

## Crystallization Instability at the Amorphous-Silicon/Liquid-Silicon Interface

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The rate at which crystalline Si nucleates at the amorphous-Si/liquid-Si interface is estimated. On the basis of this estimate and physical arguments, we propose that under certain conditions a moving amorphous-Si/liquid-Si interface is unstable with respect to nucleation of crystalline Si. Such nucleation, followed by growth, is a possible mechanism for the well-known explosive crystallization of amorphous Si. Furthermore, a similar instability can explain the formation of amorphous Si from liquid Si.

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Under certain conditions, pulsed-laser irradiation may induce transformations from amorphous Si (*a*-Si) to fine-grained polycrystalline Si by a phenomenon known as "explosive crystallization." Under different conditions, irradiation may induce the reverse transformation, from crystalline Si (*c*-Si) to *a*-Si. Both transformations are mediated by the liquid (*l*-Si) phase. Although these transformations have been widely studied, the fundamental questions of where and how the solid phases nucleate have not yet been answered.

In this Letter we present physical arguments and calculations which lead us to propose that under some conditions a *l*-Si/*a*-Si interface is unstable with respect to heterogeneous nucleation of *c*-Si. Under these conditions such nucleation, followed by growth, is a possible mechanism for explosive crystallization. Furthermore, conditions also exist for which the *c*-Si/*l*-Si interface may itself be unstable with respect to heterogeneous nucleation of *a*-Si. Such nucleation instabilities provide a simple, self-consistent explanation for these two apparently different phenomena.

A thin layer of *a*-Si on *c*-Si can be transformed completely into *c*-Si by irradiation with a laser pulse of sufficient fluence. In that case, the entire *a*-Si layer is melted and the underlying *c*-Si seeds subsequent epitaxial solidification. Markedly different behavior is observed for fluences only slightly above the threshold for melt initiation. At these lower fluences, the *a*-Si is partially transformed into polycrystalline Si with an unusual microstructure: The near-surface region contains large-grained poly-Si, and the underlying region contains equiaxed, randomly oriented, fine-grained poly-Si.<sup>1,2</sup> Transient conductance,<sup>3</sup> impurity redistribution,<sup>4</sup> and optical<sup>5</sup> measurements show that the fine-grained Si formation is mediated by a buried *l*-Si layer. This buried layer is at a temperature higher than the melting temperature  $T_{al}$  of *a*-Si, but lower than the melting temperature  $T_{cl}$  of *c*-Si ( $T_{cl} - T_{al} \approx 225$  K<sup>6</sup>), and propagates into the substrate by simultaneous melting of *a*-Si and freezing into *c*-Si. Because the latent heat of melting of *c*-Si is greater than that of *a*-Si propagation may be

self-sustaining or "explosive."<sup>7</sup>

Two distinct scenarios have been proposed to describe explosive crystallization. In one scenario, propagation of the buried *l*-Si layer occurs by melting at the leading *l*-Si/*a*-Si interface and freezing at the trailing *c*-Si/*l*-Si interface. However, in this scenario, one would expect the microstructure to be textured with columnar grains oriented along the faster growing directions, rather than fine grained. In a second scenario,<sup>8</sup> crystallization of the buried *l*-Si layer occurs by homogeneous nucleation from the undercooled melt. While such nucleation is consistent with the observed microstructure, the rate required to explain the grain size is far higher than that measured<sup>9</sup> for even greater undercooling.

Thus neither scenario is satisfactory. We propose a third: random nucleation (followed by growth) of *c*-Si at the moving *a*-Si/*l*-Si interface. In this scenario, *c*-Si forms at the *leading* liquid-solid interface, despite the high (meters per second) velocity of that interface and despite continued melting of the *a*-Si "catalyst" itself. Although counterintuitive, this proposal explains the fine-grained microstructure without invoking unreasonable homogeneous nucleation rates, and is consistent with the observation that nucleation usually occurs at interfaces rather than in the bulk.

Furthermore, this proposal can account not only for the self-sustained propagation of the buried liquid layer, but also for the *initiation* of explosive crystallization, which is difficult to explain otherwise. Early transient conductance and reflectance measurements during 30-ns FWHM pulsed-laser irradiation revealed that the explosive process could be initiated while the surface is still molten.<sup>3</sup> The final microstructure indicated that the large-grained *l*-Si nucleated beneath, and grew towards, the surface.<sup>1</sup> Hence, it was originally believed that explosive crystallization is initiated by nucleation at the *stationary a*-Si/*l*-Si interface as it stops to turn around.

