PHYSICAL REVIEW B VOLUME 53, NUMBER 11 15 MARCH 1996-I

Atomic arrangement at the AlN/SiC interface

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(Received 9 June 1995)

The lattice structure of the AlN/SiC interface has been studied in cross section by high-resolution transmission-electron microscopy. Lattice images show planar and crystallographically abrupt interfaces. The atomic arrangement at the plane of the interface is analyzed based on the image characteristics. Possible bonding configurations are discussed. Variations in local image contrast and interplanar separations are used to identify atomic bonding configurations consistent with the lattice images.

AlN and SiC are very similar from the crystallographic point of view. Both occur in the hexagonal crystal structure with similar lattice parameters and thermal expansion characteristics. With cohesive energies per bond of 2.88 and 3.17 eV, respectively, both compounds are stable at elevated temperatures. These properties make SiC a suitable substrate and AlN a suitable buffer layer for GaN-based III-V nitride thin-film growth for optoelectronic applications in light-emitting devices in the green to ultraviolet region of the electromagnetic spectrum.[1] Some characteristics of these lattices are given in Table I. AlN has the hexagonal wurtzite structure. SiC exists in many crystallographic variations. The hexagonal α-6*H* form is commercially available as single crystals. The lattice mismatch on the basal plane between AlN and 6H SiC is less than 1%. The thermal-expansion coefficients along the basal planes are also quite close with quoted values of $(4.2\times10)^{-6}$ °C^{-1} for both materials. This superb match at the basal planes is expected to facilitate the formation of nearly perfect junctions. In most heteroepitaxial cases, the structure of the interface with the substrate is critical for the overall properties of the epilayer. In the case of AlN/SiC, the atomic arrangement at the interface should determine the stable growth configurations, as well as the polarity of growth of the AlN.

The structure of GaN thin films grown on α-6H SiC substrates, using AlN buffer layers, has been recently reported in the literature.[2] In this paper, we present further analysis of the results presented there, with emphasis on the implications of the characteristics of the lattice images on the atomic arrangement at the AlN/SiC interface. Electron diffraction patterns of the AlN/SiC interface region show that the epitaxial relationship between the lattices corresponds to parallel epitaxy with $[0002]_{\mathrm{AlN}}\|[0006]_{\mathrm{SiC}}$ and $[1120]_{\mathrm{AlN}}\|[1120]_{\mathrm{SiC}}$. Cross-section TEM specimens were produced by mechanical thinning and ion milling. High-resolution TEM was performed at 800 kV with an instrumental point resolution of less than 1.5 A. A lattice image of the AlN/SiC interface region is shown in Fig. 1. The SiC lattice is viewed in the $\langle 1120\rangle$ projection, with the basal (0006) and a $\{1100\}$ plane appearing in horizontal and vertical projections, respectively. The AlN layer is observed in its $\langle 11\bar{2}0\rangle$ projection, where the horizontal corresponds to the basal (0002) plane and the vertical to a $\{1\bar{1}00\}$ plane. The respective interplanar separations are shown in Table I. Direct measurements of the interplanar distances, using the SiC lattice image as a reference, indicate that the lattice parameters for the AlN layer are within 0.5% of their bulk values, well within the expected

TABLE I. Lattice parameters, thermal-expansion coefficients, and interplanar distances for indices relevant to epitaxy on the basal planes (in Å). 6*H*-SiC and AlN belong to the space group $P6_3mc(186)$.

Crystalline properties	Index	AlN	SiC-6H
Lattice Parameter	*a*	3.1114	3.081
	c	4.9792	15.092
Thermal Exp. coefficient	*a*	4.2	4.2
	c	5.3	4.68
Interplanar separations	Basal	2.49	2.516
	$(1\bar{1}00)$	2.695	2.669
	(11–20)	1.556	1.541

