Nonequilibrium Segregation and Trapping Phenomena during Ion-Induced Crystallization of Amorphous Si

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The segregation and trapping of Au at the moving crystal-amorphous Si interface has been measured. Epitaxial crystallization was induced by 2.5-MeV Ar-ion irradiation. The Au segregation is analogous to behavior at liquid-solid interfaces except that the interfacial segregation coefficient of 0.007 at 320 °C is independent of velocity between 0.6 and 6 Å/sec. The Au is trapped in crystalline Si at concentrations some 10 orders of magnitude in excess of equilibrium concentration.

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The behavior of impurity atoms at moving phase boundaries can provide important information on basic crystal growth and solidification processes. Great strides 1,2 were made in the 1950's in the understanding of the redistribution and zone-refining of solute atoms during solidification. In general, the redistribution can be characterized by a segregation or partition coefficient between the solid and liquid equilibrium phases. If the equilibrium concentration of solute in the liquid is greater than in the solid, rejection will occur ahead of a solidifying interface. The final profile of the rejected solute depends on both the velocity of the interface and the diffusivity of the solute in the liquid. Renewed interest in these segregation phenomena has occurred because of the very rapid interface motion and nonequilibrium crystal growth associated with laser melting^{3,4} of surface layers. Under such conditions, solute can be segregated in quite novel fashions with interfacial segregation coefficients exceeding the equilibrium values by several orders of magnitude.^{5,6} This solute trapping^{7,8} is a direct consequence of the undercooling (or chemical potential driving force) produced by the high interface velocities and occurs when the liquid-phase diffusive velocity of the solute is comparable to the interface velocity.

In this Letter we describe Si crystal growth and segregation in an entirely new regime. Rather than studying liquid-to-solid segregation, we have observed analogous segregation phenomena in amorphous Si (a-Si) to crystalline Si (c-Si) transformations. Like a solidifying liquid, *a*-Si is thermodynamically unstable in contact with *c*-Si, and elevated temperatures result in epitaxial regrowth⁹ via a thermally activated process. We have recently discovered that impurities such as Cu, Ag, and Au have high solubilities^{10,11} in *a*-Si as compared with their solubilities in *c*-Si. We estimate Au to be 8 orders of magnitude more soluble in *a*-Si than in *c*-Si at 515°C by comparing the measured solubility 10,11 in *a*-Si with the extrapolated solubility 12 in *c*-Si. Gold also has a high diffusivity 10,11 in *a*-Si and can be uniformly diffused within an implanted *a*-Si layer at temperatures ≈ 500 °C. Solid-phase epitaxy at these temperatures results in the Au being retained within the narrowing amorphous layer because of its low segregation coefficient. Consequently, impurity segregation should occur at a regrowing *c*-Si-*a*-Si interface with behavior similar to liquid-solid interfaces. Because the entire process occurs in the solid phase, however, the dynamics and impurity profiles may be studied with unprecedented accuracy. Indeed, since *a*-Si exists metastably at room temperature, the solute profile can be thermally quenched at any particular phase of the regrowth process.

Solid-phase epitaxial crystallization can also be induced by ion irradiation^{13,14} at temperatures as low as 200 °C with an activation energy of only 0.3 eV and with interface velocities of $\simeq 1$ Å/sec. At these temperatures, the Au diffusive velocity is comparable to the interface velocity. Parameters important in the characterization of the segregation process are the interfacial segregation coefficient k' (the ratio of the solute concentration in the c-Si to that in the a-Si at the interface) and the diffusive escape distance D/v (the ratio of diffusivity away from the interface to the interface velocity). In liquid-phase bulk crystal growth, D/v is $\simeq 50 \ \mu m$, whereas in surface laser melting it is $\simeq 50$ Å. As D/v approaches the interatomic spacing, the probability increases for solute atoms to be engulfed or trapped by an advancing interface. For ion-beam-induced crystal growth at 250°C, D/v is ≈ 0.1 Å if the diffusivity retains its usual thermal value. As discussed below, however, the diffusivity is also enhanced above thermal values by the ion-beam irradiation which results in longer escape distances of $\simeq 20$ Å. These values should result in an intriguing segregation and trapping regime.¹⁵

