Prediction of Kinetically Controlled Surface Roughening: A Monte Carlo Computer-Simulation Study

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The existence of a surface roughening under far-from-equilibrium conditions is demonstrated. Roughening is critically controlled by surface kinetic processes, such as the atomic migration rate. Monte Carlo simulations are presented for a model of molecular-beam epitaxial growth of tetrahedrally bonded compound semiconductors. It is proposed that the roughening reported for GaAs/AlAs(100) growth, if intrinsic, corresponds to the kinetic surface roughening predicted here rather than that predicted by Burton, Cabrera, and Frank for surface-vapor equilibrium.

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Roughening of a solid surface, at or near equilibrium with its vapor, was anticipated in the work[1] of Burton, Cabrera, and Frank (BCF), and has been extensively investigated[2-4] during the past two decades—first via analytical model studies based upon kinetic Ising models and subsequently via Monte Carlo (MC) computer simulations on a simple-cubic elemental solid within the so-called solid-on-solid (SOS) approximation. These MC studies have shed light on the so-called surface roughening transition, indicating the existence of a roughening temperature, T_R (where $k_B T_R \sim 0.6$ times the nearest-neighbor bond energy in the SOS model), above which the surface becomes rough and consequently, in the presence of even a small driving vapor overpressure, crystal growth proceeds by a three-dimensional (3D) island growth mechanism. Below T_R, if the vapor overpressure is very small the surface remains smooth and consequently growth takes place via the layer-by-layer growth mechanism or, at high vapor overpressure, the surface profile is again rough with a certain diffuseness which depends upon the vapor overpressure and the substrate temperature. These features are also found in recent MC studies on elemental tetrahedral structures.[5,6] An essential feature of these studies is that they do not concern themselves sufficiently with certain essential kinetic processes (such as surface migration) occurring at the growing crystal surface since the very issue of focus has been the behavior of the solid surface at or close to equilibrium.

In recent years, however, vapor-phase epitaxial growth techniques such as molecular-beam epitaxy (MBE) have emerged which rely significantly on surface kinetic processes for successful growth of high-quality interfaces between reasonably compatible materials.[7] This technique has, so far, been most extensively employed for growth of tetrahedrally bonded III-V compound semiconducting materials on suitable substrates and, for various pragmatic reasons—some relating to the kinetics of growth—typically under far-from-equilibrium conditions at usually low growth temperatures (700 to 950 K). Indeed, multiple-interface structures of $(\mathrm{GaAs})_m/(\mathrm{AlAs})_n$ (where m and n denote the number of atomic layers) have been grown[8,9] along the [100] direction and, in transmission electron microscopy (TEM) studies, shown to exhibit interfaces which are structurally and chemically perfect to within two, or even one, monolayer.[10,11] Such remarkable control on the interface sharpness is, however, found to be sensitive to the growth temperature employed. Results of TEM, photoluminescence linewidth, and recently, Hall mobility of single and multiple interface structures[12] of GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$(100) systems grown at increasing substrate temperatures have shown the occurrence of a worsening in the interface sharpness beyond a certain temperature in the neighborhood of 950 K. While the experiments do not reproduce this temperature precisely enough, a situation largely thought to be a consequence of differing background impurity content in the MBE growth chamber even under the ultrahigh vacuum (UHV) conditions employed, the occurrence of interface roughening is unmistakable and substantiated by independent groups. This has led to the view that growth of GaAs proceeds by a layer-by-layer mechanism for growth temperatures below ~950 K, whereas above such a temperature, it proceeds via a 3D island growth mechanism.

The change in the surface profile of the growing GaAs layer (upon which subsequent deposition of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ defines the sharpness of the interface) occurring near 950 K has been attributed[13] to the surface roughening transition of BCF. However, given the far-from-equilibrium nature of MBE growth involved, the extremely low growth temperature (~950 K ≡ 0.08 eV) compared to the relevant bond energies (~2–4 eV), the molecular nature of the group-V vapor species employed, and the tetrahedral geometry of the growing structure (the SOS model assumes atomic species, elemental solid, and simple-cubic structure), it is easily realized that the proposed identification of the observed interface roughening is neither quantitatively nor qualitatively in conformity with the primarily thermodynamic basis of the surface roughening predicted by BCF. Moreover, for crystal growth under conditions of constant flux as in MBE growth, no indication of a roughening transition is found in the MC studies on the SOS model.[14]

It is the aim of this paper to demonstrate the existence of a new kind of surface roughening which occurs under far-from-equilibrium conditions, is critically controlled by surface kinetic processes, such as the surface migration rate at the growth front, and is severely influenced by the structural constraints imposed on surface kinetic processes by the structure of the growing solid. We shall refer to this as "kinetic roughening" and denote the appropriate temperature as T_{KR}.

