Growth-Site-Limited Crystallization of Amorphous Silicon

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The ion-beam-induced epitaxial crystallization rate of amorphous Si was measured by time-resolved reflectivity on crystal substrates with orientations every 5° from (100) to (111) to (011). The measurements show that the (011) regrows 3% slower than the (100), and the regrowth rate steadily decreases with increasing misorientation towards the (111). These data can be explained using a growth-site-limited model wherein a beam-induced defect flux to the interface results in a growth rate dependent on the interfacial bonding configuration.

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Ion-beam-induced epitaxial crystallization (IBIEC) is a nonequilibrium epitaxial growth process induced by ion irradiation through an amorphous-Si (*a*-Si)-crystal-Si (*c*-Si) interface. At low temperatures (200–400 °C), IBIEC can lead to growth rates many orders of magnitude faster than conventional thermal solid-phase epitaxy (SPE) [1,2]. This extremely nonequilibrium growth leads to kinetic processes similar to those observed in rapid liquid-phase solidification [3]. The existence of two very different solid-state epitaxial growth regimes naturally leads to the question of whether the atomistic growth mechanisms of IBIEC and SPE are related. However, even with the wealth of experimental data available [1], the best current IBIEC model is purely phenomenological [4]. Thus, understanding IBIEC, and its relation to SPE, requires new data to construct an atomistic growth model for IBIEC.

The dependence of the growth rate on substrate orientation is crucial information for atomistic growth models because it probes the interaction of the growth mechanism with the different interface structures. To date, the IBIEC growth rate v has been measured only on the (100), (111), and (011) orientations, with $v_{111} \approx \frac{1}{3} v_{100}$, and $v_{011} \approx v_{100}$ [5–7]. In contrast, the SPE rate has been measured for orientations every 5° along (100)-(111)-(011) [8–10]. The SPE results show large changes versus orientation, with $v_{111} = \frac{1}{25} v_{100}$, and $v_{011} = \frac{1}{3} v_{100}$. This places stringent requirements on atomistic growth models, which are met by current SPE theories [11,12]. The quantitatively different response of IBIEC to substrate orientation could be caused by a separate atomistic growth mechanism, changes to the interface structure, or a combination of these factors. Without complete data, however, constructing and testing atomistic IBIEC models are impossible.

In this Letter, we will present accurate measurements of the IBIEC growth rate versus substrate orientation every 5° along the (100)-(111)-(011) arc, allowing for direct comparison with SPE. The variation in IBIEC rate with orientation differs significantly from the SPE data as well as from previous predictions [7,13]. To explain the measured IBIEC orientation dependence, we present a new atomistic model within which an orientation-independent defect flux from the bulk to the interface causes crystallization at an interface-structure determined rate, and also alters the interface structure itself. This provides an atomistic basis for the existing phenomenological model of IBIEC [4], and also provides a direct link to atomistic models of SPE [11,12].

Samples with orientations every 5° from (100) to (111) to (011) were cut from a single *p*-type (B-doped), 30-Ω cm float-zone Si boule [14]. These wafers have also been used for studying SPE as a function of orientation, allowing for direct comparisons between SPE and IBIEC [10]. The orientation samples, along with (100) Si reference samples (B-doped *p*-type, 5–15-Ω cm float-zone Si), were amorphized by implanting $2 \times 10^{15}/\mathrm{cm}^2$ 80-keV Si ions at liquid-nitrogen temperature. The samples were then annealed at 400 °C for 1 h in a vacuum furnace ($\leq 1 \times 10^{-7}$ Torr) to remove damage in the crystal substrate without inducing SPE. The *a*-Si thickness was 150 nm as measured by Rutherford backscattering spectrometry (RBS) in the channeling configuration.

