Critical thickness of GaN thin films on sapphire (0001)

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Synchrotron x-ray diffraction was employed to measure the lattice constants *a* and *c* of GaN films grown with an AlN buffer layer on sapphire (0001) over a thickness range of 50 Å to 1 μm. We used multiple reflections and a least-squares fit method for high reliability. As the thickness increased, the lattice constant *a* increased from 3.133 Å to 3.196 Å and *c* decreased from 5.226 Å to 5.183 Å. The expected trend was fitted to an equilibrium theory, allowing the critical thickness of GaN on AlN to be estimated at 29 Å $\pm$ 4 Å in good agreement with a theoretical prediction. © *1996 American Institute of Physics.* [S0003-6951(96)03442-0]

The fact that GaN has a wide and direct band gap has led people to consider GaN as a candidate material for short wavelength optical devices, especially for a laser diode. Due to this high interest, much work has recently been reported on the various physical properties of GaN. There has been little work on the lattice constants of GaN, however, compared with the amount of work on other properties.[1,2] Since the lattice constant couples to the electronic as well as optical properties of material, it is very important to accurately measure these values for different thicknesses of the epitaxial layer. This is especially important for GaN because the potential substrate materials for GaN epitaxy, such as sapphire and SiC, have such a sizable lattice mismatch with GaN that the lattice constants of GaN in layers as thick as 1000 Å would be expected to deviate significantly from those of bulk GaN. This could cause observable deviation on the expected performance of practical optical devices. Our study also helps us gain a fundamental understanding of the relationship between strain and lattice mismatch in an anisotropic material.

Using Bond's double crystal x-ray method[3] Hiramatsu *et al.*[2] previously measured the lattice constant of GaN grown by hydride vapor phase epitaxy and metalorganic vapor phase epitaxy in the thickness range 0.6–1200 μm and found that the lattice constant *c* of GaN decreased with increasing film thickness of GaN. They explained it by a strain relaxation mechanism resulting from cracks, assuming that the origin of the stresses was just the difference in the thermal expansion coefficient because their samples were considered to be thick enough to ignore the stress coming from lattice mismatch. Furthermore, only lattice constants near the surface of GaN were measured because the penetration depth was less than the thickness.

In this work, GaN samples with smaller thicknesses in the range from 50 Å to 1 μm were grown by molecular beam epitaxy (MBE) on sapphire (0001) using a 32 Å AlN buffer layer. We used an AlN buffer layer because its in-plane lattice constant is intermediate. This redistributes the substantial mismatch between two interfaces. In order to have a workable signal from the thinnest films, a synchrotron x-ray source was employed to measure lattice constants *a* and *c* of GaN films using a least-squares fit method. Our data therefore extend Hiramatsu's work to thinner films. We could estimate the critical thickness of GaN grown on AlN using an equilibrium energetic relationship between the lattice constant *a* and the film thickness.

Sapphire substrate preparation consisted of degreasing in successive rinses with trichloroethane, acetone and methanol. Then the substrate was etched in 3:1 H_2SO_4:H_3PO_4. Both rinsing and etching were done at a temperature of 150 °C. After rinsing and etching, the substrate was inserted into the ultrahigh vacuum chamber. Thermal cleaning at 800 °C resulted in sharp reflection high energy electron diffraction patterns typical of the clean sapphire surface. An AlN buffer layer was then grown at a substrate temperature of 550 °C and an Al effusion cell temperature of 1030 °C for 15 minutes. A radio frequency plasma source was used for nitrogen. Using the relation of $Nd \approx 2\pi/\Delta q$, where Δq is the momentum transfer difference between successive minima of fringes near the (002) Bragg peak and *Nd* is the film thickness, an AlN buffer layer thickness of 32 Å was obtained. The full width at half-maximum of the (002) rocking curve of AlN was 4.8 arcmin which confirmed that it was epitaxial with the sapphire substrate. On top of the AlN buffer layer, the GaN layer was grown with the substrate temperature of 700 °C and a Ga effusion cell temperature of 910 °C. Using a profilometer, the thickness of the thickest GaN sample was measured to be 1 μm $\pm$ 0.05 μm. This calibration allowed the thickness of the other samples to be derived from their growth time. The thickness of our GaN films was found to range from 50 Å to 1 μm. Using the fringe method we determined the thickness of the 50 Å GaN film to be within

