# Energetics of AlN thin films and the implications for epitaxial growth on SiC

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We present an *ab initio* study of the energetics of thin films of AlN on the Si-terminated SiC(0001) surface. We demonstrate the existence of a vacancy-stabilized NAl wetting layer that can be obtained in both the $\sqrt{3} \times \sqrt{3}$ and 2×2 reconstructions through an N-rich deposition of Al and N. We show that the latter reconstruction is compatible with a nonabrupt neutral interface which promotes the formation of thick overlayers. Our study of the competition between two-dimensional and three-dimensional growth reveals that only large islands ($r_c \geq 60$ Å) are stable with respect to the initial two-dimensional phase. [S0163-1829(96)50548-5]

AlN is a wide-band-gap semiconductor that has attracted interest, along with other III-V nitride materials, for its possible applications in optoelectronics and high-temperature electronics. One factor inhibiting the development of nitride-based solid-state devices is the lack of a suitable substrate for epitaxial growth. The most commonly available substrate for nitride growth is sapphire. However, its large lattice mismatch with AlN gives rise to threading defects, which are expected to reduce the electrical and optical efficiency of the epitaxial materials. A promising alternative to sapphire is silicon carbide, which has a 1% lattice mismatch with AlN and a 3% mismatch with GaN. Due to the good lattice match, high-quality nitride films have been obtained using AlN as a buffer layer for nitride growth on SiC both with molecular-beam epitaxy[1–4] (MBE) and metal-organic chemical vapor deposition[5] (MOCVD) techniques. Sitar *et al.*[3] have shown that AlN has a layer-by-layer growth mode on SiC up to a film thickness of ~15 Å. A two-dimensional growth mode is desired since it is expected to reduce the density of extended defects in the films.

The goal of the present study is to understand the growth mode of an AlN epitaxial film on SiC by analyzing the energetics of possible film structures. We are particularly interested in the existence of thin films which are stable with respect to AlN cluster formation, i.e., wetting layers. We have calculated the formation energies for a number of possible structures which could be formed in the initial stages of growth. We have considered N- and Al-terminated films of AlN with 1×1, $\sqrt{3} \times \sqrt{3}$, and 2×2 periodicities. In addition to ideally terminated AlN bilayer films we have considered films having Al or N vacancies in the outermost layer, and structures having Al adatoms decorating the surfaces of such bilayers. Studies of the AlN(0001) surface have indicated[6] that the formation energies of N adatom structures are quite high, and so we have not considered them in the present study. We have also performed calculations for nonabrupt interfaces at which the local charge dipole that prevents the formation of thick films[7] can be neutralized.

Our results indicate that, independently of the surface structure, films with the (0001) orientation are favored energetically over films with the (000$\bar{1}$) orientation.[8] We find that

a $\sqrt{3} \times \sqrt{3}$ Al-terminated AlN film with $\frac{1}{3}$ monolayer (ML) of Al vacancies, and a 2×2 Al-terminated AlN film with $\frac{1}{4}$ ML of Al vacancies and $\frac{1}{4}$ ML substitution of Si by Al at the interface, are both stable with respect to aluminum nitride cluster formation on the substrate. We present results which indicate that the (2×2)-reconstructed structure is more conducive to layer-by-layer growth.

The interface systems have been modeled using $\sqrt{3} \times \sqrt{3}$ and 2×2 supercells containing five bilayers of SiC and one or two bilayers of AlN. The vacuum region in each cell has a thickness of ~10 Å. C or Si dangling bonds at the bottom of the slabs are saturated by H atoms, and all atomic positions are relaxed. Total-energy and force calculations are performed in the scheme of the density-functional theory within the local-density approximation.[9] A dynamical approach towards the ground state is used, as in the Car-Parrinello scheme.[10] The code is highly optimized for surface calculations[11] and uses optimized starting conditions.[12] The electron-ion interaction is described by pseudopotentials generated in the Martins and Troullier scheme.[13] The kinetic-energy cutoff in the plane-wave expansion of the electronic wave functions is 40 Ry. Monkhorst-Pack grids[14] are used for reciprocal space integration. We have used a grid of six **k** points in the irreducible two-dimensional (2D) Brillouin zone (BZ) of the $\sqrt{3} \times \sqrt{3}$ lattice, and two or four **k** points in the irreducible 2D BZ of the 2×2 lattice.

SiC polytypes differ among each other only in the stacking sequence,[15] while the local bonding configuration is tetrahedral in each case. In our calculations we have employed the 3C polytype. However, we expect the results obtained to be valid for all other polytypes as well.

A detailed account of the structures we have studied is given elsewhere.[6] Here we focus on the selected configurations that should play a role in the growth process. In Fig. 1 we illustrate some of the $\sqrt{3} \times \sqrt{3}$ adatom and vacancy structures. The (2×2)-reconstructed interfaces are similar, but include a $\frac{1}{4}$ ML substitution of Si atoms by Al atoms in the outermost substrate layer, and have $\frac{1}{4}$ ML rather than $\frac{1}{3}$ ML of Al vacancies and adatoms on the surface.