Motivated by the possible significance of the surface kinetic processes in far-from-equilibrium growth from the vapor phase in general, and the roughening observed for MBE growth of the GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}$As(100) system in particular, we have performed Monte Carlo computer simulations of the [100] homoepitaxial growth of a tetrahedrally bonded compound semiconductor BC (for example GaAs) on an anion-terminated ideal surface. In particular, the role of the structural constraints arising from the tetrahedral geometry, the molecular nature of the group-V beam, and the diffusion of cations (B) during growth is examined.

The model assumes that the cations impinge upon the substrate (held at a temperature T_S) at a constant flux, F_B. The anion beam is taken to be in the diatomic molecular state (C_2) and at a vapor pressure high enough so that the growth is controlled by the cation flux, in keeping with the experimental findings.[7–12] Following the suggestion[15] by Arthur, we take C_2 to exist in a mobile physisorbed state at the growth front. This precursor state acts as the bath from which C_2 chemisorbs dissociatively whenever it can find a geometry in which at least three cation atoms exist in appropriate consecutive tetrahedral epitaxial sites as determined by the (100) surface.[16,17] A cation atom may chemisorb onto the growing structure directly from the vapor only when it impinges upon a site which allows it to form two nearest-neighbor bonds with the anions in the layer below. Details of this model for incorporation of cations and anions will be presented elsewhere.[14] The chemisorbed atom will migrate on the surface (no bulk diffusion or exchange is allowed) prior to its possible evaporation or incorporation. Since the growth rate is cation-flux controlled and generally occurs under anion overpressure, diffusion of chemisorbed anions is not expected to play as rate limiting a role in the growth profile as the diffusion of cations. This is plausible since the need for only two anions to be present at consecutive tetrahedral sites (thus providing an appropriate site for chemisorption of the cation) can be achieved with higher probability. The migration of anions may, however, influence the anion vacancy concentration but for simplicity, in this model, we only consider cation diffusion. A typical cation may, depending upon the growth condition, make a large number of hops before it becomes part of the bulk crystal.

The hopping rate of a "free" cation (i.e., one forming only two cation-anion bonds and four cation-cation bonds with the layers below) is taken to be of the form

$$R_d^0 = R_{0d}\exp(-E_d/KT), \tag{1}$$

where E_d is an activation barrier. The hopping rate of any other surface cation is given by

$$R_d^{\,i} = R_{0d}\exp[-(E_d + E^i)/KT], \tag{2}$$

where E^i is the energy gained by the cation at site i by virtue of additional bond formation. Hopping will therefore take place primarily among the "free" cation atoms. During the growth, some of the atoms will evaporate. The rate of evaporation of cations is also taken to be given by an Arrhenius form,

$$R_e = R_{0e}\exp(-E_{\mathrm{tot}}^{\,i}/KT), \tag{3}$$

where $E_{\mathrm{tot}}^{\,i}$ is the total binding energy of the cation at site i. Thus

$$E_{\mathrm{tot}}^{\,i} = E^i + 2E_{BC} + 4E_{BB}, \tag{4}$$

where E_{BC} is the cation-anion bond energy, and E_{BB} is the cation-cation bond energy.

The computer simulation of the random impingement, chemisorption, diffusion, and evaporation processes is carried out via a new Monte Carlo technique which differs from the ones used in the literature in a fundamental way. The technique involves keeping track of two matrices, one of which contains real-time information about the crystal sites (occupied or empty) and the other, the information on the most probable time when the next kinetic event (i.e., a hop or evaporation) is to take place for a given site. The latter information is also generated via MC simulation of the kinetic rates. This new method leads to a significant improvement in the efficiency of the computer program. Its details will be published elsewhere.[14] The Monte Carlo studies were carried out on substrate sizes of 20×20, 30×30, and 40×40 with periodic boundary conditions. It was found that the 30×30 size was sufficient for convergent results. Three different random number sequences were used and the average results reported here are reliable to within 5%. The parameters used for the simulations are

$$R_{0d} = 5\times10^{7}\ \mathrm{sec}^{-1};\quad E_d = 0.75\ \mathrm{eV};$$

$$R_{0e} = 1\times10^{11}\ \mathrm{sec}^{-1};\quad E_{BC} = 1.0\ \mathrm{eV};\quad E_{BB} = 0.2\ \mathrm{eV}.$$

The flux of the impinging cation atoms is maintained such that if all of them were incorporated, the substrate would grow at the rate of approximately 1.1 monolayers per second. Under the present growth conditions the incorporation rate lies between 25% and 35%, consistent with available information. The parameters chosen are expected to represent realistic situations, although they do not represent any specific system.

