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Evidence for relaxed and high-quality growth of GaN on SiC(0001)

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By using polarization-dependent x-ray absorption spectroscopy at the Ga edge, we study the growth of GaN on SiC(0001) in the thickness range 0.7–150 nm. We find that the growth is always relaxed (i.e., nonpseudomorphic) even for the thinnest epilayers, i.e., below the expected critical thickness. No evidence is found for a mixed Ga/Si interface plane, while a C/N mixed interface plane cannot be ruled out. The results are discussed with reference to the electronic structure of the SiC/GaN heterojunction and in particular to band offsets and strain-induced piezoelectric polarization. © *1999 American Institute of Physics.* [S0003-6951(99)03722-5]

GaN and related III–N compound semiconductors possess unique material properties which make them extremely attractive for optoelectronic and high temperature, high power microelectronic applications; they are the subject of much current interest, for example for the realization of blue–violet diode lasers.[1] All the devices which have been fabricated up to now are based on heterostructures. One example is the GaN/SiC heterobipolar transistor with a GaN emitter realized by growth on a SiC p-n junction,[2] the system subject of the present letter.

The importance of strain in determining electronic properties is well known.[3] There are some peculiar characteristics of nitrides which make this relationship even more important. Besides spontaneous polarization, nitrides exhibit an important strain-dependent piezoelectric polarization which determines a significant band bending.[4] We note that the elastic properties of the nitrides are still a matter of research[5,6] and that there is no experimental measurement of the critical thickness in epitaxial growth. The abrupt GaN/SiC interface is expected to be electrically charged[7] and thus unstable; atomic intermixing at the interface is thus predicted to be an intrinsic phenomenon which stabilizes the system. Supplementary intermixing originating from nonoptimized growth procedures may of course occur in the layers further from the interface. Finally, a variation of the lattice spacing near the junction with a significant effect on the band offsets has been predicted for the related SiC/AlN system.[8] While there are some theoretical predictions available in the literature, quantitative experimental determination of atomic structure at nitride heterostructures is not yet available.

X-ray absorption fine structure (XAFS) spectroscopy in the fluorescence mode is a powerful tool used to determine the local atomic structure of thin semiconductor heterostructures.[9–12] It has also been recently applied to nitrides,[13,14] obtaining a local characterization of pure and alloy thin films. In this letter we present a study of the local structure for GaN epilayers grown on SiC(0001) in the nominal thickness range 0.7–150 nm. This range was chosen because the available estimates of the critical thickness for strain relaxation range, for the related AlN/GaN system, between 1.5 and 4 nm.[6,15] By exploiting polarization-dependent measurements we determine the local structure in the first and second coordination shell, thus providing important information for modeling the heterostructure.

GaN samples were grown on Si-terminated SiC(0001) substrates by molecular beam epitaxy with a rf plasma source for the activated nitrogen supply. The substrates were prepared, after the usual chemical procedure, by annealing in ultrahigh vacuum (UHV) at 1000 °C in Si flux, in order to obtain a surface free of oxygen, which showed a $\sqrt{3}\times\sqrt{3}R30°$ reconstruction, as checked by low-energy electron diffraction (LEED). The GaN growth temperature was 600 °C and the rate 1.5 nm/min. A series of epitaxial layers was grown with nominal thicknesses between 0.7 and 150 nm (Table I). The four thinnest GaN epilayers, up to 6 nm of thickness, were also analyzed *in situ* by x-ray photoemission spectroscopy (XPS) providing information on the electronic properties of the ultrathin SiC/GaN heterostructures, with particular reference to the valence band offset and the macroscopic polarization fields.[4] The samples were characterized by atomic force microscopy (AFM), showing an increase in root-mean-square (rms) roughness from 0.75 nm for the thinnest sample to a constant rms roughness of 1.4 nm for the two thickest ones.

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TABLE I. Sample nominal thickness and local structural parameters for the Ga–Ga second shell: interatomic distance R, coordination numbers CN, and Debye–Waller factors (σ^2).

