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Supersaturating silicon with transition metals by ion implantation and pulsed laser melting

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We investigate the possibility of creating an intermediate band semiconductor by supersaturating Si with a range of transition metals (Au, Co, Cr, Cu, Fe, Pd, Pt, W, and Zn) using ion implantation followed by pulsed laser melting (PLM). Structural characterization shows evidence of either surface segregation or cellular breakdown in all transition metals investigated, preventing the formation of high supersaturations. However, concentration-depth profiling reveals that regions of Si supersaturated with Au and Zn are formed below the regions of cellular breakdown. Fits to the concentration-depth profile are used to estimate the diffusive speeds, $v_D$, of Au and Zn, and put lower bounds on $v_D$ of the other metals ranging from $10^2$ to $10^4$ m/s. Knowledge of $v_D$ is used to tailor the irradiation conditions and synthesize single-crystal Si supersaturated with $10^{19}$ Au/cm$^3$ without cellular breakdown. Values of $v_D$ are compared to those for other elements in Si. Two independent thermophysical properties, the solute diffusivity at the melting temperature, $D,(T_m)$, and the equilibrium partition coefficient, $k_e$, are shown to simultaneously affect $v_D$. We demonstrate a correlation between $v_D$ and the ratio $D,(T_m)/k_e^{0.67}$, which is exhibited for Group III, IV, and V solutes but not for the transition metals investigated. Nevertheless, comparison with experimental results suggests that $D,(T_m)/k_e^{0.67}$ might serve as a metric for evaluating the potential to supersaturate Si with transition metals by PLM. © 2013 AIP Publishing LLC.

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I. INTRODUCTION

A potential strategy for producing an intermediate band in silicon (Si) that could be useful for sub-bandgap photodetectors or photovoltaics1,2 is to incorporate a dopant that creates a filled and an empty level near mid-gap. At sufficiently high concentrations, the two levels may overlap to form a single partially filled band. This approach necessitates multiple mid-gap levels. Transition metals could introduce such a combination of states, but are typically avoided in Si devices because they significantly reduce minority-carrier lifetime even at dilute concentrations.3–5 To achieve the overlap, solute concentrations well beyond the equilibrium solubility limits of most solutes in Si must be achieved.6,7

When nanosecond-scale pulsed laser melting (PLM) is applied to ion-implanted Si, the ultra-fast resolidification that follows melting can produce single crystalline Si supersaturated with the implanted solute. To achieve supersaturation, the solidification speed $v$ must be high enough, compared to the diffusive speed $v_D$ of the solute, for deviations from local interfacial equilibrium to cause significant solute trapping.8–11 Ion implantation and PLM have been used to synthesize single-crystalline silicon supersaturated with a range of dopants from group III–group VI and their diffusive speeds have been well characterized.10–15 Transition metals, however, have proven challenging; early attempts at non-equilibrium doping of Si with transition metals resulted in complete segregation out of the solid during resolidification.16–20 There have been isolated reports of supersaturated concentrations of Au (Ref. 21) and Pt (Ref. 22) achieved in Si using PLM, but uncertainty remains about the possibility of achieving supersaturated concentrations of a wider array of transition metals in silicon. Studies have also been reported of the use of pulsed melting techniques to incorporate supersaturations of Mn into Si23,24 and Ge25,26 in search of carrier-mediated ferromagnetism. Motivated by the potential synthesis of an intermediate band semiconductor, we set out to improve the understanding of the phenomenology and mechanisms dictating the incorporation of transition metals into silicon during the PLM process.

In this work, we investigate dopant incorporation of nine different transition metals (Au, Co, Cr, Cu, Fe, Pd, Pt, W, and Zn) ion-implanted into Si and melted and rapidly resolidified using nanosecond PLM. Using scanning electron microscopy (SEM), cross-section transmission electron microscopy (XTEM), and secondary ion mass spectrometry (SIMS), we...
fully characterize the extent of dopant incorporation, dopant segregation, and cellular breakdown. We use this information to extract estimates of or lower limits to $v_D$ for each transition metal. These investigations inform the selection of laser irradiation conditions that lead to the successful incorporation of self into monocrystalline Si at supersaturated concentrations. Finally, we combine our estimates (or lower limits) of $v_D$ for transition metals with knowledge about the behavior of group III–VI solutes in silicon to elucidate the relationship between $v_D$ and thermophysical properties of the solute. We propose and rationalize a correlation between $v_D$ and more readily available solute properties. This correlation provides insight into the behavior of solute atoms at the solid-liquid interface and leads to a parameter that might serve as a metric for evaluating the potential for significant solute trapping of transition metals in Si.

