

## Growth of metallic superlattices by sequential deposition of atoms

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(Received 5 August 1992; revised manuscript received 12 November 1992)

In an effort to better understand the formation, epitaxy, and interfacial properties of metallic superlattices, we have performed an exploratory molecular-dynamics (MD) study of the growth of a simple Lennard-Jones multilayer system. We find indeed that “large” heterostructures can be epitaxially grown using the technique of MD, a steady-state growth regime being rapidly attained. In the present model, we observe that growth is Volmer-Weber with, at any instant, three or four layers in formation. The interfaces, as a result, are not sharp and extend in all cases over two monolayers. Several possible improvements to the model will be discussed.

There is a great deal of interest in metallic superlattices since it is now possible — by judicious choice of components combined with appropriate fabrication methods — to tailor their properties for specific applications exploiting their electronic, mechanical, or magnetic properties. Progress in the development of new technology, however, is hampered by the lack of understanding of their properties at the fundamental level, in particular structure and growth. The most eloquent example of this state of affairs is, perhaps, the “supermodulus effect.” Evidence has been reported that some metallic superlattices see their biaxial moduli, depending on modulation wavelength, suffer extraordinary increases.<sup>1</sup> Though it appears that the observation of such dramatic enhancement of elastic constants is simply erroneous<sup>2</sup> (being due to deficient experimental conditions), it also appears that “anomalies,” of the order of 10–15 %, may exist,<sup>3,4</sup> but this is still controversial.<sup>2,5</sup> Other problems with superlattices include the nature of defects (such as voids and grain boundaries), the effect of strain on their structure, and the structure of interfaces, including diffusion processes.<sup>6</sup>

For most applications, it is necessary that the interface between layers of different species be as sharp as possible, and therefore it is essential to understand formation and growth in order to optimize fabrication. In particular, it is important to gain a detailed understanding of the dynamic structure of the interfaces, which may be altered during growth. In some cases, such as NiZr and CoZr, the energy transferred from the incoming particle beam to the growing sample may in fact be enough to cause partial, or even complete, amorphization by solid-state reaction.<sup>7</sup>

In an effort to better understand the formation, epitaxy, and interfacial properties of metallic superlattices, we have performed, and report on, a molecular-dynamics (MD) simulation of the growth of a simple Lennard-Jones superlattice. The usefulness of computer-simulation methods, and in particular MD, in understanding materials fundamentals and optimizing materials design, as well as predicting new properties, is no longer to be demonstrated.<sup>8</sup> MD has been used quite extensively to investigate semiconductor layer growth, being concerned

almost exclusively with *homoepitaxy* [e.g., Si on Si(100)];<sup>9</sup> very rarely has *heteroepitaxy* [e.g., Ge on Si(100)] been studied.<sup>10,11</sup> In the case of metallic systems, a relatively larger proportion of published studies addresses the problem of heteroepitaxial growth.<sup>12–18</sup> This, to a large extent, can be attributed to the fact that simple models such as Lennard-Jones give adequate results, while in the case of covalent semiconductors, the use of more complex (but poorly known) “three-body” potentials, such as that proposed by Stillinger and Weber for Si,<sup>19</sup> is essential to a proper description of bonding. For metals, however, more realistic than Lennard-Jones, the recently developed embedded-atom-method (EAM) potentials<sup>20</sup> have been employed successfully to model the bilayer growth of Au on Ni(100) and Ni on Au(100),<sup>12</sup> and of Ag on Ag(111).<sup>17</sup> To our knowledge, however, there has been no published account of the simulation of the growth of metallic superlattices.