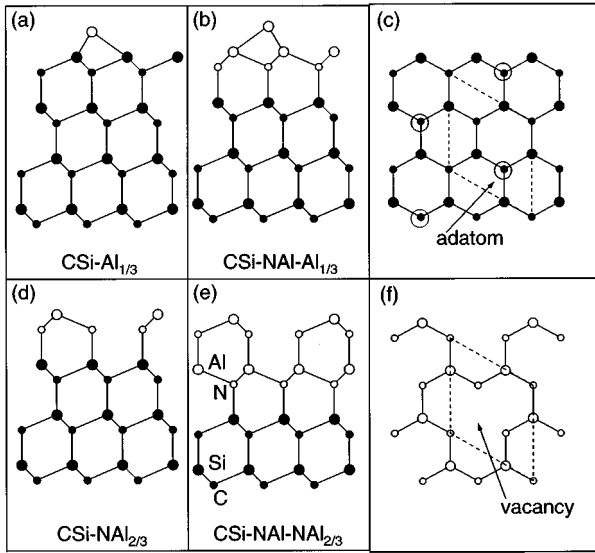A clear 2×2 diffraction pattern has been observed for a 30-nm-thick AlN film grown on Si-terminated SiC(0001) by

FIG. 1. Configurations studied in the $\sqrt{3}\times\sqrt{3}$ reconstruction. (a) Al-terminated SiC(0001) surface [top view in (c)]; (b) Al adatom on the 1 bilayer NAl film deposited on SiC(0001); (d) Al vacancy in the 1 bilayer NAl film deposited on SiC(0001) [top view in (f)]; (e) Al vacancy in the 2 bilayers NAl film deposited on SiC(0001). Si (C) atoms are marked by large (small) dots, Al (N) atoms by large (small) circles. The structures are labeled in the panels according to their composition. The corresponding structures studied in the 2×2 reconstruction with partial substitution of Si by Al will be labeled $CSi_{3/4}Al_{1/4}$-$Al_{1/4}$, $CSi_{3/4}Al_{1/4}$-$NAl$-$Al_{1/4}$, $CSi_{3/4}Al_{1/4}$-$NAl_{3/4}$, and $CSi_{3/4}Al_{1/4}$-$NAl$-$NAl_{3/4}$, respectively, for (a), (b), (d), and (e).
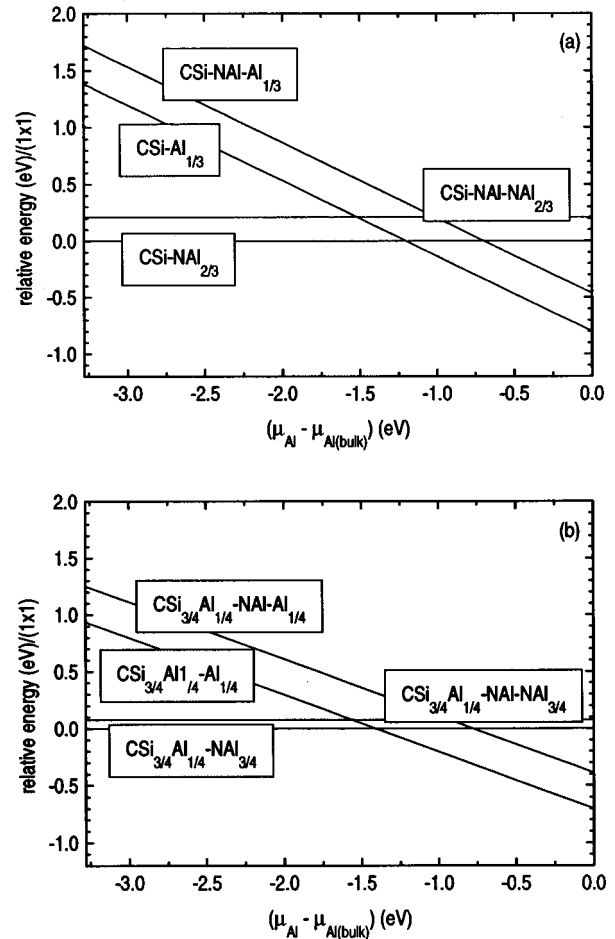


FIG. 2. (a) Relative stability of the $\sqrt{3}\times\sqrt{3}$ phases as a function of the Al chemical potential in equilibrium with bulk AlN. (b) Relative stability of the 2×2 phases as a function of the Al chemical potential in equilibrium with bulk AlN. The physically allowed values of $\mu_{Al}$ range between $\mu_{Al(bulk)}-\Delta H$ and $\mu_{Al(bulk)}$, with $\Delta H = 3.28$ eV being the heat of formation of bulk AlN.

