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Growth mechanism for molecular-beam epitaxy of group-IV semiconductors

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The microscopic homoepitaxial growth dynamics of Si and Ge are probed by the application of a Monte Carlo computer simulation, with attention focused upon the substrate temperature dependence of reflection high-energy electron-diffraction (RHEED) specular beam intensity oscillations. A model that involves short-range site selectivity by the incident atoms, but without surface diffusion, is found to produce a low-temperature layer-growth mode. By incorporating diffusion on a stepped surface at higher substrate temperatures, simulated RHEED profiles are obtained that are in qualitative agreement with those measured.

The evident technological importance of semiconductor superlattices fabricated by molecular-beam epitaxy (MBE) has prompted a number of experimental[1,2] and theoretical[2-8] investigations into the fundamental kinetics of the growth process. To date, most effort has been directed towards the III-V compound semiconductors, such as GaAs and AlGaAs. However, the possibility of monolithic integration of optoelectronic devices with Si circuits has turned some attention toward homoepitaxial and heteroepitaxial growth on Si and Ge substrates.

Of considerable importance to the development of MBE has been the application of reflection high-energy electron diffraction (RHEED) as an *in situ* surface analytical technique. The appearance of oscillations in the intensity of diffracted beams with a period equal to the deposition time for single or double atomic layers has facilitated control of film thickness to atomic-layer precision, as well as providing a time-dependent probe of surface structure and surface morphology. Indeed, a fairly complete picture has emerged of growth on vicinally cut (stepped) GaAs(100) from an interpretation of RHEED measurements.[1] At low temperatures, growth proceeds by two-dimensional nucleation on terraces, leading to a periodic variation in the step density and thus in the RHEED specular intensity. At higher temperatures, the enhanced surface mobility leads to direct incorporation of migrating atoms at the terrace edges. Thus, in the high-temperature regime, growth proceeds by step propagation, wherein the step density remains approximately constant and RHEED oscillations are absent. In both regimes, there is considerable surface mobility, as evidenced by the rapid recovery of the RHEED intensity once the molecular beam is turned off and the surface relaxes by a smoothening of the growth front. The interpretation of Neave, Dobson, Joyce, and Zhang[1] is supported by numerous simulations on both flat[7,8] and stepped[5] surfaces, including the effects of relaxation in the post-growth phase.[6]

The picture that emerges for group-IV MBE is somewhat different. Aarts, Gerits, and Larsen[9] and Aarts and Larsen[10] have recently investigated the epitaxial growth of Si(100) and Ge(100), and identified two important features from (RHEED) measurements:

(i) During the growth of Ge(100) at room temperature, oscillations in the specular RHEED intensity are plainly visible, exhibiting a large amplitude and appearing over an extended period of time. However, upon termination of the incident flux, the RHEED intensity remains approximately constant, in contrast to the behavior just described for III-V compounds.[2,6] This suggests that at room temperature, Ge surface atoms are essentially immobile, which must be reconciled with the generally accepted view that the layer-by-layer growth mode in MBE results from a kinetically controlled island-growth process, driven by surface diffusion.

(ii) As the substrate temperature is progressively increased, the amplitude of the RHEED oscillations diminishes, until beyond a certain temperature oscillations are no longer observed. The disappearance of RHEED oscillations is accompanied by an increase in the mean diffracted intensity. Thus, in the high-temperature regime, the epitaxial growth of Si(100) and Ge(100) appears to be qualitatively similar to that found for III-V compounds.

Additionally, an earlier study of Si MBE by Sakamoto *et al.*[11] revealed the following.

(iii) Stable RHEED oscillations occurred only after preheating treatments which, for the Si(100) surface, have been shown to result in a single-domain 2×1 structure with biatomic steps.[12]

To obtain a qualitative understanding of the microscopic growth kinetics that could give rise to these phenomena we have employed a Monte Carlo simulation of epitaxial growth based upon an extension of the basic solid-on-solid (SOS) model[13] used earlier[5-7] to investigate the origin of RHEED intensity oscillations observed during the epitaxial growth of III-V compounds. In the SOS model, the substrate is described as a simple cubic lattice in which interatomic bonds are formed only with nearest neighbors, while vacancies and overhangs are forbidden. The growth process is modeled by two steps, involving the deposition of a monatomic species onto the surface, and the migration of surface atoms. Evaporation is neglected, as the residence time of incident Si atoms has been estimated to be $\approx 10^7$ sec,[14] and the incorporation probability is unity.

