Peripheral roughening in a monolayer: A molecular-dynamics study

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(Received 12 December 1988)

We have performed a molecular-dynamics simulation of the peripheral roughening of a two-dimensional triangular lattice on a bcc substrate. The model in which the peripheral atoms exhibit a weakened bond to the inner atoms shows a smooth increase in the roughness as a function of temperature. The dependence of the roughness on the strength of the interaction is in agreement with a theoretical spin model but, however, disagrees with earlier claims based on thermodynamic measurements of epitaxial films. The implications for epitaxial growth are also discussed.

INTRODUCTION

The behavior of monolayer solids[1] and noble gases on solid substrates[2] is a problem of current interest. The growth of epitaxial monolayer films is the basis for the preparation of novel materials and for the study of unusual physical phenomena.[3] The understanding of growth mechanisms and dynamics of epitaxial growth is receiving more and more attention.[4,5]

In a stimulating experimental study Kolaczkiewicz and Bauer[6] claimed that the periphery of a monolayer Au film on a W(110) surface exhibits a roughening transition in two dimensions (2D) in analogy to the roughening transition predicted[7] for the surface of a three-dimensional crystal. The peripheral roughening transition was claimed to be due to the weakening bonds between the peripheral to inner atoms (J_1) (presumably due to substrate mediated dipolar interactions). In this fashion Kolaczkiewicz and Bauer claimed that the roughening temperature (T_R) increases with decreasing $J_1=\alpha J$, if the inner atom interaction strength J is kept constant. A further analogy was made with a 2D spin model developed earlier by Abraham[8,9] in which the system is bound by rigid walls and which under certain conditions in effect produces a roughening transition.

The existence of a roughening transition clearly has serious implications for the epitaxial growth. One of the most important implications would be that above T_R it is incorrect to think of well-defined islands on a substrate, which would modify the growth dynamics considerably.

The growth of an epitaxial film is quite well suited for numerical simulation, especially using molecular-dynamics techniques.[10–13] In a realistic simulation the epitaxial film grows in an atom-by-atom fashion, and it is of major interest to understand if the existence of a roughening transition below the melting temperature is real for *finite* size islands, in what fashion the possible weakening of peripheral bonds affects T_R, whether the transition is sharp or broad, etc. In order to answer some of these questions we have performed extensive molecular-dynamics simulations of the behavior of a triangular monolayer on a bcc(110) substrate as a function of temperature and relative bond strength factor α.

THE MODEL

The model consists of a finite sized, triangular monolayer crystal to simulate a fcc(111) plane on an infinite, rigid bcc(110) substrate.[14] The particles are interacting via ordinary Lennard-Jones potentials;

$$V(r)=4\varepsilon d[(r_0/r)^{12}-(r_0/r)^6]\,. \tag{1}$$

In order to stabilize the fcc monolayer on top of the bcc substrate the interaction parameter between the fcc particles was chosen $d_1=14$ and the interaction between the fcc particles and the bcc substrate was chosen as $d_2=4$. Recall that the equilibrium configuration of a Lennard-Jones crystal is fcc. The melting temperature of the monolayer is $T_m\sim 1.6$ in 2D, with our parameter values for the potential. The ratio of the triangular to bcc lattice parameter was chosen to be equal to the one which gives minimum of the epitaxial energies (1.33) (Ref. 15) and is quite close to the ratio of Au to W lattice parameters (1.291) as studied experimentally.[6] As suggested in Ref. 6 the interaction between the peripheral and inner atoms is weakened by a factor α, when compared to the inner atom interactions, i.e., $J_1=\alpha J$ with $\alpha<1$. A few studies with $\alpha>1$ were also performed.

The equations of motion of all particles are solved simultaneously as is customary in molecular-dynamics calculations,[16] with the unit of time being given by $t_0=r_0(m/\varepsilon)^{1/2}$ and the unit of energy is ε. The temperature is controlled by periodically resetting all the velocities in order to keep the total kinetic energy equal to the desired temperature. Once the system is in equilibrium,

the temperature control is removed and the system is allowed to move freely.

An atom is defined as being on the periphery of the 2D layer if within a distance, slightly larger than the midpoint between the first and the second nearest-neighbor distance in the 2D triangular lattice, it has less than 6 neighbors. This computational criterion defined the same atoms as being in the periphery as the ones determined from a simple visual inspection. The size of the triangular lattice was varied from 225 to 900 particles without appreciable change in the results. The number of steps to obtain equilibrium typically were 5000 to 100000 time steps depending on the value of α [i.e., from 7 to 140 h of central processing unit (CPU) time on a VAX 8600 at the Catholic University in Santiago].

