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Epitaxial GaN Thin Films Prepared by Polymer-Assisted Deposition

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Epitaxial GaN thin films have been deposited on (0001) sapphire substrates by a chemical solution approach of polymer-assisted deposition. The films are smooth with no detectable cracks or pores, as observed by scanning electron microscopy and atomic force microscopy. Microstructural studies by X-ray diffraction and transmission electron microscopy show that the GaN films have a hexagonal structure with an epitaxial relationship between the film and the substrate of $(0001)_{\text{GaN}} \parallel (0001)_{\text{Al}_2\text{O}_3}$ and $[11\bar{2}0]_{\text{GaN}} \parallel [10\bar{1}0]_{\text{Al}_2\text{O}_3}$. The films with a room temperature resistivity of around $0.13 \, \Omega \cdot \text{cm}$ exhibit photoluminescence characteristic of wurtzite hexagonal GaN.

1. Introduction

Tremendous efforts have been devoted to epitaxially grow GaN films, since GaN is one of the most attractive materials for high-efficiency light-emitting diodes and lasers.^{1,2} Sapphire (Al_2O_3) is the most widely used substrate for the growth of wurtzite GaN. In general, the difficulty in heteroepitaxial growth of high-performance nitride films lies in the large mismatches in either lattice parameters or thermal expansion coefficients between the film and the substrate.³ The most common and successful techniques for the growth of epitaxial GaN films are metalorganic chemical vapor deposition (MOCVD) and molecular-beam epitaxy (MBE).^{4–13} MOCVD uses metalorganic precursors, such as trimethylgallium or triethylgallium, at reduced pressure to form GaN at high temperature, where nitrogen and hydrogen are typically used as the carrier gas.^{4–11} The MBE method generally uses metallic gallium and molecular nitrogen (plasma-enhanced or excited by electron cyclotron resonance) as material sources to form GaN.^{12,13} An alternative approach for the growth of thin films is chemical solution deposition in which a nonvolatile precursor solution is deposited by spin- or dip-coating onto a single-crystal substrate.¹⁴ The potential advantages of this technique are the low cost, easy setup, and coating of a large area. There have been some reports on the growth of GaN films by chemical solution deposition.^{15–24} These films have been successfully used as buffer layers for the growth of GaN films using MOCVD.¹⁵ However, much more effort is needed to make it a viable approach for the growth of GaN, since the films deposited by the chemical solution method were often noncontinuous, leading to porous or cracked

surfaces.^{15–22} In this paper, we report the growth of epitaxial hexagonal GaN films with smooth surface morphology from polymer-assisted deposition (PAD). In the PAD process, stable metal–polymer solution was used as the film precursor, in which the polymer not only controls the solution viscosity but also binds the metal ions to form a homogeneous solution.^{25,26}

2. Experimental Section

In the PAD process, the procedures to form nitride films consist of the following two steps: (1) the formation of a homogeneous metal polymeric liquid precursor by binding polymer with metal ions and (2) the ammonolysis of the coated films in flowing ammonia gas to yield the metal nitride films. To form a Ga–polymer solution, 2 g of gallium chloride was dissolved in 2 g of polyethyleneimine (PEI, BASF Corporation of Clifton, NJ) in 10 g of ethanol. After removing unbound ions by Amicon filtration, the final Ga concentration of 156 mM was determined by using a Varian Liberty 220 inductively coupled plasma atomic emission spectrometer (ICP-AES). The solution was spin-coated onto (0001) sapphire substrates at 2000 rpm for 30 s. The films were then heated in ammonia gas at 510 °C for 2 h with a ramping rate of 1 °C/min and then annealed in ammonia gas at 900 °C for 1 h with a ramping rate of 10 °C/min. Films with a thickness in the range of 35–45 nm were obtained from one spin-coat. Thicker films could be deposited by multiple spin-coats.

X-ray diffraction (XRD) was used to characterize the crystal structure of the films. The surface morphology of the films was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The microstructure of the films was analyzed by transmission electron microscopy (TEM). Fourier transform infrared (FTIR) absorbance was taken using a Nicolet spectrum. The electrical resistivity (ρ) was measured from 5 to 300 K using a standard four-probe technique by a Quantum Design Physical Properties Measurement System (PPMS).

