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Electron beam induced rapid crystallization of water splitting nanostructures

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ABSTRACT

Titanium dioxide (TiO_2) loaded with gold (Au) as noble metal, acts as an efficient photo-catalyst that has been extensively investigated for water splitting processes. In this paper, we report on the microstructure of atomic layer deposited titanium dioxide and the crystallinity modification of the material using energetic electron beam irradiation. A rapid high-energy electron beam induced crystallization of the nanostructures has been observed *in-situ* inside a High-Resolution Transmission Electron Microscope (HRTEM). The systematic crystallization of the nanomaterial occurring under the electron beam irradiation (300 KV) indicates the transformation of the near amorphous material into a mixture of two nuances of TiO_2 polymorphs, namely rutile and anatase. We believe that this transformation will enhance the efficiency of water splitting process, as the mixed phases of rutile and anatase are known to possess better optical properties than the individual polymorphs of TiO_2. This finding may be of particular interest in developing appropriate heat treatment methods for these nanostructures dedicated to water splitting to increase their efficiency.

INTRODUCTION

The energy solutions for the future suggest the realization and development of eco-friendly and economic energy sources. Many natural sources such as, solar energy, wind energy and biofuels have been used in order to reduce the carbon emission. In this regard, solar energy assisted water splitting and hydrogen production has shown a promising potential. In 1972, Fujishima and Honda showed that TiO_2 could be a potential catalyst in water splitting process [1]. Since then, a large amount of studies have been performed on TiO_2 and other equivalent photonic structures. TiO_2 has a band gap of 3.2 eV, which falls in the UV region of the light spectrum. Thus, water splitting (WS) efficiency is limited within the UV region. However by adding localized surface plasmon resonance (LSPR) particles to the oxide material, the optical activity of the composite plasmonic-metal/semiconductor photocatalysts (MPhC) can be significantly enhanced [2, 3].

In the MPhC structures used in our studies, TiO_2 acts as the WS catalyst and Au nanoparticles as the LSPR material. In this case, the WS activity fundamentally can depend on the (i) production rate of hot electrons in the Au part through plasmon resonance, (ii) the

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transport of the hot electrons produced in Au to the TiO_2 material, and (iii) the degree of crystallinity of the catalyst (TiO_2).

Considering the third parameter mentioned above the band gap might change due to change in the order of crystallinity and this could effect on the efficiency of the WS process. In this study we focus on investigating the stability of the catalyst nanostructure using *in-situ* heating inside HRTEM. We report our investigation on the dynamic change of the crystallization in TiO_2 during the *in-situ* electron beam treatment and discuss the role of the degree of crystallization of the MPhC material on the WS activity.

EXPERIMENTAL

Figure 1 gives the workflow used to generate the MPhC nanostructures. The fabrication process is well explained and documented in previous published paper [4]. The process includes fabricating Alumina shells using sidewall lithography process and subsequent deposition of TiO_2 layer via atomic layer deposition (ALD) at 220 °C for a thickness of ~ 80 nm and further annealing at 350 °C for 1 hour. The last step involves Au deposition using sputtering process. The purpose of the annealing step at 350 °C is to release the residual stress in TiO_2 and to make it suitable to receive Au layer without forming blisters.

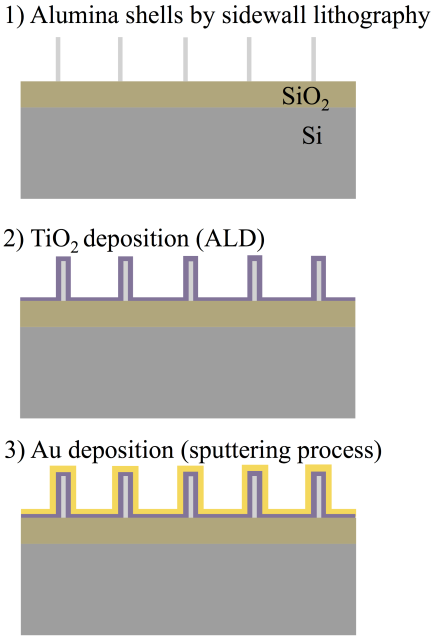

Figure1: Schematic diagram shows the fabrication steps of the MPhC structures. 1) Alumina shells are fabricated using sidewall lithography process, 2) TiO_2 is deposited on the Alumina shells using ALD, 3) Au layer was deposited using sputtering process.

