was then multiplied by the nanowire density to give a non-dimensional c-plane area ratio.

4.3 Results and discussion

4.3.1 Areal density control with dynamic deposition spincoating

We dispersed ZnO seeds uniformly and controllably over the substrate surface using dynamic spincoating of the zinc acetate sol-gel seed solution. This involved dispensing the seed solution onto a substrate that had already been ramped to the final spin speed; the seed solution was observed to immediately cover the full substrate. The final spin speeds used varied from 2000 – 10000 rpm, which are achievable on most common semiconductor processing spincoaters. To achieve a high degree of reproducibility, the spincoating was performed in a nitrogen glovebox (H2O < 0.1 ppm) to regulate the solvent evaporation rate due to its controlled humidity. The seeded substrates were subsequently annealed in ambient atmosphere on a 400 °C hotplate to achieve vertical texturing. Discrete ZnO seeds were imaged using SEM and the seed density was measured from three different regions on the substrate to ensure uniformity: Figure 4-4a – d shows that discrete ZnO seeds were controllably and uniformly dispersed over the substrate surface.
Figure 4-4. Seed layer deposition. (a – d) SEM images of density-controlled ZnO seeds on Si substrate showing their uniform distribution. As the spin speed increases, the seed density decreases. (e) Dense seed layer deposited by spincoating produces closely packed seeds ~ 10 nm in diameter. (f) Dense seed layer deposited by sputtering produces seeds 20 – 30 nm in diameter. All micrographs at same scale.
Dynamic deposition spincoating causes seed dewetting and the subsequent high temperature annealing forms discrete ZnO seeds of ~5 nm diameter (Figure 4-5a, inset), with seed densities that decrease controllably over an order of magnitude with increasing spin speed (Figure 4-5a). Hydrothermal synthesis of ZnO nanowire arrays from these sparse seed layers yielded arrays aligned normal to the substrate (Figure 4-5c–f), indicating that the seeds were well aligned with the c-axis normal to the substrate [38] due to the high temperature annealing step [8]. The order parameter is greater than 0.85 for all the nanowire arrays shown in this study.

Figure 4-5. Control over areal density of ZnO nanowire arrays. (a) Seed density vs. spincoating speed. Control of ZnO seed density between $4 \times 10^{10}$ to $1.7 \times 10^{12}$ cm$^{-2}$ by varying a 10 mM sol-gel seed solution spincoating speed from 2000 to 10000 rpm. Error bars are standard error and omitted where smaller than the symbol size. Inset: SEM image showing discrete ZnO seeds ~5 nm in diameter on Si (100) substrate. (b) Linear relationship observed between nanowire density and seed density; nanowire density is about two orders of magnitude lower than seed density. Dashed line is a guide to the eye. (c) – (f) Cross sectional SEM images of density-controlled ZnO
nanowire arrays. nanowire arrays grown on Si(100) substrates at $[\text{Zn}^{2+}] = 10 \text{ mM}$, 90°C for 60 min on seed layers spincoated at 4000, 6000, 8000 and 10000 rpm, respectively. All micrographs at same scale.

Sparse and dense ZnO seeded Si substrates were subjected to hydrothermal synthesis in a homebuilt continuous flow reactor that maintains homeostatic reactant concentration and temperature growth conditions (Figure 4-2). For the pH range 4 – 5 and zinc concentrations between 5 – 20 mM, speciation plots show that the dominant zinc species in the growth solution was $[\text{Zn(H}_2\text{O)}_6]^{2+}$ (Figure 2-6). We obtained well-aligned, uniform nanowire arrays comparable to those grown using bulk (non-homeostatic) synthesis, producing both sparse and dense ZnO nanowire arrays (Figure 4-5c – f). On density-controlled sparse arrays, nanowire density varies linearly with the seed density (Figure 4-4b), indicating a narrow seed grain size distribution [39]. The nanowire density is two orders of magnitude lower than the seed density, which we attribute to the seed dissolution-growth equilibrium in the initial stages of growth [35,39].

Based on the range of nanowire densities obtained and shown in Figure 4-4b, we were able to control average nanowire spacing between 70 – 600 nm. The capability to change nanowire spacing in this range (100 nm – 1 μm) [40,41] is key to enhancing QDPV device performance; it also has practical importance because nanowire density affects the net consumption of Zn$^{2+}$ growth units, which in turn has an impact on the local Zn$^{2+}$ concentration at the crystal-solution interface and thus nanowire $c$-plane growth rate.
4.3.2 Reaction vs. diffusion rates in nanowire array growth

Figure 4-6. Diffusion/reaction-limited analysis applied to ZnO nanowire growth. Top down SEM images of (a) high and (b) low nanowire density arrays with similar c-plane area ratios $S$, shaded in yellow. (c) c-plane growth rate vs. c-plane area ratio. High (A) and low (B) nanowire density arrays (shown in (a) and (b), respectively) are indicated. The crossover from reaction-limited to diffusion-limited growth (dashed line) takes place at $S = 0.11$. Error bars are standard error and omitted where smaller than the symbol size. (d) Schematic showing serial processes of diffusion and reaction in the vicinity of the nanowire array growth front. Zn$^{2+}$ diffusion (dotted arrow), adsorption, and subsequent incorporation (solid arrow) into nanowire top faces (c-plane). The local variation in Zn$^{2+}$ concentration in the vicinity of the c-facets is shown for diffusion- and reaction-limited growth scenarios (left and right inset, respectively). Arrow thickness represents process rate; thinner arrow refers to a “slow” process.

To identify the effects of changing growth parameters on the nanowire arrays, we quantified nanowire length, diameter, and array density from multiple regions on the substrate (Section 4.2.3). Notably, we found that the c-plane growth rate does not increase with decreasing nanowire density per se (as previously found for dense seed layers and by assuming nanowires with the same facet area [35,36]), but rather with the total area ratio of c-planes exposed to
growth solution (Figure 4-6a – c). To quantify the total area of the growing crystal facet, we defined the unitless c-plane area ratio \( S \), given by:

\[
S = \rho A
\]

where \( \rho \) is the nanowire areal density (cm\(^{-2}\)) and \( A \) is the mean nanowire c-facet area (cm\(^2\)). This value gives an instantaneous measurement of the area ratio of substrate consisting of c-planes upon which Zn\(^{2+}\) growth units are impinging (Figures 4-6a and b).

To fully investigate this phenomenon throughout parameter space, we grew a total of 40 substrates encompassing a range of growth and seeding parameters. Sparse seed layer density was varied from \( 4 \times 10^{10} \) cm\(^{-2}\) to \( 1.7 \times 10^{12} \) cm\(^{-2}\), and dense seed layers deposited by spincoating or sputtering (Figures 4-4e and f) were also used to eliminate any possible effects of the seed deposition method [42]. All samples were grown at \([\text{Zn}\,^{2+}] = 10 \) mM and temperature of 90 °C to ensure identical reactant transport conditions. The c-plane growth rate increases with decreasing \( S \) (Figure 4-6c), \textit{i.e.} nanowire arrays with less total c-facet area exposed to growth solution grow faster than those with greater c-facet area. Interestingly, nanowire density does not affect the growth rate; both sparse and dense arrays show the same behavior such that nanowire arrays with the same c-plane area ratio \( S \) have similar c-plane growth rates. Therefore, a dense array of thin nanowires (Figure 4-6a) grows at the same rate as a sparse array of thick nanowires (Figure 4-6b), since they have similar \( S \) (points A and B, respectively, in Figure 4-6c). To extend the range of accessible \( S \) values, five samples were grown with various concentrations of added Al\(^{3+}\) up to 0.1 mM and six samples were grown with added Mg\(^{2+}\) up to 0.08 mM, both of which inhibit m-
plane growth [11] and yielded nanowire arrays with \( S \) below 0.1. This allowed us to confirm that the relationship between growth rate and \( S \) extends to \( c \)-plane area ratios down to \( S = 0.02 \), the lowest value measured in our work.