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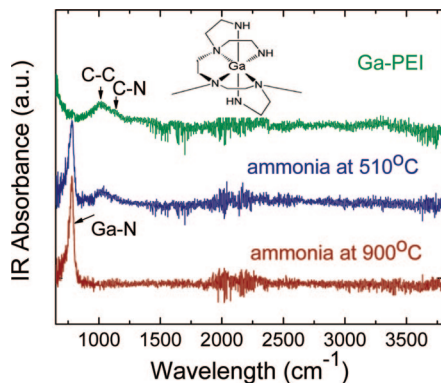


Figure 1. FTIR absorbance spectra of the Ga-PEI precursor film at room temperature, the precursor film annealed in ammonia gas at 510 °C, and the precursor film annealed in ammonia gas at 900 °C, respectively. Inset shows the putative structure of Ga metal ions bound to PEI.

3. Results and Discussion

Figure 1 shows FTIR absorbance spectra of the films of Ga-PEI precursor at room temperature, annealed in ammonia gas at 510 °C, and annealed in ammonia gas at 900 °C, respectively. The inset shows the putative structure of Ga metal ions bound to PEI. It is clear that the Ga-PEI precursor has stretching bands associated with C-C and C-N from PEI. On the other hand, the Ga-N band in the Ga-PEI precursor is extremely weak. After annealing the precursor films at 510 °C in ammonia gas, the sharp Ga-N bond at 780 cm^{-1} appears. The decrease in the intensity of C-C and C-N bonds indicates that PEI undergoes thermal depolymerization, although this process does not remove polymer completely at this temperature. The presence of only a Ga-N bond after annealing the film in ammonia gas at 900 °C implies the full formation of GaN. The absence of other stretching bands, compared with the precursor film, is reasonable, considering that PEI can be completely depolymerized at high temperature when the precursors are treated in different environments.²⁶

Figure 2 shows the XRD θ - 2θ scan, rocking curve, and ϕ -scans of a GaN film on sapphire substrate annealed in ammonia gas at 900 °C. Only (0002) peak from hexagonal GaN is observed, indicating that the film is preferentially oriented along the c -axis perpendicular to the substrate surface. The full width at half-maximum of the (0002) rocking curve is 0.61°. From the d -spacings of the (0002) and (10 $\bar{1}$ 2) diffraction peaks, the lattice parameters of the epitaxial GaN film were determined to be $a = 3.17$ Å and $c = 5.19$ Å. As compared to $a = 3.189$ Å and $c = 5.185$ Å of bulk GaN,⁴ the strain makes the in-plane lattice parameter of the GaN film slightly smaller and the out-of-plane lattice parameter slightly larger. The in-plane orientation between the film and the substrate was determined by XRD ϕ -scans from (10 $\bar{1}$ 2) GaN and (10 $\bar{1}$ 4) sapphire, respectively. Three peaks are observed for sapphire, whereas six peaks are observed for hexagonal GaN with 30° rotation in-plane to the sapphire substrate. The epitaxial relationships between the film and the substrate can be described as (0001)_{GaN}|| (0001)_{Al₂O₃} and [11 $\bar{2}$ 0]_{GaN}|| [10 $\bar{1}$ 0]_{Al₂O₃}, consistent with the GaN films on sapphire grown by other techniques.

Different mechanisms to form GaN powders from a solution approach have been proposed.^{27,28} Generally, the mechanisms for the formation of GaN are mainly controlled by the precursors. If Ga₂O₃ is used as the precursor to form GaN, Ga₂O₃ is first reduced to Ga₂O by reacting with decomposed ammonia (such as NH₂, NH, N₂, and H₂). Ga₂O then further reacts with

