Molecular beam epitaxial growth of atomically smooth scandium nitride films

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(Received 31 May 2000; accepted for publication 24 August 2000)

High quality scandium nitride films have been grown on magnesium oxide (001) substrates by molecular beam epitaxy using a rf plasma source for nitrogen. Both reflection high energy electron diffraction and x-ray diffraction confirm that these films have (001)-orientation. Atomic force microscopy reveals a surface morphology consisting of large plateaus and pyramids. The plateaus are found to be atomically smooth and have a 1×1 surface structure, as revealed by *in situ* scanning tunneling microscopy. © *2000 American Institute of Physics.* [S0003-6951(00)00142-X]

The growth and surfaces of nitride semiconductors have recently been subjects of great interest.[1–4] Most of the work has concentrated on group XIII nitrides, and GaN in particular. Yet there are other nitrides with interesting properties, an example of which is scandium nitride, a group III transition metal nitride. For this unusual material, there is evidence that it is a semiconductor having a direct band gap in the range 2.1–2.4 eV.[5–10] Different from most conventional semiconductors, ScN is known to stabilize in the rock-salt crystal structure.[5,7,9] Due to the strong bonding between Sc and N, ScN is also thought to have a very high melting point of over 1500 °C.[7,11] Finally, ScN has a very small lattice parameter mismatch with GaN ($<0.3\%$), which might allow the growth of GaN/ScN heterostructures or ScGaN alloys.[6]

For a potentially useful electronic material, it is important to demonstrate that smooth epitaxial growth of singly oriented films can be achieved. Dismukes *et al.* grew ScN using chemical vapor deposition on sapphire, resulting in (111)-oriented, but rough, films.[5] Moustakas grew ScN on sapphire(0001) using electron cyclotron resonance (ECR) molecular beam epitaxy (MBE), which also resulted in (111)-oriented, but rough, films.[9] Gall *et al.* grew ScN on MgO(001) using reactive magnetron sputtering, resulting in films having both (001) and (111) orientation.[7] A subsequent paper by Gall *et al.* reported that the use of a 20 V substrate bias during growth resulted in single (001) orientation but that these films were also rough.[8]

In this letter, we report the smooth growth of ScN using radio frequency (rf) MBE. We find that rf MBE growth results in well-oriented ScN films, having either (001), (110), or (111) orientation, depending on the starting substrate orientation. We find that (111) and (110) oriented ScN films grow in a 3D growth mode with rough surfaces, but (001)-oriented ScN films can be grown in a 2D growth mode, resulting in atomically smooth surfaces.

The experiments are performed in a custom-designed vacuum system consisting of a MBE chamber coupled to a surface analysis chamber. The substrates are first cleaned with solvents, then loaded into the MBE chamber and heated up to ~1000 °C for 30 min (for growth on sapphire, the nitrogen plasma is also applied during this heating step). Then the sample temperature is lowered to ~800 °C prior to beginning the growth of ScN. The nitrogen flow rate is 1.1 sccm with the rf power set at 500 W. The effective Sc flux, estimated from the measured film thickness and the growth time, is in the range 4×10^{13}–$3\times10^{14}/\mathrm{cm}^2\,\mathrm{s}$. The growth condition is monitored using reflection high energy electron diffraction (RHEED). Following growth, the sample is analyzed by *in situ* scanning tunneling microscopy (STM). After removal from the surface analysis chamber, the sample is analyzed using x-ray diffraction (XRD) and atomic force microscopy (AFM).

Initially, we grew ScN on sapphire (0001) substrates, resulting in (111)-oriented ScN. While the RHEED patterns during growth showed good ordering along the high symmetry directions, $\langle 11\bar{2}0\rangle$ and $\langle 1\bar{1}00\rangle$, the patterns were very spotty, indicating a rough growth surface. The roughness of these surfaces was later confirmed in AFM images, and XRD confirmed the (111) orientation. We also tried growth on MgO(110), and although the RHEED patterns showed good (110) orientation, they were also very spotty.