To explain this relationship, we adapted the diffusion/reaction-limited analysis [36] that relates the serial processes of consumption of \( \text{Zn}^{2+} \) growth units at the \( \text{ZnO} \) crystal growth front, parameterized by \( c \)- and \( m \)-plane growth rates, and \( \text{Zn}^{2+} \) diffusive transport from the bulk solution (Figure 4-6d). We modified the model by combining \( m \)-plane growth rate and nanowire density under the \( c \)-plane area ratio \( S \) (as derived in Chapter 2) to obtain the following equation:

\[
R_{c\text{-plane}} = \frac{k_1 C_\infty}{\rho (\phi + 1)} = \frac{k_1 C_\infty D}{\rho D + \rho \delta k_1 S} ; \quad \phi \equiv \frac{k_1 S \delta}{D}
\]  

where \( R_{c\text{-plane}} \) is the \( c \)-plane growth rate, \( k_1 \) is the surface reaction rate for dehydration of \( [\text{Zn(H}_2\text{O)}]^2+ \) (surface adsorbed) to \( \text{ZnO} \) (crystal), \( \rho \) is \( \text{ZnO} \) molar density \( (4.20 \times 10^{28} \text{ m}^{-3}) \), \( C_\infty \) is the bulk solution concentration of \( \text{Zn}^{2+} \), \( D \) is the \( \text{Zn}^{2+} \) aqueous tracer diffusion coefficient \( (2.91 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}) \) [43], \( \delta \) is the stagnant layer thickness (the thickness of fluid adjacent to the substrate surface without flow and with only diffusive transport), and \( S \) is the \( c \)-plane area ratio.

Since \( c \)-plane growth rate \( R_{c\text{-plane}} \) and \( c \)-plane area ratio \( S \) are readily available from the experimental measurements, we take the reciprocal to obtain a relationship that is linear with \( S \), to facilitate fitting:
The reciprocal growth rate versus c-plane area ratio is shown in Figure 4-7 for the nanowire arrays grown with CF synthesis at [Zn$^{2+}$] = 10 mM and 90°C shown in Figure 4-5a – c. Fitting the data using Equation (3) yields an $R^2$ of 0.9161, a surface reaction rate $k_1 = 3.19 \times 10^{-6}$ ms$^{-1}$ and stagnant layer thickness $\delta = 1.6 \times 10^{-2}$ m. $\delta$ is higher than expected [36] (around $10^{-3}$ m) likely because the stagnant layer model used for this calculation assumes diffusive reactant transport, and does not take into account advective transport. A more precise reactant transport model would take into account advective flux, but such analysis is technically challenging since no analytical solution is available [44].

$$\frac{1}{R_{c\text{-plane}}} = \frac{\rho}{k_1 C_\infty} + \frac{\rho \delta}{C_\infty D} S$$

(3)

Figure 4-7. Reciprocal c-plane growth rate vs. c-plane area ratio. Experimental data for c-plane growth rate and c-plane area ratio are shown along with linear (blue) and allometric (green) fits to the data. Error bars are standard error and omitted where smaller than symbol size.

To check that the data was indeed linear, we also used a power law fit ($y = Ax^B + C$), shown in Figure 4-7. We determined a slight deviation from linearity – the exponent obtained
from fitting was 0.86 ± 0.15, which could also be due to discrepancies in the reactant transport model. The exponent $B$ could thus be taken as an ideality factor to determine to what degree reactant transport was diffusive, with an ideal value of 1. Despite this slight deviation, both the linear and allometric fits had fairly high $R^2$ values and similar fitting parameters, giving us confidence in using this model to explain our data.

Having validated our model, we now turn our attention to its practical implications for growth control. The Thiele modulus $\phi$ measures the ratio of surface reaction rate to reactant diffusion to the crystal growth front – since they are serial processes (Figure 4-6d), $\phi$ determines the degree to which growth is reaction- or diffusion-limited. By solving the Thiele equation for $\phi = 1$, the $S$ value for which the growth regime changes from reaction-limited to diffusion-limited can be determined. In our case ([Zn$^{2+}$] = 10 mM at 90 °C), this crossover point is at $S = 0.11$, as depicted in Figure 4-6d. Therefore, when the c-plane area ratio is above 0.11, the large area of c-planes at which reactants are being incorporated cause the growth rate to be constrained by reactant transport to the nanowire growth front (Figure 4-6d left inset). However, growth of nanowire arrays with a c-plane area ratio below 0.11 is reaction-limited, i.e. transport of reactants to the nanowire growth front is faster than incorporation of reactants (Figure 4-6d right inset).

We next show the utility of this analysis in two applications: (1) fundamentally, we extract the actual variation in c-plane growth rate with Zn$^{2+}$ concentration and demonstrate that the c-plane grows by the direct incorporation mechanism; (2) practically, we achieve excellent nanowire height uniformity over an electron-beam lithography patterned nanowire array with a graded pitch by inducing reaction-limited nanowire growth with c-plane citrate adsorbents.
4.3.3 Identifying the c-facet growth mechanism

As mentioned above, measuring the c-facet growth rate as a function of supersaturation would allow unique identification of the growth mechanism. However, changing the Zn$^{2+}$ concentration causes the diffusion environment to change because nanowire density and diameter also increase with Zn$^{2+}$ concentration. Therefore, the individual contributions of each process (diffusion vs. reaction) to measured c-plane growth rate are indistinguishable. The diffusion/reaction analysis gives us a tool to separate these two processes, effectively accounting for the effect of variation in $S$ on measured c-plane growth rates as Zn$^{2+}$ concentration is changed. In practice, we remove the effect of diffusion by multiplying the measured c-plane growth rate $R_{c\text{-plane}}$ by $S$. This leaves the desired relationship between solely reaction rate and Zn$^{2+}$ supersaturation, which we term the diffusion-corrected growth rate ($R_{c\text{-plane}} \times S$). In doing this normalization, we assumed that growth took place in the diffusion-limited regime ($\phi \gg 1$), which is plausible due to high values of $S$ (between 0.2 to 0.6), as shown in Equations 4 and 5.

\[
R_{c\text{-plane}} \approx \frac{k_1 C_\infty}{\rho \phi} = \frac{C_\infty D}{\rho \delta S} \tag{4}
\]

\[
R_{c\text{-plane}} S = \frac{D}{\rho \delta} C_\infty \tag{5}
\]
Figure 4-8. Identifying the c-plane growth mechanism. (a) Diffusion-corrected c-plane growth rate vs. Zn$^{2+}$ concentration. Results from twenty growth runs are binned in 5 mM intervals for clarity. Error bars omitted where smaller than the symbol size. A linear fit to the data is shown in red. The calculated growth rate for layer-by-layer mechanism (gray) is a poor fit to the experimental results due to the exponential relationship with supersaturation. (b) SEM image showing a typical roughened nanowire top face.

We grew 36 nanowire arrays at Zn$^{2+}$ concentrations between 5 – 20 mM on sparse and dense spincoated and sputtered seed layers. The diffusion-corrected c-plane growth rates of these arrays show a linear relationship with Zn$^{2+}$ concentration (Figure 4-8a), indicative of growth by direct addition of Zn$^{2+}$ growth units to the c-plane. The direct incorporation growth rate given by classical crystal growth theory [28] is:

$$R_{c-plane} = a v \left(\frac{a}{d}\right)^2 v_{atom} e^{-\frac{\Delta U}{kT}} (C_{\infty} - C_{eqm})$$

where $a$ is the unit cell dimension (3.2 Å), $d$ is the distance between kink sites (32 Å)[28], $v$ is the vibration frequency (10$^{13}$ Hz), $v_{atom}$ is the Zn$^{2+}$ hydrated volume (74.01 Å$^3$)[45], $\Delta U$ is the Zn$^{2+}$ dehydration barrier, $kT$ is available thermal energy (3.02 kJ/mol at 90°C), and $C_{eqm}$ is the
equilibrium Zn$^{2+}$ concentration. Fitting our data with Equation (6) (Figure 4-8a) gives a Zn$^{2+}$ dehydration barrier of $\Delta U = 65$ kJ/mol, which is in the range of dehydration barrier values for transition metal ions (40 – 80 kJ/mol, depending on aqueous charge and size, among other factors [28]). Together with speciation calculations (Figure 2-6), this result strongly suggests that it is indeed the [Zn(H$_2$O)$_6$]$^{2+}$ species crystallizing on the c-facet. We also considered the layer-by-layer (LBL) growth mechanism by calculating the growth rate [26] as a function of Zn$^{2+}$ concentration (Figure 4-8a), but it varies non-linearly and greatly overestimates the c-plane growth rate at higher Zn$^{2+}$ concentrations.