MBE.[1] However, a thin overlayer at an abrupt interface naturally saturates all the dangling bonds in a $\sqrt{3}\times\sqrt{3}$ periodicity. Structural modifications and changes in the surface reconstruction can occur as the film becomes thicker in order to realize a charge-compensated interface.

Since different geometries examined involve different numbers of atoms, it is necessary to calculate their relative formation energies as a function of the chemical potentials of the atomic species. For structures containing the same number of Si and C atoms, the relative surface energy depends on the Al and N chemical potentials through the relation

$$\Delta E = \Delta E_{\text{tot}} - \Delta n_{Al}\mu_{Al} - \Delta n_N\mu_N. \quad (1)$$

Under conditions in which a bulklike AlN phase is present, e.g., because of island formation, it is possible to assume equilibration between the film and the bulk phase. In this case the relation $\mu_N + \mu_{Al} = \mu_{AlN(bulk)}$ holds and the relative energy may be written as

$$\Delta E = \Delta E_0 - (\Delta n_{Al} - \Delta n_N)(\mu_{Al} - \mu_{Al(bulk)}), \quad (2)$$

where $\Delta E_0$ is the relative surface energy in Al-rich conditions determined from the total-energy calculations. The relative surface energy has been calculated for the sets of $\sqrt{3}\times\sqrt{3}$ and 2×2 structures as a function of $\mu_{Al}$ for the case in which the films are equilibrated with large islands, and the results are shown in Fig. 2. For each set of structures, we find that for $\mu_{Al} \gtrsim \mu_{Al(bulk)} - 1.4$ eV the most stable configuration

consists of an Al-adatom-terminated SiC surface. For smaller values of $\mu_{Al}$, corresponding to N-rich conditions, NAl bilayers with $\frac{1}{3}$ ML or $\frac{1}{4}$ ML of Al vacancies are stable. These results indicate that stable 2D structures containing both N and Al may be obtained in N-rich conditions in the initial stages of growth. On the other hand, if growth takes place in Al-rich conditions, N and Al atoms will accumulate in islands, with the excess Al terminating the SiC surface in the form of adatoms.

Continued growth on the vacancy-stabilized NAl bilayer structures would lead to an (0001)-oriented film. The results of Capaz et al.[16] for the preferred polarity of a 1×1 film of GaN on SiC is consistent with our calculations. The present result for the preferred polarity does not require the assumption of equilibrium between the 2D film and bulk AlN, and refers to a situation in which Al and N deposition begins on a clean or Al-covered Si-terminated SiC(0001) surface. Different procedures in substrate preparation could, in principle, affect the polarity of the overlayer. While we have examined only thin films (≤2 bilayers), we think it likely that the polarity would be frozen in after the first few bilayers.
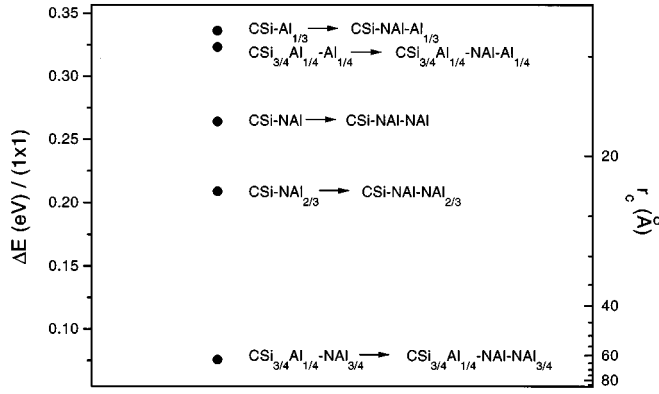
FIG. 3. Left axis: energy cost ($\Delta E$) for various structural transitions involving the deposition of an NAl bilayer. Right axis: minimum radius ($r_c$) of bulk islands required to activate a 3D growth mode.
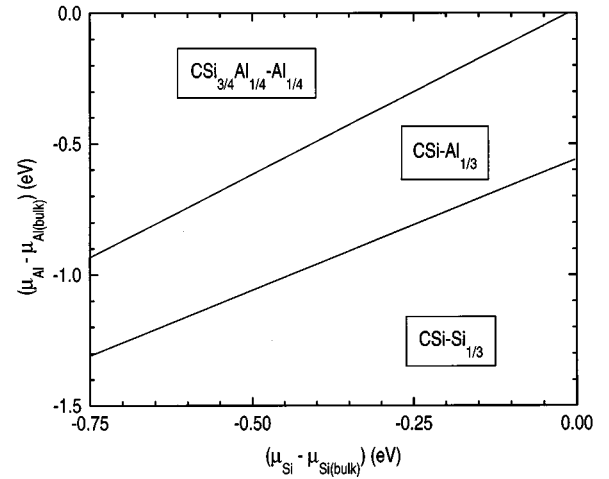


FIG. 4. Energetical comparison among plausible structures obtained by Al deposition on the SiC(0001) surface as a function of Al and Si chemical potentials. The physical range for the Si chemical potential is fixed by assuming equilibrium with SiC. For $\mu_{Al} \geq -1.3$ eV the Al adatom structures become stable with respect to the Si-adatom-terminated SiC(0001) surface.