Evidently, ScN takes on the crystalline orientation of its substrate, but smooth growth is difficult (under our MBE conditions) for (110) and (111) orientations. This could be due to very small adatom diffusion lengths on surfaces with these orientations, as was suggested by Gall *et al.* in the case of (111) orientation.[7,8]

If adatom diffusion lengths are larger for the (001) surface, then smooth growth may be possible. To grow (001)-oriented ScN, we use MgO(001) as a substrate. MgO also has rock-salt structure, and the lattice mismatch of ScN with MgO is 7.3%.

The RHEED patterns shown in Fig. 1 illustrate the stages of the growth process. Prior to heating, the as-loaded substrate has good crystalline quality, as seen in Fig. 1(a), which shows the RHEED patterns along the [100] and [110] azimuths. Clear diffraction spots are seen along both azimuths, as well as Kikuchi lines. However, the patterns are spotty, indicating some roughness.

After heating the substrate to 1000 °C for 30 min, the diffraction spots elongate and sharpen into the distinct streaks shown in Fig. 1(b). These streaky patterns suggest that the MgO surface may be smoothened by the heating.

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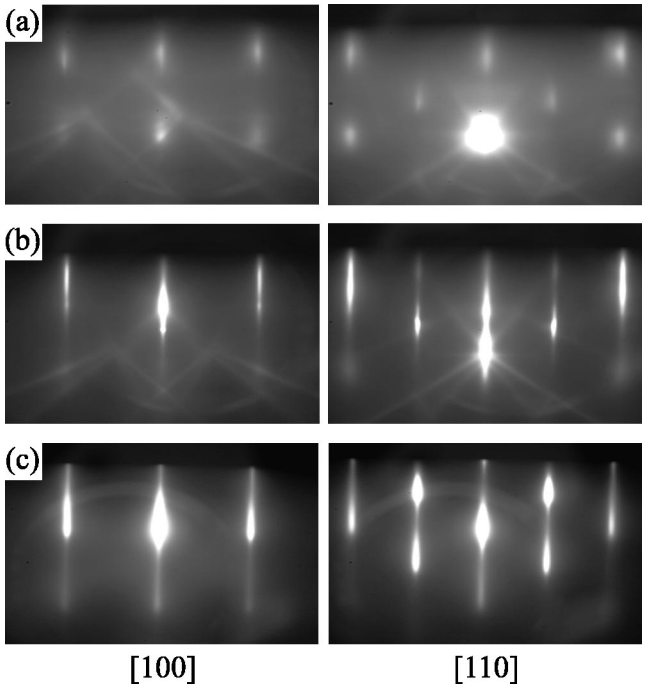

FIG. 1. Sequence of RHEED patterns for ScN growth process on MgO(001). (a) As-loaded MgO surface prior to heating; (b) MgO surface after 30 min of heating at 1000 °C; (c) ScN(001) surface during growth.

Scandium nitride growth is initiated on this smoothened MgO(001) surface. The RHEED patterns show good epitaxy from the very beginning. Figure 1(c) shows the RHEED patterns during growth for a ScN film of thickness about 1200 Å. These patterns are fairly streaky, indicating smooth growth. The ratio of the line spacing along [100] to the line spacing along [110] is close to $\sqrt{2}$, indicating four-fold surface symmetry.

Detailed analysis of the RHEED patterns can be used to estimate the in-plane lattice constant of the film surface. This is done by dividing the spacing between the first-order diffraction lines for the ScN [Fig. 1(c)] by the spacing between the first-order lines for the MgO substrate [Fig. 1(b)]. For the 1200 Å thick sample, we get a ratio of about 1.04, 2.5% less than the ratio of the expected bulk lattice constants for ScN and MgO at 800 °C, 1.065.[5,8] For thicker films ($\geqslant$2000 Å and grown with higher Sc flux), we have measured ratios which are very close to the expected bulk ratio.

Figure 2 shows XRD spectra for two films—one about 1200 Å thick and the other about 2400 Å thick. The two spectra have been normalized to the height of the ScN (002) peak which occurs near 40°. The peak in each spectrum near 43.1° is the MgO (002) peak. No ScN (111) peaks (which would be at 34.5°) are observed for these or for any of our films grown on MgO(001). We conclude that rf-MBE growth on MgO(001) results in single oriented ScN(001).