We further bolster our experimental results by recalling that the diffusion/reaction-analysis (Equation (2)) also shows a linear relationship between c-plane growth rate ($R_{c-plane}$) and Zn$^{2+}$ concentration ($C_o$). Using Equation (5) for the case of diffusion-limited growth, we calculate the expected gradient $\frac{D}{\rho \delta}$ of $4.33 \times 10^{-36}$ m$^4$ s$^{-1}$ for the growth rate-concentration plot, which is remarkably close to the experimentally determined value of $4.19 \times 10^{-36}$ m$^4$ s$^{-1}$. The close agreement between our experiments and values predicted by both macroscale reactant transport mechanisms as well as atomistic-scale classical crystal growth theory confirms that these analytical models accurately describe the ZnO nanowire growth system.

The linear relationship between growth rate and supersaturation is not uncommon in aqueous growth of other inorganic semiconductor crystals [28,46]. Discrete interface models [46–48] predict linearity at high supersaturation, where adatom surface diffusion becomes less significant than volume diffusion. In all these cases, growth units enter directly into kinks – crystal positions of high surface energy – that are present on the surface in high density. We
confirmed a high kink density by observing high $c$-plane surface roughness using high resolution SEM (Figure 4-8b), which has also been observed by others [7].

Identifying the $c$-facet growth mechanism means that the growth rate can be controlled by changing the $\text{Zn}^{2+}$ concentration. This result also has implications for interaction of the $c$-facet with impurities because dopant incorporation frequently takes place at the $c$-facet due to its higher surface energy compared to the $m$-facet [24,49]. Impurity adsorption also offers the opportunity for growth control through modification of the growth rate. The variation of facet growth rate with additive concentration strongly depends on the facet growth mechanism [22,50], and so this understanding will allow further tuning of growth rates via impurity addition, which we show next.

4.3.4 Impurity-mediated reaction limited growth for uniform arrays

Diffusion/reaction analysis suggests that growth under reaction-limiting conditions yields growth rates independent of the nanowire diffusion environment. To test this hypothesis, we used electron-beam lithography to define a set of nanowire rows with varied distances (Figure 4-9a – c) – thereby locally tuned nanowire environment – and used citrate ion adsorbents to achieve reaction-limited growth by limiting incorporation of $\text{Zn}^{2+}$ into the $c$-facet surface [51]. As can be seen in Figures 4-10a and b, each individual row of nanowires has a different local environment due to the graded row spacing – $S$ peaks towards the left of the array, where rows are most closely packed, and decreases as the pitch is increased.
Figure 4-9. Achieving uniform nanowire growth rates. (a) Cross sectional SEM images of nanowire arrays with graded pitch varying from 150 nm to 830 nm grown with increasing citrate concentration. Arrays grown at 1.25, 2.5, 5 and 7.5 μM citrate (artificially colored) are superposed on nanowire grown without citrate, showing decrease in nanowire length and greater uniformity with increasing citrate concentration. All growths performed with bulk synthesis: equimolar zinc nitrate and HMTA concentration of 2.5 mM, at 90°C for 100 min. (b) Top down SEM image of a typical patterned substrate. Example micrograph of the six arrays patterned on
each substrate and grown at a certain citrate concentration. (c) Top down SEM image of the cleaved edge (red arrows) of a substrate. The measured pitch between individual rows is as labelled. (d) Nanowire length for each citrate concentration vs. measured pitch. Error bars represent standard error. Six arrays were grown for each citrate concentration, as shown in (b). (e) Reciprocal c-plane growth rate $R_{c-plane}$ versus c-plane area ratio for each growth and linear fits.

Four samples were grown under varying citrate concentrations from 0 to 7.5 μM, displaying shorter nanowires, i.e. reduced growth rate, with increasing citrate concentration (Figure 4-9a). More quantitatively, from Figure 4-9e and by using Equation (3), we showed that the surface reaction rate constant $k_l$ decreases with increasing citrate concentration (Table 4-I), indicating that citrate adsorbents are indeed limiting the c-plane growth rate. The stagnant layer thickness $\delta$ and Thiele modulus $\phi$ also decrease (Table 4-I), all of which confirm reaction-limited growth regime with less dominant diffusion (Figure 4-6d, right inset). Notably, the reaction-limited growth achieved here using c-plane adsorbent yields superior nanowire length uniformity (decrease in length variation from 41% to 16%) across the patterned substrate (Figure 4-9d and Figure 4-10), according to our expectation. This independence of nanowire growth rate from pattern fill factor is particularly useful for device applications where nanowire length must be uniformly controlled over the entire substrate, regardless of the nanowire density.
Figure 4-10. Electron-beam lithography patterned ZnO nanowire arrays. (a) Top-down SEM image of nanowire array grown without citrate. Image consists of six images stitched together. c-plane areas shaded according to individual row, for measuring $S$. (b) c-plane area ratio vs. measured pitch, for each individual row, calculated by measuring nanowire top face area. (c) nanowire length for each row, normalized to shortest nanowire length for each array, plotted against measured pitch.

Table 4-I. $k_1$ and $\delta$ values extracted from Figure 4-9e

<table>
<thead>
<tr>
<th>Citrate concentration (µM)</th>
<th>Surface reaction rate constant $k_1$ (ms$^{-1}$)</th>
<th>Stagnant thickness $\delta$ (mm)</th>
<th>Thiele modulus $\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$7.42 \times 10^{-6}$</td>
<td>2.62</td>
<td>0.46</td>
</tr>
<tr>
<td>1.25</td>
<td>$5.95 \times 10^{-6}$</td>
<td>1.14</td>
<td>0.28</td>
</tr>
<tr>
<td>2.5</td>
<td>$4.84 \times 10^{-6}$</td>
<td>0.84</td>
<td>0.24</td>
</tr>
<tr>
<td>5</td>
<td>$4.14 \times 10^{-6}$</td>
<td>0.61</td>
<td>0.23</td>
</tr>
<tr>
<td>7.5</td>
<td>$3.27 \times 10^{-6}$</td>
<td>0.35</td>
<td>0.14</td>
</tr>
</tbody>
</table>
4.4 Conclusion

In summary, we outlined a way to independently tailor all dimensions of ZnO nanowire arrays. By controlling the nanowire density over an order of magnitude, we showed that the nanowire c-plane growth rate greatly accelerates as the c-plane area ratio decreases, which we attribute to a transition from a diffusion-limited to a reaction-limited growth regime. Our diffusion/reaction analysis yields a linear relationship between c-plane growth rate and Zn$^{2+}$ concentration, which is indicative of a direct incorporation mechanism operative on the ZnO c-plane, corroborated by both the reactant transport model and classical crystal growth theory. This analysis allowed us to tune the c-facet growth rate by changing Zn$^{2+}$ concentration and by impurity adsorption, giving precise control of growth rates critical for obtaining nanowire arrays with uniform and controlled length. We then applied our model to achieve reaction-limited growth and consequently spatially uniform c-plane growth rates regardless of the nanowire areal density. This study emphasizes the importance of tuning the growth conditions to operate under rate-limiting conditions for precise growth rate control. Having this set of nanowire array design guidelines will streamline processing by facilitating optimization of nanowire array morphology for a wide variety of specific device purposes.
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CHAPTER 5

