High Quality Transferable AlN Thin Film by PLD

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Abstract. AlN thin film was epitaxial grown on c-plane sapphire substrate by pulsed laser deposition. To reduce structural defects from largely lattice mismatched substrate, MgO or ZnO buffer layer was inserted between AlN and sapphire. Crystal structure and surface morphology of as prepared AlN were characterized by XRD, AFM, and SEM. It was found that buffer layers significantly improve crystalline quality of AlN, especially using ZnO. Furthermore, a general and steady wet chemical process was developed to selectively etch away ZnO layer, so that high quality free-standing AlN thin film was obtained. This film could be transferred onto any other host substrates such as Si, quartz, etc. Moreover, with no clamping effect from the substrate, the as-prepared free-standing AlN thin films may find potential applications in high sensitivity piezoelectric devices, flexible wearable detectors and so on.

1. Introduction

Aluminium nitride (AlN) is a wide bandgap semiconductor with a variety of outstanding physical and chemical properties, which make it one of the most promising next-generation semiconductor materials for several applications. With its wide bandgap of 6.2 eV[1], high electrical resistivity, high temperature stability, and high breakdown voltage, AlN can be used to fabricate power devices. Thin films of AlN are commonly exploited to manufacture optoelectronic devices covering wavelength range from visible spectral to deep ultra-violet. Moreover AlN exhibits high sound and piezoelectricity that make it suitable candidate for resonators and surface acoustic wave devices [2]. And AlN is a suitable buffer layer not only for GaN but also for SiC with similar crystal structure and lattice mismatch as little as 2% [3].

Since high quality single crystal AlN had yet been successfully fabricated, several deposition techniques were used to prepare thin films of AlN, for instance, magnetron sputtering, MOCVD, MBE and PLD. Compared to those reactive deposition techniques, PLD is a physical process with low cost and high efficiency, so it remains a challenge to enhance the activity of N element and improve the quality [4]. It was reported that introducing NH3 or N plasma during the deposition can result in better epitaxial quality of AlN [5]. In this paper, N components ablated by laser were found remaining active in high vacuum, based on this result, quality of AlN film was further improved by inserting MgO or ZnO buffer layer. More importantly, the buffer layer can be selectively etched in solution and AlN film was lifted off from original substrate and transferred onto any other substrate, which provided a versatile way to fabricate high quality free-standing semiconductor nanosheets on large scale with various potential applications.

2. Experiment

Epitaxial AlN films were deposited through a standard PLD process. Single crystalline c-plane sapphire was used as substrate and temperature was up to 600°C during deposition. Laser energy density varied from 1 J/cm² to 3 J/cm² for the pre-deposition of MgO or ZnO and deposition of AlN. After finishing deposition, N2 gas was introduced into the chamber and the films cooled down to room temperature.

MgO or ZnO inserted between AlN and sapphire substrate also acted a sacrificial layer to transfer AlN film onto any substrate. PMMA photoresist was spread on AlN surface and after baked on the hot plate, the photoresist turned to be a firm and stable protector. Then these multilayers were immersed into (NH₄)₂SO₄ solution and the MgO or ZnO was selectively etched away. Free-standing AlN film
was lifted off from original substrate and transferred onto Si or transparent quartz, while acetone was used to dissolve PMMA. This process was graphically illustrated in Figure 1.

![Etching and transfer process of AlN film](image)

**Figure 1.** Etching and transfer process of AlN film

### 3. Results and discussion

#### 3.1 Multilayer structure

As prepared MgO or ZnO buffer layers between AlN film and sapphire substrate were carefully characterized. Figure 2a showed the cross section of AlN thin films with MgO layers on c-plane sapphire. Clear boundaries across the section were used to measure different thicknesses of layers on the interface. The deposition rates was evaluated as 200 nm AlN of 5000 pulses, 80 nm MgO of 5000 pulses, and 90 nm ZnO of 3000 pulses approximately. The thickness data were further verified by fitting results of ellipsometer. And from the top view of AlN film as Figure 2a, the surface morphology is extremely smooth with very low density of particulates.

![SEM cross section, top view, and XRD scans](image)

**Figure 2.** (a) SEM cross section, (b) top view of AlN/MgO/sapphire multilayer structure, (c) XRD 2θ-ω scans of different multilayer structures

Figure 2c was 2θ-ω scan result of as prepared multilayer samples by X-ray diffraction (XRD). The diffraction pattern showed that all the AlN films from different structure were highly c-axis oriented grown. And the MgO peak located at 35.9° was indexed to (111) orientation, and ZnO at 34.4° was of (002) orientation [6-7].

