Dominant Influence of Beam-Induced Interface Rearrangement on Solid-Phase Epitaxial Crystallization of Amorphous Silicon

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Bombardment with 0.6–3-MeV Ne^+ ions has been employed to stimulate solid-phase epitaxial growth of amorphous silicon at temperatures 200–500 °C. Two distinctly different regrowth regimes have been identified. In the temperature range 200–400 °C the activation energy for beam-induced regrowth is 0.24 eV, whereas, in the temperature range above 400 °C, it is higher (>0.5 eV), but less well defined because of competing thermal effects. Results indicate that ion irradiation generates (athermally) nucleation sites for crystal growth, a process which has a high ($\sim$2.4 eV) activation energy in the absence of ion-beam excitation.

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Amorphous layers in the near-surface region of crystalline silicon recrystallize by solid-phase epitaxial growth (SPEG) when heated to temperatures of >500 °C.[1] This process is characterized by an activation energy of $\sim$2.7 eV.[2] Phenomenological models of the SPEG process[3-7] have been successful in providing a qualitative explanation for the dependence of the growth kinetics on both substrate orientation and concentration of dopants; however, details of the growth mechanism are yet to be determined, in particular the interpretation of the activation energy.

Recently, it has been observed that SPEG can be induced in silicon at ambient temperatures in the range 200–500 °C by irradiation with energetic ions.[8-13] These studies have adequately demonstrated that crystallization is not a consequence of local beam heating but results more directly from ion-atom interactions in the substrate. However, the experimental conditions employed in these studies often precluded the identification of the factors responsible for beam-induced SPEG. In particular, the competition between damage production and crystallization induced by the ion beam often complicated the interpretation of results.[8,10,11] In the present study, by simplifying the bombardment conditions we have been able to demonstrate the dominance of defect generation at the amorphous-crystalline interface in controlling SPEG.

We have studied SPEG of $\sim$1000-Å-thick amorphous silicon layers produced in (100)-oriented single-crystal silicon samples, held at $\sim$77 K, by irradiation with 50-keV Si^+ ions to a fluence of 2.5×10^{14} cm^{-2}. We have used 0.6–3-MeV Ne^+-ion bombardment to stimulate SPEG. These high-energy ions penetrate to depths of 0.95 to 2.5 μm, respectively. Over the first 4000 Å of their penetration the ions lose energy at a nearly constant rate (<5% variation even in the 0.6-MeV case), so that the amorphous layers are uniformly excited throughout their thickness. Before neon-ion bombardment all samples were preannealed thermally at 450 °C for 15 min to remove partial amorphous regions and thus provide an abrupt crystal-amorphous interface for beam-induced SPEG studies. Both Ne^+-induced crystallization and subsequent analysis of the extent of growth using 1.5-MeV-He^+ ion channeling and backscattering were performed *in situ* in a vacuum chamber operating at 10^{-7} Torr. Samples were mounted on a two-axis goniometer with the ability to operate at substrate temperatures up to 600 °C. The Ne^+ beam employed for SPEG was electrostatically scanned across a 3-mm aperture placed 5 cm from the sample. Beam fluxes of 2.2×10^{12} to 8.8×10^{12} cm^{-2} sec^{-1} were used. Although most irradiations were performed in a random direction with respect to the underlying crystal, beam collimation in the scanned mode was sufficient to allow channeling in single-crystal silicon with an $x_{\min}$ of 5%. Substrates could be translated to allow several sample regions to be irradiated sequentially under varying conditions. The He^+ beam for ion-channeling analysis was defined by a 1-mm aperture aligned coaxially with the 3-mm aperture employed for Ne^+ irradiation.

Typical results of SPEG induced by Ne^+ irradiation are illustrated by the 1.5-MeV-He^+ ion-channeling spectra in Fig. 1. The spectra from as-implanted samples are shown as dashed curves and the preannealed samples (450 °C for 15 min with no Ne^+ irradiation) are indicated by open circles. As shown, preannealing removes about 200 Å of partially amorphous disorder at the amorphous-crystal interface and sharpens the interface. For all cases in which the substrate temperature was maintained at <400 °C during Ne^+ irradiation, the extent of epitaxial growth, for a given Ne^+ energy, was found to be linearly dependent on the incident ion fluence. This is illustrated in Fig. 1(a), the case for successive 1.5-MeV-Ne^+ irradiation at 318 °C. The ion-channeling spectra in this figure depict SPEG of $\sim$170 Å for each fluence increment of 3×10^{16} cm^{-2}. Following a dose of 1.2×10^{17} cm^{-2}, the regrowth is almost complete, with <100 Å of amorphous silicon remaining. In this case, the crystal quality is good, as indicated by a channeling minimum yield of <6%. Figure 1(b) illustrates similarly good re-