Sample	Thickness (nm)	R parallel (± 0.01 Å)	R perpendicular (± 0.01 Å)	CN parallel (± 1)	CN perpendicular (± 1)	σ^2 parallel ($\pm 1\times10^{-3}$ Å^2)	σ^2 perpendicular ($\pm 1\times10^{-3}$ Å^2)
A72	150	3.18	3.17	12	12	2.4	2.6
A73	15	3.18	3.17	12	12	3.1	2.9
A74	5	3.18	3.17	12	12	2.6	2.9
A75	3	3.18	3.17	12	12	2.7	3.4
A76	1.5	3.16	3.17	11	11	4.7	3.6
A79	0.7	3.16	3.16	7	6	4.4	3.2

XAFS experiments at the Ga K edge were performed at the BM8 ''GILDA'' CRG beamline of the European Synchrotron Radiation Facility. A Si(113) dynamically sagitally focusing monochromator was used[16] and harmonics were eliminated with a pair of Pd-coated grazing incidence mirrors. The Ga K_α fluorescence intensity was monitored using a seven element hyper-pure Ge detector. Spectra were acquired in two geometries: with the angle between the electric vector of the photon beam and the [0001] direction either 15° or 75°; these two geometries preferentially probe the structure either perpendicular or parallel to the growth plane, respectively.

XAFS data were analyzed using standard procedures, using Fourier-filtering techniques. The background-subtracted raw data are shown in Fig. 1 and the good signal-to-noise ratio, even for the 0.7 nm sample, is apparent. The raw data was Fourier transformed in the range 2.5–13 Å^{-1} with a k^2 weight and the result is shown in Fig. 2. The peak in the range 1–2 Å is due to the N nearest neighbors which occur, in bulk GaN, at an average distance of 1.95 Å. The strong peak at $\sim$2.8 Å is due mainly to the Ga second shell at an average distance in the bulk of 3.184 Å; there is also a weak contribution from the N third shell at 3.74 Å.[13]

We will focus our attention on the Ga second shell since in the wurzite structure it bears a simple relation to the in-plane and out-of-plane lattice parameters a and c; in fact, in bulk GaN, six Ga atoms lie in the same (0001) basal plane as the central atom at a distance a, while the other six Ga atoms, positioned in parallel basal planes (three atoms above and three below), are at a distance $\sqrt{(1/3)a^2+(1/4)c^2}$. The measurement of the second shell distances thus provides a direct probe of the lattice parameters for the epilayers. To a good approximation, in the perpendicular geometry only the out-of-plane second shell correlations are probed, while in the parallel geometry the in-plane correlations have approximately three times the relative weight compared to the out-of-plane correlations.

From Fig. 2 we observe that there are no apparent shifts in the position of either the first or the second peaks of the Fourier transforms. On the other hand, there is a clear decrease of the intensity of the second peak with decreasing thickness.

Quantitative analysis was performed by inverse Fourier transforms and k-space fitting. Analysis of the first shell data showed that for all thicknesses Ga is surrounded by four N atoms at an average distance of 1.96 ± 0.015 Å, with no significant changes in the Debye–Waller (DW) factor. The inverse Fourier transform of the second peak in the range 2.12–3.8 Å was fitted with two theoretical contributions, both simulated with the GNXAS[17] package: a Ga–Ga contribution with variable coordination number (CN), DW and distance, and a Ga–N contribution (third shell); due to the weakness of this contribution its CN and distance were kept fixed at the bulk value. The quality of the fits thus obtained is illustrated in Fig. 3, while the local structural parameters for the second shell are listed in Table I for all samples and both polarizations.

It is clear that within 0.02 Å, there is no change (and no apparent trend) in the second shell distance with epilayer thickness. This is even more evident if compared to the 0.1 Å difference of a between GaN and SiC which, if pseudomorphic growth were occurring, would lead to measured second shell distances of 3.224 and 3.116 Å in the perpendicular and parallel geometries, respectively; these values have been calculated using $2C_{13}/C_{33}=2.09$,[5] and taking into account the XAFS polarization factor. Our data thus indicate that a re-

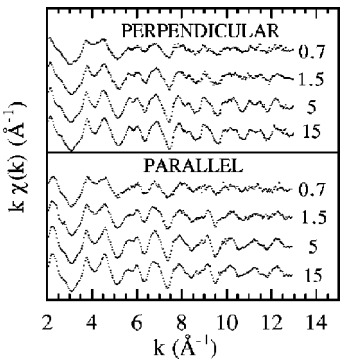

FIG. 1. Representative background-subtracted raw XAFS data in the two polarizations used; sample thickness (nm) is indicated.

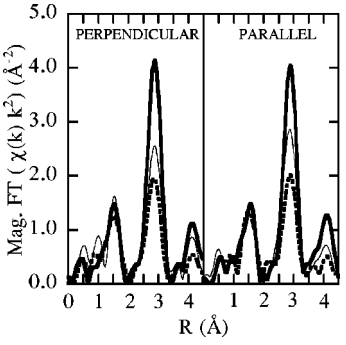

FIG. 2. Magnitude of the Fourier transforms (in the range 2.5–13.1 Å^{-1}) in the two polarizations for samples of thickness 15 nm (thick continuous line), 1.5 nm (thin continuous line), and 0.7 nm (dotted line).