Here we do so using the technique of sequential deposition of energetic atoms. The primary purpose of this exploratory study (our model, described below, is certainly not optimal) is to assess the feasibility of such an enterprise, i.e., to verify whether or not “large” metallic heterostructures can be epitaxially grown using MD. We find that it is indeed the case, a “steady-state” growth regime being rapidly attained: though such conclusions could to some extent be anticipated from the study of bilayer systems,<sup>12–18</sup> it is important to verify that accumulation of strain and defects does not result in poor-quality growth on the multilayer scale. In the Lennard-Jones model used here, we find that growth is Volmer-Weber (i.e., nucleation and growth of three-dimensional clusters)<sup>21</sup> with, at any instant, three or four layers in formation. The interfaces, as a result, are not sharp and extend, in all cases, over two monolayers. We find no interfacial diffusion, but the model is not appropriate for the study of such processes: As mentioned earlier, the model used here was designed to assess the main features of superlattice growth, rather than the detailed processes that take place during deposition. Several conceivable improvements to the model will nevertheless be discussed.

The procedure we use for simulating the superlattice

growth process resembles closely that used to investigate the growth of  $\text{Si}_{1-x}\text{Ge}_x$  on  $\text{Si}(100)2\times 1$  presented in Ref. 11, where additional details can be found. In essence, high-energy atoms of the proper type are projected sequentially onto the surface of a substrate, and allowed to interact dynamically with it until the system relaxes completely. Starting with a substrate which consists of four 50-atom layers of *A*-type material arranged in a fcc pattern along the (001) direction, growth proceeds by the deposition of alternate layers of *B*-type and *A*-type atoms, each also equivalent to four complete monolayers (200 atoms). The final structure, therefore, contains 1000 atoms (20 monolayers) in the sequence *A/B/A/B/A*. Interactions between atoms are taken to be of the Lennard-Jones form, viz.,  $V_{IJ}(r) = 4\epsilon_{IJ}[(\sigma_{IJ}/r)^{12} - (\sigma_{IJ}/r)^6]$ , with  $IJ = AA, AB$ , and  $BB$ . The energy parameter  $\epsilon_{IJ}$  is taken to be the same for all three types of interaction, namely  $\epsilon = 0.0106$  eV (appropriate to Ar), while the length scales are chosen as determined in earlier studies of single-layer growth, namely  $\sigma_{AA} = 3.446$  Å (also corresponding to Ar),  $\sigma_{AB}/\sigma_{AA} = 0.95$ , and  $\sigma_{BB}/\sigma_{AA} = 0.9$ . In all cases, the potential is truncated at a distance  $r_{c,IJ} = 2.5\sigma_{IJ}$ . The substrate is held at an essentially constant temperature of 25 K, using a procedure similar to that described in Ref. 11, which consists in continuously renormalizing the velocities of the atoms in a number of cooling layers to the desired temperature. The substrate temperature here corresponds to a fraction of 0.30 of the melting point of Ar,  $T_m$ , a value which appears to be optimal for metallic growth.<sup>13</sup> The bottom layer is held fixed (i.e., at zero temperature) in order to mimic the effect of the bulk; the lattice parameter for the  $xy$  plane (note that the surface is free),  $a = 5.402$  Å, was determined from an independent constant-pressure run of a bulk system at the temperature of the substrate. The “beam temperature,”  $T_d$ , was taken to be 110 K ( $= 1.29T_m$ ). Thus, particles were created at random  $xy$  positions on a plane at a distance  $2r_{c,AA}$  above the surface (defined, at any instant, as the top-most layer), with velocity pointing towards the substrate given by  $mv_d^2/2 = kT_d$ , where  $k$  is Boltzmann’s constant. Atoms were deposited at a rate of one every  $\tau = 100$  time steps  $\Delta t$ , where  $\Delta t = 5.0$  fs. We have verified that, under these conditions, the substrate does not suffer excessive heating. Note that even though atoms are created far from the surface (which raises with time), they can (and do, as we will see shortly) interact with one another. As a final point, we have found it convenient to define an atom as belonging to the substrate when its velocity (originally pointing towards the surface) changes sign for the first time.