For the Scanning Electron Microscope (SEM) imaging and cross sectional characterization a dual beam Focused Ion beam (FIB) system (FEI™ Helios NanoLab™ 650) was used.
A thin TEM lamella was prepared using standard FIB process as described below. First, a protective layer of platinum (Pt) of 20 µm × 2 µm × 2 µm in size, was deposited on the top of the

WS nanostructures. Then, using regular cross section and cleaning cross section methods available in the FIB system, a rectangular slice of 20 μm × 1 μm × 8 μm was obtained. Subsequently, the prepared slice was lifted out using an Omniprobe and placed on a Cu TEM grid for further thinning. Ion beam having energy of 30 keV and current of 0.43 - 0.79 nA was used for rough thinning and for the final thinning beam energy of 5 keV and beam current of 41 pA was implemented. Using this approach a TEM lamella of thickness <80 nm was prepared for further HRTEM investigation.

The TEM experiments were carried out in an FEI™ image corrected Titan TEM microscope. The TEM experiments were done using electron beam of 300 keV beam energy, beam current of 3.12 nA and at spot size of 3.

RESULTS & DISCUSSION

Figure 2 shows SEM images of MPhC nanostructures. The fabricated MPhC samples have cylindrical shapes with ~ 0.8 μm in diameter. Given the high aspect ratio of the structure, we observe a non-uniform Au coating, with a continuous film of about ~ 40 nm deposited at the top of the structures and dispersed nanoparticles at the sides and bottoms of the structures.

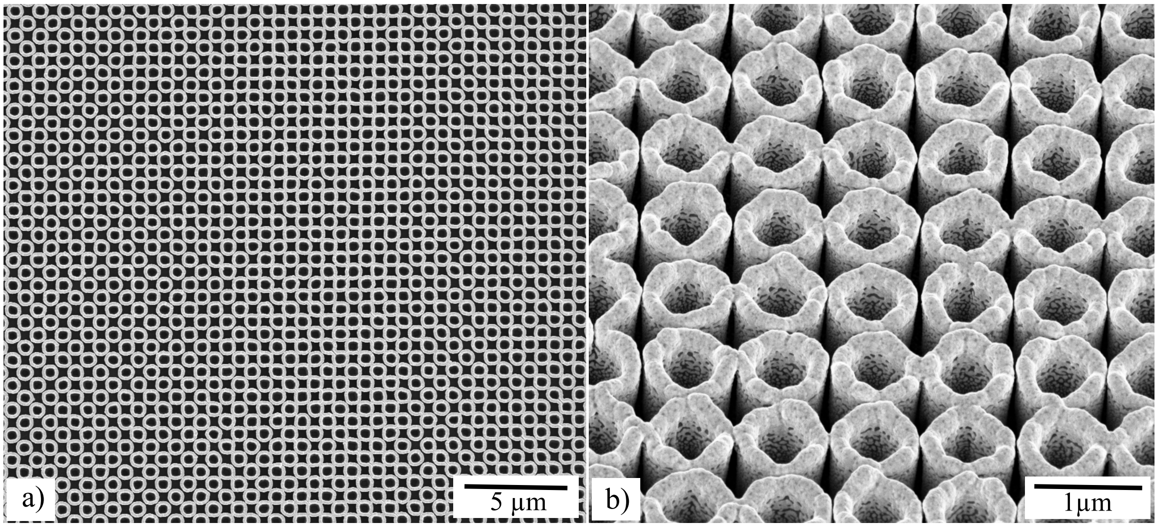

Figure 2: SEM images of the MPhC nanostructures fabricated using the steps given in the experimental section; a) top view and b) tilted view (at 40°).