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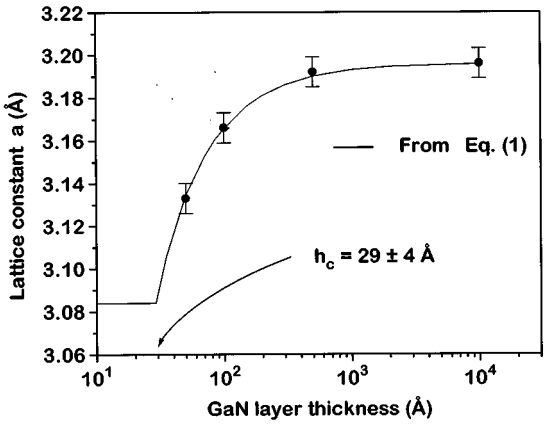

FIG. 1. Fit of lattice constant a as a function of GaN layer thickness.

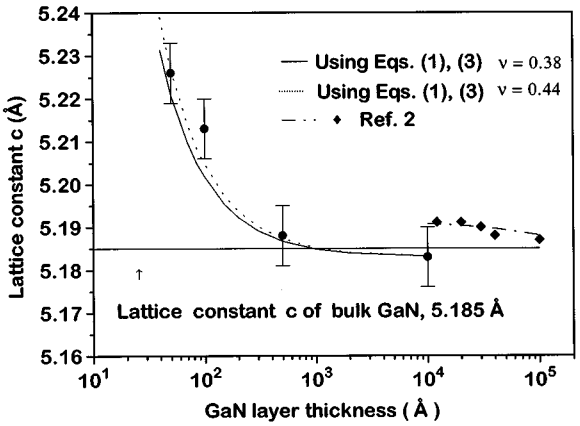

FIG. 2. Lattice constant c as a function of GaN layer thickness.

± 5 Å, which assured us that the thickness calibration was accurate for the thinner films, too.

The x-ray measurement was done using the beamline X16-C of the National Synchrotron Light Source (NSLS). The way we measured the lattice constants was as follows. The same method was used for each sample. (1) Optimize each of the diffractometer angles for N (typically N=10) in the different Bragg peaks of GaN, (2) build N corresponding reciprocal lattice vectors from the angles of each Bragg peak and (3) use a least-squares fit method to get a best fit of lattice which goes through all the Bragg peaks observed. In this way, lattice constants a and c were obtained for each sample. The same method was applied separately to a blank sample containing only the 32 Å AlN buffer layer in order to measure its lattice constant a, which turned out to be 3.084 Å compared with its bulk value 3.112 Å indicating a partial compression of the buffer layer.

Because of instrumental limitations, the resulting lattice constants will depend slightly on which Bragg peaks are used in the calculation as well as on the accuracy of the setting. Since the values were substantially overdetermined, we were able to use this redundancy to obtain a reliable error estimate. We carefully chose as many peaks isotropically distributed as possible in the reciprocal space. In order to estimate the error connected with the choice of Bragg peaks, we systematically omitted one or more Bragg peaks from the set and repeated the refinement. The resulting error was 0.007 Å for both a and c, including a correction for the systematic (misalignment) error of the diffractometer.

Our results for lattice constants a and c of the GaN films are plotted in Figs. 1 and 2 as a function of their thickness. They both show a progressive trend away from the bulk GaN lattice constants for thinner films. In the case of the in-plane lattice constant (Fig. 1), the values are found to lie between those of bulk GaN and the AlN buffer layer. It is clear that if the trend towards thinner films were extrapolated slightly, the GaN lattice constant would cross that of the AlN buffer layer. This is the situation that occurs at the critical thickness h_c of GaN: thinner films would simply have a pseudomorphic epitaxial relationship with the AlN substrate. In order to establish a quantitative estimate of h_c, it is necessary to make a theoretical fit to the data for the trend of lattice constant with thickness, which we explain next.

At thermodynamic equilibrium, misfit dislocations appear at the interface of strained layer heterostructure when the strained layer is thick enough that it is energetically favorable for the mismatch to be accommodated by a combination of elastic strain and interfacial misfit dislocations, rather than by elastic strain alone.[4] Therefore, in the initial stage of growth, when the film is below the critical thickness, GaN is expected to grow pseudomorphically on AlN. Above the critical thickness, the strain begins to relax by spontaneous creation of dislocations at the GaN/AlN interface. Subsequently the lattice constant begins to approach the bulk value as the thickness of GaN increases further.