The Role of ZnO Nanowire Arrays in Charge Collection in PbS Quantum Dot Photovoltaic Devices

Abstract

PbS quantum dot photovoltaics (QD PV) have achieved high efficiencies while also demonstrating cost-effective, scalable, low-temperature fabrication in ambient atmosphere. Leveraging quantum confinement for bandgap tunability puts technologies like flexible and/or tandem devices within reach. However, efficient charge collection in QD PV devices has proven challenging due to low carrier diffusion lengths and the presence of sub-bandgap states in QD films that limit $J_{sc}$ and $V_{oc}$, respectively. Here, we incorporate dimension-tailored nanowires to improve charge collection in QD PV devices; by tuning nanowire length and active layer thickness, we achieve an 8% $J_{sc}$ improvement and champion power conversion efficiency (PCE) for an optimized device architecture consisting of 200 nm long ZnO nanowires and 470 nm thick QD film. We use quantum efficiency and total reflectance measurements to identify key loss mechanisms, demonstrating consistently high internal quantum efficiency (IQE) in nanowire QD PV devices. We find that ZnO-PbS QD interfacial recombination is likely to be significant in nanowire devices and use surface passivation to yield even higher current collection and PCE in morphology tailored nanowire devices.
5.1 Overview

In this chapter, we present ZnO nanowire/PbS QD PV devices with varying combinations of nanowire length and active layer thickness. This sweep through parameter space allowed us to isolate specific optical and electronic effects by accounting for the changes in device architecture. First, we made devices with constant nanowire length of 200 nm and varying PbS QD (tetrabutylammonium iodide (TBAI) and ethylenedithiol (EDT) ligands) active layer thickness from 335 – 575 nm. As the total active layer thickness increased, $J_{sc}$ increased monotonically even after the active layer thickness exceeded the p-type diffusion length (~ 300 nm). In devices made with planar ZnO n-type layer, $J_{sc}$ plateaus as ‘dead zones’ appear when the active layer exceeds the p-type diffusion length [1] confirming that nanowires allow us to increase QD active layer thickness without sacrificing charge collection [2]. Subsequently, the number of QD layers was held constant while changing ZnO nanowire length between 150 – 440 nm. For all nanowire devices, $J_{sc}$ increased compared to planar devices. Moreover, the nanowire devices displayed a distinct maximum in $J_{sc}$ for 200 nm long nanowires; increasing nanowire length beyond 200 nm was detrimental to charge collection. Increasing nanowire length also caused $V_{oc}$ to decrease – this tradeoff between $J_{sc}$ and $V_{oc}$ thus led to maximum device performance (8.5% champion PCE) obtained with a 470 nm PbS QD/ 200 nm ZnO NW device architecture. The drop in $V_{oc}$ with longer nanowires suggests that interfacial recombination is an additional loss mechanism for $V_{oc}$ in ZnO nanowire QD PV devices compared to planar devices.

We then performed external quantum efficiency (EQE) measurements, total reflectance measurements, and optical and electrical modeling to fully elucidate the effects of nanowires on generation and extraction processes. Notably, the $J_{sc}$ obtained from EQE measurements increases
monotonically with nanowire length, in contrast to $J_{sc}$ obtained from J-V measurements. In seeking to explain this discrepancy and identify possible loss mechanisms, we used total reflectance measurements to exclude the effect of scattering from external surfaces. We discovered that internal quantum efficiency (IQE) also increases with nanowire length, that is, incorporating longer nanowires increasingly enhances the intrinsic ability of the active layer to convert light into charge. Optical modeling using Finite Domain Time Difference (FDTD) reveals that nanowires spatially alter the optical generation rate, causing enhanced optical scattering in the active layer that improves light-harvesting efficiency. This suggests that changes in charge collection with illumination intensity cause the excess in EQE, which, in conjunction with the decrease in $V_{oc}$ points towards interfacial recombination as a significant loss mechanism in longer nanowire arrays. Passivation of the nanowire surface therefore has the potential to greatly increase device efficiency, which we confirm experimentally.

5.2 Experimental methods

ZnO nanowire arrays were fabricated by hydrothermal synthesis of ZnO nanowire arrays on 150 nm thick patterned ITO electrodes (Thin Film Devices Inc). ITO substrates were sonicated in acetone for 10 min, boiled in IPA for 10 min, and finally subjected to O$_2$ plasma cleaning for 2 min. Dense seed layers were then spincoated from sol-gel solution (0.3 M zinc acetate, 0.3 M monoethanolamine in 2-methoxyethanol, all from Sigma-Aldrich) at 4000 rpm for 60 s, and annealed at 200 °C for 10 min. Two layers were spincoated to produce ~ 30 nm thick seed layers. ZnO nanowire arrays were then grown from the seed layers at 25 mM zinc nitrate and 25 mM HMTA aqueous solutions at 90 °C for varying growth times between 40 and 100 min to yield nanowire arrays with controlled lengths.
For studying interfacial recombination, a subset of planar and nanowire arrays was surface passivated using atomic layer deposition (ALD) of TiO$_2$, carried out on a Cambridge Nanotech Savannah ALD system. Each layer deposition cycle consisted of a 200 ms pulse of tetrakis-dimethylamido-titanium, a 20 ms pulse of water, and a 7 s nitrogen purge. Deposition temperature was 150 °C and 20 cycles were carried out to conformally surface passivate ZnO with 1 nm of TiO$_2$.

These nanowire arrays, along with planar control n-type layer consisting of only the dense seed layer (30 nm thickness), were then used as substrates for QD PV device fabrication. Deposition of a single QD layer was conducted as follows: 50 mg/ml PbS QDs in octane was spincoated at 1500 rpm for 35 s. Following deposition, ligand exchange was carried out. Two types of ligands were used: 10 mg/ml TBAI in methanol, and 0.02 wt% EDT in acetonitrile (ACN). The QD film was soaked in either TBAI/methanol or EDT/ACN for 30 s, and spun off at 2500 rpm for 30 s. The substrate was then rinsed with methanol or ACN respectively, depending on the ligand exchange solution, (2500 rpm, 30s) three times. The thickness of each layer was ~30 nm; layers were repeated until the desired thickness was obtained. The final two layers of every device were always EDT layers, i.e. a device with 8 layers would consist of the first 6 layers done with TBAI, finished off with 2 layers of EDT. Finally, gold top electrodes (100 nm) were deposited using thermal evaporation to complete the device. The nominal active device area is 5.44 mm$^2$ as defined by the overlap of the ITO and gold electrodes. For measurements, masks with 3 mm$^2$ apertures were used to define the device area in order to obtain accurate current density measurements.
Current-voltage (J-V) testing was carried out using a Keithley 2636A source-meter and a Newport 96000 solar simulator with an AM1.5G filter. Before measurements, the light intensity was calibrated to 1-Sun, 100 mW cm\(^{-2}\) using a Newport 91150V reference cell. EQE measurements were conducted using monochromatic light obtained by passing white light from a xenon lamp (Thermo Oriel 66921) successively through a chopper, monochromator, and finally through an optical fiber butt-coupled to the device. The device was illuminated through the glass substrate in an underfilled geometry. The output photocurrent was measured with a lock-in amplifier (Stanford Research System SR 830). Total reflectance measurements were taken on a Perkin-Elmer LAMBDA 1050 UV/Vis/NIR spectrophotometer with 100 mm Integrating Sphere accessory.

5.3 Results and discussion

5.3.1 Effect of active layer thickness

For each device, we used scanning electron microscopy (SEM) to image the device cross-section prepared by focused ion beam (FIB) milling (Figure 5-1). As defined in Figure 5-1, nanowire length was measured from the ITO layer to the top of the nanowire array, whereas the device or active layer thickness was measured from ITO to the gold contact. Device thickness therefore includes a certain length of nanowires infiltrated with QDs.
Figure 5-1. (a) Cross-section SEM images of FIB-milled nanowire-QD devices. (b) Device thickness and nanowire length measured from cross-section SEM images vs. number of QD layers spincoated on nanowire arrays with the nominal length of 250 nm.

