

Interfacial Structure and Chemistry of GaN on Ge(111)

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(Received 31 August 2013; published 16 December 2013)

The interface of GaN grown on Ge(111) by plasma-assisted molecular beam epitaxy is resolved by aberration corrected scanning transmission electron microscopy. A novel interfacial structure with a 5:4 closely spaced atomic bilayer is observed that explains why the interface is flat, crystalline, and free of GeN_x. Density functional theory based total energy calculations show that the interface bilayer contains Ge and Ga atoms, with no N atoms. The 5:4 bilayer at the interface has a lower energy than a direct stacking of GaN on Ge(111) and enables the 5:4 lattice-matching growth of GaN.

DOI: [10.1103/PhysRevLett.111.256101](https://doi.org/10.1103/PhysRevLett.111.256101)

PACS numbers: 68.35.bg, 68.37.Ma

GaN-based materials are an important class of wide band gap semiconductors widely used in optoelectronic and electronic devices. The combination of wide band gap and narrower band gap semiconductors (such as Si and Ge) has been used for various devices, such as heterostructure bipolar transistors [1] and multijunction solar cells [2]. Therefore, integration of GaN-based semiconductors with Si and Ge has been of much interest, and it is important to understand the interfaces between them.

GaN has been directly grown on Si(111) by plasma-assisted molecular beam epitaxy (PAMBE), although an amorphous SiN_x interlayer forms in between and degrades the epitaxial growth quality [3–5]. Therefore, an AlN layer grown on Si before the GaN growth was found to improve the crystal quality [6]. Similarly, GaN grown on Si(111) by metal-organic vapor phase epitaxy (MOVPE) requires an AlN interlayer to prevent etching. However, an amorphous SiN_x interlayer was found at the AlN/Si interface, which is believed to be formed due to interdiffusion between Si and AlN [7,8]. GaN and AlN films grown by PAMBE were generally found to be of N polarity, that is, the growth direction is parallel to [000 $\bar{1}$] and the surface terminates at N-face planes. However, thus far, only the structure of the Al polar (opposite to the N polarity) AlN/Si(111) interface has been determined at atomic resolution [8].

Despite the difficulty of growing GaN on Si(111) without an interlayer, GaN directly grown on Ge has been determined to have very good crystal quality [1]. Moreover, GaN has a closer match of the thermal expansion coefficient with Ge than with Si [1], which avoids problems such as wafer cracking upon cooling from the growth temperature. Therefore, growing GaN on Ge may allow for a much wider range of wafer size or the thickness ratio of the thin film over the substrate. However, the interface structure is unknown, although GeN_x phases have been

observed by *in situ* characterization during PAMBE growth [9]. Studying the atomic structure and chemistry of the interface will not only help in understanding the high quality growth of GaN on Ge, but may also shed light on the interface between N-polar nitrides and Ge in general.

Using transmission electron microscopy (TEM), the interface between GaN and Si was found to be domain matched by the integer ratio 6:5 [4], whereas AlN on Si [7,8] and GaN on Ge [1] are matched by 5:4. However, in order to fully understand the atomic structure of such interfaces, aberration corrected TEM [10], or scanning TEM (STEM) [7,8] is required.

In this Letter, we examine a GaN film (~100 nm) grown by PAMBE on a Ge(111) substrate. The growth conditions have been optimized to a growth temperature of 850 °C to avoid the formation of misoriented domains and beam fluxes at a Ga-rich condition that optimizes the crystal quality [11]. The GaN film has an x-ray (0002) rocking curve full width at half maximum of 422 arcsec and a threading dislocation density of $5 \times 10^9 \text{ cm}^{-2}$ [12]. We have used aberration corrected STEM and density functional theory (DFT) to determine the structure of the GaN/Ge(111) interface.