We plot in Fig. 1 the trajectories — projected onto (a) the  $xy$  plane and (b) the  $yz$  plane — for the last 50 *B*-type atoms of the final stage of deposition. Though such plots carry limited information (an animation of the growth process is much more instructive), they are nevertheless useful in providing qualitative understanding of the problem. Indeed, it is already clear from this figure that growth is three dimensional (Volmer-Weber), i.e., it does *not* proceed layer by layer; quantitative information will be presented later. Thus, a layer starts forming be-

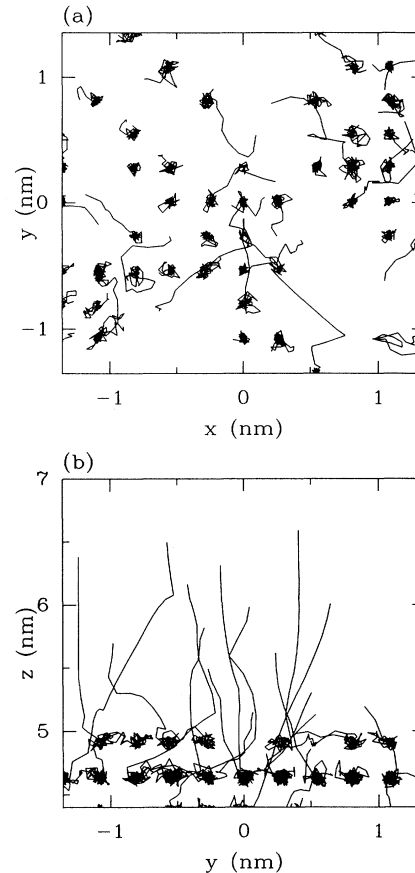


FIG. 1. Trajectories of the last 50 atoms during the final (*A*-type) stage of deposition, projected onto (a) the  $xy$  plane and (b) the  $yz$  plane.

fore the previous one is complete. Such results, of course, may depend on details of the model, and in particular the potential. For instance, pseudomorphic Volmer-Weber growth has been observed in the case of Ni on Au(100), while interestingly, Au on Ni(100) proceeds in the mode of Stranski-Krastanov (i.e., three-dimensional growth following an initial two-dimensional growth), in the (111) direction.<sup>12</sup> It can be further remarked, from Fig. 1(a), that atoms undergo substantial surface diffusion before settling down. Note finally that atoms interact with one another already well above the surface, owing to the relatively large deposition rate; this, however, has little effect on their actual trajectories, dominated by a large downwards velocity — cf. Fig. 1(b).

The details of the growth of a single layer on the substrate is not our main concern, and we proceed, rather, with the growth of the superlattice as a whole, as described earlier. The final structure, consisting of five layers (with each four monolayers), i.e., two-and-a-half periods, we find, is perfectly crystalline. This is evidenced in Fig. 2, where we plot the density function along the  $z$  axis, calculated during a 50-ps period of relaxation following the final stage of deposition; the contributions of the two species are indicated by a full line and a dashed

line, respectively. This function,  $\rho(z)$ , counts the average (over time) number of atoms in a sheet of width  $\Delta z$  at  $z$ . Thus, a peak in  $\rho(z)$  corresponds to the presence of a plane of atoms, i.e., a monolayer; the integral of a peak measures the number of atoms in the monolayer. Peaks are well defined and unambiguously separated here, and the system is therefore perfectly crystalline; visual inspection of “slices” through the system confirms this, and also establishes that the packing arrangement of the monolayers is free of defects. The integral of each peak, irrespective of the atomic type, is exactly equal to 50 (except for the last two, because of the presence of the surface), the maximum number of atoms that a perfect fcc(100) layer can accommodate in the present case. (The increase in intensity at small  $z$  is an artifact of the presence of the fixed layer, located at  $z = 0$ ; at large  $z$ , on the other hand, i.e., close to the surface, the loss of symmetry causes the intensity to decrease and the vibrational amplitudes — measured by the width of the peaks — to increase.)