ZnO nanowire/PbS QD PV devices with varying active layer thicknesses between 335 – 575 nm and constant nanowire length of 200 nm (Figure 5-1) were fabricated by successively increasing the number of spincoated QD layers on ZnO nanowire arrays. We achieved excellent nanowire length uniformity of ± 10 nm from substrate-to-substrate, while the active layer thickness increased linearly with number of spincoated layers, as expected. This provided us a platform to investigate the effect of QD overlayer (i.e. the thickness of QDs above the nanowire array) on device properties, summarized in Figure 5-2. Furthermore, the investigated thicknesses span both the electron and hole diffusion lengths of ~ 100 nm and 300 nm, respectively, so the effect on each can be observed.
Several important relationships between the device thickness and relevant PV metrics are immediately obvious from Figure 5-2. Figure 5-2a shows that $J_{sc}$ increases with device thickness even as the thickness exceeds the majority carrier diffusion length. This indicates that nanowire arrays are indeed enhancing charge extraction by extending the depths to which carriers can be collected efficiently. Furthermore, net optical absorption increases with thickness (the total volume of QDs is increasing thus absorbing more light); this effect coupled with enhanced carrier extraction causes $J_{sc}$ to increase. To ascertain that the obtained $J_{sc}$ values were accurate,
we performed EQE measurements. Figure 5-3 shows $J_{sc\,EQE}$, the predicted $J_{sc}$ obtained by convolving EQE with the AM 1.5G photon flux and integrating under the resulting curve. These measurements confirm that $J_{sc\,EQE}$ is in good agreement with the $J_{sc}$ obtained from J-V testing, thus strengthening our observation that $J_{sc}$ is increasing with increasing active layer thickness.

![Figure 5-3](image)

Figure 5-3. $J_{sc\,EQE}$ and $J_{sc}$ vs. device thickness. Nanowire length is 200 nm ± 10 nm.

The enhancement in current collection arising from increasing device thickness involves a tradeoff in $V_{oc}$ (Figure 5-2b) and FF (Figure 5-2c), both of which decrease with device thickness. We attribute these relationships to bulk recombination and increasing series resistance, respectively. Sub-bandgap state recombination in the QD bulk has been established as the dominant mechanism for carrier loss in QD films [3]. Therefore, as the QD overlayer thickness increases, the $V_{oc}$ deficit steadily worsens. These competing processes result in a maximum PCE for devices with an active layer of 475 nm and nanowire length of 200 nm (Figure 5-2d).
5.3.2 The effect of nanowire length

![Graph showing the effect of nanowire length on device thickness.](image)

Figure 5-4. Thicknesses measured from SEM images of FIB cross-sections of PV devices vs. nominal NW length, which is the length expected from hydrothermal synthesis growth time.

Having ascertained the effect of QD thickness while holding nanowire length constant, we then fabricated devices with varied nanowire length (Figure 5-4 and Appendix A) to investigate the role of nanowires in charge collection. Series of devices with 9, 12, and 15 QD layers were fabricated, with each series featuring increased nanowire lengths in 50 nm intervals, beginning from planar n-type layers (~30 nm) until device failure (short-circuited device due to excessive nanowire length). Figure 5-4 shows that nanowire length was well controlled across each series and increased linearly with growth time. Furthermore, device thickness also increased linearly with number of QD layers. These device architectures span a significant parameter space and therefore allow us to probe the effects of nanowire length and device thickness on PV metrics.
Figure 5-5. PV device metrics (a) $J_{sc}$, (b) $V_{oc}$, (c) FF, and (d) PCE for series of nanowire length-varied devices with 9, 12 and 15 spincoated QD layers.

Figure 5-5 shows the relevant PV metrics for the aforementioned devices. It is immediately obvious that both device thickness and nanowire length have a strong effect on $J_{sc}$. First, $J_{sc}$ increases with the number of QD layers (Figure 5-5a), thus once more confirming the results presented in the previous section. However, while the 9-layer device series does not show much variation in $J_{sc}$ with nanowire length within the error of the measurement, both the 12- and 15-layer device series display a distinct maximum in $J_{sc}$: compared to planar devices, $J_{sc}$ increases until nanowires are about 200 nm long, subsequently decreasing rapidly as nanowires
become longer. The initial increase in $J_{sc}$ shows that nanowires improve charge collection over planar devices. Furthermore, even small differences in nanowire length (200 nm vs. 150 nm) are sufficient to increase $J_{sc}$ by $\sim 2$ mA cm$^{-2}$ (about 8%), showing that precise control of nanowire length is critical for maximizing device performance.

Further increase in nanowire length past 200 nm causes a drop in $J_{sc}$. There are several possible reasons for this behavior where a maximum in $J_{sc}$ is observed, and we qualitatively discuss them here. First, as nanowire length (and consequently device thickness) increases, collection of electrons improves, since ZnO nanowires provide high n-type mobility pathways. The region of the device where electrons are efficiently collected is thus extended deeper into the device. However, the distance travelled by holes to the Au anode necessarily increases with nanowire length – since the optical generation rate decreases exponentially with path length, the bulk of carrier generation takes place at the cathode (ZnO-QD interface) in this inverted device architecture. Therefore, upon exceeding a certain critical thickness, $J_{sc}$ drops due to poor collection of holes [4]. Second, optical effects play a part in decreasing $J_{sc}$ at longer nanowire lengths. As nanowire length increases, a greater volume of the active layer thickness is occupied by non-absorbing ZnO instead of absorbing PbS QDs. This decrease in active material could result in less optical overall absorption. Third, incorporating increasingly longer nanowires into the active layer introduces defects into the QD film or ZnO-QD interface, which cause poorer film quality and hence reduction in light absorption and charge collection efficiency. Because one or more of the abovementioned reasons could be causing this behavior, in the next section we provide more in-depth investigation of individual effects.
5.3.3 Quantum efficiency characterization

Quantum efficiency of optoelectronic devices refers to the ratio of charge to photon conversion (and vice versa). In PV devices, it is the product of efficiencies corresponding to various processes that occur between light incidence and charge extraction. Apart from being an important metric for comparing various device architectures and active layers, performing different types of quantum efficiency measurements isolates specific processes, thus allowing us to identify and address the limiting factors to improve overall device efficiency.

![EQE spectra for 15-layer device series including spectra for planar, 150, 210, 370 and 570 nm long nanowires. All spectra display the PbS QD exciton peak at ~ 930 nm; the drop in EQE at short wavelength corresponds to the ZnO bandgap. Interference effects in the spectrum for planar device (black dashed line) can be seen in the peaks at 380 and 725 nm. Black arrows at 400 and 930 nm indicate change in EQE arising from increasing nanowire length.](image)

EQE spectra for the 15-layer device series are shown in Figure 5-6. The planar device spectrum is significantly different from nanowire device spectra; interference peaks are more pronounced for the planar device whereas the spectra for nanowire devices are smoother. These results indicate that enhanced optical scattering in nanowire devices prevents formation of the
optical modes that cause interference peaks in the active layer. Nanowire arrays thus improve light harvesting efficiency by increasing the optical pathlength through scattering. Furthermore, by comparing EQE spectra as a function of the nanowire length, it can be observed that the quantum efficiency behavior varies for short and long wavelength regions. At short wavelengths (∼ 400 nm) the quantum efficiency decreases with increasing nanowire length. Because these wavelengths are absorbed near the substrate, i.e. at the ZnO-QD interface, increasing the nanowire length causes poorer carrier collection as holes have to travel further to the Au contact. However, at the long wavelength region (∼ 900 nm, at the excitonic peak) quantum efficiency increases as nanowires become longer. These wavelengths are absorbed deeper in the device, near the QD-Au contact interface, and therefore this behavior reflects enhancement of carrier collection in this region of the device from longer nanowires.