By observing the trend of the lattice constants as a function of thickness, the thickness at which $a=a_s$, where a_s is the lattice constant of the substrate, which is called the critical thickness h_c, may be extrapolated using a fitting function. We derived a functional form that was based on Van der Merwe's equilibrium theory.[5] The total energy of an epitaxial film is given by the sum of (i) the strain energy which is proportional to square of in-plane strain as well as film thickness and (ii) the energy due to dislocations. By assuming that the effective range of the dislocation field is constant, the energy due to dislocations depends on their density alone, which is linearly proportional to in-plane strain. By differentiating this total energy with respect to the in-plane lattice constant we can obtain the theoretical dependence of a on h

$$a=a_0+\frac{h_c}{h}(a_s-a_0), \tag{1}$$

where a is the in-plane lattice constant of the GaN film, h is the thickness of the film, a_0 is the lattice constant of unstrained GaN, a_s is the lattice constant of the substrate. h_c= 29 Å ± 4 Å was obtained to fit our data in the entire region of the thickness (Fig. 1) by adjustment of only the parameter h_c. The resulting fit curve is the solid line through the data points. Using Kasper's[6] energetic correction estimates for the dislocation interactions we obtained a different expression for Eq. (1).[7] Quantitatively, using the logarithmic correction for the effective range of the dislocation field did not give a significantly different result at the level of accuracy of our data.[7]

The critical thickness has been calculated and discussed by many authors.[8,9] However, there have been many reports[10,11] on experimental determinations of the critical thickness indicating that coherence apparently persists to thicknesses much greater than that predicted by classical theories. Recently, Fischer *et al.*[12] reported a new approach in equilibrium theory for strain relaxation in metastable heteroepitaxial semiconductor structures. In this equilibrium theory, they included the elastic interaction between straight misfit dislocations and obtained h_c by setting the excess resolved shear stress required to produce misfit dislocations to zero. According to Fischer *et al.*, the critical thickness is given by

$$\frac{(a_0-a_s)}{a_s}=\left(\frac{b\cos\lambda}{2h_c}\right)\times\left(1+\left(\frac{1-(\nu/4)}{4\pi(1+\nu)\cos^2\lambda}\right)\ln(h_c/b)\right), \quad (2)$$

where, as before, a_0 and a_s denotes the lattice constant of the fully relaxed film and that of the substrate, respectively. λ is the angle between the Burgers vector and the direction in the interface, normal to the dislocation line. Inserting appropriate material parameters, $\lambda = \pi/3$, $\nu = 0.38$ and $b = 3.084$ Å, the calculated critical thickness of GaN is 31.5 Å which is in good agreement with our result.

The expansion of c as a result of the contraction of a is simply explained by the Poisson ratio, ν, so c can be related to a from its definition.

$$c=c_0+\frac{c_0\nu}{a_0}(a_0-a), \quad (3)$$

where c_0 is the bulk (relaxed) lattice constant. Shown in Fig. 2 are our data of lattice constant c, the data from Hiramatsu *et al.*,[2] and the best fit of Eq. (3) with $c_o=5.183$ Å and $a(h)$ taken from Eq. (1). The solid line is obtained using $\nu=0.38$ from Detchprohm *et al.* We obtained a slightly better fit (dotted curve) with $\nu=0.44 \pm 0.05$, which can be considered as an experimental estimation of the Poisson ratio for a thin GaN film. Compared with Hiramatsu *et al.*'s results, the changes in the lattice constant c were very large because our samples were so thin that the effect of lattice mismatch was dominant. However, our result of lattice constant c sits on Hiramatsu's data without any discontinuity. Although the apparent trend in Hiramatsu's data overlies a region where our values appear to be constant, they are still consistent within error. Since the determination of the critical thickness is more sensitive to data obtained for thin samples, this uncertainty of the lattice constant in a thicker region does not seriously change the fitting value of the critical thickness.

In summary, synchrotron x-ray diffraction was utilized to measure lattice constants a and c of thin GaN films grown on a 32 Å AlN buffer layer by MBE using a least-squares fit method. Due to the lattice mismatch, changes in the lattice constants of GaN films were observed. The critical thickness of GaN was estimated to be 29 Å ± 4 Å. It is worth noting that an equilibrium energetic argument appears to explain our observations, and gives good quantitative agreement with the predicted h_c. This is not the case in other systems, such as Ge_xSi_{1-x}, where critical thicknesses ten times the equilibrium value are found, and kinetic models are needed to explain the phenomenon.[13]

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