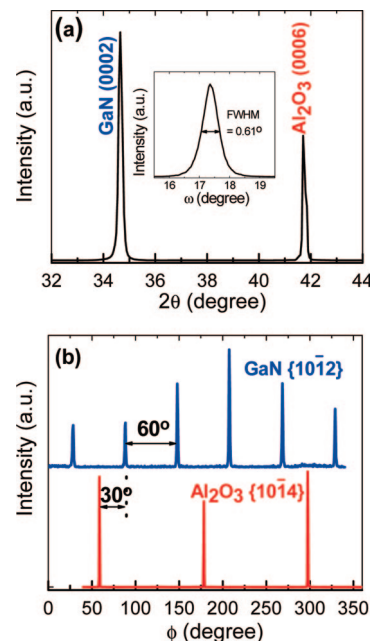


Figure 2. XRD patterns: (a) θ - 2θ scan of GaN film on sapphire. Inset shows the rocking curve of (0002) reflection; (b) ϕ -scans from (10 $\bar{1}$ 2) reflection of GaN and (10 $\bar{1}$ 4) reflection of sapphire.

ammonia or amine species (NH₂ and NH) to form GaN.^{20,27} On the other hand, if gallium dimethyl amide (Ga-N(CH₃)₂) is used as the precursor, it will react with ammonia in a transamination or deamination process to yield gallium imide Ga(NH)_x. Upon further heat treatment, GaN is formed from gallium imide with the release of ammonia.²⁸ In the PAD process, it is possible that the formation of GaN happens through different routes due to the use of PEI in the precursor. First, the Ga-PEI precursor can react with ammonia to form GaN by the amine groups from ammonia decomposition at high temperature. Interestingly, we have observed the formation of single-phase epitaxial GaN films when the precursor films were annealed in 94% Ar with 6% H₂ at 900 °C. This indicates that the PEI in the precursor can provide enough N to form GaN.

The surface morphology and surface roughness of the films were analyzed by both SEM and AFM. All the films are dense and smooth with no detectable microcracks. Figure 3a shows an AFM phase image of a GaN film on sapphire. The GaN film has an average grain size (surface) of around 30 nm with a root-mean-square surface roughness of about 4 nm. Figure 3b shows the cross section high-resolution transmission electron microscopy (HRTEM) images of a hexagonal GaN film on sapphire. It is clear that the interface between the film and the substrate is flat. The corresponding selected area electron diffraction (SAED) pattern (insert in Figure 3b) confirms the epitaxial growth of hexagonal GaN film on sapphire, evidenced by the distinguished diffraction dots from the film and the substrate. The epitaxial relationships between the film and the substrate deduced from the SAED pattern are consistent with the XRD analysis.

It is known that the lattice mismatch between GaN and substrate leads to high density dislocations that affect the electronic and photoluminescence properties of GaN. It is interesting to note that GaN films by PAD were more conductive when the films were annealed in Ar/H₂ gas. On the other hand, the films were highly resistive when they were annealed in ammonia gas. Figure 4 shows the temperature dependence resistivity of a GaN film on sapphire annealed in Ar/H₂ gas by

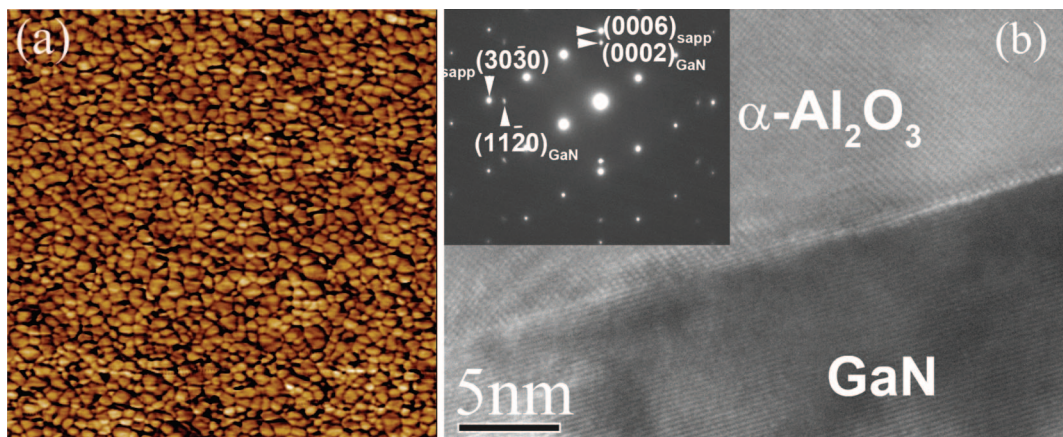


Figure 3. (a) AFM phase image ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of GaN film on sapphire; (b) cross section HRTEM image of a hexagonal GaN film on sapphire. Inset shows the SAED patterns taken from the interface between the film and the substrate.