The deposition of atoms is performed in two stages. Random sites on the substrate are first generated in time intervals of $\delta t = 1/FA$, where F is the incident beam flux and A is the area of the substrate. In the simulations re-

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ported below, we have used a 30×30 square lattice with an incident beam flux of 10^{18} $m^{-2}sec^{-1}$. To investigate the possibility of a layer-by-layer growth mode at temperatures too low to stimulate surface migration, we consider an additional stage to account for the incorporation kinetics of an incident Si/Ge atom. Recent molecular dynamics simulations of the epitaxial growth of Si(111) (Ref. 15) have revealed that for a molecular-beam incidence of 30° with respect to the surface normal, up to 50% of the incident atoms come to rest at the surface, usually skipping up to 10 Å from the point of initial contact with the surface. The remaining atoms come to rest as interstitials between the first two double atomic layers. Though the incident kinetic energy employed in Ref. 15 (10 eV) is considerably greater than that produced in growth chambers for Si MBE ($\approx 1600\,^\circ$C), the transient migratory behavior of the adatoms will be shown below to provide a possible pathway to epitaxial growth in Si and Ge even without surface diffusion. We model an arriving atom in this transient state as being able to select a site within a search region S (Fig. 1) that maximizes the number of nearest-neighbor bonds which, in the case of several such sites, is in the deepest layer nearest to the point of arrival.

As in our earlier work,[5-7] surface migration is modeled by an Arrhenius expression for the nearest-neighbor hopping probability: $D(E,T)=(2k_BT/h)\exp(-E/k_BT)$, where E is energy barrier to diffusion of a given atom, T is the substrate temperature, k_B is Boltzmann's constant, and h is Planck's constant. The prefactor $2k_BT/h$ represents the vibrational frequency of an adatom, modelled as a two-dimensional harmonic oscillator to which the equipartition theorem has been applied to obtain the characteristic frequency at substrate temperature T. The energy barrier consists of two terms: a barrier E_S to surface diffusion for a free atom, and a (site-dependent) term E_N that is proportional to the number of nearest neighbors. Thus, $E=E_S+nE_N$, where $n=0,\dots,4$ and we have taken $E_S=1.3$ eV and $E_N=0.25$ eV, which is to be compared with measured *average* values for diffusion barriers on Si of 1.1 eV,[14] 1.3 eV,[16] and 1.57 eV.[17]

Analysis of the simulation is achieved by continuous monitoring of the surface step density of the growth front, defined as the number of unsaturated nearest-neighbor bonds parallel to the surface. Previous work has demonstrated this procedure to produce a strong correspondence with the measured evolution of RHEED specular spot profiles in a variety of circumstances.[5-7]

In Fig. 2 we show the step-density evolutions formed during simulated growth in the absence of migration (i.e., $T=0$) over a range of allowed search areas, characterized by the search parameters S (Fig. 1). Extended runs of the simulation with $S=2$, 3, 4 are shown in Fig. 3. The experiments of Aarts *et al.*[9] and Aarts and Larsen[10] showed sinusoidal oscillations with a strongly decaying envelope over approximately 20 oscillations. The growth profile with $S=3$ is found to most closely reproduce the measured RHEED data and so will form the basis for the finite-temperature simulations below. We also conclude from Fig. 2 that a plausible explanation of the feature (i) above is provided by a mobile precursor state with an effective range corresponding to $S=3$ or $S=4$. Feature

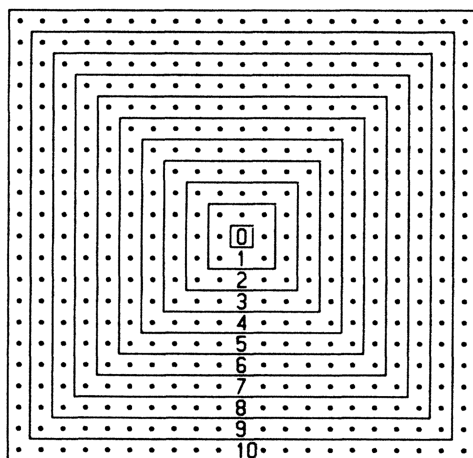

FIG. 1. The surface area corresponding to the value of the search parameter S. Lattice sites are indicated by small filled circles. For a given value of S, the search area includes all sites within and including the indicated band of sites.

