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First-principles calculation of energy of an epitaxial system

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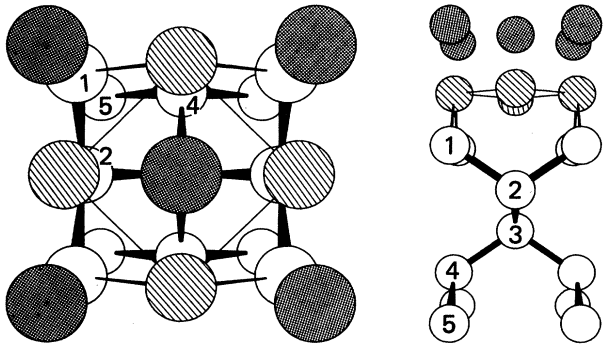
A self-consistent pseudopotential calculation of the energetics of aluminum growth on Ge(001) in the epitaxial relationship (001)[100]Al||(001)[110]Ge is presented. We observe that the equilibrium Al-Ge interplanar distance increases with the overgrowth thickness t and, more significantly, rapidly saturates ($t \lesssim 3$) to a value equal to the average interplanar distances of the two systems. We also conclude that the Frank–van der Merwe growth sequence of Al would begin at the bridging sites on Ge(001).

Despite a widespread interest in the field of epitaxy,[1-10] there appears to be a serious shortage of first-principles atomistic calculations dealing with the energetics of bicrystals. Much of the work[5-9] which has guided our thinking in this field has been based on the continuum theory of elastic media. There has been some discussion about an *ab initio* approach[10] but no specific epitaxial system has been treated to date. The problem is admittedly difficult for two major reasons. First of all, one does not know the exact atomic positions in any epitaxial system and thus a laborious process of double self-consistency is required. Secondly, the system is generally too large to be handled microscopically. Recently, much progress[11-13] has been made in the area of solid films on graphite but relatively little is known about the energetics of technologically important systems (metal/semiconductor interfaces) at the microscopic level. In this paper we consider a prototype metal-semiconductor epitaxial system and carry out a limited set of doubly self-consistent calculations. We present results as a function of the size of the system which we enlarge systematically.

Epitaxy is the growth of one naturally occurring crystal on another but with some definite and unique orientational relationship. Broadly speaking one can distinguish[1,4] three types of growth sequences following the nucleation. These depend on the value of γ, which is defined as the ratio of the interfacial binding energy (E_I) to the binding energy of the overgrowth particles (E_C). A type-I or a layer-by-layer growth occurs if $\gamma \approx 1$ and the lattice mismatch is not too severe ($< 15\%$). Furthermore, for large values of E_I there would be no nucleation barrier. For this growth mode the crystals strain elastically[6,7] to bring the lattice constants closer together. Such a pseudomorphic growth goes by the name of Frank–van der Merwe (FVDM). A type-II growth mode is characterized by $\gamma \gtrsim 1$ but the lattice parameters of the overgrowth and the substrate are very different. Because of the strong interaction with the substrate the initial growth commences with the first layer being pseudomorphic or chemisorbed in an $n \times m$ superstructure. The subsequent growth takes place by the nucleation of islands. This growth mode is also known as the Stranski-Krastanov (SK) mode. A type-III or the Volmer-Weber growth occurs for $\gamma < 1$ and the lattice misfit is of little consequence. Because of the weak interaction with the substrate the overgrowth particles are very mobile and lead to the formation of stable clusters. Metals on ionic substrates tend to grow in this fashion. It is believed[1,4] that semiconductors on semiconductors follow FVDM growth and metals on semiconductors grow according to the SK mechanism. Metals on metals show both of the growth modes and thus the divisions are by no means rigid.

In this paper we employ the total energy calculations to the important problem of epitaxy under somewhat idealized conditions. This work should be viewed as a first step in the direction of determining metal-semiconductor interatomic potentials. The prototype system we study is the growth of aluminum on Ge(001). We present the results of total energy calculations starting from submonolayer coverages of Al to multilayer deposition of metal in an epitaxial relationship (001)[100]Al||(001)[110]Ge. One can expect to grow abrupt interfaces for this system because the bulk phase diagram[14] indicates low solubility up to the eutectic temperature (~424 °C). The interdiffusion can also be reduced by improved semiconductor surface ordering.[15] This system has been experimentally grown[16] by molecular-beam epitaxy and characterized[16] using high-energy-electron diffraction and total-reflected x-ray diffraction techniques. The Al(001) film grew 45° rotated with respect to the Ge(001) lattice, i.e., the [100] axis of the Al(001) face coincided with the [110] axis of the Ge(001) plane. The first deposited Al(001) layer was found to be in registry with the Ge(001) substrate which implied that the planar lattice constant of the first deposited Al(001) layer is 4.00 Å. Since the bulk lattice constants of Ge and Al are 5.658 and 4.05 Å, respectively, there is a lattice mismatch of about 1.2%. From our discussion above, this amount of lattice misfit suggests the possibility of a FVDM growth mechanism. It was also reported[16] that it takes approximately 30 ± 5 Al layers before the bulk Al lattice constant of 4.05 Å is achieved. Thus in the region close to the interface we are justified in assuming the pseudomorphic growth.