A cross sectional view of a thin lamella prepared from a WS sample is shown in figure 3. The SEM picture shows the layout of the WS structures. The thickness of the alumina ring is ~ 40 nm, which is covered by the ALD deposited ~ 80 nm thick TiO_2 layer. The alumina, which is in an amorphous form, acts as supporting post for the WS material and does not participate in the WS process.

In order to look into the irradiation effect on the MPhC structure, the prepared lamella was placed inside the TEM and locally irradiated on the Au, TiO_2 boundary region.

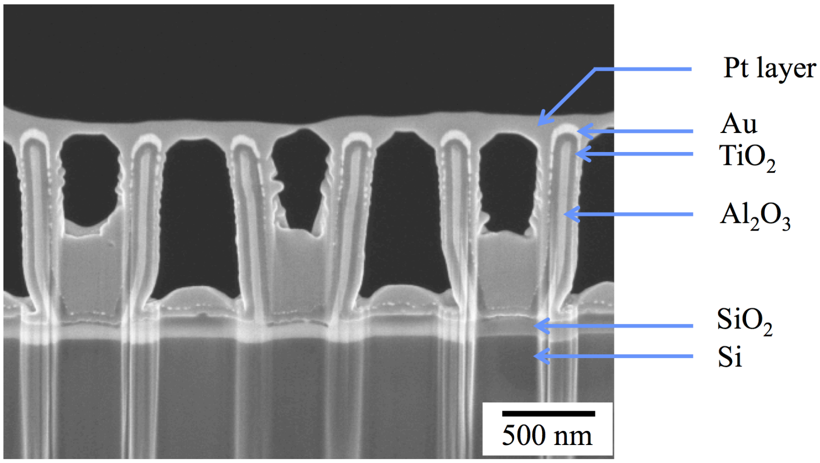

Figure 3: A cross sectional view of a thin lamella depicting the layers.

Due to the irradiation of energetic electron beam on the material, the irradiated TiO_2 region was found to change its crystallinity systematically and rapidly. It can be seen in the sequential TEM micrographs in figure 4. 4a) is the image captured at t = 0 s when the irradiation was started. 4b) is an intermediate state and 4c) is the image captured after 50 s of continuous irradiation. Fast Fourier Transform (FFT) patterns corresponding to the selected areas (shown by the rectangular boxes) were taken simultaneously and are shown in the insets of each frame. It can be seen that the crystallinity of the material (TiO_2) changes with time and it is becoming more pronounced with the electron beam dose. Further, the FFT patterns are compared with the available database of anatase and rutile TiO_2. The overlapped diffraction pattern of rutile [001] and anatase [100] TiO_2 with the collected FFT pattern is shown in figure 5. This indicates that the grown crystalline patterns correspond to the mixed phases of anatase and rutile.