Given the existence of a stable 2D film, we may ask whether it is more favorable to add another NAl bilayer to this film or incorporate the additional material in an AlN island. The energy cost of adding an NAl bilayer to the $\sqrt{3} \times \sqrt{3}$ and $2 \times 2$ Al-vacancy structures is, respectively, 0.21 eV/(1×1) and 0.075 eV/(1×1). The endothermicity of this reaction suggests that the evolution towards thicker films would be accompanied by island formation *under equilibrium conditions*. However, in reaching this conclusion we have assumed that the islands are sufficiently large that it is possible to neglect their surface energy in estimating their formation energy. The surface energy of the islands can affect the energetic competition between 2D films and 3D islands. For an island containing $n$ AlN, pairs a rough approximation for the formation energy is

$$E_I = n \mu_{AlN(bulk)} + \gamma A, \tag{3}$$

where $\gamma$ is the surface energy of the island and $A$ is its total surface area. If $\Delta E$ is the energy cost of adding a NAl pair to a film and $\Omega$ is the volume per pair, then only hemispherical islands with radius $r \geq r_c = 2\Omega \gamma / \Delta E$ are stable with respect to the film. For $\Delta E = 0.075$ eV, corresponding to growth on the 2×2 vacancy stabilized NAl bilayer, we obtain $r_c \sim 60$ Å. This corresponds to islands containing $n_c \sim 5 \times 10^4$ pairs.[17] Layer-by-layer growth will occur under conditions in which surface diffusion is too slow to enable the formation of islands larger than this size.

In Fig. 3 we report the energy cost $\Delta E$ for deposition on different structures and the minimum size $r_c$ of the stable islands. The figure shows that structures containing Al vacancies have the lowest $\Delta E$'s, and consequently should exhibit the best wetting behavior. It also shows that 2×2 Al vacancy structures, with Si-Al mixing at the interface, are more conducive to layer-by-layer growth than the corresponding $\sqrt{3} \times \sqrt{3}$ structures. Continued growth on a film exhibiting an abrupt interface, such as in the $\sqrt{3} \times \sqrt{3}$ reconstruction, would lead to accumulation of charge at the interface. It is therefore preferable to create the 2×2 vacancy-stabilized bilayer (VSB), since the 75% Si and 25% Al mixture eliminates the interface charge for arbitrarily thick overlayers.

It seems natural to form such a 2×2 VSB by an N-rich deposition of AlN on a substrate in the 2×2 adatom +substitution reconstruction ($CSi_{3/4}Al_{1/4}$-$Al_{1/4}$, denoted 2×2-$\sigma$). The question therefore arises: Is the 2×2-$\sigma$ model a stable Al-induced reconstruction of SiC? To address this question we have considered four possible Al-terminated structures for the SiC(0001) surface (1×1 CSi-CAl, 1×1 CSi-Al, $\sqrt{3} \times \sqrt{3}$ CSi-$Al_{1/3}$, and the 2×2-$\sigma$ model) and have calculated their relative energies as a function of the Si and Al chemical potentials.[18] The results are presented in Fig. 4, which shows that the 2×2-$\sigma$ model is stable under Al-rich conditions, while the $\sqrt{3} \times \sqrt{3}$ CSi-$Al_{1/3}$ structure is stable under Si-rich conditions if the Al chemical potential is high enough to destabilize the $\sqrt{3} \times \sqrt{3}$ Si adatom reconstruction of SiC. Both the 1×1 substitutional model (CSi-CAl) and the 1×1 adlayer model (CSi-Al) are found to be unstable. The 2×2-$\sigma$ model is predicted by our calculations as a possible structure that can be obtained through the deposition of Al on SiC, and the stability of such a substrate reconstruction supports the possibility of forming the 2×2 VSB, on which 2D growth can proceed. The 2×2 VSB is also favorable on an energetical basis, since it minimizes the energy cost for deposition of additional bilayers of AlN.

In conclusion, by calculating the energies of possible configurations of AlN on Si-terminated SiC(0001) we have demonstrated the stability of a two-dimensional film with respect to island formation. This film consists of an Al-terminated AlN bilayer with $\frac{1}{4}$ ML of Al vacancies in the surface layer. In this structure mixing between Si and Al in the interfacial layer enables charge neutrality to be achieved for arbitrarily thick overlayers.

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