More recently, for long-pulse (>40 ns FWHM) laser irradiation *c*-Si has been observed<sup>10</sup> to nucleate even while the *a*-Si is *in motion*. This indicates that initial nucleation may occur at a temperature *above*  $T_{al}$ . In

these experiments, the location at which nucleation occurred could not be resolved. However, the other possible locations for *c*-Si nucleation, the free surface and the bulk liquid, can be ruled out by an indirect argument.

In numerous laser-melting experiments,<sup>11</sup> neither surface nor bulk nucleation of *c*-Si has been observed for quench rates beyond those required for amorphization. Therefore, *c*-Si does not nucleate on these time scales either at the surface or in the bulk at temperatures at least as low as  $T_{al}$ , and therefore not at the higher temperatures associated with explosive crystallization. Bulk nucleation can also be ruled out by independent experiments in which melt droplets have been cooled below  $T_{al}$  for times long compared to those considered here.<sup>9</sup> The only remaining possibility is nucleation of *c*-Si at the *a*-Si/*l*-Si interface.

Our proposal is further supported by calculated rates of heterogeneous *c*-Si nucleation at the *l*-Si/*a*-Si interface. Three important parameters that enter into this calculation are the energies  $\sigma_{cl}$ ,  $\sigma_{al}$ , and  $\sigma_{ac}$  associated with the *c*-Si/*l*-Si, *a*-Si/*l*-Si, and *a*-Si/*c*-Si interfaces, respectively. Here, the energy per atom at the solid-liquid interfaces is estimated by  $\sigma_{sl} = 0.45\Delta h_{sl}$ , where  $\Delta h_{sl}$  is the heat of fusion. The value of 0.45 is intermediate between those observed for simple metals and for materials with markedly different bonding in the liquid and solid

phases,<sup>9</sup> and is consistent with recent measurements.<sup>9</sup>

The *a*-Si/*c*-Si interfacial energy is not accurately known. Model-building studies of planar interfaces separating bulklike *c*-Si and *a*-Si yield 0.12 eV/atom.<sup>12</sup> Because the small *c*-Si embryos considered here contact *l*-Si on one side, which may permit additional strain relaxation, we take 0.12 eV/atom to be an upper limit for  $\sigma_{ac}$ . An estimate of  $\sigma_{ac}$  based on studies<sup>13</sup> of *c*-Si nucleation in *a*-Si films yields values near 0.04 eV/atom; however, it also contains uncertainties. If there were contributions from heterogeneous nucleation, it would be an underestimate. It could also be an overestimate for the case here, since *c*-Si in contact with *l*-Si may permit additional strain relaxation. Although values  $\approx 0.04$  eV/atom appear reasonable because of the uncertainties noted, we calculate nucleation rates for values of  $\sigma_{ac}$  from 0.04 to 0.12 eV/atom.

We calculate the steady-state nucleation rate<sup>14</sup> by applying the classical Becker-Doring treatment to heterogeneous nucleation at a smooth interface,<sup>15</sup> and then extending that treatment in a simple way to account for the important effect of interfacial roughness. Because the treatment is straightforward, we do not describe it in detail here, except to note that the most important determinant of the nucleation rate is the free-energy barrier  $\Delta G_c$  to formation of a critical embryo. In the notation of Christian,<sup>16</sup>

$$\Delta G_c = \frac{4}{3} \pi (\sigma_{cl})^3 [2 - 3 \cos(\Theta^{(a) \rightarrow c}) + \cos^3(\Theta^{(a) \rightarrow c})] / \Delta g_{cl}^2, \quad (1)$$

where  $\cos(\Theta^{(a) \rightarrow c}) = [\sigma_{la} - \sigma_{ca}] / \sigma_{lc}$  is a wetting angle factor, and  $\Delta g_{cl} = \Delta g_{cl} [1 - T/T_{cl}]$  is the molar free energy of transformation.<sup>17</sup>

This free-energy barrier is appropriate for heterogeneous nucleation at a smooth interface. At a rough interface, nucleation will be enhanced. Since the *a*-Si/*c*-Si interface energy is estimated to be lower than the *c*-Si/*l*-Si interface energy, *c*-Si embryos will prefer to increase *a*-Si/*c*-Si interface area at the expense of *c*-Si/*l*-Si interface area, i.e., by forming in *l*-Si pockets at the *a*-Si/*l*-Si interface. The enhancement will be maximum for pockets with size comparable to that of the critical nuclei, which is a few atomic diameters. It is unlikely that the *a*-Si/*l*-Si interface will be smooth on this spatial scale. Indeed, fluctuations of subcritical embryos at such an interface would be expected to alter local melting kinetics and contribute greatly to roughness.<sup>18</sup>