#### 3.2 Improvement of AlN with buffer layer

The MgO or ZnO layer of the multilayer structures was used to improve the quality of epitaxial AlN film as a buffer layer. Further researches have been carried out to reveal this. The full-width at half maximum (FWHM) of the ω-scans (rocking curves) by XRD could be used to describe the crystal quality of as deposited AlN films [8]. According to Tab.1, AlN film on ZnO buffer layer showed the narrowest FWHM of 0.74°, which indicating the highest degree of epitaxial quality, compared to the films on MgO buffer layer or bare sapphire substrate.
Table 1. FWHM of AlN films

|                | AlN (002) on Al2O3 (006) | AlN (002) on MgO (111) | AlN (002) on ZnO (002) |
|----------------|--------------------------|------------------------|------------------------|
| mismatch       | 13.2%                    | 4.4%                   | 4.1%                   |
| FWHM           | 2.01°                    | 1.02°                  | 0.74°                  |

Atomic force microscopy (AFM) was used to study the surface morphology of AlN films. A smooth surface is an essential requirement for various applications, for example, to provide a suitable substrate for epitaxial growth of GaN [9]. As shown in Figure 3, the direct grown AlN film without buffer layer showed a relatively rough surface with root mean square (RMS) roughness of 2.699 nm. By pre-depositing MgO buffer layer, the RMS roughness was significantly reduced to 0.5642 nm as shown in Figure 3b. And ZnO buffer layer can further improve the surface morphology of AlN films with RMS roughness as low as 0.2684 nm as shown in Figure 3c.

Figure 3. AFM images of AlN films surfaces (a) AlN/Sapphire (b) AlN/MgO/Sapphire (c) AlN/ZnO/Sapphire

3.3 Transferred AlN thin films

After the etching and transfer process of AlN thin film, XRD and SEM measurement were firstly carried out to characterize the quality of transferred AlN film on Pt coated Si substrate. As the XRD result shown in Figure 4a, only AlN (002) peak was found, indicating a c-axis crystal orientation AlN as same as the original one. Figure 4b and 4c were the top view of transferred AlN film by SEM. Smooth and uniform AlN nanosheets were found in large scale up to tens of micrometers, and the close-up SEM image in large magnification revealed a similar surface topography to the surface in Figure 2b. All these results confirmed that crystal structure and surface morphology of free-standing AlN films were maintained, and the process of etching and transfer was steady and highly reliable.

Figure 4. Characterization of AlN film transferred on Pt-Si (a) 2θ-ω result from XRD (b) SEM image in large scale (c) large magnification SEM image of a part

Optical transmittance spectra was also used to investigate the bandgap of transferred AlN film on full wavelength transparent quartz. Using the method proposed by Swanepoel, the absorption coefficient was calculated therefore the bandgap could be obtained from intercept of the plot [10].
shown in Figure 5, light transmittance remained above 80%, until strong absorption started at about 250 nm wavelength. The bandgap of transferred AlN film was then calculated from this spectra data to be nearly 6.0 eV, which is very close to the theory value 6.2 eV [11]. This result revealed that the transferred AlN film on transparent quartz may find promising applications in ultraviolet photoelectric field, as well as in other fields on respective substrate.

**Figure 5.** (a) photo of AlN film transferred on quartz (b) transmit of AlN film before transfer and after transfer (c) fitting of AlN optical bandgap

4. Conclusion

MgO or ZnO film was epitaxial growth on c-plane sapphire substrate as a buffer layer to improve the quality of PLD deposited AlN film. Through XRD, AFM, and SEM measurements, ZnO was found to be a better choice compared with MgO, since its similar crystal structure and less lattice mismatch towards AlN. And then ZnO was selectively etched away in (NH₄)₂SO₄ solution, releasing AlN layer from the original sapphire substrate. As obtained free-standing AlN film could be transferred onto any substrate. Researches of the films on Pt-Si and quartz substrate revealed that the AlN remained chemical stable, morphology steady and performance outstanding. This high reliable transferable AlN thin film provides a variety of promising applications, for instance, heteroepitaxial growth of GaN on any substrate, flexible and wearable ultraviolet photo detectors, clamping free SAW devices and so on.

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