The total energy calculations being reported here were performed using the pseudopotential technique.[17] The self-consistent version of the method has been described before[18] along with relevant references to the earlier work. It suffices here to state that we used a repeating slab geometry and represented the infinite substrate with five layers (labeled 1–5 in Fig. 1) of ideal unreconstructed Ge(001) held rigid in their bulk truncated positions. On top of this we placed an appropriate number of aluminum layers t and an equivalent of five Ge layers of empty space. Figure 1 shows the case of $t = 2$, commencing with a bridge configuration. We also made the additional assumption of holding the Al lattice constant fixed at 4.0 Å. The effect of strain caused by this compression (from 4.05 Å) is later estimated. The only distance we optimize self-consistently is the interfacial interplanar distance $r_\perp$.



(a) Top (b) Side

FIG. 1. (a) Top and (b) side views for the pseudomorphic growth of Al on Ge(001) in the epitaxial relationship (001)[100]Al||(001)[110]Ge. Two layers of aluminum ($t=2$) have been shown for the FVDM growth sequence commencing at the bridge site.

Plane waves (PW) with kinetic energy less than 5 Ry (373 PW at Γ) were treated exactly and another 125 PW were included by means of Löwdin's perturbation scheme. During the self-consistency iterations, the electronic valence charge was sampled at nine k points in the irreducible part of the Brillouin zone. We carried out calculations for t values in the range 0.5 to 3.0. The value $t=0.5$ corresponds to a $p(1\times 1)$ structure in the language of chemisorption, i.e., there is one overlayer atom for every substrate atom. However, measuring coverage in metal equivalent layers a $p(1\times 1)$ structure corresponds to $t=0.5$. The interfacial binding energy $E_I(t)$ per unit cell was obtained from the relation

$$E_0(t)=E_I(t)+E_M(t)+E_S \ . \tag{1}$$

Here $E_0(t)$ is the total energy of the metal-semiconductor system, and $E_M(t)$ and E_S are the total energies of the separated metallic and semiconductor systems, respectively.

There are two possible interface atomic orientations in which the Al(001) film can grow coherently on Ge(001) in the epitaxial relationship (001)[100]Al||(001)[110]Ge. These are the bridge (see Fig. 1) and on-top sites. Our total energy calculations can distinguish which registry pattern is more likely to grow. To this end we carried out total energy calculations as a function of $r_\perp$ for both the on-top and bridge sites. From this curve, we obtained the equilibrium normal distance $R_\perp$ (and hence the Ge-Al interatomic distance d) by a parabolic fit of the total energy around the minimum value. For the on-top site, we found $R_\perp = 2.4$ Å, $d=2.4$ Å, and $E_I = 1.8$ eV. For the bridge site our calculated values are $R_\perp = 1.2$ Å, $d=2.3$ Å, and $E_I=3.0$ eV. These calculations clearly demonstrate that the bridge site is more stable, by ~ 1.2 eV, than the on-top site even though the absolute binding energies may be somewhat reference energy dependent.[18] The bridge site provides a natural hybridization for the bonding of Al with the surface Ge dangling bonds. In fact, our calculation gives the Ge-Al-Ge bond angle to be $\sim 118°$ indicating that the chemisorbed Al is in an sp^2-like configuration. In this configuration the Al essentially continues the bulk lattice and provides substantial bonding. In the literature, there are attempts[8,9] to represent the interfacial potential of an overgrowth atom to a rigid substrate by a sinusoidal model of the form

$$V=\tfrac{1}{2}W[1-\cos(2\pi x/s)] \ , \tag{2}$$

where x is the displacement from the potential minimum and s is the spacing of the substrate atoms. Our calculation gives the amplitude $W=1.2$ eV and may be useful in carrying out model calculations based on realistic parameters. Having established that the bridge site is energetically favorable for the initiation of the FVDM epitaxial growth, the rest of the calculations for $t>0.5$ were only carried out for this configuration.