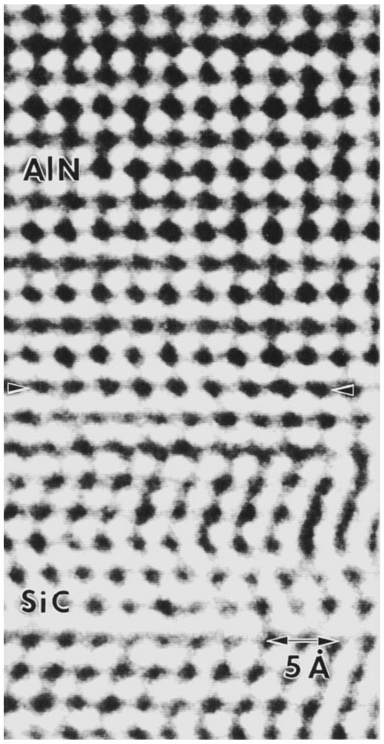

FIG. 1. Lattice image of the AlN/SiC interface.

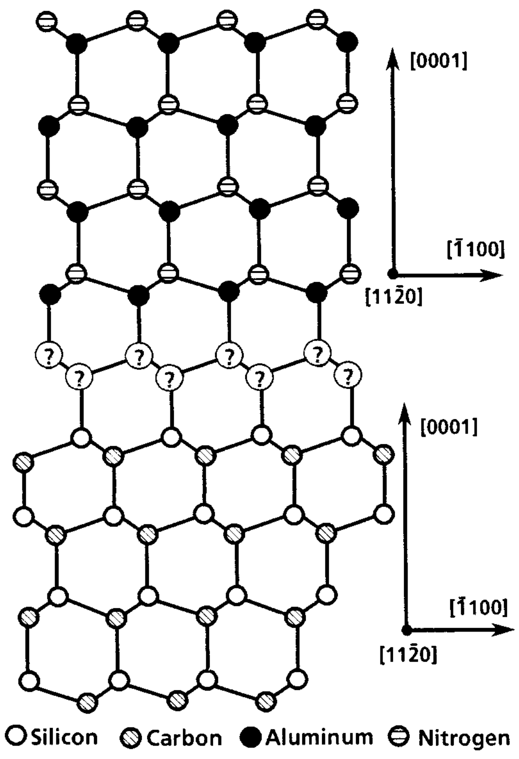

FIG. 2. Schematic diagram of the atomic arrangement at the AcN/6*H*-SiC interface.

experimental accuracy of the measurement, indicating negligible strain. The interface between the SiC substrate and the AlN layer is atomically abrupt and follows (006) SiC basal planes.

The lattice image in Fig. 1 corresponds to a specimen thickness close to 8 nm (determined by interpolation to the first extinction distance in a wedge sample), taken close to the ⟨1120⟩ AlN axis, at a value of defocus of ~ -105 nm (determined from the minimum contrast image from a through focus series). A schematic diagram of this crystalline projection is shown in Fig. 2. The bright spots in the lattice image have special significance. In the AlN, the bright spots appear aligned vertically, without any significant offset. The dark spots, on the other hand, are slightly offset every other lattice plane. This signature is associated with bright spots corresponding to the center of the Al-N dumbbell observed in this projection.[3] The situation is similar in SiC, where we observe that the arrangement of bright spots in the direction normal to the basal planes has a dull corner at the twin reflection plane, indicative of white spots at the center of the Si-C dumbbell. These considerations based on the symmetry of the images in this projection are consistent with lattice image simulations obtained for AlN and SiC at 800 kV, for -105 nm defocus, in the range of 6–10 nm in specimen thickness.[4]

The focus of the present work is on the understanding of the bonding at the AlN/SiC interface, i.e., the chemical composition in the plane where the AlN and SiC lattices meet (see Fig. 2). There are two features in Fig. 1, which have interesting implications. The first is that the intensity of the image spots remains fairly constant across the interface. Figure 3(a) plots the maxima of the image intensity integrated parallel to the basal planes. No averaging nor filtering was applied to the image since, although such operations potentially remove noise and improve the image quality, they can also remove important aspects of the data. The observed variations follow the periodicities of the lattices, i.e., sixfold for SiC and twofold for AlN. Detailed image simulations by O'Keefe and Radmilovic[5] have shown that these small variations are due to very slight tilts (less than one degree) of the lattice, with respect to the incident electron beam during the recording of the image. Experimentally it is very difficult to completely correct the electron-beam tilt, and these lattice structures are extremely sensitive to it. The important aspect is that the intensity of the interface plane closely matches the average intensities of the adjacent planes. The intensity of lattice images for thin TEM specimens (less than 12 nm for SiC and AlN) have been shown to follow the projected charge-density approximation[6] where the image intensity I is proportional to the projected charge density ρ of the atomic columns: $I(x,y) \approx 1 + A\rho_p(x,y)$, where A is a constant proportional to the value of image defocus and the electron wavelength, and ρ_p is the projected charge density. Therefore, the variation in $I(x,y)$ is linearly proportional to the