Regrowth was induced by 600-keV Kr^{++} irradiation at a nominal temperature of 310 °C resulting in a growth rate of typically $\sim$(1 nm)/(10^{14} ions/cm^2). The Kr beam was scanned across a 2.5-cm-diam circular aperture with a dose rate on target of 1×10^{12} Kr/cm^{2}sec. Because run-to-run variations in temperature or dose could obscure the small velocity changes expected in this experiment, both an orientation sample and a (100) reference (each $\sim 0.5 \times 0.5$ cm^2) were mounted within the irradiated area so that the velocity of each orientation *relative* to the reference could be directly determined. The samples were attached to the sample holder with silver paint to ensure good thermal contact. The temperature was measured directly by a thermocouple on the sample holder and indirectly through the reference sample regrowth rate. Temperature variations were less than 2 °C during a given irradiation, and all runs were within 10 °C of each other. Within a run, the doses for each sample were the same within $\leq 1\%$ as measured by RBS, and the absolute implant doses were within 5% of the current integrator value, with the uncertainty due to low levels of pulse pileup and uncertainties in the absolute RBS cross sections [15].

The position of the *a*-Si/*c*-Si interface of each sample was measured as a function of dose *in situ* using time-resolved reflectivity [2]. In this technique, optical interference between the surface and the moving *a*-Si/*c*-Si interface modulates the sample reflectivity, with a complete oscillation corresponding to the regrowth of 65 nm [1]. A single HeNe laser beam was split and directed onto the two samples, and the reflections were focused onto reverse-biased photodiodes. The signals from the photodiodes and the target current integrator were recorded by a personal computer. Analysis of the reflectivity data directly yields the interface velocity [2]. Regrowing two reference samples simultaneously results in measured velocities within 0.5% of each other, so we believe that the relative regrowth rates between different orientations can be determined within less than 2%.

Figure 1 shows, as an example, reflectivity traces versus dose (normalized relative to the reference sample) for several orientations. The position of the final maximum is indicated. Regrowth on the (011) is slightly (3%) slower than the (100), while orientations near the (111) are clearly slower. From such signals, the regrowth rate for each orientation can be determined. Figure 2 shows the IBIEC regrowth rates (solid circles) for each orientation relative to the (100). For comparison, SPE data from the literature [8–10] are also reported (dotted line). The IBIEC rate steadily decreases with increasing misorientation from (100) or (011). However, within 10° of the (111) the rate is nearly constant, and cross-section transmission electron microscopy indicates that growth on these orientations leads to twins. IBIEC on the (111) is known to twin after ≈ 20 nm of growth [5], resulting in nonepitaxial growth and an increasing velocity [7]. It is interesting to note that the orientation range for twinning under IBIEC is similar to that observed for SPE [9,16].

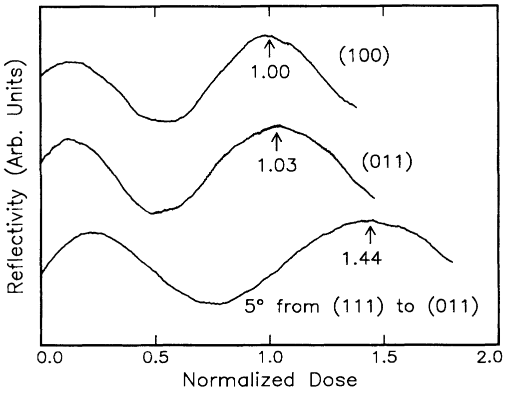

FIG. 1. Example reflectivities vs dose (normalized vs the references) for the (100), the (011), and 5° from the (111) towards the (011).

Comparing the IBIEC and SPE data shows two important distinctions. First, the (011) velocity is almost equal to the (100) velocity under IBIEC, while during SPE $v_{011} \approx \frac{1}{3} v_{100}$. Second, the decrease in velocity with misorientation from (100) or (011) is much less dramatic during IBIEC. These results indicate that the IBIEC and SPE growth mechanisms must have significant differences. Using the complete IBIEC orientation data we are able to discriminate between atomistic models of growth.