Silicon wafers (100) were implanted with Au ions at an energy of 3 MeV to a dose of 10^{16} ions/cm². This implantation produces an a-Si surface layer approximately 1.6 μ m thick with the Au at a depth of approximately 1 μ m. The samples were then furnance annealed to redistribute the Au uniformly throughout the amorphous layer. Typical annealing conditions were 485 °C for 24 h at 10^{-7} Torr, resulting in *a*-Si layers 1.1 μ m thick with Au concentrations ≈ 0.2 at.%. Ion-beam-induced crystallization experiments were then carried out at temperatures of 250, 325, 375, and 420 °C, with 2.5-MeV Ar-ion bombardment. Irradiations were made through 1-mm-diam apertures at doses of 2×10^{16} - 4×10^{17} ions/cm² and at low dose rates (1.4×10^{13} - 1.4×10^{14} ions/cm² sec) to avoid beam heating. The a-Si thicknesses and Au-depth profiles were measured by the Rutherford backscattering and channeling techniques with 2-MeV ⁴He ions. The samples were also analyzed by transmission electron microscopy.

Figure 1 shows Rutherford backscattering and channeling spectra of a sample before and after irradiation at 320 °C with 2.5-MeV Ar at a dose of 2×10^{17} ions/cm² and dose rate of 7×10^{13} ions/cm² sec. The Au depth profiles as functions of dose are plotted in Fig. 2. The dose rate was constant at 7×10^{13} ions/cm² sec yielding an interface velocity of $\simeq 3$ Å/sec. The zone-refined profiles display the characteristic features of the segregation process: buildup of segregated solute at the interface and the concomitant removal of material-"the initial transient." At steady state (cf. lower part of Fig. 2), the amount of material in the segregation spike remains constant and solute is rejected behind the moving interface at the initial concentration. There are several novel features to this crystal-growth and impurity-segregation process. First, it is remarkable that Au is trapped in c-Si at concentrations of at least 10 orders of magnitude



FIG. 1. Backscattering and $\langle 100 \rangle$ channeling spectra of 2.0-MeV He from 1.1- μ m *a*-Si containing Au before (circle) and after (triangle) ion-beam-induced crystallization with 2.5-MeV Ar at a dose of 2×10¹⁷/cm² and temperature of 320 °C.

greater than the equilibrium solubility in c-Si.¹² Transmission electron microscopy shows this c-Si to be defect free without evidence of Au precipitation. However, Rutherford backscattering and channeling measurements give no evidence of the Au atoms residing on substitutional lattice sites.

The velocity dependences of the processes also show some intriguing features. The interface velocity scales with the Ar dose rate: i.e., the rate of defect production at the interface. The velocity can therefore be controlled easily and reproducibly. We observe that an order-ofmagnitude change in velocity (i.e., same dose but an order-of-magnitude difference in dose rate) produces identical segregation profiles. This is in direct contrast to the liquid-solid case where the width of the segregation transient scales inversely as velocity.

The fact that the segregation profiles are independent of interface velocity suggests that the defect-production rate controls not only the interface velocity but also the diffusive motion of Au ahead of the interface. Specifically, the equilibration distance D/k'v (the width of the "initial transient") must remain constant for all interface velocities. We have, therefore, measured the diffusion of implanted Au in *a*-Si in the presence of the Ar beam. The diffusivity scales linearly with the dose rate, as does the interface velocity, and is considerably enhanced over the thermal values,¹⁶ showing an Arrhenius behavior with an activation energy of 0.37 eV. (The athermal ballistic-mixing or recoil-implantation



FIG. 2. Gold depth profiles in c- and a-Si before and following 2.5-MeV-Ar-induced crystallization at different doses. The equilibration distance X_c is indicated.

component of the radiation-enhanced diffusion coefficient is at least an order of magnitude less than the thermally activated component). Experimentally then it is observed that both the diffusivity and velocity scale the same way with dose rate. A direct consequence of this result is that the parameter D/v is independent of interface velocity. Combined with the result that the segregation profiles (i.e., D/k'v) are velocity independent, we conclude that k' is also independent of velocity.

We have fitted¹⁷ the experimental solute profiles using only one free parameter-that of the interfacial segregation coefficient k'. Figure 3 shows a fit to the 320 °C data with the measured interface velocity of 2.85 Å/sec and radiation-enhanced diffusivity of 4.4×10^{-15} cm²/ sec. The fit gives k' to be 0.007 \pm 0.004. To allow for detector resolution, straggling, and the waviness of the interface (as measured by transmission electron microscopy), these fits have been convoluted with a Gaussian of $\sigma \approx 300$ Å. The width (D/v) of the segregated spike is expected to be $\simeq 20$ Å, and we do not have the experimental resolution to measure the depth profile directly. The fitted k' values indicate that the peak concentration of Au at the interface should be 20 at.%. This value is clearly in excess of equilibrium solubilities of Au in a-Si which, for example, we measure to be 0.7 at.% at 515 °C. The solubility of Au in a-Si in the interface region is therefore markedly enhanced by the ion irradiation over the 20-Å spike width.