The theoretical short circuit current $J_{sc, \text{EQE}}$ can be calculated from EQE spectra; this was carried out by convolving the EQE spectrum with the photon flux given by the AM1.5G spectrum, and then integrating under the resulting curve. The results for $J_{sc, \text{EQE}}$ are shown in Figure 5-7 for 9-, 12-, and 15-layer device series. Typically, $J_{sc, \text{EQE}}$ is an underestimate for $J_{sc}$ because EQE is a low light intensity measurement whereas J-V testing is performed under 1-Sun intensity. Therefore, trap-filling by the larger numbers of generated carriers may take place during J-V testing, causing observed $J_{sc}$ to be larger than $J_{sc, \text{EQE}}$. We observe such behavior in each device series at nanowire lengths < 300 nm. However, as nanowires exceed 300 nm in length, $J_{sc, \text{EQE}}$ exceeds $J_{sc}$ substantially. This behavior is consistent across each device series – as nanowire length increases, $J_{sc, \text{EQE}}$ initially lies below $J_{sc}$, but while $J_{sc}$ reaches a maximum and subsequently decreases, we do not observe a similar precipitous drop in $J_{sc, \text{EQE}}$. Furthermore, we
recall from section 5.3 (Figure 5-3) that $J_{sc, EQE}$ remains a good indicator for $J_{sc}$ even as device thickness is increased while nanowire length is held constant.

Figure 5-7. $J_{sc, EQE}$ and $J_{sc}$ vs. nanowire length for (a) 15-layer, (b) 12-layer, and (c) 9-layer device series. The shaded region is the current shortfall between $J_{sc, EQE}$ and $J_{sc}$. (d) the difference between $J_{sc, EQE}$ and $J_{sc}$ as a function of nanowire length for each device series showing deficit and surplus predicted current.
At this juncture it is instructive to consider the processes occurring between light absorption and charge generation during J-V and EQE testing, depicted in Figure 5-8, to understand discrepancies in the measured \( J_{sc, EQE} \) and \( J_{sc} \) currents. In our inverted device architecture, incident AM1.5G illumination enters the device through the rear glass surface. At each material interface (namely air-glass, glass-ITO, ITO-ZnO, ZnO-QD, and QD-Au) light is transmitted, reflected specularly, or reflected diffusely. Light that is transmitted into the QD
active layer is absorbed; light intensity decreases according to Beer's law as it proceeds on its particular path. Upon reaching the back electrode, the light is almost fully reflected at the QD-Au interface, thus completing a double pass before exiting the active layer. Absorption of light in the active layer causes generation of electrons and holes via the photovoltaic effect. The charge generation rate is highly spatially non-uniform—shorter wavelengths have a lower penetration depth and are absorbed near the ZnO-QD interface, while longer wavelengths are absorbed towards the QD-Au interface. Irrespective of the spatial distribution of generation rate, the ratio of incident photon flux to total charge generation rate is known as absorption efficiency. Generated carriers are then collected, either by diffusion or by drift, to their respective electrodes. The ratio of total charge generation rate to collection rate is known as collection efficiency; the ratio of collection efficiency to absorption efficiency is termed internal quantum efficiency (IQE), that is, the ability of a material to generate charge from light. IQE and EQE differ in that EQE reflects collected carriers as a function of total incident photons, whereas IQE only considers photons that are actually absorbed in the material.

Figure 5-9. Light harvesting efficiency (LHE) vs. wavelength for 15-layer device series including spectra for planar, 200, 250, 350 and 450 nm long
In order to calculate IQE, we performed integrating sphere measurements – this measures the ratio of the amount of light reflected from the device to the incident light, as a function of wavelength, thus yielding the total reflectance. The light harvesting efficiency (LHE) of the device is shown in Figure 5-9a, where 0% corresponds to total reflectance. Comparing the general shape of the LHE spectra and the EQE spectra for 15-layer devices (Figure 5-6), we immediately notice some qualitative similarities: both LHE and EQE spectra for the planar device exhibit interference peaks. However, the LHE and EQE spectra for nanowire devices are much smoother, which is indicative of scattering preventing optical modes from being set up. Also, nanowire devices have generally higher LHE over the visible and NIR region. This thus confirms that part of the enhancement seen in EQE comes from nanowire optical scattering in the PV device. IQE is given by:

\[
IQE \equiv \frac{EQE}{1 - LHE}
\]

and therefore we do not expect IQE to vary much from the EQE, given that LHE is almost identical for all the nanowire devices.

Light harvesting from external surface scattering is therefore unlikely to be the reason for the discrepancy between \( J_{sc, EQE} \) and \( J_{sc} \). Apart from optical absorption, processes like transmission, refraction, and reflection are not intensity-dependent (at the intensities involved in PV operation). Therefore, we do not expect the ability of a PV device to trap incident light through scattering to vary with the intensity of light during measurement, whether it is low-intensity (EQE) or 1-Sun (J-V testing). We can therefore conclude that the current extraction becomes a function of light intensity when nanowire length increases.
Variation of photocurrent with light intensity is likely due to changes in the type and relative rates of recombination. Between low-intensity EQE measurements and 1-sun illumination, the number of generated carriers increases by several orders of magnitude. Since each recombination mechanism has a specific relationship with carrier concentration, their relative rates are dependent on intensity. However, as EQE is a function of absorption efficiency and collection efficiency (we have excluded external scattering), the changes in recombination may stem from different factors. We put forward several possibilities, all related to recombination, to explain \( J_{sc, \text{EQE}} \) diverging from \( J_{sc} \):

1. As nanowire length increases, scattering within the active layer increases, causing the optical pathlength to become longer. The spatial optical generation profile also changes, with generation taking place deeper into the device. The altered generation profile could cause increased recombination rates in certain parts of the device where light is unintentionally concentrated as the carrier concentration is higher than for the equivalent planar device. These rates could change drastically with light intensity, thus reducing collection efficiency.

2. Increases in nanowire length are associated with greater interfacial recombination at the ZnO nanowire-QD interface as the total interfacial area increases. The dominant recombination mechanism could be either interfacial recombination or Shockley-Read-Hall (SRH) recombination via sub-bandgap states. While sub-bandgap state recombination dominates in planar devices [3], the large interface area in ZnO nanowire devices could make interfacial recombination dominant. It has been shown that the
recombination at the ZnO-QD interface can cause sub-linear scaling in photocurrent with respect to illumination intensity [5], so this is a possible reason for the increased EQE.

Identifying the reason for this deficit is important because EQE represents an upper bound on collected current. The favorable EQE obtained for our active layer shows that the material is of generally good quality, and therefore further improvements in efficiency are possible if we can address the reason for the deficit. Subsequently, we investigate which of these two effects are at work in our device: optical simulation will yield information about scattering at the nanowire-QD interface, while we make use of atomic layer deposition (ALD) to passivate titania on the nanowire surface to investigate the effect of interfacial recombination.

5.3.4 Optical simulation

We used finite element modeling to visualize the spatial variation of generation rate in the device cross-section. Frequency-domain time difference (FDTD) simulation software from Lumerical divides complex device architectures into smaller regions and solves Maxwell’s equations stepwise across boundaries. Using the FDTD method is crucial for modeling nanowire devices because the features have sub-wavelength dimensions, and therefore methods such as ray tracing do not yield accurate solutions to Maxwell’s equations. We used dielectric constant and extinction ($n, k$) values measured using spectroscopic ellipsometry as the material parameters for FDTD simulation, these can be found in Appendix A. FDTD yields both the spatial distribution of generation rate and the integrated generation rate, which corresponds to the expected $J_{sc}$ assuming 100% collection efficiency. Simulating the actual device cross sections measured from
FIB (Figures 5-1, 5-4 and Appendix A) thus allows us to visualize regions with high generation rate in the device cross-section, as well as to estimate the total generated charge.