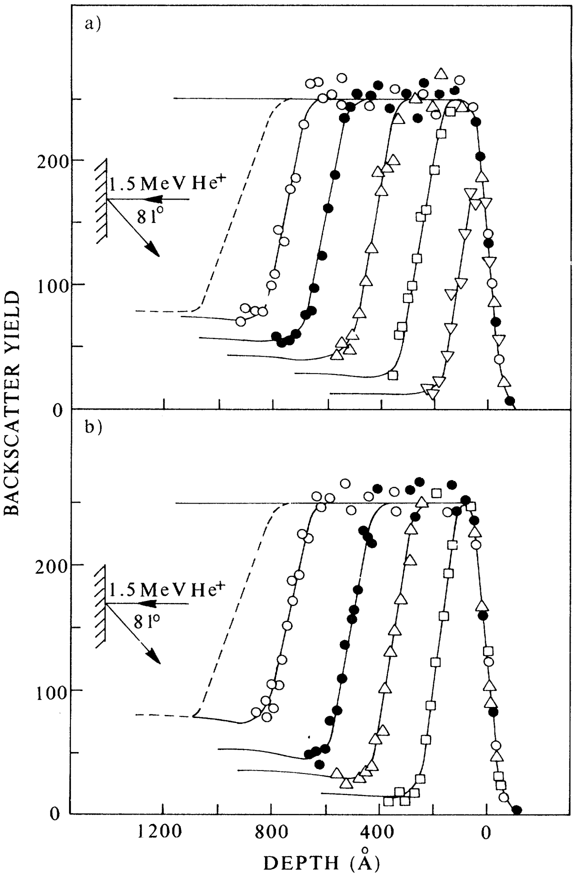

FIG. 1. Aligned Rutherford backscattering spectra displaying the thickness of an amorphous silicon layer as-implanted (dashed curve), following a preanneal at 450 °C for 15 min (open circles), and after successive Ne^+ irradiations. Results are shown for (a) samples irradiated at 318 °C with equal fluence steps (3×10^{16} Ne^+ cm^{-2}) of 1.5-MeV Ne^+, and (b) samples irradiated at 450 °C with equal fluence steps (5×10^{15} Ne^+ cm^{-2}) of 0.6-MeV Ne^+.

growth for 600-keV Ne^+ irradiation of substrates held at a temperature of 450 °C. However, in Fig. 1(b) and at all temperatures >400 °C, the growth is not simply proportional to beam fluence.

SPEG measurements, obtained from data such as those depicted in Fig. 1, are plotted as a function of $1/T$ in Fig. 2. Regrowth per 10^{16} Ne^+ cm^{-2} is shown for three Ne^+-ion energies, 0.6, 1.5, and 3.0 MeV. Thermal SPEG data, with an activation energy of 2.68 eV drawn through our 520 °C (thermal only) measurements, have been included on the figure for comparison. The thermal curve has been scaled by normalizing to the time taken to irradiate to a fluence of 10^{16} Ne^+ cm^{-2}, employing a constant beam flux of 4.4×10^{12} cm^{-2} sec^{-1}. Two distinct beam-induced annealing regimes are evident in this figure. We will concentrate on the regime at temperatures <400 °C in which regrowth is linear with neon-ion fluence and independent of neon-ion flux. In this regime, ion-beam–induced SPEG enhances regrowth by several orders of magnitude and has a single activation energy of 0.24 eV, independent of the incident ion energy. This value is less than 10% of the activation energy for thermally induced SPEG and is close to the migration energy of point defects in silicon.[14]

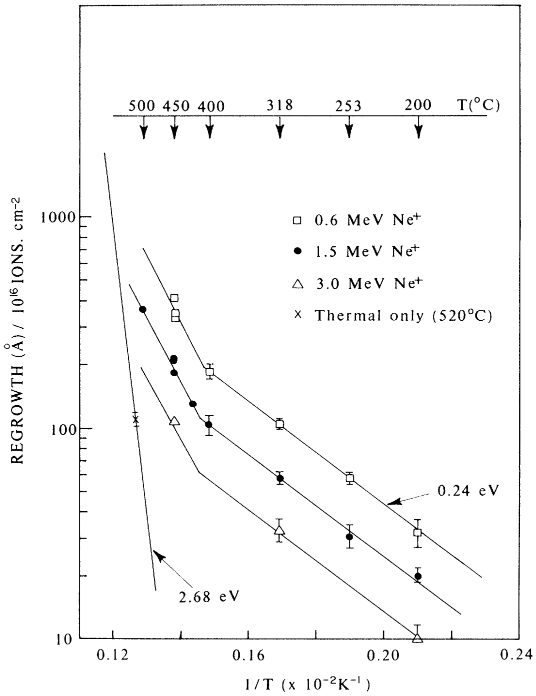

FIG. 2. Temperature dependence of beam-induced regrowth as a function of Ne^+ irradiation energy. Thermal-only regrowth is depicted by the line labeled 2.68 eV. It has been normalized to the Ne^+ data by scaling to the time taken to irradiate to a fluence of 1×20^{16} Ne cm^{-2} sec^{-1}.