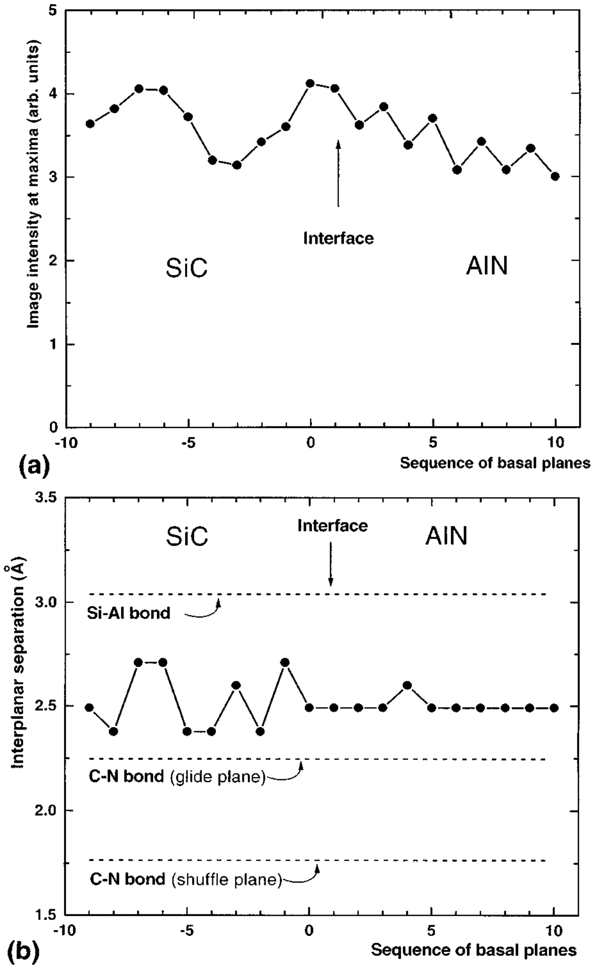

FIG. 3. Characteristics of image in Fig. 1. (a) Image contrast distribution across the AlN/SiC interface. (b) Interplanar separation for basal planes, showing the values corresponding to C-N and Si-Al tetrahedral bonds at the interface.