NUMERICAL RESULTS

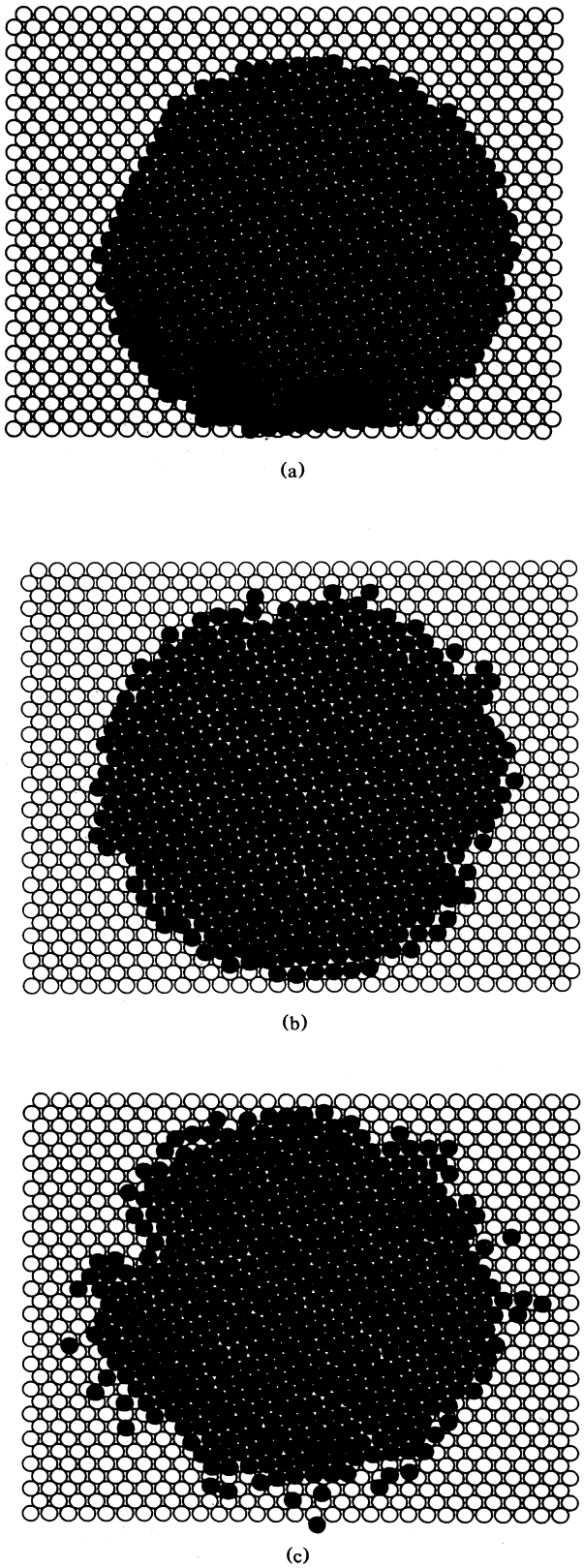
Figure 1(a) shows the configuration of a 487 atom island with an $\alpha=0.2$ at a low temperature $T=0.1$. Clearly the island is well-formed with the number of peripheral atoms being mostly given by the fact that the system has a finite size. As the temperature is raised the number of peripheral atoms increases and the surface of the 2D layer becomes rougher as shown in Fig. 1(b) and Fig. 1(c), for $T=0.5$ and $T=0.7$, respectively.

Figure 2 shows the number of peripheral atoms as a function of temperature for various values of α. It is clear from this figure that there is not a well-defined roughening temperature, but the transition is smooth. This qualitative conclusion was obtained for a variety of α's and system sizes. Clearly, in these finite sized systems, there is a cutoff of the long wavelength fluctuations, and this could be the cause for the absence of an abrupt roughening transition. On the other hand, experimentally, the growth of epitaxial films must proceed from the growth of finite size islands and possibly the roughening transition, if present, is only important for very large islands. Moreover, in order to observe a large increase in the peripheral roughness the value of α has to be made unreasonably small ($\alpha < 0.2$).

In order to understand the effect of α, at fixed temperature we have performed a variety of studies keeping the temperature constant. Figure 3 shows the number of peripheral atoms as a function of α at a fixed temperature for $T=0.5$ and 0.8. Recall that the melting of a 2D Lennard-Jones crystal is $T_M \sim 1.6$ in our units. Down to an $\alpha \sim 0.2$ no appreciable roughening is observed showing that a sizeable weakening of the peripheral bonds is necessary in order to observe the phenomenon. At present, it is not clear to us whether such a large weakening is possible, especially due to a substrate mediated indirect interaction such as the one suggested by Kolaczkiewicz and Bauer.[6]

DISCUSSION

Abraham[8,9] developed a spin model in which the boundary spins are pinned to two rigid walls. If the interaction strengths of the boundary spins at one of the two walls is lowered, a roughening transition is obtained for



(a)

(b)

(c)

FIG. 1. (a) Atomic configuration for a 487-particle layer at $T=0.1$ and $\alpha=0.2$; (b) at $T=0.5$ and $\alpha=0.1$; and (c) at $T=0.7$ and $\alpha=0.1$.