The STEM characterization used an FEI Titan operated at 300 kV, with an aberration corrector on the probe forming lens giving a probe size of ~1.0 Å (convergence angle of ~16 mrad). A high angle annular dark field detector (HAADF, inner collection angle of 50 mrad) and an annular bright field detector (ABF, inner collection angle of 12 mrad) were used for imaging. In the absence of strain, the HAADF image intensity is approximately proportional to Z^α , where Z is the atomic number of the atom and $\alpha \sim 1.7$. Hence, the contrast of light elements is very low in HAADF images, and it is difficult to visualize N in GaN. Therefore, ABF imaging, which has enough contrast to show N in GaN, was also used.

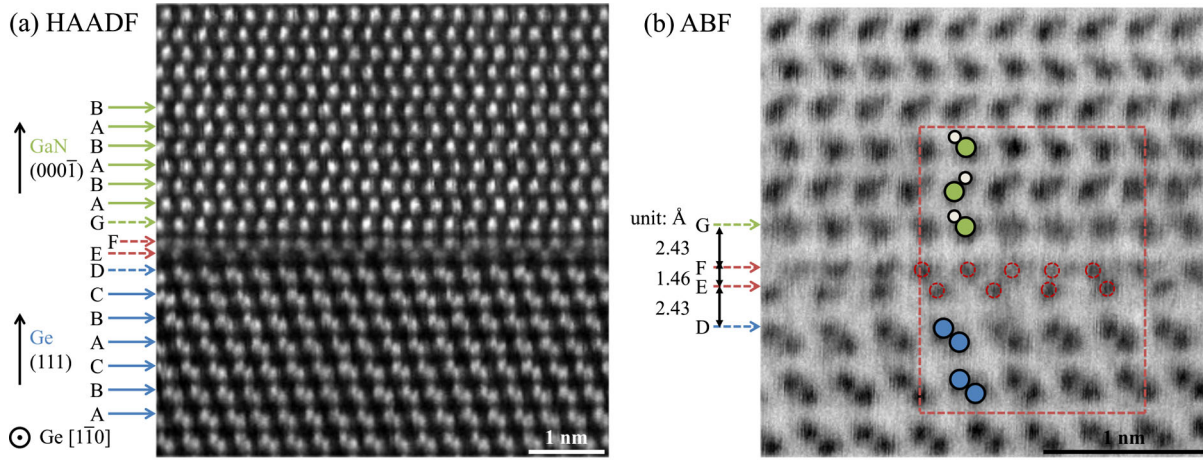


FIG. 1 (color online). (a) HAADF and (b) ABF images of GaN on Ge(111) viewed along Ge[$\bar{1}\bar{1}0$]. Atomic layers and their interplanar distances are labeled. The dotted lines show the size of the supercell used in DFT calculations.

As shown in Fig. 1(a), Ge dumbbells have $ABCABC\dots$ cubic stacking along [111], whereas GaN dumbbells [observable in the ABF image, Fig. 1(b)] have the hexagonal stacking $ABABAB\dots$ along $[000\bar{1}]$. The polarity of GaN is determined as N polarity from the ABF image. The epitaxial relationships, GaN(000 $\bar{1}$) parallel to Ge(111) and GaN[11 $\bar{2}0$] parallel to Ge[$\bar{1}\bar{1}0$], are readily observed. The 5:4 domain matching epitaxy is also apparent from the micrographs.

As illustrated in Fig. 1, the interface between GaN and Ge is flat and crystalline. Layer D is a layer of Ge dumbbells, stacked as a layer A in Ge. Layer G is a layer of GaN dumbbells, stacked as a layer B in GaN. Layer E follows the Ge stacking, but has single atoms rather than dumbbells. Another single atomic layer F shows a 5:4 matching to the layer E , and a 1:1 correspondence to the GaN layer G on top of it. The layers E and F have a very close spacing, 1.46 Å, and constitute a bilayer between GaN and Ge. However, it is not clear which types of atoms are in the bilayer. Unfortunately, due to delocalization of the inelastic scattering, the resolution of microanalysis is limited, for example, to 2 Å for Ga-L and Ge-L (at electron energy loss 1100–1300 eV) and to 6 Å for N-K (at electron energy loss ~ 400 eV). In addition, there may be some probe spreading onto adjacent atoms [13]. Therefore, determination of the chemistry of individual layers E and F by microanalysis may not be accurate. To study the interface chemistry with confidence, we make use of the structural information from the micrographs, especially the distances between the interfacial layers D , E , F , and G , as labeled in Fig. 1(b).