Atomistic models of SPE use the *a*-Si/*c*-Si interface construction of Spaepen [17], consisting of (111) terraces separated by $[01\bar{1}]$ ledges to minimize the number of unsatisfied crystal bonds. To be considered part of the crystal, an atom must be bonded to two other crystal atoms, so crystallization can only occur on ledges (although twinning is likely caused by a small chance for crystallization on the terraces). The sole SPE growth mechanism compatible with all experimental data [12] is dangling bond generation and propagation on the ledges, or, equivalently, defect-assisted motion of kinks along the ledges [11,18]. Kinetic modeling suggests that one SPE event crystallizes some 200 atoms along a ledge [12], so the ledges remain very straight during growth. In this case, the orientation dependence of the growth rate is determined by the ledge density, i.e., by the number of geometry-determined growth sites.

In contrast, the best picture for IBIEC is the phenomenological model of Jackson [4], consisting of rate equations for (unspecified) defect creation and annihilation in the bulk, with the resultant defect density at the interface determining the crystallization rate. This model does not require long-range defect migration, only that a non-

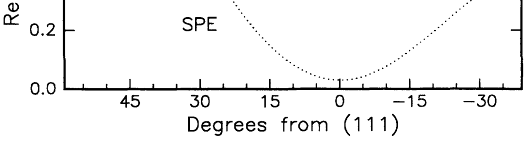

FIG. 2. IBIEC regrowth velocity relative to the (100) velocity (solid circles) for orientations along (100)-(111)-(011). The region of twinned crystal growth is indicated. The open circles are from Monte Carlo simulations using the atomistic growth model discussed in the text, while the dashed line corresponds to the best-fit analytical roughening model. For comparison, the dotted line shows the general shape of the SPE rate vs orientation (from Refs. [8–10]).

equilibrium concentration of defects is generated by the ion beam and interacts near the interface. One suitable defect candidate is the dangling bond in the amorphous phase, but crystal defects cannot be ruled out. Temperature, dose rate effects, and the transition to the SPE regime are well described for IBIEC growth on the (100) orientation. However, the model contains neither an explicit orientation dependence nor a clear atomistic basis for including such a dependence. A previous suggestion for an atomistic basis was that the defects in Jackson's model were kinks on the interfacial ledges, analogous to SPE [13]. The result does not, however, match the current results. In general, a beam-generated interface-specific defect cannot account for $v_{100} \approx v_{011}$ because of the different areal densities of ledges.

The experimental IBIEC data can be explained by a new model where an orientation-independent beam-generated defect flux from the bulk to the interface interacts with interface bonds and catalyzes a limited number of crystallization events per defect. On a Spaepen-type interface, the defects must break bonds on ledges to cause crystallization, while breaking bonds out on the terraces is useless. Thus, for IBIEC, the controlling factor will be the *ratio* of interface bonds where crystallization can occur ("useful" bonds) compared to the total number of interface bonds. In this case, $v_{011} \approx v_{100}$ occurs because on either the (100) or (011) interface all bonds are on ledges. This is in contrast to SPE, where the absolute areal density of ledges controls growth.

The full orientation dependence of the IBIEC growth rate arises not only from the initial geometry of the *c*-Si/*a*-Si interface structure (the bonding configuration), but also from how growth in turn affects this structure. Once growth begins, the bonding at the interface is altered, which affects the chance of the next defect causing growth. On interfaces misoriented from (100) or (011), crystallizing a small number of atoms roughens the ledges, increasing the number of useful bonds at the interface. This is shown in Fig. 3, where the addition of several pairs of Si atoms (open circles) modifies the ideal interface. It is the atoms crystallized out onto the terrace (indicated in the figure) which allow the ledge to wander over the terrace, increasing the ratio of useful bonds to total bonds at the interface.

The wider the terrace adjacent to a ledge, the rougher the ledge may get because it can wander more. A simple analytical model for this roughening is that the ratio of useful to total bonds increases as the terrace width (in unit cells) to a power, W_t^n. For $n=0$ there is no roughening, while $n=0.5$ would represent a sawtoothed ledge. Fitting this model to the data [except in the twinned region near the (111)] yields a best fit n of 0.38, and results in the dashed line in Fig. 2. This means that roughening a ledge next to a terrace with $W_t=2$ makes the ledge ~30% more effective at crystallization.