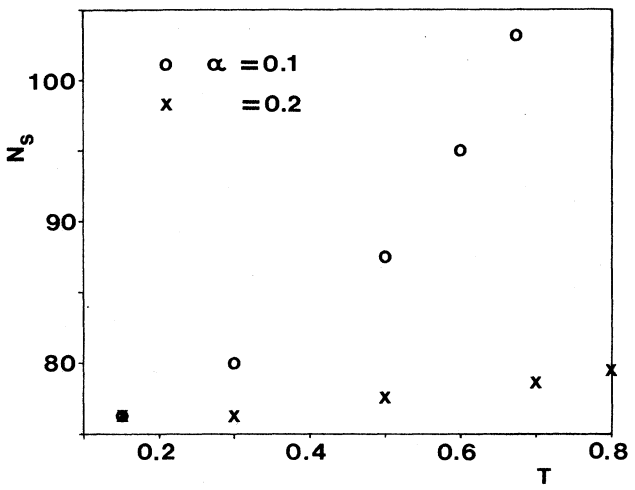


FIG. 2. Temperature dependence of the number of peripheral atoms for various values of α.

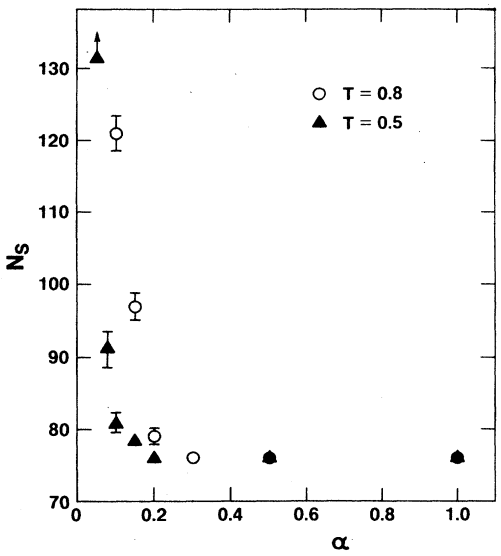


FIG. 3. Dependence as a function of α, of the number of peripheral atoms at a fixed temperature.

the situation for which the interaction between the boundary and the inner spins is weakened by a factor β. The roughening thus decreases with decreasing β.

The translation of the spin model to the lattice gas model is not clear. If the occupied sites are assumed to be of spin up and the unoccupied are of spin down the weakening should be assumed between the *last occupied sites* and the *unoccupied sites* ("vacuum"). If the interaction to the "vacuum" is weakened by a factor β, the last row of atoms is bound tighter to the new inner row of atoms and therefore the roughness is expected to decrease. This is contrary to what Kolaczkiewicz and Bauer claimed. The reason for this is that they translate the Abraham model to the lattice model by assuming that the peripheral atom interaction *with the inner atoms* is weakened whereas the correct interpretation is that the weakening is assumed to occur between the peripheral atoms and the *unoccupied sites.*

It has also been claimed[17] that the presence of a rigid wall is an essential feature required for the presence of the roughening transition in the Abraham model. Whether the existence of the rigid wall can be assumed in the monolayer model is not clear to us.

As shown above, the intuitive ideas presented are in good agreement with molecular-dynamics calculation. It should be stressed that the dependence of the roughness on α is unrelated to the size of the system and to the existence of a sharp roughening transition.

The existence of the peripheral roughening possibly does not affect epitaxial growth in a major way. Since, in our simulations, islands smaller than a few hundred atoms do not show peripheral roughening it is unlikely that this phenomenon will affect the growth in a major way.

SUMMARY

We have performed a molecular-dynamics calculation to study the roughening of a 2D fcc layer on top of a bcc substrate in which the interaction of the peripheral atoms with the inner atoms is weakened (by a factor α) when compared to the interaction of the inner atoms themselves. We find that in accordance with intuitive expectations and a spin model by Abraham, the roughness increases with decreasing α. No abrupt roughening transition is observed as a function of temperature possibly due to the finite size of the islands. The possible implications for epitaxial growth were discussed.

ACKNOWLEDGMENTS

Part of this work was done in collaboration with the late Professor A. Rahman. Work supported by the National Science Foundation under Grant No. DMR-87-01921 (at University of California at San Diego) and the Fondo Nacional de Ciencias (Chile) under Grant No. 0368/8. International travel was supported by the National Science Foundation Grant No. INT-87-19950.

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