We used DFT calculations to study the energetics of the interface. The calculations used the Vienna *ab initio* simulation package (VASP) [14], with the functional of Perdew *et al.* [15], and a projector augmented wave basis set with plane wave cutoff energy of 300 eV. Periodic supercells were constructed following the domain matching epitaxy, the epitaxial relationships, and the N polarity observed

from our STEM micrographs, with three layers of (5×5) GaN dumbbells and two layers of (4×4) Ge dumbbells, as shown by dotted lines in Fig. 1(b). In addition, the terminating Ge and GaN surfaces were saturated with pseudohydrogen atoms to retain the bulk bonding environments of Ge and GaN, with enough vacuum thickness (>10 Å) introduced in between to avoid interactions between the saturated surfaces and their periodic images. One end of the Ge substrate was fixed, with all other atoms being free to move in all degrees of freedom. Each supercell was relaxed to its energetically most favorable configuration, including the registry of GaN with respect to Ge and the interplanar distances between atomic layers.

Permutations of Ga, Ge, and N atoms were used to occupy the unknown layers, E and F with each case denoted as (atom E)-(atom F). For example, the Ga-Ge interface means the layer E is occupied by Ga atoms, and the layer F by Ge atoms. To compare the interface energy among the cases, the energy of a Ge-Ge interface was chosen as the reference, and chemical potentials μ_{Ga} and μ_{N} were set between the Ga-rich [$\mu_{\text{Ga}} = \mu_{\text{Ga}}(\text{bulk})$] and the N-rich conditions [$\mu_{\text{N}} = \mu_{\text{N}}(\text{N}_2\text{gas})$] of GaN growth [$\mu_{\text{Ga}} + \mu_{\text{N}} = \mu_{\text{GaN}}(\text{bulk})$]. μ_{Ge} was set to its bulk value because the conditions required to form a flat, high-quality crystalline interface should suffice to bring the interface into equilibrium with the underlying Ge substrate. As shown in Fig. 2, the Ge-Ge interface has the lowest energy except at the end of the Ga-rich condition, where the Ga-Ge interface is the lowest in energy. The presence of N in the interfacial layers is never favorable, even under N-rich conditions.

Moreover, the configuration $\frac{1}{2}\text{Ga}\frac{1}{2}\text{Ge} - \text{Ge}$, with eight Ga and eight Ge atoms occupying layer E was relaxed, and its interface energy $E(\frac{1}{2}\text{Ga}\frac{1}{2}\text{Ge} - \text{Ge})$ is almost degenerate with a mixture of the pure interfaces at $T = 0$ K [with $\Delta E = 0.3 \text{ meV}/\text{\AA}^2$ in Eq. (1)]. At finite temperatures, the free energy of mixed layers is further lowered by the

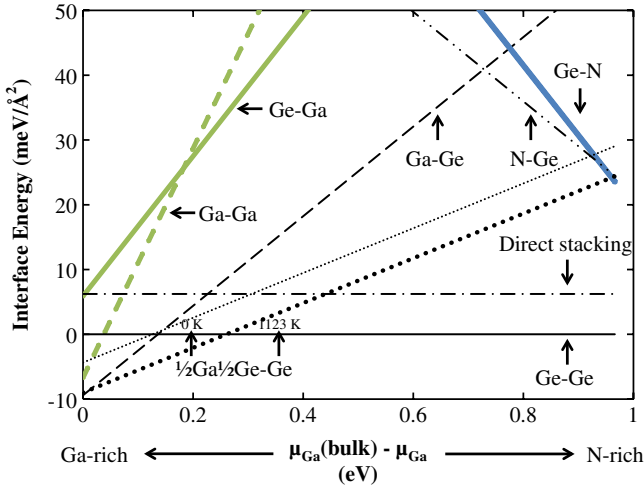


FIG. 2 (color online). Calculated interface energies between GaN and Ge(111), relative to the Ge-Ge interface.