The effect of roughness can be incorporated into the calculation by making the simplifying assumption that the interface is everywhere characterized by roughness with radius of curvature equal to that of critical nuclei. Then it can be shown that Eq. (1) also applies to a rough interface provided *a* and *l* are interchanged everywhere except in the  $\Delta g_{cl}$  free-energy difference which drives the transformation.<sup>19</sup>

The resulting nucleation rate is plotted in Fig. 1 for various values of  $\sigma_{ac}$ , normalized by the number of lat-

tice sites per unit area  $N$  and by the frequency of collisions at the interface  $q_0$ .<sup>17</sup> Above  $T_{cl}$ , the driving force for crystallization is negative and the nucleation rate vanishes. Below  $T_{cl}$ , the driving force for crystallization, and hence the nucleation rate, increase extremely rapidly

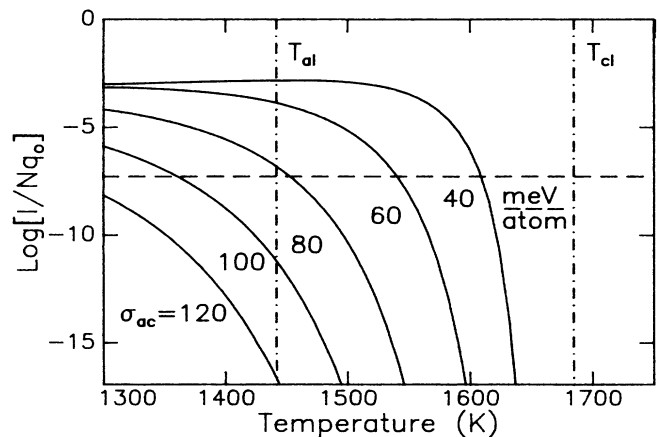


FIG. 1. Heterogeneous nucleation rates of *c*-Si at a rough *a*-Si/*l*-Si interface, plotted for various *a*-Si/*c*-Si interface energies  $\sigma_{ac}$ . The dashed line is the rate required to form nuclei separated in three dimensions by 100 Å if the interface were moving at 10 m/s.

ly. Physically, nucleation involves the creation of  $c$ -Si/ $l$ -Si and  $a$ -Si/ $c$ -Si interfaces and the destruction of an  $a$ -Si/ $l$ -Si interface. Therefore, the lower the  $a$ -Si/ $c$ -Si interface energy, the lower the barrier to nucleation and the higher the nucleation rate.

Also shown in Fig. 1 is the nucleation rate required to form nuclei every 100 Å at an interface moving at a velocity 10 m/s estimated from transient conductance measurements.<sup>3</sup> For temperatures  $\geq T_{al}$ , nucleation rates exceed this for  $\sigma_{ac} < 0.08$  eV/atom. We conclude that, for the assumptions given above, heterogeneous nucleation of  $c$ -Si at the  $a$ -Si/ $l$ -Si interface is significant for reasonable values of  $\sigma_{ac}$  and can be a basis for explaining explosive crystallization.

Note that our treatment has overestimated the nucleation rate, since the interface will not be everywhere as rough as assumed. For example, for  $\sigma_{ac} = 0.04$  eV/atom, the nucleation rate at a smooth interface is too low to account for experimental observation. Some roughness is crucial to this mechanism. However, in order for the rate to be decreased enough to invalidate this mechanism, the fraction of the interface that has approximately the optimal roughness would have to be less than one part in 10000. Moreover, we have not incorporated suboptimal roughness, which will also enhance nucleation, into our calculation. Significant enhancements may occur for steps at the  $a$ -Si/ $l$ -Si interface only one or two atomic diameters in height. Therefore, uncertainties of many orders of magnitude in the assumed roughness do not qualitatively alter our principal conclusions.

It is also of interest to apply a similar treatment to the inverse case of  $a$ -Si nucleation at a moving  $c$ -Si/ $l$ -Si interface. The results are shown in Fig. 2 for nucleation at a smooth interface for various values of  $\sigma_{ac}$ . Below  $T_{al}$ , the driving force for  $a$ -Si formation from  $l$ -Si, and hence the nucleation rate, increases. As before, the nucleation