Fits to the experimental profiles at 250 °C and 375 °C with measured diffusivities of 1.6×10^{-15} cm²/sec and 9×10^{-15} cm⁻²/sec, respectively, give k' values of 0.013 ± 0.007 and 0.005 ± 0.004 . The absolute errors in k' arise mainly from uncertainties in diffusivity. The relative errors, however, are much smaller and are $\approx 10\%$. The interfacial segregation coefficient is therefore temperature dependent. Figure 4 shows k' as a function of velocity at a temperature of 320 °C. The rel-



FIG. 3. Gold depth profile in c- and a-Si following 2.5-MeV-Ar-induced crystallization at a temperature of $320 \,^{\circ}\text{C}$ and dose of $2 \times 10^{17}/\text{cm}^2$. The smooth line is a numerical solution to the diffusion equation with a moving boundary, fitted to the experimental profile with the assumption of only one free parameter, k'.

ative errors are given by the size of the data points while the absolute errors are given by the error bars. At a fixed temperature, k' is therefore independent of interface velocity. This segregation behavior is different from that occurring in liquid-phase epitaxy, where k' scales with v because the chemical driving force for trapping increases with the velocity-dependent undercooling in the liquid.

The measured values for k' are approximately 3 orders of magnitude greater than the equilibrium value observed during liquid-phase crystal growth^{12,18} and are independent of interface velocity. There are several possible explanations for this enhanced segregation coefficient. One possibility follows classical segregation thermodynamics. The driving force for trapping is related to the chemical potentials of the impurities in the *a*- and *c*-Si which depend on temperature but are independent of the interface velocity. The concentration of impurities in the growing *c*-Si phase (and hence the chemical potential) will be proportional to the impurity concentration in *a*-Si. Furthermore, the nonequilibrium defect concentrations produce by the ion irradiation will contribute further to the trapping.

On the other hand, ballistic mixing (or recoil implantation) at the interface may also provide the nonequilibrium mechanism for driving Au at the interface into the growing crystalline phase. As in thermodynamiccontrolled segregation, the concentration of impurities incorporated into the crystalline phase by ballistic mixing will be proportional to the impurity concentration in *a*-Si at the interface. Indeed, the two mechanisms are almost indistinguishable. We can estimate the magnitude of this mixing segregation from our measurements of the athermal ballistic-mixing diffusivity $(2 \times 10^{-16}$ cm²/sec) and interface velocity of 3 Å/sec which pertain



FIG. 4. The interfacial segregation coefficients, k', of Au at the *c-a* Si interface as a function of interface velocity at a temperature of 320 °C.

to the data of Fig. 2. From an atomistic model of diffusivity, ¹⁹ where $D = 1/6\Gamma a^2$ ($a \approx 3$ Å is the jump distance), we obtain an atomic-jump frequency (Γ) of order 1 per second. At interface velocities 3 Å/sec, every atom consequently makes one jump during the time the interface advances one atomic layer. This mixing can therefore account for a maximum segregation coefficient of order $\frac{1}{6}$, the probability of a Au atom at the interface ballistically diffusing across the interface and being trapped by the advancing growth front. This is clearly an upper limit since the nonballistic diffusional mixing (an order of magnitude faster in the a-Si) across the interface will tend to return the system to equilibrium and reduce the trapping coefficient. Estimates of the return of the system are difficult since the atomic exchange rate across the interface is not known. Further experiments with alternative ions and dopant impurities are necessary to resolve this question. However, to first order, both the ballistic mixing model and the free-energy trapping arguments are consistent with the observed increase of k'with decreasing temperature.

In conclusion, we have presented results on a novel regime of crystal growth had segregation. Amorphous Si films on c-Si have been doped with Au to high concentrations. Ion-beam irradiation has been used to recrystallize the a-Si epitaxially at temperatures where the usual Si bond breaking and rearrangement are completely frozen out and diffusion of Au in the a-Si layer is greatly suppressed. The resulting Au profiles exhibit the classic shapes of segregation at phase boundaries. The process, however, is highly nonequilibrium with Au being trapped in c-Si at concentrations far in excess of solubility limits. At a given temperature, interface velocity and solute diffusivity scale linearly with ion-induced defect production. Interface segregation therefore is velocity independent at a fixed temperature.

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