Our calculated energies and equilibrium distances for the Al-Ge system in an epitaxial relationship (001)[100]Al||(001)[110]Ge as a function of layer thickness t are given in Table I. Notice that the interfacial bonding energy is nearly constant but there is a striking change ($\sim 35\%$ increase) in the interplanar distance in going from the chemisorption regime to the multilayer overgrowth regime. The Ge-Al-Ge angle which was nearly 118° at $t=0.5$ shrinks to $\sim 90°$ at $t=1.0$. The absolute value has increased from about 1.2 Å to about 1.7–1.8 Å. An important observation we wish to make from the calculated value of $R_\perp$ is the following. The average value of the interplanar separation of Ge(001) and Al(001) layers is $\frac{1}{2}(a_{\mathrm{Ge}}/4+a_{\mathrm{Al}}/2)$ which is equal to 1.72 Å. The normal interplanar distance between two epitaxially grown systems rapidly tends to stabilize at the average interplanar separation of the constituents. There are some indications[19] that average values are, in fact, obtained in metal superlattices but there the interplanar values of the constituents were already fairly close. Our calculation is for dissimilar systems and its further verification[20,21] would have important consequences. We suggest that this might be a general result. If so proven, one could readily obtain a reasonable preliminary estimate of the interplanar separation for superlattices[19–21] and metal-semiconductor interfaces.

We should subtract an overall strain energy contribution from the adhesion energy since Al lattice has been constrained to match the substrate lattice. A simple estimate of the elastic strain energy (per unit area) can be obtained from[10,22] $E_e=\frac{1}{2}B(\delta V/V)^2 h$, where δV is the change in volume due to strained Al lattice, h is the Al film thickness, and B is the bulk modulus. Assuming that the elastic misfit energy is only associated with the overgrowth (rigid sub-

TABLE I. Calculated minimum (pseudo) energy E_0 at equilibrium interplanar separation $R_\perp$ and the metal-semiconductor interfacial energy E_I as a function of metal thickness t. The thickness is defined in terms of metal equivalent layers, and in the epitaxial relationship (001)[100]Al||(001)[110]Ge each aluminum layer contributes two atoms per unit cell. Also given in the table are calculated [the semiconductor reference energy $E_S=-38.771$ Ry has been reported earlier (Ref. 18)] values of the total metal (pseudo) energy E_M and the metal-semiconductor bond length d.

t	E_0 (Ry)	E_M (Ry)	$R_\perp$ (Å)	d (Å)	E_I (eV)
0.5	−42.936	−3.944	1.2	2.3	3.0
1.0	−47.085	−8.113	1.8	2.7	2.7
2.0	−55.382	−16.410	1.8	2.7	2.7
3.0	−63.690	−24.729	1.7	2.6	2.6

strate) B can be expressed in terms of bulk aluminum elastic constants, i.e., $B=\frac{1}{3}(C_{11}+2C_{12})$. From these expressions, for $h=20$ Å the total strain energy is estimated to be ~ 0.1 eV. Thus the overall strain energy is small compared with the bonding energy and the epitaxial growth seen by Weng and co-workers[16] is consistent with these estimates. We have, of course, not addressed the issue of the formation of the misfit dislocations.[7-10] In general, the system optimizes the strain to minimize the sum $E_p=E_e+E_d$, where E_d is the energy of the misfit dislocations. Since E_e increases with thickness, beyond a critical value of t, it is energetically more favorable to accommodate all misfit by forming misfit dislocations.[7-10] If they are formed[1] they can only reduce the strain-dependent energy and will further strengthen our conclusion.

In summary, we have presented a microscopic study of the energetics of the growth of Al on Ge(001) in an epitaxial relationship (001)[100]Al||(001)[100]Ge from submonolayer to multilayers of Al. It is found that the FVDM growth is likely to commence in a bridge site. The energy lost due to coherent strain is found to be well below the energy benefit due to interfacial bonding. Our calculation has also shown that at multilayers of Al coverage the interplanar Al-Ge distance is larger than the value found in the chemisorption regime. In fact, our calculated value is nearly equal to the average of the interplanar separations of the constituents. Even though our calculations are for a specific system, we suggest that this might be more generally applicable. An experimental corroboration of this fact should be very valuable. For example, one could readily estimate a reasonable value for the interplanar separation in superlattices and metal-semiconductor interfaces. We have also provided a value for the parameter W often used in doing semiempirical calculations in the area of epitaxy. We hope this work will stimulate further research on epitaxial growth using *ab initio* schemes. In particular, it should lead to the generation of realistic interatomic potentials suitable for molecular dynamics.

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