II. EXPERIMENTAL

Si wafers ((001), p-type, 1–10 Ω-cm) were ion implanted with $^{197}$Au $^{+}$, $^{58}$Co $^{2+}$, $^{52}$Cr $^{2+}$, $^{63}$Cu $^{+}$, $^{56}$Fe $^{+}$, $^{184}$W $^{+}$, $^{66}$Zn $^{-}$ and the natural isotopic mixes 

\[ k = \frac{k_e + (v/v_D)}{1 + (v/v_D)}, \]

where $k$ is the partition coefficient (the ratio of the solute concentration in the solid to that in the liquid at the interface), $k_e$ is its equilibrium value, and $v$ is the solidification speed.

III. RESULTS

Our investigation into the behavior of nine transition metals (Au, Co, Cr, Cu, Fe, Pd, Pt, W, and Zn) following PLM using a XeCl$^{-}$ excimer laser is summarized in Table I. Cellular breakdown of the solidification front occurred for Au, Co, Cr, Pd, Pt, and the highest dose of Fe ($1 \times 10^{16}$ cm$^{-2}$). Lower doses of Fe ($1 \times 10^{14}$ cm$^{-2}$–$1 \times 10^{15}$ cm$^{-2}$) and Cu did not contain transition metal concentrations above the detection limit of SIMS (Cu) and RBS (Fe), suggesting surface segregation of the transition metal solutes. XTEM characterization of all the samples presented in Table I is available in the supplementary material. Transition metals leading to surface segregation at low concentrations and cellular breakdown at higher concentrations, as observed here, is consistent with previous investigations into PLM of transition metals ion implanted in Si.

As an example of typical cellular breakdown morphology, Figure 1(a) shows a SEM micrograph of the sample implanted with $10^{16}$ $^{56}$Fe$^{+}$ cm$^{-2}$ and then laser-melted. The XTEM micrograph in Figure 1(b) shows solute-rich walls between cells of the host semiconductor, the signature feature of cellular breakdown. The spacing between cell walls, as visible in Figure 1(b) and the supplementary material, is on the order of $D_L/v$, where $D_L$ is the solute diffusivity in the liquid. The high density of cell walls prevents the determination of the level of dopant incorporation in the crystalline Si grains (i.e., between the cell walls) using SIMS. Accordingly, the values of or bounds on the maximum trapped solute concentration, $c_{\text{max}}$, reported in Table I are based on the maximum...
concentration of the solute in monocrystalline silicon below the breakdown region. Because we are modeling large supersaturations, $k$ is assumed to be negligible compared to unity when modeling dopant diffusion and segregation using Eq. (1).

We interpret the observed difficulty of incorporating high non-equilibrium concentrations of low-$k$ transition metals into Si to be a consequence of the large $v_D$ exhibited by the transition metals in comparison with conventional Si dopants. Large values of $v_D$ cause a spike in solute concentration in the liquid at the solidification front due to strong solute partitioning at the liquid-solid interface, and this build-up of solute increases the probability of cellular breakdown, a morphological instability in which local freezing-point depression due to solute partitioning causes runaway amplification of small perturbations to the solidification front, leading to a cellular microstructure. In most samples studied, the diffusive speed was large enough that $c_{\text{max}}$ was below the detection limit of the concentration-depth profiling measurements. The values or lower limits of $v_D$ determined here for Au, Co, Cr, Cu, Fe, Pd, Pt, W, and Zn are at least an order of magnitude larger than values of $v_D$ previously reported for group III–VI elements in Si during PLM. Although $v_D$ has not been explicitly reported previously, these results are consistent with previous investigations into PLM of Si implanted with transition metals. The values of $k$ reported are consistent with the upper limits previously reported for transition metals in Si ($k < 10^{-2}$) and agree with previously reported values for Au in Si.

As presented in Table I, the Au concentration was well above $10^{19}/\text{cm}^3$. Zn was detectable slightly above the SIMS noise floor of $10^{18} \text{ cm}^3$, and both are at least an order of magnitude higher than the solubility of Au in Si (4.8 $\times$ 10^{16} \text{ cm}^{-3} at 1100 °C) and Zn in Si (1.1 $\times$ 10^{17} \text{ cm}^{-3} at 1211 °C). Though the Zn concentration profile approached the SIMS noise floor, the data still allowed us to estimate $v_D$. Figure 2 shows a XTEM image overlaid on a concentration-depth profile of the Au-doped sample described in Table I, illustrating that a supersaturated layer with thickness $> 100 \text{ nm}$ formed below the depth at which cellular breakdown began.

