Ab initio studies of GaN epitaxial growth on SiC

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(Received 4 January 1995)

Ab initio methods were used to investigate the initial stages of GaN epitaxial growth on (0001) 6*H*-SiC. Total energies of four types of interfaces were calculated. Polarity matching at the interface plays a fundamental role in determining the lower-energy structures, yielding strong binding for Si-N and C-Ga interfaces and very weak binding for Si-Ga and C-N. We therefore predict that Si-terminated substrates will produce ideally Ga-terminated films, whereas C-terminated substrates will produce ideally N-terminated films. This prediction suggests reinterpretation of recent experiments.

Gallium nitride (GaN) is one of the most promising materials for future electronic and optoelectronic devices.[1] Because of its wide (3.4 eV) and direct band gap, it would serve well for applications in light-emitting devices operating in the blue and ultraviolet region. However, the technology of GaN fabrication is still in the early stages. Bulk single crystals or wafers are not yet available, and the choice of adequate substrates for heteroepitaxy has been a nontrivial problem for experimentalists. Sapphire (Al_2O_3) is commonly used, but its large misfit with respect to GaN (13.8%) has been a limiting factor in the quality of the grown epilayers. Recently, SiC substrates[2,3] have been considered as possible candidates for GaN heteroepitaxy, not only due to the lower misfit (3.4%), but also because SiC itself is a wide band-gap semiconductor with superior electrical and structural properties.

Epitaxial growth is a long-standing unsolved problem in condensed matter physics. An atomistic theoretical approach to it is extremely difficult because of the number and complexity of the different physical processes involved, such as adsorption, diffusion, and reevaporation, all occurring simultaneously at high temperatures. Computer simulations such as Monte Carlo or molecular dynamics are the natural way to describe these phenomena. However, large-scale simulations can only be done for a restricted class of materials that can be accurately described by empirical or semiempirical interatomic potentials. This is not the case for GaN and SiC, for which an *ab initio* treatment is required.

Although large-scale simulations of growth kinetics using *ab initio* methods is still beyond the capabilities of today's supercomputers, many useful predictions about the growth process can be obtained simply by considering the energetics of the few initial epilayers and the substrate. For instance, a simple "rule-of-thumb" for determining whether a film will undergo two-dimensional (2D) layer-by-layer growth instead of the undesirable 3D island growth is to consider the interfacial energy between the film and substrate. If the interfacial energy is low, strong binding occurs between the film and substrate, favoring layer-by-layer growth. Another basic piece of information concerns the polarity of the film with respect to the substrate. SiC substrates oriented in the hexagonal [0001] direction can be either Si-terminated or C-terminated, and the resulting GaN film can be either ideally Ga-terminated or ideally N-terminated.[4] It is clear that the final polarity of the film will be determined in the initial stages of the growth process. But since both SiC and GaN are partly ionic and partly covalent bonded materials with different degrees of ionicity and bond strengths, it is not obvious which bonding configuration will prevail at the interface. Although fundamental for the understanding of the growth process in these materials, very little attention has been given in the literature to the issue of GaN polarity on SiC substrates. As far as we know, there is only one experimental work, by Sasaki and Matsuoka,[2] which addresses this problem in an indirect way by measuring the shift in the x-ray photoelectron spectroscopy spectrum of the Ga atoms close to the surface due to the presence of oxygen bonds. Based on assumptions about the amount of oxygen incorporation for each surface, they claim that Si-terminated substrate will produce N-terminated films, and C-terminated substrates will produce Ga-terminated films.

In this paper we employ *ab initio* total energy methods to address these issues. Our calculations are based on the local-density-functional theory,[5] with the exchange-correlation functional as described by the Perdew-Zunger parametrization[6] of Ceperley-Alder results.[7] Wave-function relaxation to the Born-Openheimer surface is performed by conjugate gradient minimizations of the electronic energy.[8] Separable norm-conserving nonlocal pseudopotentials with optimized plane-wave convergence[9] were used. This allowed us to obtain a faithful description of the strongly attractive C and N potentials with a plane-wave cutoff of 40 Ry. Reciprocal space summations[10] were performed using 3 special **k** points for the interface and 12 special **k** points for test calculations involving bulk SiC and GaN.

