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Low-temperature growth and ion-assisted deposition

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Using standard molecular-dynamics methods, we have simulated silicon molecular-beam epitaxy on a (100) substrate, subject to a second beam of low-energy argon atoms. We find that the presence of the ion beam has an important effect on the structure of the deposits formed: good crystalline material forms at significantly lower temperatures, where otherwise a thermal beam yields an amorphous deposit. This is because the ion beam provides local excitations, which allow the deposited atoms to find their proper crystal lattice sites.

Modern crystal growth techniques such as molecular-beam epitaxy (MBE), chemical vapor deposition, and sputter deposition, have made possible the growth of semiconductor thin films important for the fabrication of solid-state devices. In turn, device applications have driven a continuing effort, whose aim is to understand and ultimately control the growth processes. In recent years, it has become clear that low-energy ion beams play an important role in influencing the processing of semiconductor thin films, thereby providing yet another mechanism of control.[1] Low-energy ion beams are used to sputter surfaces,[2] clean and etch them,[3] enhance dopant incorporation,[4] modify strain,[5] and change the growth modes of the films.[6]

In this paper, we present molecular-dynamics (MD) simulations of another application of low-energy ion beams, namely, their ability to enhance the formation of crystalline material. In many situations, one would like to grow crystals at low temperatures in order to suppress dopant diffusion, thereby preventing surface segregation. However, if one works at too low a temperature, then only amorphous materials form. What is therefore needed is a way of promoting epitaxial growth, without increasing the thermal budget of the system. By simulating Si MBE on a (100) substrate concurrent with a second beam of low-energy argon (Ar) atoms, we show that such an effect may be achieved.

These results are in agreement with a number of experimental studies: Wehner *et al.*[7] have shown that epitaxial growth may be achieved when ~23-eV mercury ions are codeposited with Si, while more recently Ohmi *et al.*[3] obtained good epitaxial growth at temperatures as low as 320–350 °C using a second beam of Ar atoms. The effect of ion beams on surfaces has previously been explored via simulations. However, these have concentrated on studying the defects and damage induced by the ion beam in the crystal.[8–10] Simulations of Murthy and Atwater[11] of the effects of ion beams on a rough Si(100) surface, show that for ion beams in the 20-eV range, damage is essentially restricted to the top two layers, and that above room temperature the ion beam increases the number of adatoms on the surface.

The quality of the epitaxial growth depends upon the mobility of condensed atoms on the crystal surface. Indeed, one can think of the growth of Si as taking place in several different temperature regimes: at high temperatures, when the adatoms are quite mobile, growth takes place preferentially at the edges of steps (the step-flow regime); at intermediate temperatures, this process is in competition with the nucleation and coalescence of islands; while at low temperatures, limited epitaxy or an amorphous deposit forms. By low temperatures, we imply a temperature where surface diffusion is almost completely inhibited. Simulations of Si MBE (Refs. 12 and 13) show that the transition from amorphous to crystalline material occurs at about 450 K for (100) substrates. Experimental studies of Si MBE show that the transition occurs at a temperature of about 100 K lower than in the simulations.[14]

In the low-temperature regime, good crystalline material can still form, provided that the atoms can somehow reach their proper crystal lattice sites. For Si(100) substrates, this entails breaking the dimer bonds of the reconstructed surface. MD studies of low-temperature Si MBE were recently carried out by Gilmer and Roland (GR),[15] who found that deposits formed from a beam of 5-eV Si atoms yielded much larger fractions of crystalline material at low temperatures than from a corresponding thermal beam. As an atom approaches the surface, it begins to be affected by the attractive force field of the surface and is accelerated towards it. As it condenses onto the surface, it deposits both its kinetic energy and latent heat of condensation, so that for a brief moment the average kinetic energy of the atom may be larger than at the melting temperature of Si. The deposited atom then thermalizes in ~1 ps. The simulations show that there is little or no additional diffusion induced by the condensation. Rather, the local heating has an effect similar to annealing. Excitations are provided which break local bonds and jar the atoms into their proper crystal lattice sites. Here, we show that a similar effect may be achieved with the use of a second beam of ions in the 10–20-eV range: good crystalline material can be obtained at temperatures 200–300 K below the transition temperature. The amount of crystalline material in the deposits may be further increased by increasing the flux of the ion beam.

We now give details of our simulations. Silicon MBE was modeled as in Ref. 12. Standard MD methods were used.[16] The Si atoms were modeled with the empirical

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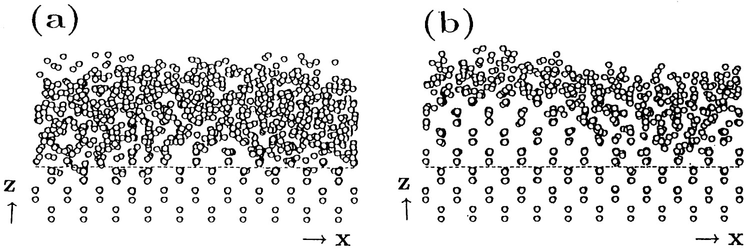

FIG. 1. Vertical cross sections through relaxed deposits (a [110] projection is shown) obtained from the MD simulations: (a) control sample (no Ar beam) and (b) with a 10-eV Ar beam. The temperature during growth was 300 K. The initial substrate is marked by a dashed line. The Ar flux is the same as that of the Si atoms.