To explore in more detail the atomistic effects of our growth model on the interface structure, we performed Monte Carlo simulations. Starting from ideal *a*-Si/*c*-Si interfaces, crystallization was attempted at random interface bonds. By crystallizing a minimum number of atoms at a time (1 or 2), and by not considering the configuration energy, these simulations should lead to maximal roughening. The relative growth rates resulting from this ledge-roughening growth-site-limited model are shown in Fig. 2 (open circles) for direct comparison with the experimental data. The excellent agreement between the model calculations and the data indicates that the proposed growth mechanism is plausible. This atomistic mechanism is entirely consistent with Jackson's phenomenological model and can be easily incorporated within that framework, yielding a complete and unified picture of silicon epitaxial regrowth.

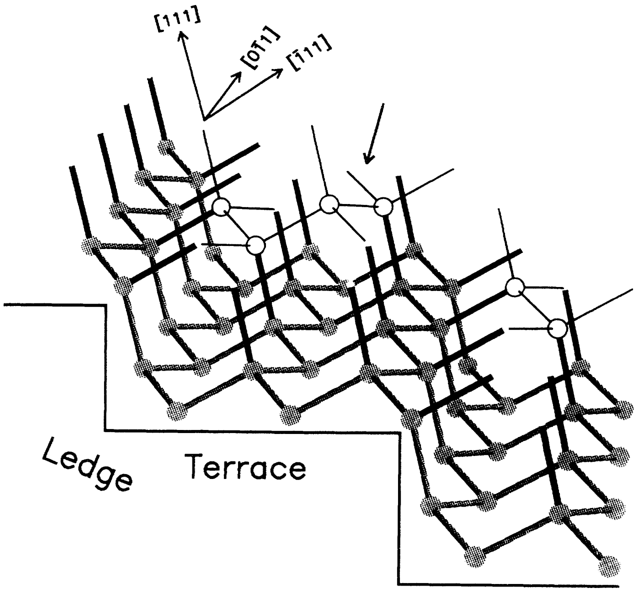

FIG. 3. Schematic picture showing how a roughened IBIEC interface increases the chances of crystallization. The crystal atoms at the initially perfect SPE interface [in this case the (133), with a terrace width $W_t=2$] are shown in light grey, with the original amorphous-crystal bonds as thick black lines. Adding a few additional atoms (open circles) with their bonds (thin lines) increases the number of bonds where crystallization can occur and decreases the number where crystallization cannot occur.

In conclusion, we have measured the ion-beam-induced epitaxial crystallization rate of *a*-Si on orientations every 5° along (100)-(111)-(011). The data show that the (011) regrows slightly (3%) slower than the (100), and that the velocity decreases with increasing misorientation toward the (111). The data can be explained with a growth-site-limited model, resulting in ledge roughening, which provides an atomistic basis for Jackson's phenomenological IBIEC theory. This also provides a close connection to SPE models, resulting in a coherent view of epitaxial crystallization of Si.

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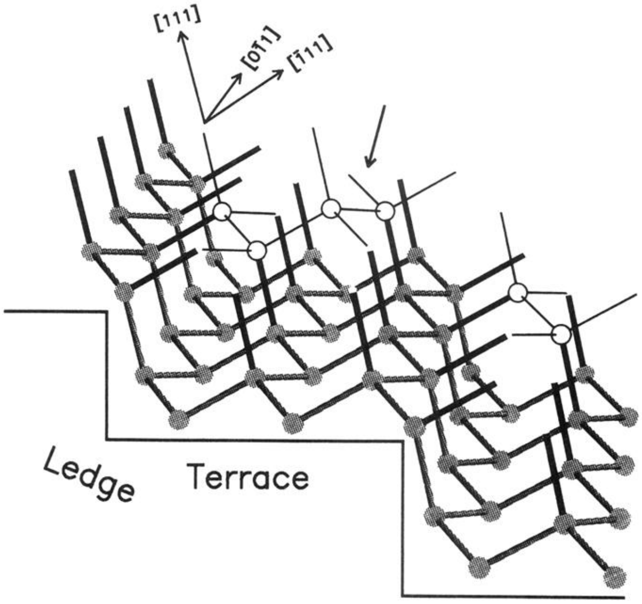

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