Figure 5-10. Cross-sections of 15-layer device series showing the spatial distribution of optical generation rate $G_{op}$ in devices with increasing nanowire length. The predicted $J_{sc}$, which assumes 100% collection efficiency, is given for each device.

The $J_{sc, FDTD}$ predicted by FDTD increases with nanowire length (also summarized in Figure 5-11), which is in agreement with the EQE results. Furthermore, there are some notable differences between the planar and nanowire device cross sections that are reflected in the corresponding generation profiles. First, in the case of the nanowire devices, the spatial generation rate profile is not uniform along the $x$-axis, with carrier generation concentrated in nanowire interstices. This contrasts the case of planar devices in which the generation profile remains independent of the $x$ coordinate. Second, optical generation extends deeper into the device (along the $z$-axis) in nanowire devices as compared to planar devices because of the optical scattering provided by nanowires in the active layer. Finally, the absolute value of the maximum generation rate rises, from $15 \times 10^{27}$ to $18 \times 10^{27}$ cm$^{-3}$ indicating that light concentration in the nanowire interstices can raise the carrier concentration rate by about 20%; such regions would thus experience a somewhat higher recombination rate and lower collection
efficiency. This is, however, unlikely be the cause of the large current discrepancy between $J_{sc, EQE}$ and $J_{sc}$. In Figure 5-11 we present the predicted $J_{sc}$ from FDTD simulations ($J_{sc, FDTD}$) for the 9-, 12- and 15-layer device series. $J_{sc, FDTD}$ tracks $J_{sc, EQE}$ closely: $J_{sc, FDTD}$ increases with increasing number of QD layers, and also increases with nanowire thickness. We can thus conclude that it is changes in collection efficiency that are causing the current deficit, moving on to probe interfacial recombination as a possible carrier loss mechanism in nanowire devices.

![Figure 5-11](image-url)

Figure 5-11. $J_{sc, FDTD}$, $J_{sc, EQE}$, and $J_{sc}$ vs. nanowire length for (a) 15-layer, (b) 12-layer, and (c) 9-layer device series.
5.3.5 Surface passivated nanowire QD PV devices

Having excluded light scattering effects both externally and internally using integrating sphere and FDTD simulations respectively, we now turn our attention to possible collection efficiency losses via interfacial recombination. The electronic properties of ZnO nanowires have been shown to be particularly sensitive to their surface structure due to propensity of the surface to interact with adsorbed molecules. In addition, the crystal facet is likely to be atomically rough following the hydrothermal synthesis process, a phenomenon that we discussed in Chapter 4 while investigating growth mechanisms. It is therefore likely that a significant concentration of surface states exists within the bandgap that could contribute to interfacial recombination – indeed, changes in band offset and Fermi level pinning [3] have been observed in QD PV devices due to surface states. These surface states reduce carrier collection efficiency and therefore need to be passivated to improve $J_{sc}$. Their existence may also be the reason for the EQE deficit observed in our devices. We therefore fabricated two series of 12-layer devices including planar, 200, 300, and 400 nm long nanowire arrays – one series was surface passivated with 1 nm of ALD TiO$_2$, while the other series was fabricated without surface passivation. Comparing device performance and EQE would then allow us to investigate the effect of surface states on device properties as nanowire length is increased.
Figure 5-12. PV device metrics (a) $J_{sc}$, (b) $V_{oc}$, (c) FF, and (d) PCE for series of nanowire length-varied devices with and without ALD surface passivation. All devices were fabricated with 12-layers.

The device performance for surface passivated and unpassivated devices is shown in Figure 5-12. As can be seen in Figure 5-12a, $J_{sc}$ for both sets of devices follow the familiar relationship with nanowire length observed in Section 5.4 – current increases from planar to 200 nm nanowire arrays, but subsequently decreases precipitously with nanowire length. Notably, all surface passivated nanowire devices show higher $J_{sc}$ than unpassivated devices, showing that ALD TiO$_2$ was successful in improving current collection. However, $V_{oc}$ and FF (Figures 5-12b and c) follow similar decreases with nanowire length. The enhancement in carrier collection
leads to generally higher PCE in surface passivated nanowire devices, especially for devices with longer nanowire arrays (~ 400 nm). Finally, the metrics presented for these device series are marginally lower than those presented in Section 5.3.2 because they were measured relatively earlier (after 6 days) while improvement in device performance over time (up to 21 days) is expected due to solvent evaporation from the QD layer. Notwithstanding, we are able to draw conclusions based on relative differences, and not absolute values, from this comparative study of surface passivated vs. unpassivated devices.

$J_{sc, \text{EQE}}$ for unpassivated and surface passivated nanowire devices is shown in Figure 5-13a and b respectively. As expected, a large discrepancy (ranging from 1 – 5 mA cm$^{-2}$) between $J_{sc, \text{EQE}}$ and $J_{sc}$ is observed in devices without ALD surface passivation. Conversely, EQE is a much better predictor of $J_{sc}$ for surface passivated nanowire devices. While there is a small deficit, it is greatly reduced compared to unpassivated nanowire devices. This strongly suggests that recombination via surface states at the nanowire-QD interface significantly affects current collection, especially at low light intensity such as that used for EQE characterization. More importantly, we show that engineering of surface states, in conjunction with nanowire array morphology tailoring, adds to our toolbox for boosting PCE of nanowire devices. Our work indicates a clear pathway toward development of effective surface passivation schemes that will be investigated in future.
Figure 5.13. $J_{sc, \text{EQE}}$ and $J_{sc}$ vs. nanowire length for (a) unpassivated and (b) ALD surface passivated device series. The shaded region is the current shortfall between $J_{sc, \text{EQE}}$ and $J_{sc}$. (c) the difference between $J_{sc, \text{EQE}}$ and $J_{sc}$ as a function of nanowire length for each device series showing deficit and surplus predicted current.

5.4 Conclusion

In this chapter, we used morphological tailoring and surface engineering of ZnO nanowire arrays to investigate a myriad of convoluted optical and electronic processes in nanostructured PbS QD photovoltaic devices. We first showed that $J_{sc}$ increases with QD overlayer thickness in devices with constant nanowire length, suggesting that nanowires allow QD active layer to be made thicker than would be possible on a planar device by enhancing
current collection. Subsequently, we explored parameter space by fabricating devices with varying nanowire length and active layer thickness to identify the optimum nanostructure for enhancing device performance, and also to elucidate limiting optical or electronic processes in such devices. We achieved a champion PCE of 8.5 % for an optimized device architecture consisting of 200 nm long ZnO nanowires and 470 nm thick QD film, also showing that current collection was maximized at this nanowire length. We carried out quantum efficiency measurements to validate our observed $J_{sc}$ enhancement and found that $J_{sc}, EQE$ calculated from EQE spectra significantly exceeded that observed during J-V testing. In seeking to understand this phenomenon, we excluded the effect of external and internal light scattering using integrating sphere and FDTD optical simulation respectively, showing that nanowires contribute to enhanced light scattering and thus improved optical absorption. Finally, we used ALD to passivate the ZnO nanowire surface with TiO$_2$, achieving improved $J_{sc}$ over a range of nanowire lengths from planar to 400 nm as compared to unpassivated devices. $J_{sc}, EQE$ was also a better predictor of $J_{sc}$ on passivated vs. unpassivated devices, showing that surface states have a significant effect on current collection. Our work demonstrates that precise control of all aspects of nanostructured architecture – morphology and surface structure – can be used to probe multiple optical and electronic phenomena and subsequently utilize their interaction to enhance device performance.
References


CHAPTER 6

Conclusion
6.1 Summary and implications

In this thesis, we sought to transform conventional hydrothermal synthesis of seeded ZnO nanowires – a low-cost, high throughput, scalable technique – into a more deterministic process by understanding key mechanisms governing nanowire morphology and crystal quality. Most optoelectronic devices incorporating hydrothermally grown ZnO nanowire arrays used bulk synthesis, in which precise control over nanostructural morphology is limited by non-homeostatic growth conditions. Independent control over array parameters such as nanowire spacing, diameter, length, and alignment was previously carried out by trial-and-error rather than by design. Beginning from the ZnO seed layer and moving on to incorporation of reactants during solution phase crystal growth, we use top-down and bottom-up lithographic techniques to control nanowire spacing and also to investigate important fundamental processes such as the effect of annealing on nanowire alignment, as well as the competition between diffusive transport and reactant incorporation at the solution-crystal interface. Harnessing the knowledge gained from these fundamental investigations allowed us to achieve precise control over nanowire array morphology and use these arrays as a platform for enhancing the performance of ZnO nanowire/PbS quantum dot photovoltaic devices. Our work opens up many possible avenues for exploration, which we outline in the next section.