By measuring the positions of the ScN (002) peaks in comparison to the MgO (002) peaks, we calculate the perpendicular lattice constants for these two films. In the case of the thinner film, we get a value of 4.48 Å, slightly smaller than the expected value of 4.501 Å. For the thicker film, the ScN(002) peak gets closer to 40.0°, giving a perpendicular lattice constant of about 4.51 Å, slightly larger than the expected bulk value.

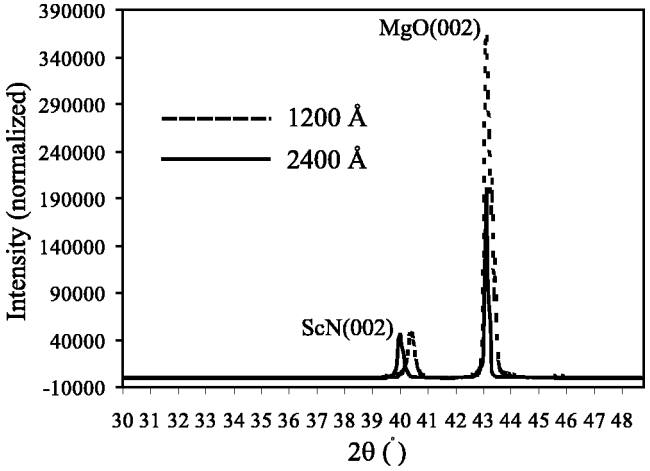

FIG. 2. 2θ x-ray diffraction spectra for two different ScN films grown on MgO(001). Neither film shows any (111) peaks.

Atomic force microscopy images of the ScN(001) films clearly reveal a plateau-pyramid morphology, as shown in Fig. 3. For this 1 μm$\times$1 μm image, one observes numerous plateaus with square shapes as well as many pyramids which are four-sided. The edges of these plateaus and pyramids are along $\langle 100 \rangle$ directions of the film which also coincide with the $\langle 100 \rangle$ directions of the substrate.

The pyramids have the same (001)-orientation as the plateaus. If they were (111)-oriented, we would expect to see three (001) facets and a (111) peak in XRD—but we do not. In fact, the sides are gently sloping, with typical apex angles of about 165°. Moreover, STM images reveal closely spaced steps on the sides of the pyramids. We believe the pyramids are centered on dislocations in the film. Assuming this, and counting the number of pyramids within the 1 μm^2 image of Fig. 3, we estimate a dislocation density of $\sim 10^9/\text{cm}^2$.

As seen in Fig. 1(c), the RHEED patterns for ScN(001) show only 1$\times$1 symmetry. This is expected since ScN has the rock-salt structure, and therefore the ionic character of the bonding will tend to suppress charge transfer, thus pre-

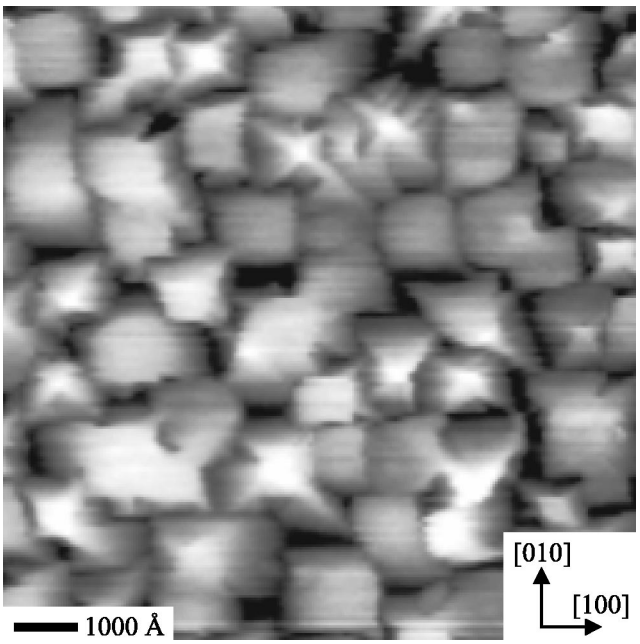

FIG. 3. Atomic force microscopy image of ScN(001) grown on MgO, illustrating the plateau-pyramid morphology. The gray scale range is 89 Å.