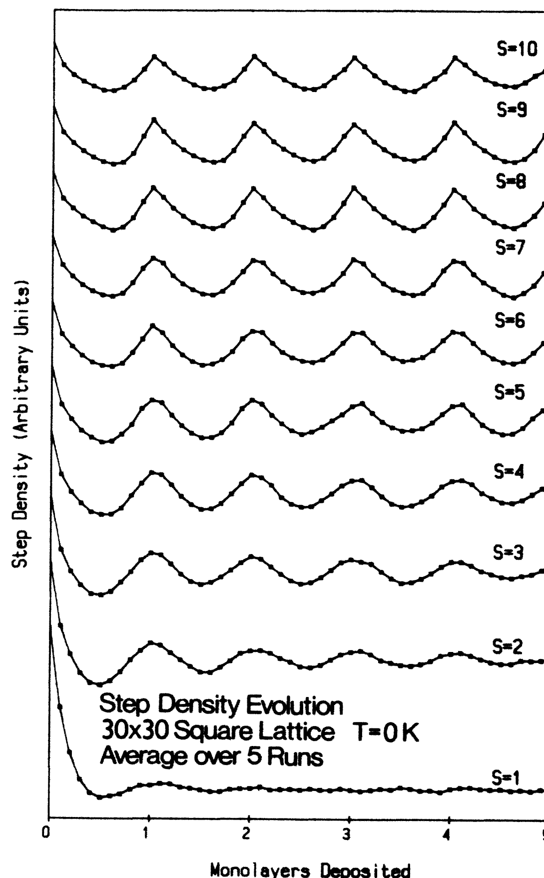

FIG. 2. The surface step-density evolutions during the growth of five monolayers over a range of values of the search parameter S (see Fig. 1) in the absence of surface adatom migration (i.e., $T=0$ K).

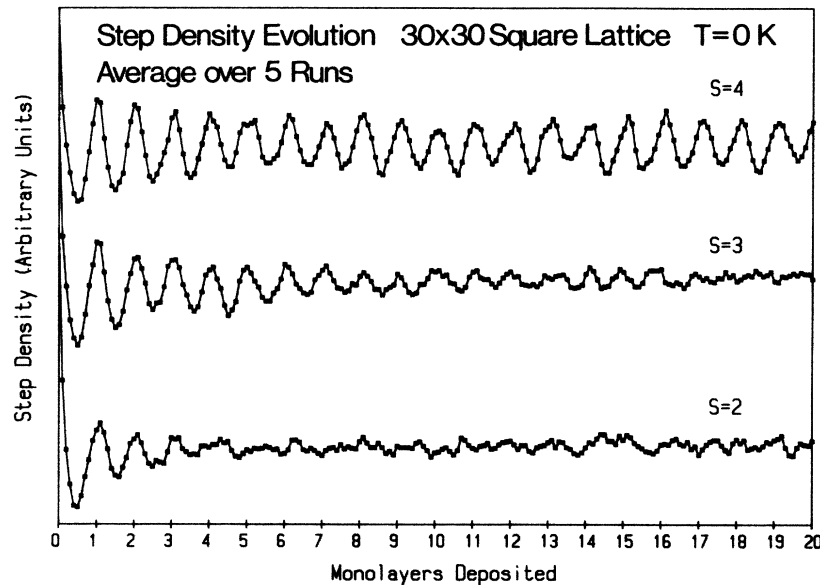

FIG. 3. The surface step density for an extended growth sample of 20 monolayers with $S=2$, 3, 4 in the absence of surface adatom migration (i.e., $T=0$ K).

(ii) may be readily explained with the observation of Neave *et al.*[1] of a loss of oscillations with increasing substrate temperature during the growth of GaAs on vicinally cut (stepped) surfaces.