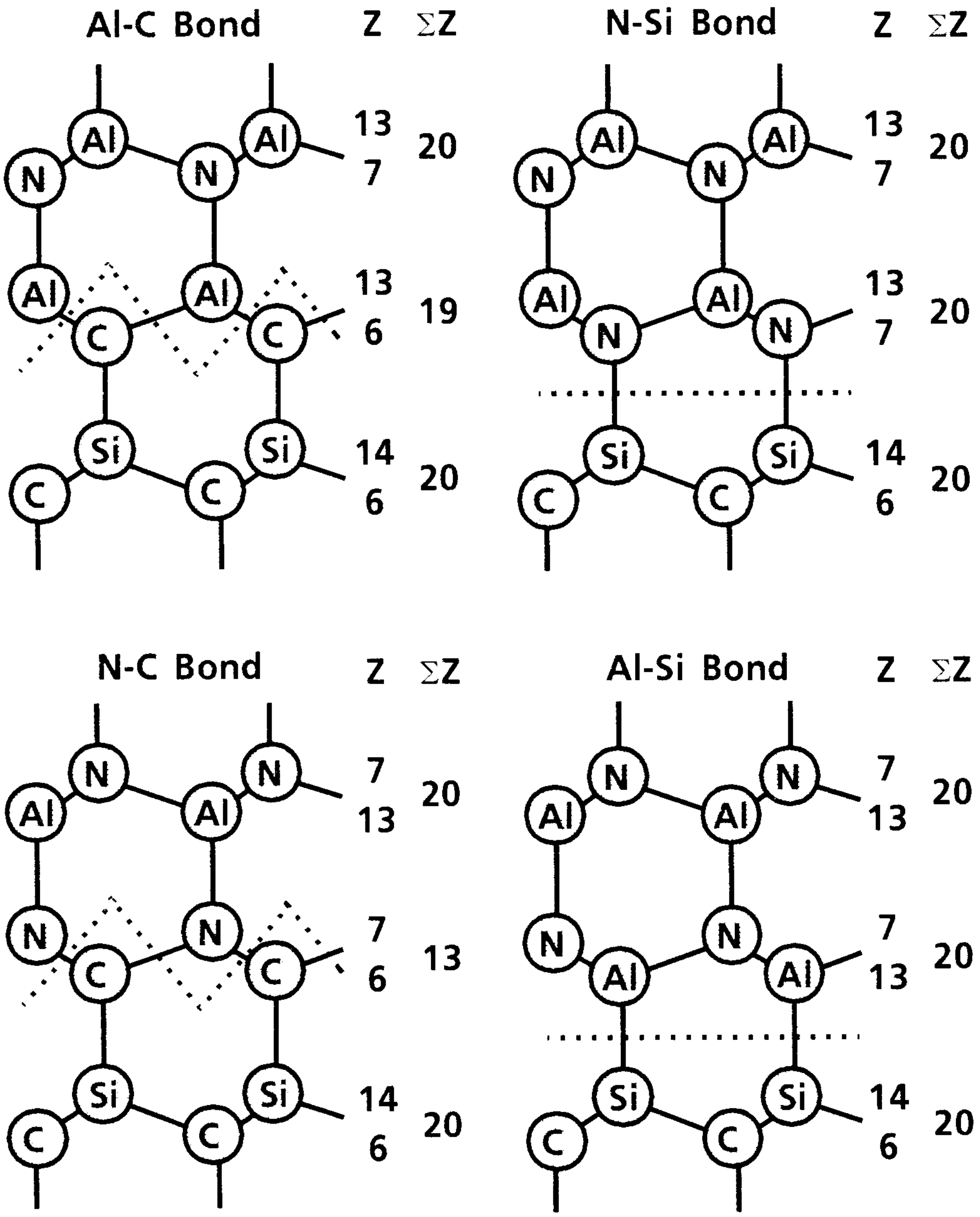

FIG. 4. Possible atomic arrangements at the AlN/SiC interface, for silicon on top of SiC basal plane. Only one element on each atomic layer of the basal planes is considered.

sum of the atomic numbers of the elemental constituents of the atomic columns. This value is 20 for both of these materials, with 13+7 for Al+N, and 14+6 for Si+C, respectively. This is the reason for the nearly identical spot intensities in Fig. 1. The fact that the interface plane itself has a similar intensity means that its atomic arrangement, shown schematically with question marks in Fig. 2, should have a sum of atomic numbers close to 20.

A second interesting feature in Fig. 1 is the value of the distance between basal planes. Figure 3(b) shows the separation of the integrated image maxima plotted in Fig. 3(a). The values of the interplanar distances in the plot are between 2.35 and 2.7 Å with an average set at 2.49 Å for AlN and 2.51 Å for SiC. The variations at the SiC side are once again due to the slight lattice tilt.[5] The interplanar separation at the interface coincides with adjacent values in Fig. 3(b).

We consider next the possible atomic bonding configurations for the interface. Figure 4 shows the four possible arrangements corresponding to the (0001) SiC lattice with Si at the top of the ⟨1120⟩ dumbbell (our experimental conditions) for atomically abrupt, planar interfaces. The values of the electronegativities and ionic radii for the various atomic species involved in this work are given in Table II.[7,8] The bond lengths can be estimated from the ionic radii when experimental values are not known, as shown in Table III.[9,10] The characteristics associated with the various potential bonds are summarized in Table IV. The Si-C and Al-N bonds have lengths of 1.88 and 1.89 Å, respectively, and have a sum of atomic numbers of 20 for both pairs. The N-C bond is short compared with the others. Its presence would require a darker line of spots in the lattice image, due to its *Z* sum of 13. Compounds containing Si-Al bonds are not commonly

TABLE II. Pauling electronegativities and atomic radii when in tetrahedral covalent bonds of relevant elements (Refs. 7 and 8).