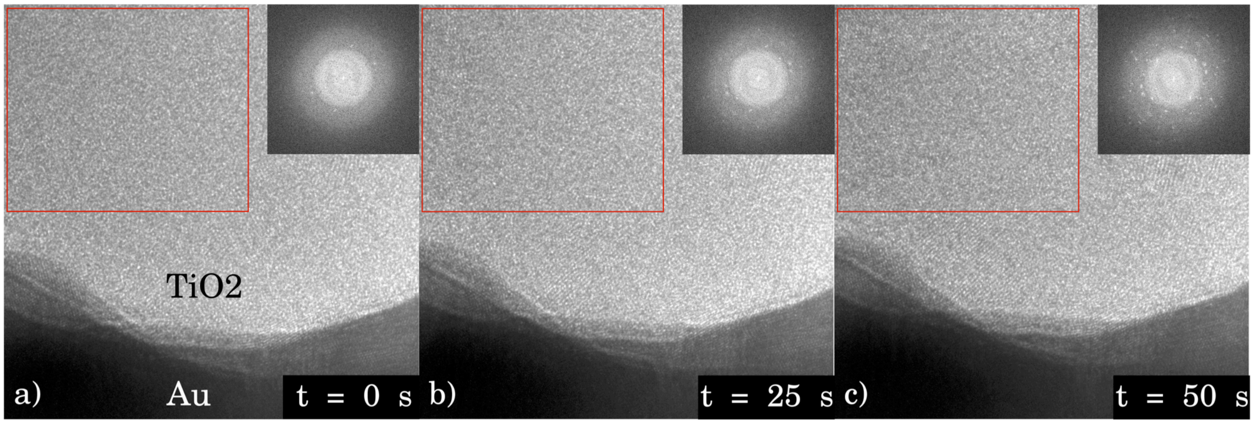

Figure 4: TEM images show the *in-situ* change of the degree of crystallinity of the MPhC material under electron beam irradiation. The FFT corresponding to a selected TiO_2 area (indicated by the red colored rectangular box) are shown in the insets of the pictures.

Due to its two dimensional nature, the thin lamella shows high internal stress. Internal stress increases with decreasing film thickness and they can significantly modify the crystallization temperature of the material. Reported crystal transformation in TiO_2 bulk material seems to occur when TiO_2 is subjected to annealing at 400 °C [5]. In the current experiment of electron beam irradiation on the thin lamella, the thickness of the irradiated material is below than 80 nm, which means that the required temperature for *in-situ* TiO_2 crystallization is likely to differ from 400 °C.

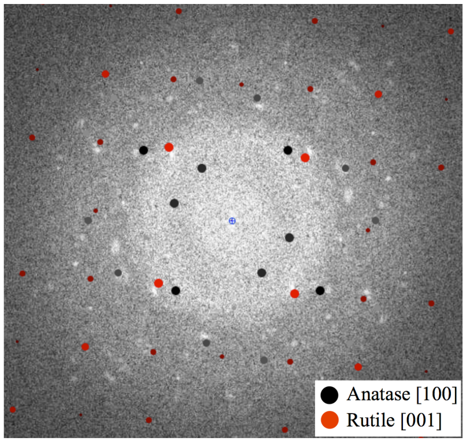

Figure 5: Using JEMS software: overlapped diffraction patterns of rutile [001] zone axis (in red) and anatase [100] zone axis (in black) with the FFT pattern taken after 50 s of irradiation.

The heating due to the high-energy electron beam is admitted to depend on the thermal conductivity of the considered material. In the current experimental geometry, the irradiated material has an amorphous structure and fairly isolated from the Silicon (Si) substrate by 200 nm of oxide layer (SiO_2). Thus the heat dissipation through conduction is expected to be low because the irradiated zone of the TiO_2 is thermally loosely connected from the rest of the specimen. This leads the local heating to build up in the irradiated region and eventually the local temperature may exceed the crystallization temperature of the catalyst, which could explain the crystallization developed in the TiO_2 layer. The most striking result is the fact that the amorphous TiO_2 turns into a mixture of its polymorphs structures both rutile and anatase. These mixed forms of crystalline TiO_2 were widely investigated for improved photocatalysis [6, 7]. The *in-situ* heating under HRTEM consisting of exposing the material under energetic electron beam seems to provide a quick route to increase photocatalytic activity of the MPhC structures. This set of electron beam induced rapid crystallization observation also infers the possibility of using energetic electron beam for annealing post fabricated MPhC structures and modifying the material property according to the defined target.

In a supplementary experiment, we have observed *in-situ* crystallization on the Alumina structures as well. This observation is indeed in agreement with other available reported results [8]. It is observed that the *in-situ* crystallization tendency in Alumina is much faster than the TiO_2 material.

CONCLUSION

Changes in the crystalline phases of amorphous MPhC material under electron beam irradiation is observed and reported in this communication. HRTEM studies of the WS catalyst (Au-loaded TiO_2) indicate that continuous irradiation of electron beam on a thin lamella induces rapid crystallization of the MPhC material. The new modified material, which is a mixed phase of rutile and anatase TiO_2, is expected to have higher water splitting activity. These observations imply that energetic electron beam can be a valuable method to increase photocatalytic activity of MPhC structures.

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