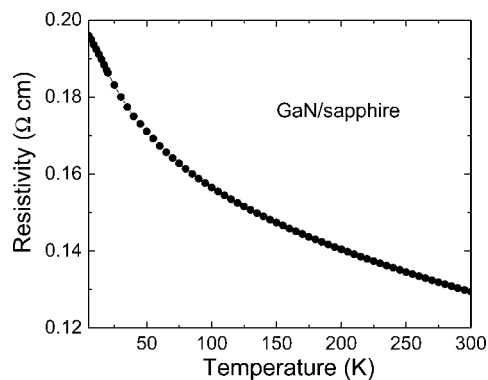


Figure 4. Temperature dependence of resistivity of a GaN film on sapphire.

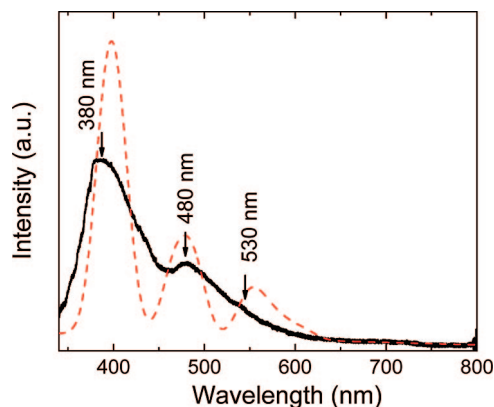


Figure 5. Room temperature PL spectrum of a GaN film on sapphire. The dashed line (red) shows the fitting peaks to the experimental results.

a four-probe technique. The GaN film is conductive with a room temperature resistivity of around $0.13\ \Omega\cdot\text{cm}$. The room temperature Hall measurement indicates its n-type conductivity with a carrier concentration of $2.1 \times 10^{20}\ \text{cm}^{-3}$ and an electron mobility of $2\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$. The carrier mobility, compared with the GaN films deposited by the MOCVD and MBE, is still relatively low. However, the demonstration of such epitaxial films with such carrier mobility by a chemical solution approach is a big step forward for practical applications.

Figure 5 shows the room-temperature photoluminescence (PL) spectrum of a GaN film on sapphire with the fitting peaks (red dashed line). Band edge emission is clearly observed centered at 388 nm, which is consistent with the band gap (3.4 eV) of

hexagonal GaN. The broad peak can be due to the shallow donor–acceptors, the conduction band acceptor recombination, and the strain from the lattice mismatch. The defect band observed at 480 nm is assigned as the aquamarine band,²⁹ indicating a slight Ga excess within the films. The shoulder present at 530 nm can come from different defects. For example, oxygen impurities can enhance this signature, as observed in the GaN powders and films.^{18,27,28} We believe that these impurities contribute to both the broadened band edge and defect PL features in our films. We would like to point out that our PL results compare well with luminescence results reported for GaN prepared by other chemical solution methods.^{7,20,27,28}

4. Conclusions

In conclusion, epitaxial hexagonal GaN films on sapphire substrates with smooth surface morphology have been produced by polymer-assisted deposition using a stable metal–polymer precursor. The formation of GaN after postannealing the Ga-PEI precursor films in either ammonia or Ar/H_2 indicates that PEI in the precursor can provide enough N to form GaN. The successful growth of GaN films with a carrier concentration of $2.1 \times 10^{20}\ \text{cm}^{-3}$ and an electron mobility of $2\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ by a polymer-assisted deposition indicates that chemical solution deposition can be an alternative approach for epitaxial nitride films.

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