Element	Al	Ga	Si	C	N	O
Electronegativity	1.5	1.6	1.8	2.5	3.0	3.5
Atomic radii	1.26	1.26	1.17	0.77	0.70	0.66

observed in nature. Thus, direct measurements of the Si-Al bond length are not available, and an estimated value from the sum of the atomic radii is given in Table II. This value is 0.55 Å longer than the Al-N and Si-C bonds and would be evident in a lattice image. Si-N bonds such as those found in Si_3N_4 are not tetrahedrally coordinated, but should be acceptable at interfaces such as the one under consideration. The same holds for Al-C bonds observed in Al_4C_3.

For *atomically abrupt* and planar interfaces, it is justified to eliminate the N-C and Si-Al bonds, based on the intensity variations in the lattice image and on the values of the interplanar separations. The two remaining possibilities, i.e., the Al-C and Si-N bonds, are in agreement with our observations and are not distinguishable by TEM.

Since AlN is a III-V semiconductor, and SiC a IV-IV semiconductor, the [0001] interface between AlN and SiC is a polar interface between heterovalent semiconductors. Ideal, abrupt polar interfaces between heterovalent semiconductors suffer from instability problems, as first pointed out by Harrison.[11] Indeed, if one calculates the electrostatic potential as a function of position along the growth direction, one finds that charge accumulation at the ideal interface gives rise to a nonzero average electric field that extends throughout the overlayer. Such an electric field could be supported in thin overlayers, but would cause the system to become unstable once the overlayer exceeds a certain thickness.

Harrison[11] pointed out that the charge accumulation at the interface could be avoided by introducing some measure of atomic mixing at the interface. The types of mixing proposed for [111] interfaces between zinc-blende semiconductors can be applied to the present case of a [0001] interface between AlN and SiC. The simplest models involve mixing of only one atomic layer at the interface; as pointed out by Harrison, such mixing eliminates the charge accumulation, but still leaves a nonzero dipole shift; different types of mixing, therefore, produce different band offsets.

The possible bonding configurations at the interface between SiC and AlN are restricted by the requirement of local change neutrality. For example, consider the abrupt interface between SiC and AlN (0001)Al, as indicated schematically below,

$$— \text{C-Si} — \text{C-Si} — \text{N-Al} — \text{N-Al} —,$$

where the interface occurs between Si and N layers. (In this notation, long dashes represent the bonds between the widely spaced layers, and the short dash represents the bonds between the closely spaced layers.) Each N atom contributes 5/4 of an electron to its bond with Si, while the Si atom contributes one electron to this bond. Therefore, there is a local charge excess at the interface of 1/4 electron per bond, and so this abrupt interface is not stable. This charge excess can be relieved by replacing one out of every four Si atoms with Al as shown in the following:

$$— \text{C-Si} — \text{C-Si}_{(3/4)}\text{Al}_{(1/4)} — \text{N-Al} — \text{N-Al} —. \qquad (1)$$

TABLE III. Bond lengths. Atomic radii correspond to tetrahedral covalent bonds from Table II. C-N values were obtained from Ref. 9. Si-N and Al-C values are from Ref. 10. Si-Al bond lengths were not available.

Compound	C-N	Si-N	Si-C	Al-N	Al-C	Si-Al
Actual	1.16	1.71–1.76	1.88	1.89	1.90–2.22	
Sum of atomic radii	1.47	1.87	1.94	1.96	2.03	2.43

TABLE IV. The quoted bond lengths are the mean value of the observed values or, in the absence of the latter, they are estimated by the sum of the covalent radii in Table III. "Δ *in Bond length*" is the difference of the bond length with respect to the SiC value. The orientation of the bond is with respect to the *c* axis. The interplanar distance value takes into consideration the component of the bond.