configurational entropy S_{conf} , stabilizing, for instance, the $\frac{1}{2}\text{Ga}\frac{1}{2}\text{Ge} - \text{Ge}$ interface by $4.6 \text{ meV}/\text{\AA}^2$ at the growth temperature (1123 K), so that it becomes more favorable than the pure layers over a range of Ga-rich growth conditions, as shown in Fig. 2. Free energies for other compositions in analogy to Eq. (1) are shown in the Supplemental Material [16]. Mixed F layers were not considered in the DFT calculations, but may likewise exist at strongly Ga-rich conditions. At less Ga-rich conditions, the preferential incorporation of Ga in layer E rather than in layer F is apparent from Fig. 2.

$$E\left(\frac{1}{2}\text{Ga}\frac{1}{2}\text{Ge} - \text{Ge}\right) = \Delta E + \frac{1}{2}E(\text{Ga} - \text{Ge}) + \frac{1}{2}E(\text{Ge} - \text{Ge}) - TS_{\text{conf}} \quad (1)$$

Furthermore, the calculated interplanar distances between layers D , E , F , and G are compared with experimental measurements, as listed in Table I. The Ge-Ge, Ge-Ga, Ga-Ge, and $\frac{1}{2}\text{Ga}\frac{1}{2}\text{Ge} - \text{Ge}$ cases match the experimental spacings best, whereas a N layer at E or F is found too close to its neighboring layers to match the experimental spacings. Combining with the interface energy results, we conclude that the interfacial layers are composed of Ga and Ge atoms, with diminishing numbers of Ga atoms as the growth condition moves away from the Ga-rich condition.

The Ge-Ge interface is shown in Fig. 3(a), where 32 of the 41 Ge atoms in layers E and F are quasifourfold coordinated (as in bulk Ge) and nine of them quasifivefold (having an extra bond with a Ge in layer F) [16]. Their average bond length is approximately equal to the bond length of bulk Ge, ranging between 94% and 112% of it. Quasifivefold coordination and sizeable bond length variations are not unusual for Ge-Ge bonds, and they are also observed in liquid and amorphous Ge [17].

TABLE I. Interplanar spacings (in \AA) between layers D , E , F , and G of the calculated cases.

	$D-E$	$E-F$	$F-G$
Expt.	2.43	1.46	2.43
Ga-Ga	2.44	1.84	2.55
Ga-Ge	2.43	1.55	2.52
$\frac{1}{2}\text{Ga}\frac{1}{2}\text{Ge} - \text{Ge}$	2.45	1.47	2.52
Ge-Ge	2.47	1.35	2.51
Ge-Ga	2.42	1.54	2.51
Ga-N	2.37	0.79	1.98
N-Ga	1.96	0.82	2.54
Ge-N	2.44	0.63	1.98
N-Ge	1.95	0.66	2.57
Direct stacking	2.51	0.90	2.46