Stillinger-Weber (SW) potential,[17] which is known to predict the proper dimerization, and other properties of the Si (100) surface to within ~ 0.1 eV,[15] which is small compared to the ion-beam energies. The Si-Ar potential was chosen to have a purely repulsive form: $V_{\text{Ar-Si}} = A \exp(-\lambda r_{\text{Ar-Si}})$, with $A = 1830.8$ eV, $\lambda = 20$ nm^{-1}, and a cutoff of 0.4 nm, as in other simulations.[11] Substrates consisted of six atomic layers of Si, with the top surface properly dimerized. Each layer consisted of either 100 or 36 (for high flux simulations) atoms arranged in a square array. The atoms of the bottom two layers were kept fixed. Velocity renormalization of the next two layers were used to maintain the system at a constant temperature. On top of these substrates, ten Si (100) layers were deposited at thermal velocities at a rate of a monolayer in ~ 0.2 ns. This high deposition rate is mandated by the computer requirements of the simulations. Note that we are essentially testing the changes brought about by the local heating mechanism induced by the Ar collisions. Because the collision and thermalization times are short, this mechanism is effectively reproduced in our high-deposition-rate simulations.[18] The Si atoms were placed at random positions ~ 10 Å above the surface with a downward thermal velocity. Similarly, the positions of Ar atoms with velocities of 5, 10, or 20 eV downwards were also chosen at random. Fluxes of 1 and 4 Ar per Si atom were studied. Once the Ar atoms had hit the surface, and bounced back, they were removed from the system. During a collision, a reduced time step, which was scaled inversely with the velocity of the energetic Ar atoms, was used.

Figure 1 shows cross sections through sample deposits obtained from the simulations. The first panel shows the control—the deposit formed without the codeposition of Ar atoms. At the low temperature of $T = 300$ K, most of the deposit consists of amorphous material. Clearly, when a second beam of 10-eV Ar atoms is allowed to strike the growing surface, the amount of crystalline material obtained is increased [Fig. 1(b)]. This effect is enhanced if a more energetic Ar beam is used.

To quantify this effect, we have measured the fraction of crystalline material in the deposits formed as a function of temperature. For each atom in the deposit, the number of nearest neighbors and the potential energy resulting from the triplet interaction term of the SW potential was calculated. Atoms having four nearest neighbors and low triplet energy (less than 0.2ϵ) were counted as crystalline atoms.[19] Only atoms found two atomic layers beneath the surface were considered. This is because even at very high temperatures, atoms in the upper two layers are amorphous until buried. There is considerable scatter in the resulting data due to the small sizes of the simulated systems.

The data are shown in Fig. 2, and constitutes the main results of this paper: through the use of a second beam of low-energy ions, the amount of crystalline material obtained at low temperatures is greatly increased.[20] Not shown in the figure are results for a 5-eV Ar beam, which are as follows: for the low flux, there is no significant increase in the amount of crystalline material, while for the high flux, we measured a crystalline fraction of about 0.67 and 0.81 for $T = 100$ and 300 K, respectively. Clearly, crystallization of the amorphous material is facilitated by increasing either the energy or the flux of the ion beam. It is interesting to compare the efficiency of ion-assisted deposition to that of an energetic beam of Si atoms. We find that the results from a beam of energetic

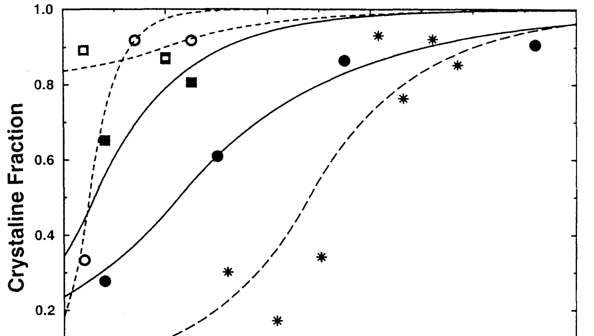

FIG. 2. Fraction of crystalline material as a function of substrate temperature for deposits. Details are as follows: stars mark the control (no Ar beam—these data are taken from Ref. 15); filled circles—deposits formed with low flux 10-eV Ar beam; open circles—high flux 10-eV Ar beam; solid squares—low flux 20-eV Ar beam; and open squares—high flux, 20-eV Ar beam. The dashed and solid lines are not fits, but simply guides to the eye.