Bond	Sum of *Z*	Bond length	Δ in Bond length	Orientation of bond	Interplanar distance
N-C	13	1.47	−0.41	tilted	2.35
Al-C	19	2.06	+0.18	tilted	2.55
Al-Si	27	2.43	+0.55	normal	3.06
N-Si	21	1.74	−0.13	normal	2.38
Al-N	20	1.89	+0.01	both	2.49
Si-C	20	1.88	-	both	2.516

The Al atoms act as acceptors residing on the Si sublattice of SiC. Alternatively, we could replace one out of four N atoms with a C as shown in the following:

$$— \text{C-Si} — \text{C-Si} — \text{N}_{(3/4)}\,\text{C}_{(1/4)}\text{-Al} — \text{N-Al} — . \qquad (2)$$

In this case, the C atoms act as acceptors residing on the N sublattice of AlN. Both of these interface structures should exhibit interlayer spacings, which are close to the experimentally observed value, and because no Si-Al or C-N bonds are introduced, no large atomic relaxations are required.

The two atomic arrangements discussed in the preceding paragraph are depicted in the top half of Fig. 5. Note that these interfaces result in an Al-terminated (0001) surface. On the other hand, consider the abrupt interface between SiC(0001)Si and AlN(0001)N indicated schematically as

$$— \text{C-Si} — \text{C-Si} — \text{Al-N} — \text{Al-N} — .$$

This type of interface results in a N-terminated (0001) surface, as suggested by Sasaki and Matsuoka for GaN on SiC.[12] In this case, the interface occurs between Si and Al layers. At the interface, each Al atom can contribute at most 3/4 of an electron to its bond with Si, and the Si atom can contribute at most one electron to this bond. Therefore, there is a local charge deficit at the interface of 1/4 electron per bond, and so this is not a stable configuration. This charge deficit can be eliminated by replacing one out of every four Al atoms at the interface with C,