The system is small here, but it is nevertheless possible to observe interfacial mixing. This can be seen directly in Fig. 2. Interfaces, in all cases, extend over two monolayers (except for the first one at  $z \sim 0.95$ , since we start with a perfect substrate). Note that, because of constraints in the number of atoms, it is not possible to have an interface “extending” over a single monolayer. The existence of a rough interface can be a consequence of nonuniform growth, or signal the presence of diffusion processes. The intimate nature of the interface depends strongly on the details of the potential. We have seen earlier that growth was three dimensional; we have not, however, observed diffusion to take place, most likely because the interaction model is not adequate, but also because our runs are relatively short. We note, however, that the first interface has “suffered” relaxation for the full duration of the simulation, a respectable 0.5 ns ( $10^5$  steps); this suggests that the diffusion constant through the interface, *at this temperature*, is less than  $10^{-6}$  cm<sup>2</sup>/s, consistent with Ref. 22, and will therefore be very difficult to observe by MD simulation. The interfacial diffusion problem, not a serious concern here, is being investigated in the case of NiZr using a more realistic semiempirical

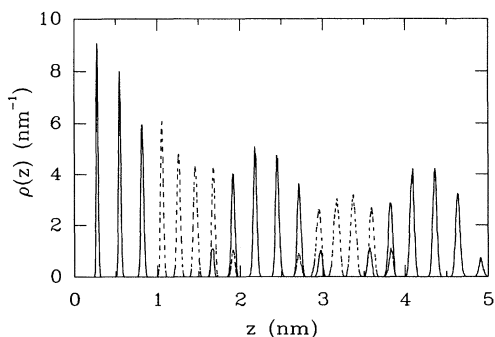


FIG. 2. Atomic density along the  $z$  axis, i.e., perpendicular to the direction of growth, for the final superlattice structure. The full and dashed lines correspond to  $A$ -type and  $B$ -type atoms, respectively. The first monolayer, which is fixed, is located at  $z = 0$  but is not indicated on this graph.

potential.

The density function  $\rho(z)$ , presented in Fig. 2, provides a precise definition of each monolayer in the system. Armed with this information, we can reanalyze the evolution in phase space of our system, and determine the occupancy, as a function of time, of each monolayer. This quantity  $n_\ell(t)$  is displayed in Fig. 3(a) for all monolayers constituting the final structure. Note that, corresponding to the plateaus at intermediate occupancy in Fig. 3(a), deposition was interrupted and the system relaxed for a period of  $10^4$  time steps ( $=50$  ps) after each stage of deposition, during which it remained virtually unchanged. The saturation of each monolayer at perfect crystalline occupancy — 50 atoms in the present case — is clearly evident. Most interesting, however, is the fact, noted earlier, that growth is not uniform but, rather, proceeds three dimensionally. This is seen more clearly in Fig. 3(b), which shows in detail the final stage of growth. At any given instant in time, there is always more than one monolayer in formation: a layer can start growing before the previous one is complete. This is easily seen in Fig. 3(b) by drawing a vertical line at a given time, and counting the number of growing layers it “crosses.”

Following Paik and Das Sarma,<sup>13</sup> we have tried fitting our data for the occupancy of the first monolayer to an expression of the form  $n_1(t) = n_1(\infty)(1 - \exp\{-(t - t_0)/\tau\}^m)$ , where  $t_0$  marks the onset of the growth,  $\tau$  is a characteristic time (which of course depends on deposi-