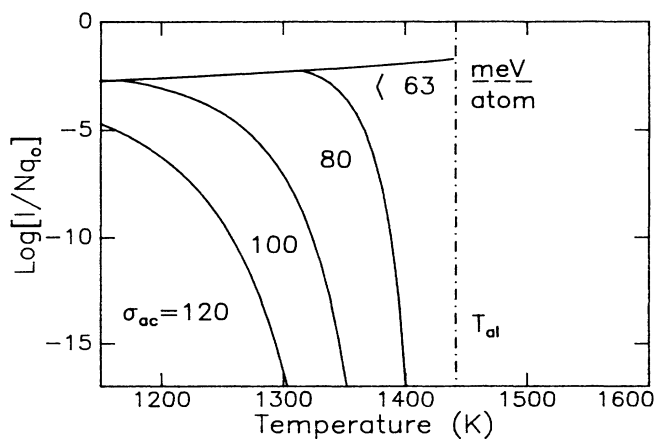


FIG. 2. Heterogeneous nucleation rates of  $a$ -Si at a smooth  $c$ -Si/ $l$ -Si interface, plotted for various  $a$ -Si/ $c$ -Si interface energies  $\sigma_{ac}$ . For  $\sigma_{ac} < 63$  meV/atom  $a$ -Si wets the  $c$ -Si/ $l$ -Si interface.

rate increases with decreasing  $\sigma_{ac}$ . For  $\sigma_{ac} \leq 0.063$  eV/atom,  $a$ -Si “wets” the  $c$ -Si/ $l$ -Si interface. No energy is required to replace a  $c$ -Si/ $l$ -Si interface with  $a$ -Si/ $l$ -Si and  $a$ -Si/ $c$ -Si interfaces. Then, for even slight undercoolings below  $T_{al}$ , the nucleation rate rises to a “collision-limited” value.

This possibility of barrier-free heterogeneous nucleation of  $a$ -Si at  $T_{al}$  is attractive, since it provides a simple explanation for amorphization. It relies only on traditional ideas grounded in classical nucleation theory, and is consistent with observation. For example, the freezing velocity into (100)  $c$ -Si at which  $a$ -Si forms is measured to be 15 m/s.<sup>6</sup> This result, combined with the measured undercooling/velocity relation for (100)- $c$ -Si of 15 K s/m,<sup>20</sup> implies that amorphization requires very little undercooling below  $T_{al}$ . In addition, the observation of sharp  $a$ -Si/(100)- $c$ -Si interfaces<sup>11</sup> implies sudden nucleation, i.e., exceedingly high nucleation rates as well as an exceedingly high dependence of nucleation rate on temperature.

Finally, wetting of the  $c$ -Si/ $l$ -Si interface by  $a$ -Si explains the subsequent stability of the  $a$ -Si/ $l$ -Si interface. Regardless of the mechanism by which  $a$ -Si is initially formed (by nucleation at the  $c$ -Si/ $l$ -Si interface or at the free surface), the results described in the major part of this Letter indicate that the  $a$ -Si/ $l$ -Si interface should be unstable with respect to nucleation of  $c$ -Si. The absence of  $c$ -Si grains within the final  $a$ -Si layer is consistent with wetting of nascent  $c$ -Si embryos.

In summary, on the basis of physical arguments and calculations, we have proposed interfacial nucleation mechanisms for two widely studied phenomena in Si: explosive crystallization and amorphization. These mechanisms represent the first unified picture for understanding the rich, and often puzzling, phenomenology of rapid solidification in Si. Furthermore, nucleation instabilities at moving liquid/solid interfaces may be more common than previously believed, with important implications for the microstructures found in other rapid-solidification studies.<sup>21</sup>

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<sup>14</sup>The existence of a self-sustained, propagating liquid layer

in explosive crystallization implies freezing velocities into *c*-Si comparable to melting velocities of *a*-Si. Therefore, a steady-state distribution of embryos at the *a*-Si/*l*-Si interface may be expected to be established in the time that the *a*-Si/*l*-Si interface moves a critical embryo size, which is only a few atomic diameters. For this reason, transient nucleation is not considered to be a major limitation.

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<sup>17</sup>We use the values  $N=5.0\times 10^{22}$  atoms/cm<sup>3</sup>,  $q_0=2.6\times 10^{13}$  s,  $\Delta h_{cl}=0.525$  eV/atom,  $T_{cl}=1685$  K, and  $T_{al}=1442$  K; and for the growth kinetics we use the entropy-limited growth model of J. Y. Tsao, M. J. Aziz, M. O. Thompson, and P. S. Peercy, Phys. Rev. Lett. **56**, 2712 (1986), with  $Q=0.1$  eV.

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<sup>19</sup>To eliminate unphysical divergences, we limit the cosine of the contact angle to the range  $\cos(135^\circ)=-0.707$  and  $1-1/r_c$ . Note that for negative values of this cosine, *c*-Si is nucleating in a *l*-Si pocket more than half enclosed by *a*-Si.

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