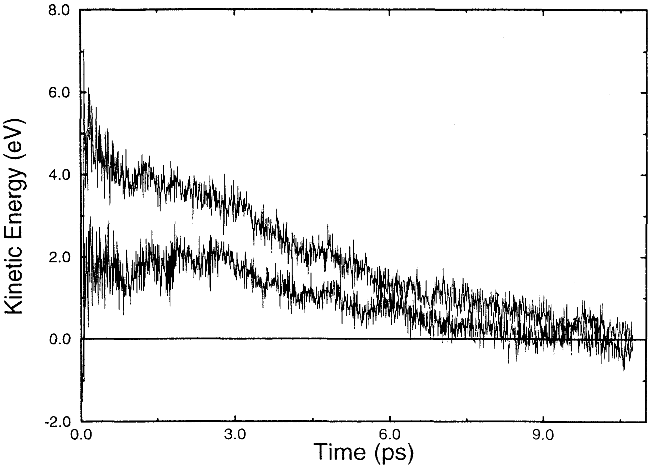

FIG. 3. Average kinetic energy of a typical system as a function of time after a 10-eV (lower curve) or a 20-eV (upper curve) Ar collision. The sample system was taken to be a five-monolayer deposit obtained from the MD simulations at a substrate temperature of 300 K. The data were averaged over 15 independent runs. The data have been displaced, so that the average kinetic energy of the system in absence of Ar collisions (solid line) marks the zero value.

(5 eV) Si atoms[15] are comparable to those of a 10-eV beam of Ar atoms. Thus, on a per energy basis, when the fluxes of Ar and Si beams are similar, a beam of energetic Si atoms is more efficient. This reduced efficiency is due to the statistical nature of the collision: because Ar atoms strike the surface at random, not every collision will help in the process of converting amorphous to crystalline material. However, this inefficiency may readily be overcome by increasing the ion-beam flux.

Crystallization is induced by the Ar atoms which transfer kinetic energy to the surface locally, thereby providing excitations of sufficient magnitude which can break dimer bonds and enabling atoms to overcome local potential energy barriers and thereby find their proper crystal lattice sites. As a measure of the excitations induced by the collisional process, we have studied the decay of kinetic energy transferred to the system as a function of time for a sample deposit (see Fig. 3). The data are averaged over 15 independent collisions. After the collision, the system thermalizes in less than ~10 ps. This rate is weakly dependent upon the ion-beam energy, so that a substrate subject to a 10-eV beam takes about 1–2 ps less time to thermalize than a substrate subject to a 20-eV beam. Different layers require a different time to thermalize. Measurements show that the upper two layers equilibrate in about 5 ps, while the lower layers take somewhat longer—7.5 ps.

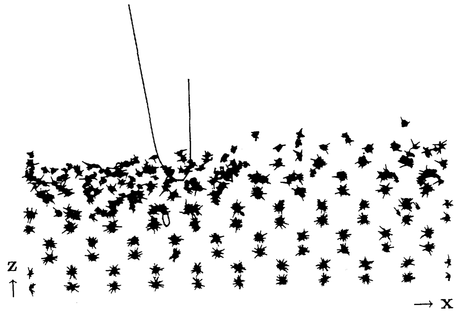

FIG. 4. Sample trajectories of atoms under a typical 20-eV Ar collision. A [110] projection is shown. Note that the Ar atom, whose trajectory is marked with arrows, here strikes the amorphous region and penetrates several monolayers into the crystal. There is no evidence of any increased diffusion induced by the collision. The substrate is at 300 K.

A sample trajectory plot of such an Ar collision is shown in Fig. 4. We find that an Ar atom may, in some cases, penetrate up to four to five atomic layers if it strikes an amorphous part of the deposit. It transfers most of its kinetic energy to the surface, and exits with a much reduced velocity. During the collision, the atoms are only displaced *locally,* by less than 1 or 2 Å. No transient enhancement in the diffusion rate was observed. This was confirmed by a direct measurement of the atomic displacements after a collision.

In summary, we have carried out extensive simulations of ion-assisted Si MBE, over a wide range of temperatures. Our results show that the amount of crystalline material obtained at low temperatures is dramatically enhanced. Crystallization of the growing deposit is induced by the excitations delivered locally to the surface, which allows atoms to overcome local potential energy barriers and find their proper crystal lattice sites. As this is accomplished without any significant increase in surface diffusion, this method may have useful applications in low-temperature growth when it is important to limit the diffusion of dopants.

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[18] During our simulation, a general temperature rise of about 50–75 K was observed. However, this is much too small of a change to have any significant effect on the amorphous to crystalline transition. Under laboratory conditions, when the deposition rate is many times lower, the temperature rise would be imperceptible.

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[20] These results are based on deposits ten atomic layers thick. Because of the small system sizes, it was not possible here to test for correlations between the amorphous to crystalline transition and the film thickness, although there is interesting experimental evidence of such an effect. See D. J. Eaglesham, H.-J. Gossmann, and M. Cerullo, Phys. Rev. Lett. **65**, 1227 (1989).