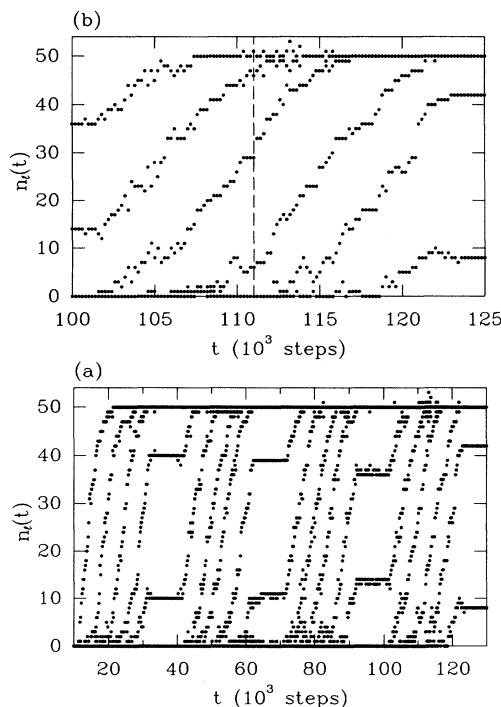


FIG. 3. Monolayer occupancy as a function of time for (a) the whole growth process and (b) the last stage of deposition. A full monolayer can accommodate 50 atoms. Plateaus at intermediate occupancies correspond to interruptions in the deposition process. The dashed vertical line in (b) indicates that, at the instant chosen as an example, three layers are simultaneously in formation.

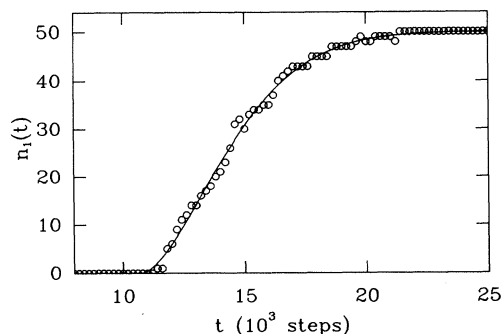


FIG. 4. Occupancy versus time for the first monolayer (open circles), fitted to a stretched exponential,  $n_1(\infty)(1 - \exp\{-(t - t_0)/\tau\}^m)$  (full line).

tion rate), and  $m$  is an exponent determined by the mode of growth —  $m = 1$  for continuous growth, and  $m = 3$  for nucleation and growth. It should be noted that this expression, which neglects such effects as surface diffusion, applies only to growth on a flat surface, i.e., in the present case, to the first monolayer. The result of our least-squares fit is shown in Fig. 4; we obtain, for the growth-mode exponent,  $m = 1.64 \pm 0.04$ . Thus, as was also found by Paik and Das Sarma, the growth is intermediate between continuous and nucleation, which is not surprising in view of the high mobility of the deposited atoms that we have observed in Fig. 1. Such an analysis cannot be reliably performed in the case of subsequent monolayers, since the substrate on which they grow is no longer flat. Nevertheless, we find that a reasonable

fit to our  $n_\ell$  data can be obtained using the above expression and values of  $m$  near 3, confirming indeed that growth crosses over to fully three dimensional after a few monolayers.

We have demonstrated that molecular dynamics can be successfully employed to simulate the growth of metallic superlattices. We have done so here using a simple Lennard-Jones interaction model, and find that perfectly crystalline layers will easily grow to “large” thicknesses. We find, in the present case, that growth crosses over from almost continuous to essentially three dimensional and, as a result, the interfaces are not flat. Such details of the growth process, however, may depend somewhat on the precise model used. It is clear, in particular, that the surface mobility — which depends in a delicate manner on substrate and beam temperatures, as well as on the energetics of the interactions (e.g., the energy of mixing) — is the key ingredient in determining the structure and quality of the interfaces. As a next step, it will be of interest to examine the corresponding problem using more realistic potentials, such as, perhaps, the embedded-atom model.<sup>20</sup> This, in addition to a detailed understanding of the growth process, could provide insights into problems such as interfacial roughening and diffusion.

This work was supported by grants from the Natural Science and Engineering Research Council (NSERC) of Canada and the “Fonds pour la formation de chercheurs et l’aide à la recherche” of the Province of Québec. E.A. would like to thank NSERC for financial support. We are indebted to the “Services informatiques de l’Université de Montréal” for generous allocations of computer resources.

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