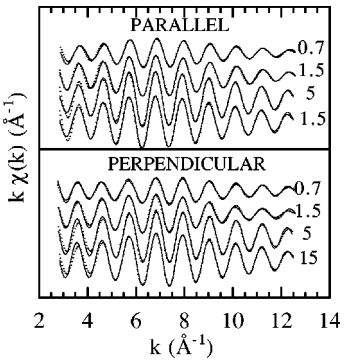

FIG. 3. Representative fits for the second and third coordination shells; sample thickness (nm) is indicated.

laxed, nonpseudomorphic growth takes place for these samples. This implies that, at least for the growth conditions employed, the critical thickness for strain relaxation is smaller than the 1.5–4 nm range expected. This is to be contrasted with the situation in III–V systems in which a transition from strained to relaxed growth is present and has significant effects on the local structure.[12] Contrary to the theoretical prediction,[8] which was made assuming pseudomorphic growth, we have found no evidence for the variation of interplanar spacing with epilayer thickness.

The CNs exhibit a decrease below 1.5 nm nominal thickness, while there is only a moderate increase in the DW. The decrease in CNs can be attributed to a size effect: as the film thickness decreases there will be a decrease in the number of second neighbors around the central atom. A simple estimate of the CNs for two-dimensional epilayers can be performed; if the number of unit cells in the (0001) direction is M, in perpendicular polarization the average CN is $\langle \mathrm{CN} \rangle = 12 - (6/M)$, while in parallel polarization $\langle \mathrm{CN} \rangle = 12 - (3/2M)$. Use of the above formula for sample A79 yields $M = 1$ for perpendicular polarization, in fair agreement with the nominal thickness of 0.7 nm = 1.35 unit cells. However, in parallel polarization the experimental CN is lower than expected for a two-dimensional epilayer; this is evidence that at low coverages the epilayer does not completely cover the substrate; this leads to a decrease of $\langle \mathrm{CN} \rangle$ in parallel polarization and an increase for the perpendicular one. This situation is qualitatively confirmed by the AFM image of this sample.

We now discuss the issue of interdiffusion. The data and analysis presented clearly rule out the presence of extensive interdiffusion: the local environment of Ga is always very similar to bulk GaN. This testifies to the validity of the growth procedures adopted. However, as already mentioned, the nitride–SiC heterostructure is expected to exhibit an interdiffused interface layer. Consideration of the ionic radii of the atoms, of their valence, and evidence from transmission electron microscopy (TEM),[18] implies that two possible interface structures are possible, with the presence of either a Ga/Si or N/C mixed plane (with relative occupancy 75%/25%). While the first shell signal is always fitted well with exclusively four N atoms at a distance of 1.95 Å the similarity of the N and C phase shifts implies we cannot exclude the presence of a N/C mixed plane; we note that a N/C intermixed plane is the most likely possibility because our substrates are Si terminated. The situation is different when considering the possibility of a Ga–Si mixed plane because a Ga–Si signal has a completely different k dependence than a Ga–Ga one. It can be calculated that, at the suggested relative occupancy, a Ga–Si CN of approximately 1 is expected in either polarization; we can exclude this amount of Ga–Si second shell correlations and thus our data do not support the presence of a Ga/Si intermixed at a relative occupancy of 75%/25%. It must be pointed out that an intermixed interface is predicted in order to neutralize the charge located at the IV–IV/III–V heterovalent interface and thus prevent the presence at equilibrium of a strong electric field in the upper layer. However, in very thin epitaxial nitride heterostructures such strong electrostatic fields, due to spontaneous polarization and/or piezoelectric contributions, have been experimentally observed.[4,19,20]

Our result provides the structural basis for an interpretation of the electronic properties probed by XPS.[4] The clear evidence for relaxed growth implies that piezoelectric polarization will be absent, the only contributions to a static electric field in the epilayer being due to the spontaneous polarization and/or to an interface charge. In fact, for these samples a shift of the Ga $3p$ core levels with overlayer thickness is observed and its sign is compatible with a relaxed growth. The valence band discontinuity of 0.8 ± 0.1 eV (with the GaN valence band maximum lower than that of SiC) should be attributed to a relaxed GaN growth.

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