The Au concentration-depth profile for the supersaturated layer was fit using the simulation described in Refs. 10, 12, and 30 in order to extract $v_D$ and $D_D$. Fitting the data in Figure 2 yields $D_D = 4.5 \times 10^{-4} \text{ cm}^2/\text{s}$ and $v_D = 350 \text{ m/s}$. Using these parameters in steady-state interface stability theory, we calculated the critical solute concentration for the stability of a liquid-solid interface traveling at $3 \text{ m/s}$, and found that a concentration of Au in the bulk liquid greater than $1.2 \times 10^{18} \text{ cm}^{-3}$ results in an unstable interface. However, if the velocity is increased to $7 \text{ m/s}$, the interface is stable for concentrations up to $9 \times 10^{18} \text{ cm}^{-3}$. Using thermal conditions from one-dimensional heat flow simulations, we find, in rough agreement with the data, that the solidification front under our experimental excimer laser PLM conditions should become unstable at a depth of about 250 nm and thus that cellular breakdown should subsequently become observable at some shallower depth. Further, modeling of interface stability and of the onset of breakdown after an interface becomes unstable is underway.

Based on our understanding of $v_D$ for Au in Si, a preliminary effort was made to produce a breakdown-free sample of Si containing even more Au by increasing the solidification speed in order to suppress solute segregation. To obtain an increased speed, the laser pulse duration was reduced by a factor of ten (by using a different, Nd:YAG-based laser) and the implant and melt depths were decreased by more than a factor of two, as explained in the experimental section. Both of these changes reduce the total thermal input into the sample, which results in a sharper temperature gradient during resolidification and a faster dissipation of heat from the melt to the underlying solid substrate. Both (001) and (111) Si
were tested because \(v_D\) is known to be significantly smaller in (111) Si (i.e., more conducive to solute trapping) than in other orientations.\(^{11}\)

Figure 3(a) shows XTEM images of the (001) and (111) samples implanted with Au and melted with the Nd:YAG laser. Whereas the (001) sample was found by XTEM to be single-crystalline and free of defects, stacking faults are clearly visible in the (111) sample. The formation of stacking faults during the rapid solidification of (111) Si is a well-known phenomenon at high solidification speeds.\(^{37,38}\) Figure 3(b) plots the concentration-depth profiles and the associated simulation fits for PLM using the Nd:YAG laser on both (001) and (111) Si: Au. These fits yielded a value for \(D_t\) estimated for the XeCl\(^+\) irradiated sample \((v_D = 350\, \text{m/s})\). The best fit was instead achieved with \(v_D = 110\, \text{m/s}\). This discrepancy appears to be too large to be explained by measurement error alone. Though it could be an artifact of differences in the background doping or laser pulse spatial and temporal profiles, this discrepancy may indicate that, although \(k\) increases with \(v\) for Au in Si(001), the partitioning behavior is not well described by Eq. (1).

Fitting the depth profile for the (111) sample using Eq. (1) under the assumption that the influence of stacking faults on SIMS is negligible yields \(v_D = 30\, \text{m/s}\). Inserting this value of \(v_D\) and the simulated solidification velocities into Eq. (1) indicates that the partition coefficient for (111) is 0.23–0.33. This is three times higher than the value for (001) of 0.06–0.09, as is consistent with results for other dopants in Si.\(^{11}\)

Figure 3 shows that we synthesized an approximately 100-nm thick layer of single-crystal (001) Si that is free of extended defects and supersaturated with Au to a concentration of roughly \(10^{19}\, \text{cm}^{-3}\), which is two orders of magnitude above the solid solubility limit. The relatively low diffusive speed of Au in Si is fortuitous, as Au impurities are known to create the filled and empty midgap energy levels required for the formation of a useful intermediate band.\(^{3}\) In principle, observing band-like conduction in the states induced by Au requires a solute concentration above both the threshold for impurity-state delocalization and the threshold concentration for overlap between the filled and empty impurity levels. One estimate\(^{39}\) suggests that elements such as Au, which create states near mid-gap in Si, should undergo a Mott insulator-to-metal transition at a concentration of approximately \(6 \times 10^{19}\, \text{cm}^{-3}\).\(^{40}\) However, this is likely to be an underestimate as the experimental thresholds\(^{7,41}\) for S and Se are above \(10^{20}\, \text{cm}^{-3}\) and, because Au creates a deeper level than does S or Se, its critical concentration would likely be higher. Considering both the substantial reduction in dopant segregation observed in the Nd:YAG melted samples relative to the XeCl\(^+\) melted sample and previous demonstrations of Au supersaturation in Si,\(^{21}\) it may be possible to increase the concentration of Au further without inducing cellular breakdown merely by increasing the implant dose. For \(v_D = 110\, \text{m/s}\) and assuming steady-state solidification conditions, we predict fully stable solidification at \(6 \times 10^{19}\, \text{cm}^{-3}\) if the solidification speed exceeds 7 m/s, which is achievable with the Nd:YAG laser used here.