We began by using electron-beam lithography patterned ZnO seed layers to investigate the effect of substrate choice, annealing, and deposition technique on final nanowire array morphology, achieving well-aligned nanowire arrays with minimal branching on a variety of device relevant substrates. We used sputtering and sol-gel spincoating, the two most commonly used seeding techniques, to deposit seed layers on Si, ITO/glass and PEN, which are commonly
used substrates for electronic device applications. Careful characterization and quantification of nanowire alignment and branching (multiple nanowires grown per template hole) allowed us to conclude that template hole diameter relative to seed layer grain size was a key processing parameter behind enhancing vertical alignment and minimizing branching. Annealing had the effect of increasing seed layer grain size and improving vertical alignment, making it a useful tool for engineering the seed layer. Our study showed that seed layer engineering, coupled with high resolution templating, provides excellent control over nanowire alignment and spacing at length scales relevant for controlling optical and electronic phenomena in nanostructured devices.

We then introduced dynamic deposition spincoating of sol-gel seed layers as a method for large scale control over nanowire spacing for photovoltaic applications, showing excellent nanowire alignment coupled with controllable areal density. In order to independently control nanowire length and diameter, we studied the effect of nanowire density on relative $c$- and $m$-facet growth rates using diffusion/reaction analysis, successfully separating the serial processes of solution phase reactant diffusion vs. adatom incorporation in nanowire growth. Fundamentally, this allowed us to show that the direct incorporation mechanism is operative on the ZnO $c$-facet during solution phase growth; from an application standpoint, we took advantage of reaction-limited growth using citrate additives to demonstrate enhanced nanowire length uniformity over a template with varying nanowire areal density. This understanding of key hydrothermal growth processes is necessary for producing nanowire arrays with sufficient precision for enhancing performance of nanostructured photovoltaic devices.
Finally, we used nanowire arrays with precisely controlled lengths in PbS quantum dot (QD) photovoltaic devices, achieving a 9% current enhancement and champion power conversion efficiency of 8.5% in a 470 nm QD/200 nm nanowire length device architecture. We used quantum efficiency measurements, coupled with diffuse reflectance measurements and optical simulation, to show that incorporating nanowires into PbS QD photovoltaic devices significantly increased scattering that improved optical absorption. Finally, we used atomic-layer deposition to surface passivate nanowire arrays, alleviating carrier losses via interfacial recombination to achieve even better performance on morphologically tailored nanowire devices.

Our work shows that judicious choice of seeding and growth parameters arising from an understanding of the fundamental processes taking place at the nanoscale is required for morphological control precise enough to modulate optoelectronic processes in nanostructured devices. Apart from enhancing device performance, dimension tailored nanowire arrays can also provide an excellent platform for elucidating the inner workings of nanostructured devices. These capabilities are attractive for facilitating optimization of nanowire array morphology for a wide variety of specific device purposes.

6.2 Future directions

We have demonstrated the utility of EBL for prototyping (i.e. precise nanowire placement over small areas) and subsequently the ability to translate the knowledge gained from prototyping into large area device fabrication using scalable dynamic deposition spincoating. Possessing easily customizable seed layers provides a solid foundation for realizing more complicated nanostructures using continuous flow synthesis. Continuous flow synthesis, unlike
bulk synthesis, offers vastly more control over growth conditions, which opens up possibilities for \textit{in situ} diameter control. The ability to vary nanowire diameter along the growth axis is important for several reasons. First, electrical conductivity is a function of nanowire diameter. In certain device architectures, especially those where ZnO nanowires are used to provide high electron mobility pathways, nanowire tapering can be advantageous since the collected current is a function of device thickness. Nanowires that are wider at the base would thus be more effective at conveying charge out of the device. Furthermore, the nanowire taper rate would need to be carefully controlled in order to produce the correct nanowire shape for the particular application. Continuous flow synthesis is particularly well-suited for growing such morphologies since the sidewall (\textit{m}-facet) growth rate can be altered using additives or by changing growth solution concentration. By changing the additive and/or reactant concentrations in real time, it is possible to access a wide range of nanowire morphologies, which greatly increases the available parameter space for optimization of charge collection in nanostructured devices.

Second, diameter modulation can be used to periodically thin the nanowire. Since the thinner regions are more mechanically fragile, sonication can be used to divide the nanowire into lengths dictated by the periodicity of the thinned regions. This method could be a way to produce large quantities of nanowires with well-defined lengths suspended in solution – the nanowires could then be spincoated on to a substrate to form part of a device. Continuous flow synthesis is ideal for producing such nanowires because additives can be added and removed as desired to thin the nanowire, and also because growth can continue indefinitely, producing nanowires as long as required.
Third, diameter modulation could also be used to produce 3D photonic crystals. One difficulty in fabricating complex 3D nanostructures is that while traditional lithography can create patterns in the plane, it is challenging to produce photonic crystals as this requires that periodic air gaps be created within the material to achieve the required variation in refractive index. Taken to the extreme, diameter modulation of nanowires using continuous flow growth could produce an inverse taper (increasing diameter with growth time) such that the top of the array coalesces. The taper would then be reduced to re-form the nanowire array. Such a process could be repeated to create a structure where air gaps alternate with ZnO crystal along all three axes – a photonic crystal. Furthermore, it is likely that the morphology could be controlled to hundreds of nanometers, which is adequate for photonic applications. Repeated bulk synthesis runs have been used to create such a structure intended to mimic seashell cross-sections [1], but the morphology was not well controlled. Continuous flow synthesis would be able to achieve greater morphological precision critical for producing a 3D photonic crystal.

Apart from changing the nanowire morphology in real time, the magnetic and electronic properties of ZnO can also be tuned by adding metal ions into the growth solution. ZnO can be made into a dilute magnetic semiconductor by adding cobalt or manganese during hydrothermal growth [2][3]. Since incorporation takes place primarily at the growing c-facet, it is possible to vary the composition along the growth axis, thus changing the magnetic properties along the nanowire axis. ZnO can also be made p-type by adding potassium during growth [4]; since ZnO is intrinsically n-type, this is attractive for producing p-n homojunctions along the nanowire axis, which could be attractive for light-emitting diode or lasing applications. While we demonstrated that dimensional tailoring can enhance charge collection in PbS quantum dot photovoltaic
devices, taking advantage of additives could make nanowires even better charge collectors by engineering the bandgap and doping concentration. The combination of continuous flow synthesis and controlling nanowire dimension, magnetic, and electronic properties \textit{via} additives thus has great potential for producing complex nanostructures that actively manipulate useful physical phenomena at the nanoscale.
References


APPENDIX A

Optical Simulation Parameters: Device Dimensions and Material Optical Dispersion
Table A-I. Nanowire length and active layer thickness measured from focused ion beam cross sections

<table>
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<tr>
<th>Number of QD layers spincoated</th>
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<th>Measured nanowire length (nm)</th>
<th>Active layer thickness (nm)</th>
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Figure A-1. Dielectric constant $n$ and extinction coefficient $k$ for glass, ITO, ZnO, PbS (TBAI ligand) and Au measured by spectroscopic ellipsometry and used in FDTD simulation.