SiC exists in a great variety of polytypes. We chose for our study the 6*H* polytype, which consists of a hexagonal Bravais lattice with a close-packing stacking (...*ABCACB*...) along the *c* axis. 6*H*-SiC is the polytype most used as a substrate for GaN growth. GaN also exists in a hexagonal structure with the simpler stacking sequence (...*ABAB*...) known as the *wurtzite* structure. Structural parameters obtained in the bulk calculations were $a = 3.040$ Å, $c/(pa) = 0.8177$, $u = 0.375$ for 6*H*-SiC and $a = 3.020$ Å, $c/(pa) = 0.8130$, $u = 0.376$ for GaN, where c and a are the lattice constants, p is the number of bilayers per unit cell (6 for 6*H*-SiC and 2 for GaN)

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and u is an internal parameter describing the relative displacement between the Si(Ga) and C(N) layers along the hexagonal [0001] direction. For ideal tetrahedral coordination we have $c/(pa) = \sqrt{2/3}$ and $u = 3/8$. These values are in good agreement with experimental results and recent *ab initio* calculations.[11]

The truly semi-infinite interface was modeled in the supercell scheme in the following way (see Fig. 1): Six bilayers of SiC were used to represent the substrate, with hydrogen saturated bonds at the bottom.[12] The bottom two bilayers (four atoms) were kept unrelaxed at the bulk positions. All the other atoms were allowed to relax along the c axis. Two bilayers of GaN model the initial epilayers of the growing film. Approximately 10 Å of vacuum between the film and the hydrogen atoms were included to prevent interaction between the two surfaces. The supercell contains one atom per layer, corresponding to the 1×1 unreconstructed surface.

Contour plots of the total valence charge density and schematic ball-and-stick models for the four types of interfaces are displayed in Fig. 1. The plane of cut for all the figures is the hexagonal $(10\bar{1}0)$ plane, which contains two of the four bonds of the tetrahedrally coordinated atoms. The ball-and-stick models superimposed on each charge density plot give faithful description of the bond lengths and bond angles for each structure. Notice that the C and N atoms are surrounded by regions of high density of contours, reflecting the displacement in the bond maximum density towards these two atoms with higher electronegativity. Accordingly, Si and Ga atoms correspond to regions of depletion of valence charge density and "look smaller" compared to C and N. Let us de-