### IV. DISCUSSION

There has been interest in understanding how \(v_D\) relates to more readily measured thermophysical properties of the alloy system, both for predicting the \(v_D\) of untested materials and for elucidating the kinetics of solute trapping at the resolidification front.\(^{11,17,19,42,43}\) To gain insight into these relationships, here we compare the \(v_D\) of transition metals in Si (or their lower limits), determined in this work, with previously reported values for a wide range of solutes.

The diffusive speed is related\(^{5}\) to the diffusivity of the impurity at the interface, \(D_i\), and the distance between atomic sites, \(\lambda\), by \(v_D = D_i/\lambda\). With little information about \(D_i\), correlations have been examined between \(v_D\) and the diffusivity of the impurity in crystalline silicon at the Si melting point \((D_i(T_m))^{17,42}\) We plot \(v_D\) vs. \(D_i(T_m)\) for 16 solutes in Fig. 4(a). A strong positive correlation between the two properties is apparent. It has been suggested that \(D_i\) can be approximated as the geometric mean of the diffusivity in molten silicon and crystalline Si at the melt temperature \((D_i = \sqrt{D_i(T_m)D_i})^{45}\) However, there is only 15% variation in \(D_i\) across all solutes presented here, and we find that taking the geometric mean of \(D_i(T_m)\) and \(D_i,\) does not improve on the correlation between \(v_D\) and \(D_i(T_m)\).

We also observe a strong inverse correlation between \(v_D\) and the equilibrium partition coefficient, \(k_e\), as shown in

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**FIG. 3.** (a) XTEM images of (001) Si and (111) Si implanted with 50 keV \(^{197}\)Au\(^{+}\) to the dose of \(10^{14}\, \text{cm}^{-2}\) and melted with an Nd:YAG laser as described in the text. The (001) Si is single-crystal and without extended defects, whereas the (111) Si exhibits stacking faults. (b) Concentration-depth profiles and associated simulation fits for (001) and (111) Si: Au. The surface concentration peak is likely a signal from the Au segregated to the surface and broadened by the SIMS instrument.
This correlation has been previously rationalized\cite{11,43} as a consequence of an energy barrier for solute redistribution that varies with the energetic component of the thermodynamic driving force within the context of the continuous growth model,\cite{5} as shown in Fig. 5. The rate at which a solute makes thermally activated transitions from a state of high redistribution potential in the crystal at the interface (state A) to an adjacent state of low potential in the melt (state B) is governed by the height of the activation barrier (state A*). The redistribution potential, $\mu'$, is the chemical potential of the solute minus the contribution from the ideal configurational entropy of mixing.\cite{9} Uniformity of chemical potential in equilibrium requires
\[
 k = \exp \left( \frac{\Delta \mu'}{RT} \right),
\]  
where $\Delta \mu'$ is the difference between $\mu'$ in the solid and that in the liquid, and $R$ is the universal gas constant. We seek a correlation among many different impurities in silicon, each of which has its own barrier height and its own value of $\Delta \mu'$.

Redistribution potential landscapes for two such impurities are sketched in Fig. 5: the solid curves represent a low-solubility impurity, and the dashed curves represent a high-solubility impurity. A proportionality has been proposed\cite{11,43} between the amount the barrier height $Q$ drops and the relative amount the potential well in the liquid drops as one considers impurities of progressively decreasing $k_e$ (increasingly more negative values of $\Delta \mu'$)
\[
 Q = Q_D + z \Delta \mu',
\]  
where $z$ is the correlation coefficient. Fig. 5(a) illustrates the case $z = 0$ (barrier height with respect to state A is independent of $\Delta \mu'$) and Fig. 5(b) illustrates the case $z = 1/2$ (barrier height drops half as much as does state B, with respect to state A). Early studies\cite{11,43} found $z \approx 0.6$. The diffusive speed itself is related to the barrier height as a thermally activated process
\[
 v_D = \text{const.} \exp \left( -\frac{Q}{RT} \right).
\]  
In this work, we are concerned only with thermophysical parameters near the pure Si melting point $T_m$ and so we replace $T$ by $T_m$ in Eq. (4). Likewise, the solid diffusivity is related to its apparent activation energy $Q_D$ by
\[
 D_S(T_m) = D_0 \exp \left( \frac{Q_D}{RT_m} \right).
\]  
We make the approximation that the barrier height in the absence of driving force, $Q_0$ in Fig. 5, is approximately the apparent activation energy for diffusion in the solid, $Q_D$
\[
 Q_0 \approx Q_D.
\]  
This is certainly an oversimplification. The variation in $D_0$ is ignored, and $Q_D$ contains contributions both from the point defect formation energy and the migration energy. The large number of impurity species we examine diffuse by a variety of mechanisms,\cite{44,45} some of which change with temperature and some of which are unknown at the melting point. Hence
we propose this simple approximation recognizing that it may fail to correlate species with different diffusion mechanisms.