The data in Fig. 2 also illustrate that the extent of crystal growth per incident ion is dependent on the incident ion energy. For the neon-ion energies we have used, the dominant loss of energy is in electronic excitation (hole-electron pair generation) which increases with increasing energy from 83 to 153 to 198 eV/Å for 0.6, 1.5, and 3.0 MeV, respectively. The neon-ion energy lost in nuclear collisions (which results in collisional displacement of silicon atoms) has the opposite trend with energy: 4.8, 2.5, and 1.5 eV/Å for 0.6, 1.5, and 3.0 MeV, respectively. In Fig. 2, for temperatures below 400 °C the growth is found to be precisely proportional to the energy lost in nuclear collisions. This is consistent with the conclusions of previous studies[10–13] but is found in the present case even at very high hole-electron pair-generation rates. There is no hint of the inverse energy trend that inelastic processes would imply.

It has been suggested that beam-induced SPEG might be due to generation of defects in the underlying crystalline silicon and their migration and interaction at the growing crystalline-amorphous interface.[11–13] To test the validity of this idea, we have used channeling of the Ne^+ beam to reduce the magnitude of the nuclear energy loss and defect production in the crystalline silicon. Figure 3 shows typical results of such a channeling experiment. In this case the substrate was held at 318 °C and irradiated with 1.5-MeV Ne^+ ions. The growth steps each represent a Ne^+ fluence of $3\times10^{16}\ \mathrm{cm}^{-2}$. The first growth step is for a randomly incident beam, the second is for a channeled beam, and the third is, once again, for a random beam. The extent of growth is exactly the same for random and channeled irradiations. Computer simulation using TRIM[15] shows that greater than 50% of the incident Ne^+ ions should be channeled after traversing an amorphous layer 800 Å thick. Therefore, if defect migration from the underlying crystal were of dominant importance we would expect approximately a factor of 2 decrease in the regrowth under channeling conditions. Additional channeling measurements utilizing Ne^+-induced SPEG of buried amorphous layers have shown that growth is not diminished when the nuclear energy loss in the surface crystalline regions is reduced by channeling to ~5% of its random value.[13] These channeling results indicate that growth is not dominated by defects generated in the crystalline material and migrating to the growing interface. In addition, the extent of epitaxial growth is independent of the amorphous-layer thickness so that defect migration within the amorphous material is also unimportant. These observations isolate the beam effect to the amorphous-crystalline interface itself, where displaced silicon atoms may contribute to growth.

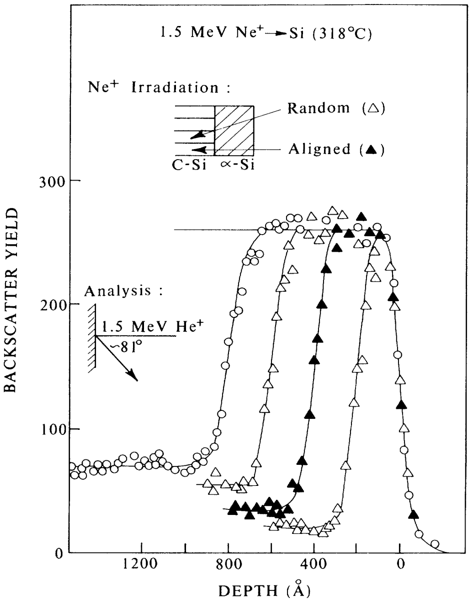

FIG. 3. Aligned Rutherford backscattering spectra depicting the thickness of an amorphous silicon layer after preannealing (open circles) and following three successive, equal-fluence ($3\times10^{16}\ \mathrm{Ne}^+\ \mathrm{cm}^{-2}$), irradiations with 1.5-MeV Ne^+. As indicated in the inset, the second irradiation was undertaken with the Ne^+ beam aligned along the ⟨100⟩ axis of the underlying crystalline silicon, whereas the other two irradiations were performed in a random direction.