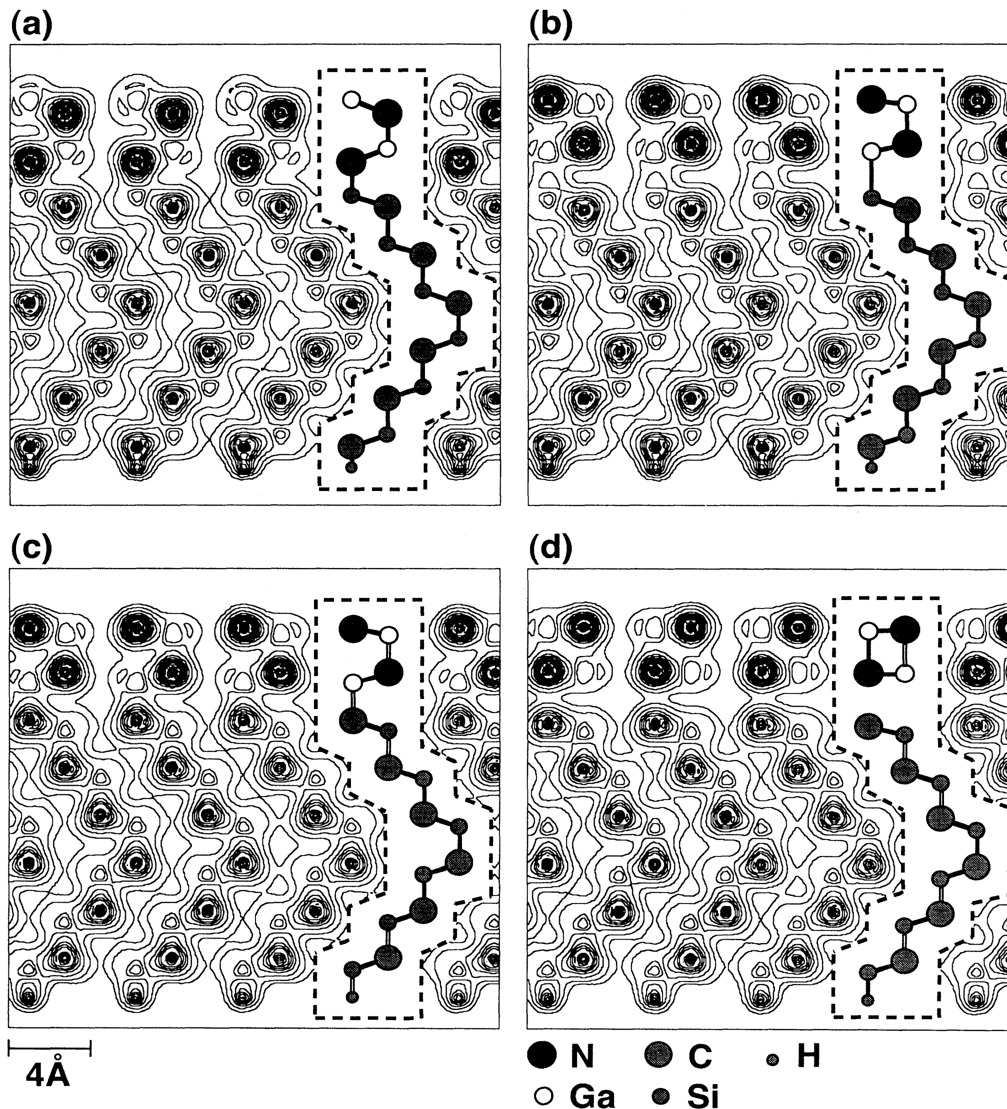

FIG. 1. Contour plots of electronic density for four interfaces. Twelve evenly spaced contours from 0.4 to 3.7 (in units of electrons/Å^3) are used. Two additional contours at 0.1 and 0.2 help to map the low charge density regions. Ball-and-stick models are superimposed for each case. Balls are placed at the actual atomic positions and differ by shade and size according to the atomic types.

note by E_a, E_b, E_c, and E_d the total energies of the four interfaces displayed in Figs. 1(a), 1(b), 1(c), and 1(d), respectively. Figure 1(a) corresponds to a Si-terminated substrate and ideally Ga-terminated film. Notice that the Si and N atoms at the interface form a nice partly covalent, partly ionic bond. The Si-N bond distance is 1.77 Å. The remaining bond lengths and angles do not change significantly from the bulk values and the initial epilayers of the film look like a smooth continuation of the substrate. Figure 1(b) still corresponds to a Si-terminated substrate, but the film is now ideally N-terminated. A covalent bond is formed between Si and Ga at the interface (the bond distance is 2.43 Å). However, this bond is very weak since most of the charge remains concentrated around the C and N atoms. Subtraction of E_b from E_a gives us $E_a - E_b = -1.08$ eV, indicating that *for Si-terminated substrates, the ideally Ga-terminated film with Si-N bonds at the interface is energetically favorable.* This result is exactly the opposite of the result proposed in Ref. 2.

A similar situation occurs for C-terminated substrates [Figs. 1(c) and 1(d)]. In Fig. 1(c), the ideally N-terminated film with C-Ga bonds at the interface is shown, and the charge density contours resemble very much those of Fig. 1(a) with inverted polarity. A strong covalent and ionic bond between C and Ga (bond length 1.99 Å) is formed at the interface. However, for ideally Ga-terminated films [Fig. 1(d)] the situation is surprisingly distinct from all the previous cases. The N atoms at the interface prefer to make bonds along the c axis to the nearby Ga atoms (bond distance 2.22 Å) than to the C atoms on the substrate, yielding a very weakly coupled film-substrate system. The angles between all the Ga-N bonds shown in the figure are very close to 90°, indicating sp^2 hybridization of the epilayers. Although carbon and nitrogen form strong covalent bonds in a large variety of situations, the presence of the surrounding atoms seems to make polarization effects very crucial, and the C and N atoms behave almost like two repelling negative charges. The total energy difference $E_c - E_d = -1.07$ eV, suggests that *for C-terminated substrates, the ideally N-terminated film with C-Ga bonds at the interface is energetically favorable.* Again, this result contradicts the experimental findings of Ref. 2.

All the results above suggest that the importance of the strength of covalent bonds is diminished by the polarization induced by the surrounding atoms and the ionic component of the bonds prevails. Thus our findings can be described in terms of a very simple rule of polarity matching at the surface. The lowest energy interfaces are those on which "positive" substrate ions bind to "negative" film ions, and vice versa. Therefore the GaN films will grow with the same polarity as the SiC substrates. Besides being intuitively appealing, this picture is strongly supported by the fairly big energy differences (~ 1 eV per surface atom) we found in our calculations. We believe that it is also robust enough to describe other possible microscopic processes during the initial stages of growth (for example, replacement of substrate ions by film ions at the interface should also satisfy polarity matching). Therefore, we believe that it may be necessary to reinterpret the experimental results from Ref. 2. Perhaps the observation of N(Ga)-terminated films on Si(C)-terminated substrates is the result of a surface reconstruction of the ideally Ga(N)-terminated film. Such reconstructions are not uncommon for polar surfaces of III-V compounds.[13] A more direct type of measurement (such as cross-sectional STM imaging, for example) could be used to resolve this controversy.

R.B.C. is grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq—Brazil) for providing financial support. H.L. would like to thank the committee for International Exchanges of Kyung Hee University for financial support. This work was partly supported by ONR Grant No. N00014-94-1-0591.

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