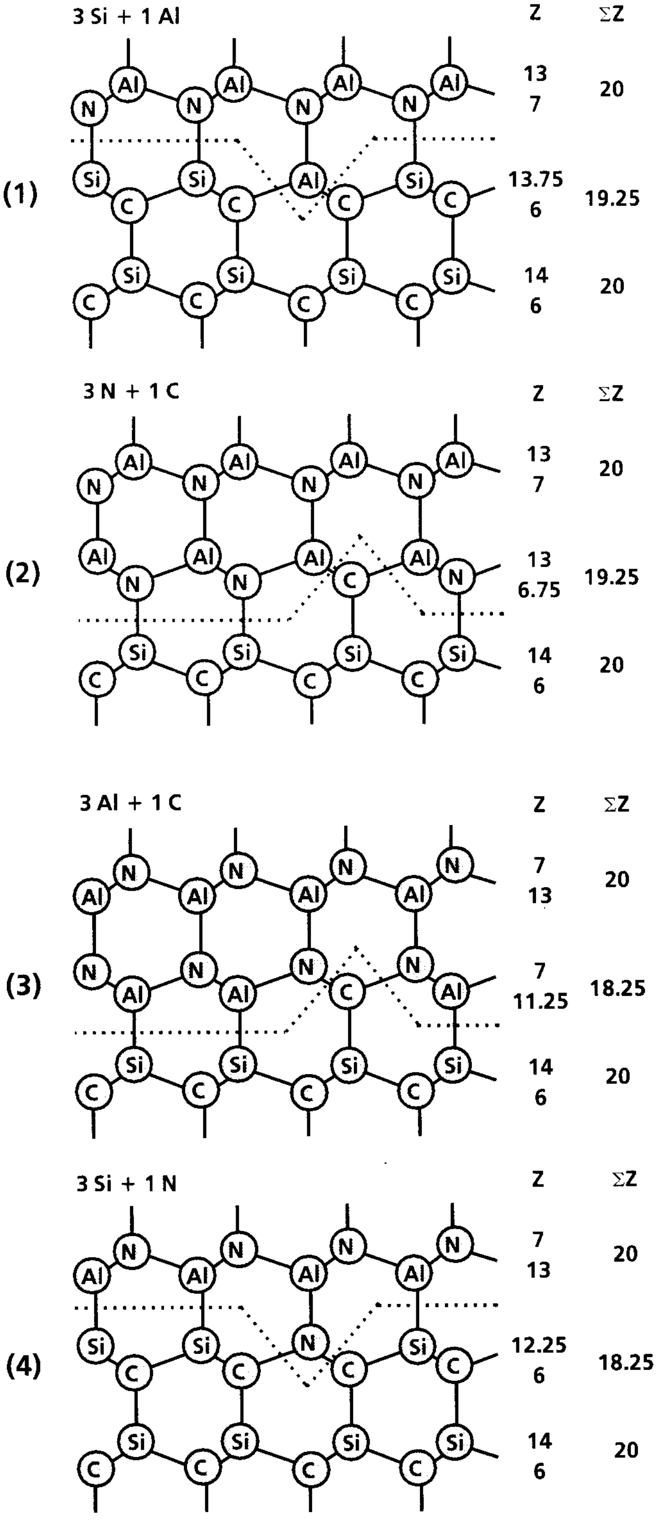

FIG. 5. Possible atomic arrangements at the AlN/SiC interface, allowing for atomic mixing at the interface. These models are related to models (1) to (4), respectively.

$$\text{— C-Si — C-Si — Al}_{(3/4)}\text{C}_{(1/4)}\text{-N — Al-N —,} \qquad (3)$$

with C acting as donors on the Al sublattice. Alternatively, we could replace one out of four Si atoms with N, with the N acting as a donor on the Si sublattice,

$$\text{— C-Si — C-Si}_{(3/4)}\text{N}_{(1/4)}\text{ — Al-N — Al-N — .} \qquad (4)$$

The spacing between interfacial layers will depend on the atomic relaxation. For this model to be compatible with the TEM images, the interplanar spacing should be approximately equal to the SiC bond length, which is 1.9 Å. To satisfy this constraint, the Si-Al bonds across the interface would be compressed by 0.5 Å relative to the sum of the atomic radii. This compression of the Si-Al bond may be relieved by a relaxation away from the interface of 0.25 Å for each Si and each Al atom. These relaxations could occur without significant changes in the Si-C or Al-N back-bond lengths, provided that there are also lateral relaxations in the plane of the interface. Structures (3) and (4) are depicted in Fig. 5(b).

The prevalence of a particular structure depends on the total energy of the system, which in turn depends on the abundance of various elements in the environment (chemical potentials)—and also on kinetic limitations, such as the ease with which various types of atoms diffuse.

It should be emphasized that Harrison's arguments[11] for intermixing apply only in the case of thick overlayers; for overlayers which are only a few atomic layers thick, an abrupt interface is possible, in principle. We note, however, that total-energy calculations for GaAs on Si(111) show that intermixing is exothermic even when the GaAs film is only three monolayers thick.[13] We expect that intermixing during the initial stages of growth of AlN on SiC is exothermic as well. In any case, the mixed configurations displayed in Fig. 5(a) should prevail in the case of a thick overlayer.

In summary, the image contrast and the interplanar separations observed in high-resolution TEM lattice images favor, for atomically abrupt interfaces, Si-N and Al-C bonds at the interface between AlN and (0001) Si-terminated 6H SiC. These bonding configurations give Al at the top of the AlN basal plane. The image contrast and interplanar distances corresponding to C-N and Al-Si bonds (providing N at the top of the basal plane) are not observed. We have also considered intermixing in order to obtain charge balance at the interface. Intermixing of the Si-N and Al-C bonds produce configurations without significant changes in the Si-C or Al-N back-bond lengths. This is not the case with intermixing of the Si-Al and C-N bonds. We, therefore, conclude that the most favorable atomic arrangements at the AlN/SiC interface are any combinations of the two intermixed configurations of the Si-N and Al-C bonds shown in the upper half of Fig. 5.

This work was partially supported by Department of Commerce Advanced Technology Program No. (70NANB2H1241). F.A.P. gratefully acknowledges stimulating discussions with Neville Connell and Jim Boyce. The authors also gratefully acknowledge the technical assistance of Mr. Chris Nelson and the use of the Atomic Resolution Microscope at the National Center for Electron Microscopy, Lawrence-Berkeley Laboratory, a National User Center supported by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. J.E.N. gratefully acknowledges the support of Naval Research (Contract No. N00014-95C-0169).

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