The substrates used in the Si/Ge(100) experiments were cleaved very accurately with a misorientation from the desired crystallographic plane of less than 0.05°.[9] However, any variation from the ideal will produce linear steps on the surface which, as for the case of GaAs growth, can act as traps for mobile surface atoms. Accordingly, in Fig. 4 are presented the step-density evolutions for the simulated growth of ten layers of material on a 30×30 site substrate which incorporates a single monatomic step. Each growth sample comprises the average of five independent runs of the simulation. Noticeable in this data are the following: (1) the presence of strong oscillations at $T=300$ K, a temperature too low to promote surface migration; (2) a progressive decrease in the amplitude of the oscillations until at $T=750$ K no more oscillations are visible; (3) the reduction of the initial decrease in step density as the substrate temperature is raised.

By application of our simulation we are able to reproduce, qualitatively, the principal aspects of group-IV semiconductor MBE, as evidenced by RHEED specular intensity evolutions. Si/Ge MBE growth at higher temperatures exhibits the same behavior as III-V growth and we may thus expect the growth kinetics to be similar, i.e., a surface-diffusion-limited process. However, at low temperatures we see a marked departure from previous observations of III-V MBE, namely, the presence of RHEED oscillations in the absence of surface migration. Our simulations and comparisons with RHEED measurements, as well as the molecular dynamics simulations in Ref. 11, suggest that this may be explained by the existence of a precursor state in which incident atoms are able to explore the potential-energy surface of the growth front before being incorporated onto the surface at a local potential-energy minima. When the surface has a low step density, incident atoms will have a low probability of being adsorbed at a step edge and will increase the mean surface step density, while when the surface has a higher step-density adsorption at a many nearest-neighbor site is

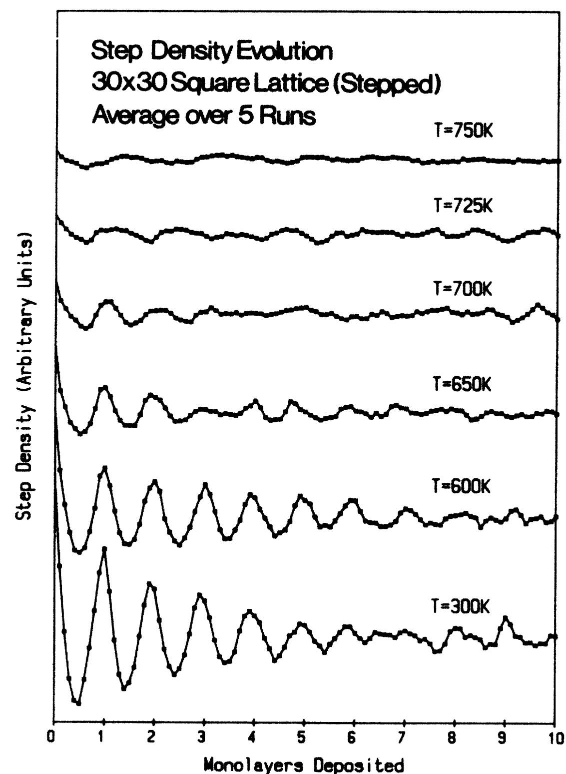

FIG. 4. The surface step density for finite-temperature growth over a range of substrate temperatures T during the growth of 10 monolayers on a surface with a single step.

probable, there is a reduction in the step density. Thus, we observe oscillations in the specular RHEED intensity.

Our model cannot address other questions concerning the nature of Si MBE, such as the requirement of a single-domain 2×1 surface reconstruction for the successful observation of RHEED oscillations[11,12] or the alternating $2\times1/1\times2$ reconstruction of progressive monolayers,[18] but does offer an understanding of other fundamental aspects of growth. Indeed, the apparent importance of incorporation kinetics in the low-temperature regime of group-IV MBE is somewhat reminiscent of the studies of Ghaisas and Madhukar[8] on the role of arsenic incorporation in III-V MBE at low arsenic overpressure. To obtain a quantitative understanding of group-IV MBE and to analyze the reconstruction problem [item (iii) above] will require the application of more advanced simulation techniques.

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