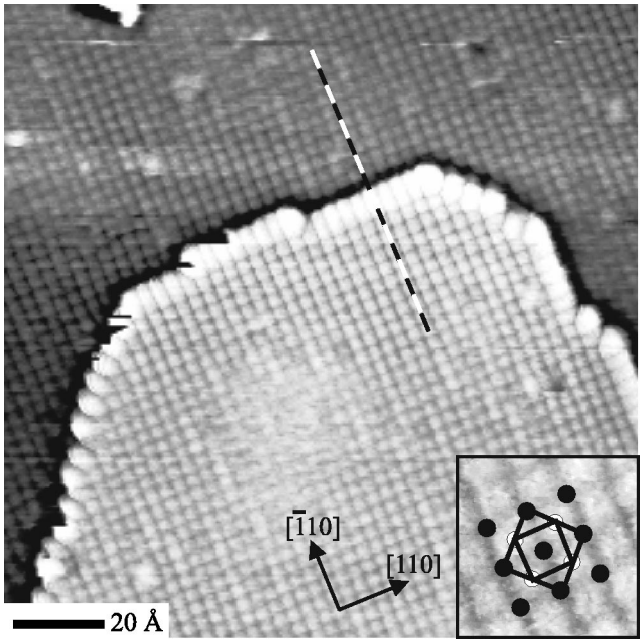

FIG. 4. Scanning tunneling microscopy image of plateau region on ScN(001). The image was acquired at a sample bias of -0.5 V and a tunneling current of 0.08 nA. The enhancement at the step edge is due to a local background subtraction. The inset is an expanded view of the surface acquired with a sample bias of -1.0 V and a tunneling current of 0.2 nA. A model of the rock-salt surface lattice is fit to the data.

venting reconstructions. Shown in Fig. 4 is a STM image of the ScN surface showing atomic resolution. The square 1×1 periodicity is clearly evident. The inset shows a magnification of the surface with a simple overlay for the rock-salt lattice. The larger square indicates the conventional surface unit cell, having an atom at the face center and sides along $\langle 100\rangle$. The smaller square inside, rotated by 45°, is the primitive surface unit cell whose sides are aligned with the atomic rows observed in the image. Therefore, the atomic rows in the image are along $\langle 110\rangle$.

The two terraces in the image are separated by a single step. The measured height of this step is very close to 2.25 Å,[12] or half the lattice constant. By sighting along the dashed line crossing the step, one can see that the atomic rows on the lower terrace are shifted by half the row spacing along the [110] direction compared to the atomic rows on the upper terrace. This shift is due to the fact that adjacent (001) planes of the rock-salt lattice are offset by $a/2$ along the [100] direction.

A single (001) lattice plane of the rock-salt structure contains an equal number of N and Sc atoms. If we assume that the surface structure is similar to the bulk truncation, then our STM image should correspond to one of the two sublattices (Sc or N). Since the STM image of Fig. 4 was acquired with a sample bias of -0.5 V, one possibility is that we are imaging the N atoms (filled states). However, dual bias images obtained at $+1$ and -1 V showed only a small relative shift, much less than the expected $a/2$. More work is needed to clearly distinguish the two expected sublattices.

While this letter has not presented data on the optical properties of these MBE-grown ScN films, from visual inspection, the films have a reddish or rusty color when white light is shined through them, consistent with an absorption near 2.2 eV. Luminescence and optical transmission measurements are currently being performed to investigate in detail the optical properties.

In conclusion, we have investigated the growth of ScN by rf MBE. We find that well-oriented ScN films can be grown which take on the orientation of their substrate. While (110) and (111) orientations have rough surfaces, (001)-oriented ScN can be grown smooth, which has been shown by RHEED, AFM, and STM data. For growth on MgO(001), we find only (001)-oriented ScN. We have shown atomically smooth terraces separated by single steps of height 2.25 Å, half the lattice constant of ScN. Work is underway to clarify the detailed surface structure, to understand the dependence of the film properties on the Sc flux during growth, and to measure the optical properties of these films for different MBE growth conditions.

The authors gratefully acknowledge the contributions of Megan Krejny and Marcus Legros for their construction of essential equipment used in this study, and Bethany Revill, who helped with AFM imaging and cataloguing of some of the data. The authors also thank the Office of Naval Research for supporting this work.

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