It is instructive to compare the magnitude of regrowth with the calculated displacement rate from nuclear collisions. From Figs. 1(a) and 2, for a sample held at 318 °C, bombardment with 1.5-MeV Ne^+ results in ~3 recrystallized atoms per incident ion. In contrast, the simple Kinchin and Pease[16] model predicts an average of only ~0.3 displaced atoms at the interface per ion (with the assumption of an atomically sharp interface and a silicon displacement energy of 13 eV). The larger number of subthreshold collisions (i.e., where the nuclear energy transfer to a silicon atom is insufficient to displace it) may contribute to crystallization. However, our results show that the recrystallized-atom/displaced-atom ratio is weakly temperature dependent even though the nuclear energy deposition is temperature independent. This leads us to suggest that displayed atoms lead to multiple rearrangements of surrounding atoms, and that the measured activation energy of 0.24 eV is associated with subsequent crystallization processes around these nucleation sites generated at the interface by nuclear collisions of the ion beam.

The nature of the nucleation and subsequent crystallization processes is, at present, unknown. It is possible to imagine, however, that an atomic displacement, or rear displacement, may give sufficient geometric freedom (and even urgency) to enable the rearrangement of neighboring atoms. This rearrangement may involve a temperature-dependent cooperative bond rearrangement process which reduces the local strain energy, a process which is similar to cooperative bond-breaking models for conventional thermally induced SPEG.[4,7] Alternatively, the nucleation site may itself move within the interface to catalyze crystallization, with a migration energy of 0.24 eV, a value typical of point-defect migration energies in crystalline silicon.

Our results for temperatures >400 °C are less clear. The apparent activation energy is larger, 0.6 eV, as drawn through the 1.5-MeV-Ne data of Fig. 2. However, this activation energy is not unique in this temperature range and depends on the irradiation history of the sample [e.g., nonlinearity of growth with ion fluence as shown in Fig. 1(b)]. Furthermore, there is an ion-flux dependence in the regrowth: The extent of SPEG is found to increase with decreasing ion flux (for constant fluence). This latter result is consistent with He^+-induced SPEG data at 440 °C.[12] The identification of different flux behaviors in the two temperature regimes reconciles the apparent consistency in the published literature.[11,12] We do not fully understand the implications of these results, but we believe that competition with thermal effects (e.g., longer-range defect migration and/or thermally induced growth) is involved in the higher-temperature regime.

Since hole-electron pair generation results in broken Si-Si bonds it might be expected that electronic excitation by neon ions would enhance the rate of epitaxial rearrangement at the amorphous-crystalline interface. Multiple broken bonds on interface atoms should be even more effective in this role. Therefore, the experimental absence of any contribution of hole-electron pair generation to interfacial growth is surprising. Although the average excitation-induced hole-electron concentrations are low (comparable to the intrinsic value of $< 10^{16}\ \mathrm{cm}^{-3}$ at 400 °C, if we assume a hole-electron pair lifetime of as long as 1 μm), the transient hole-electron density along the path of a single Ne-ion track is extremely high. For 1.5-MeV Ne^+ it is $> 5\times10^{22}\ \mathrm{cm}^{-3}$ in a 20-Å-radius cylinder around the particle track immediately following the ion's passage ($\sim 10^{-15}$ sec). The fraction of interfacial atoms within the cylinder with one broken bond is thus approximately unity and the fraction with multiple broken bonds is high. If long lived, such excitation must enhance the probability of epitaxial rearrangement of silicon atoms at the interface. However, this is inconsistent with the observed scaling of growth with nuclear energy loss. Thus, the hole-electron density must dissipate before atomic rearrangement can occur. Indeed, radial ambipolar diffusion of the hole-electron density away from the cylindrical track reduces the density by a factor of more than 10 in $\sim 10^{-13}$ sec, a time which is typical for atomic rearrangement processes. Auger recombination processes on a similar time scale further reduce the hole-electron density.

In summary, our results indicate two distinct crystallization regimes in the temperature range 200–500 °C. We have unambiguously shown that beam-induced atomic rearrangements at the amorphous-crystalline interface control solid-phase epitaxial growth at temperatures less than 400 °C. The low activation energy (0.24 eV) for crystallization around these collision-generated nucleation sites leads to the conclusion that the overwhelming fraction of the activation energy measured under thermal growth conditions is required to produce such nucleation sites. Crystallization in the temperature regime above 400 °C is more complex as a result of competing thermal effects. Broken bonds associated with hole-electron pair generation are unimportant at least at the densities accessible in our experiments.

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[14] Recently, Linnros *et al.* (Ref. 11) have reported a 0.36-eV activation energy for 300-keV-Ne^+–induced SPEG of silicon on sapphire in the temperature range <400 °C. Our significantly different result may be due to our use of higher-energy, more uniformly interacting ions which simplify both the regrowth and the data interpretation. Alternatively, the difference may be associated with the differences between the silicon-on-sapphire and bulk-silicon starting materials.

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