The Ge-Ge interface is compared to a direct stacking of GaN on top of Ge(111), as illustrated in Fig. 3(b). The direct stacking was observed for the 5:4 matching interface of Al-polar AlN on Si when grown by MOVPE at a relatively low temperature. At a higher growth temperature, an amorphous SiN_x interlayer is formed [8]. However, our N-polar GaN on Ge has a novel structure, with a 5:4 bilayer in between. The difference between the two configurations is the number of Ge atoms in layer F , (5×5) Ge atoms in the Ge-Ge interface, and (4×4) Ge atoms for direct stacking, forming dumbbells with the Ge atoms in layer E . As plotted in Fig. 2, the direct stacking leads to higher interface energy, by $6.2 \text{ meV}/\text{\AA}^2$. Therefore, the 5:4 bilayer observed in this study is confirmed to be energetically favorable. Moreover, as shown in Fig. 3, the stacking of GaN on top of the Ge-Ge interface has a smaller rumpling than the directly stacked GaN, suggesting a more favorable condition for smooth GaN growth on top of the Ge-Ge interface. Indeed, a layer F of (5×5) atoms is lattice-matching with (5×5) GaN grown on top, and there are no dangling bonds between them.

Although previous studies have suggested a GeN_x interlayer between GaN and Ge(111), its presence has been confirmed only at the nitridation step before the

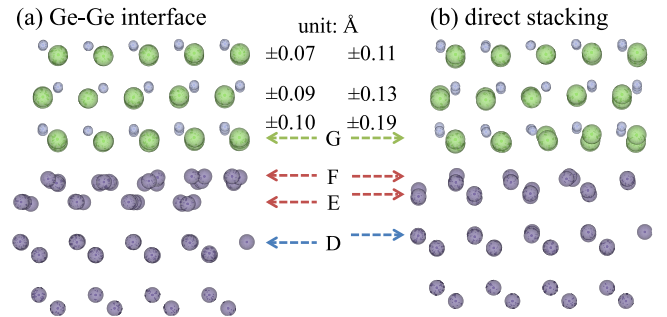


FIG. 3 (color online). Relaxed interfaces between GaN and Ge(111) by DFT calculations viewed along $\text{Ge}[1\bar{1}0]$: (a) the Ge-Ge interface, and (b) the direct stacking of GaN on Ge. The height (the coordinate along $\text{GaN}[000\bar{1}]$) variances of three GaN layers are labeled.

growth of GaN [9]. However, with the introduction of a Ga flux during GaN growth, the very thin GeN_x layer ($\sim 1\text{ nm}$) is no longer stable. This can be understood from a comparison between the formation enthalpy of GaN (-130 kJ/mol [18]) and Ge_3N_4 ($\frac{1}{4}\text{Ge}_3\text{N}_4$, -76 kJ/mol [19]). Si_3N_4 ($\frac{1}{4}\text{Si}_3\text{N}_4$, -207 kJ/mol [20]), on the other hand, is more stable than GaN, but less than AlN (-308 kJ/mol [21]). As a result, an amorphous SiN_x layer is present at the GaN/Si interface, but at the AlN/Si interface only at higher temperature during MOVPE growth [7,8]. A GeN_x interlayer is not formed between GaN and Ge, at least at the PAMBE growth temperature ($850\text{ }^\circ\text{C}$). However, the growth of GaN on top of the GeN_x layer helps the morphological change of Ge atoms at the interface to form the 5:4 bilayer. N-polar AlN on Si, which has been grown by PAMBE [22], may have a similar 5:4 closely spaced atomic bilayer, and microscopy with subangstrom resolution is required to confirm this.

In summary, a novel interface, a 5:4 closely spaced atomic bilayer, has been identified at the N-polar GaN/Ge(111) interface grown by PAMBE. The bilayer is shown to be composed of Ge atoms, plus a number of Ga atoms depending on the growth conditions, and to be free of N atoms. Having the bilayer in between GaN and Ge (111) not only lowers the interfacial energy, but also enables lattice-matched GaN growth. The flat, crystalline, and domain matched interface is suitable for applications in semiconductor heterostructures.

We acknowledge the School of Physical Sciences, University of Cambridge for funding the FEI Titan³ 80–300 electron microscope. S.Z. acknowledges a DAAD scholarship for funding. C.J.H. thanks the EPSRC for funding. R.R.L. acknowledges support from a Research Foundation-Flanders (FWO) fellowship.

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