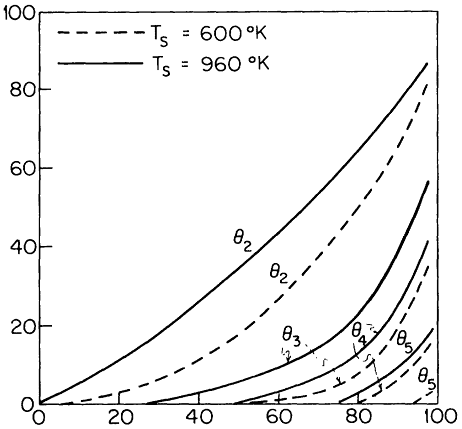

FIG. 1. Growth profile of the structure BC for two different substrate temperatures. Plotted are the coverages of the higher layers as the first layer is filled up. Dashed line, $T_S = 600$ K; solid line, $T_S = 960$ K.

The results of the MC simulations are shown in Figs. 1 and 2. Figure 1 illustrates the coverage θ_n of the layer n ($n = 2, 3, 4, \ldots$) as a function of the first-layer coverage θ_1. The plot illustrates the growth profile as a function of θ_1 for two substrate temperatures ($T_S = 600$ K and $T_S = 960$ K). These temperatures are very small compared to the bond energies used in this simulation, yet the increase in growth temperature from 600 K to 960 K reveals significant roughening of the growth profile. This aspect is brought out even more clearly in Fig. 2 which is a plot of the coverage of the cation of the fifth layer as a function of the growth temperature when the first-cation-layer coverage reaches 95% and 97% (curves I). Note the sudden increase in the concentration of the fifth-layer cations near $T_S \sim 800$ K. If an interface is fabricated from two different materials, say AC deposited on BC, the interface will reflect the roughness present in the steady-state, dynamic growth front profile of BC, giving rise to a progressive roughening of the interface with increasing temperature over a relatively small window of ~75 K.

The central role played by the surface kinetics in controlling this roughening behavior is confirmed by repeating the study with a lower diffusion barrier, $E_d = 0.65$ eV, keeping all other

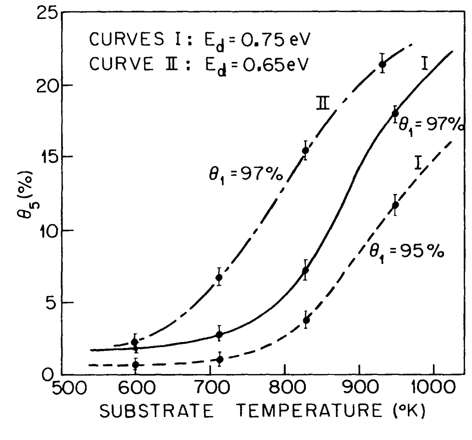

FIG. 2. Coverage of the fifth layer (third cation layer from the starting substrate) as a function of the substrate temperature. Plotted are the fifth-layer coverages when the first layer is 95% covered (dashed line) and 97% covered (solid line). The short-dash–long-dashed line gives the behavior when the activation energy for diffusion, E_d, is lowered from 0.75 eV (for curves I) to 0.65 eV (curve II).

parameters the same. The result at $\theta_1 = 97\%$ is given by curve II, Fig. 2. The temperature at which the surface roughening begins is clearly seen to be lowered by almost 100 K.

The effect of the kinetics, which is primarily controlled by the surface migration at the growth temperatures considered, is reflected in the microstructure of the growing layers. We find that for a given coverage θ_n of the nth layer ($\theta_n < 1$), at low temperatures the atoms are arranged in a rather random manner, while at higher temperatures increased surface migration allows formation of larger, 2D clusters. The ability to form these larger in-plane clusters allows vertical growth to take place since the conditions for incorporation in the next layer, as required by geometric constraints of the structure, are satisfied at a higher fraction of the covered sites. This is the main reason for the growth changing from a smooth layer-by-layer mechanism to a 3D nucleation (continuous growth) mechanism with increasing temperature. Such an effect is not expected to occur for the SOS model since there are no geometric constraints in the SOS model and atoms can be incorporated on top of any occupied site. For the same reason the kinetics is not expected to play as dominant a role in the SOS model.

It is important to note that the results reported here are based upon the growth surface profile reaching a steady-state value. Thus the results shown will not change upon further growth. The fact that steady state is reached rapidly is manifested in Fig. 2 (solid lines) where for $\theta_1 = 40\%$, $\theta_2 = 26\%$ and again for $\theta_3 = 40\%$, $\theta_4 = 26\%$.

In summary, in this Letter we have identified the existence of a kinetically controlled growth-front roughening via MC computer simulations of the [100] MBE growth of III-V semiconductors. The origin of this roughening is different from the conventional roughening transition predicted by BCF at or near thermodynamic equilibrium. It is proposed that the observed interface roughening in the growth of GaAs/AlAs(100) multiple-interface structures, if dominated by intrinsic effects, is likely caused by the kinetic and geometric effects giving rise to the kinetic surface roughening predicted here, and is most unlikely to correspond to the surface roughening transition of BCF, as previously suggested.

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