A relationship between two independent thermophysical properties ($D_s(T_m)$, $k_e$) and $v_D$ can be derived by combining Eqs. (2)–(6), yielding

$$\log v_D = \text{constant} + \log \left( \frac{D_s(T_m)}{k_e^{0.67}} \right). \tag{7}$$

The assumptions discussed above thus lead to the prediction that a scatter plot of $\log(D_s(T_m)/(k_e^{0.67}))$ vs. $\log(v_D)$ for solutes in Si should exhibit a correlation with a slope near unity.

To test this proposal, we first determine the best-fit value of $x$ by rearranging Eq. (7) to read

$$\log \left( \frac{v_D}{D_s(T_m)} \right) = \text{constant} - x \log(k_e) \tag{8}$$

and applying a linear fit to extract the slope, $-x$. The scatter plot suggested by Eq. (8) is shown in Fig. 6(a). In this plot, the solutes exhibit two distinct behaviors depending on their dominant diffusion mechanisms in crystalline Si. The group III, IV, and V solutes (As, Bi, Ga, In, Sb, and Sn) exhibit a much lower $D_s(T_m)$, which is a consequence of their vacancy-mediated diffusive mechanisms in c-Si.\cite{44,46-48} These relatively slow diffusers exhibit a linear trend as predicted by Eq. (8); yielding a best-fit slope $m = 0.91$ ($R^2 = 0.80$), in good agreement with the slope predicted ($m = 1$). Data presented in (a) and (b) were calculated from references listed in Figure 4. Elements for which $k_e$ is unavailable (Pd, Pr, Se, Te) were omitted from this analysis.

![Fig. 6](image-url)

FIG. 6. (a) Log-scale scatter plot of $v_D/D_s(T_m)$ vs. $k_e$, as suggested by Eq. (8). Group III–V solutes exhibit a linear trend (solid line) with a best-fit slope $-x$ of $-0.67$ ($R^2 = 0.69$). (b) Log-scale scatter plot $v_D$ vs. $D_s(T_m)/k_e^{0.67}$ as suggested by Eq. (7), with $x = 0.67$. A linear fit to the Group III–V solutes (As, Sb, Sn, Bi, Ga, In) yields a slope $m = 0.91$ ($R^2 = 0.80$), in good agreement with the slope predicted ($m = 1$). Data presented in (a) and (b) were calculated from references listed in Figure 4. Elements for which $k_e$ is unavailable (Pd, Pr, Se, Te) were omitted from this analysis.

V. SUMMARY

In search of a solute for the formation of an impurity band in the band gap of Si, we investigated the supersaturation of Si with transition metals using ion implantation and pulsed laser irradiation, structurally characterized the resulting material using SIMS and XTEM, and extracted $v_D$ from the composition-depth profiles. Very large $v_D$ ($10^2$–$10^4$ m/s) resulted in cellular breakdown at the solidification front for most transition metals. SIMS and XTEM characterization showed that both Au and Zn were incorporated into Si at high concentrations, but it was not immediately clear why these transition metals were incorporated whereas others exhibited cellular breakdown. Next, we identified strong correlations between $v_D$ and two independent thermophysical

\[ \text{relations between } v_D, \text{ and } k_e. \]
properties: $D_s(T_m)/k_e$. These independent trends were consolidated into a single correlation parameter by assuming the barrier height for unbiased thermally activated jumps across the crystal-melt interface is the same as the apparent activation energy for solid-state diffusion at the melting point. The resulting correlation, described by Eq. (7) and Figs. 6(a) and 6(b), is established only for solutes that exhibit vacancy-mediated diffusion. Nevertheless, the combination $D_s(T_m)/k_e^{0.67}$ might serve as a metric for evaluating the potential for supersaturating Si with transition metals using PLM.

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