Influence of the texture on Raman and X-ray diffraction characteristics of polycrystalline AlN films

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A B S T R A C T

The phonon modes of various polycrystalline aluminum nitride (AlN) films deposited by RF reactive sputtering with different textures have been studied. The comparison between Raman spectra and X-ray diffraction (XRD) patterns was performed to find out the influence of the texture on the phonon mode in polycrystalline AlN films. The E2 (high) mode and the A1 (TO) mode were observed in Raman scattering along the growth c axis. The orientation and the crystal quality of AlN film have a great impact on the phonon vibration. The deterioration of (002) orientation and the appearance of other orientations on the XRD pattern lead to enhancement of A1 (TO) mode in the film. The broadening of the Raman peaks can be associated with degeneration in crystal quality. Furthermore, by combining the energy shift of E2 (high) mode with the measured residual stress, the Raman-stress factor of the polycrystalline AlN films is found to be ~4.1±0.3×10−9 cm−1/Pa for E2 (high) phonon.

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1. Introduction

Aluminum nitride (AlN) is a refractory III–V compound semiconductor with hexagonal (wurtzite type) equilibrium crystal structure. The growth and properties of this material are under intensive theoretical and experimental investigations due to unique combination of its useful properties such as considerable hardness, high thermal conductivity, high electrical resistivity, good stability at high temperature, low coefficient of friction, and chemical inertness. The large range of its excellent properties has made AlN thin films useful in many applications, such as hard coatings with good wear resistant, electroacoustic devices, buffer layers for GaN epitaxial growth, dielectric layer in metal-insulator-semiconductor capacitors, and a buried dielectric layer in future silicon-on-insulator devices [1,2]. A variety of methods including molecular beam epitaxy [1–3], chemical vapor deposition [4,5] and reactive sputtering [6,7] have been used to grow AlN films. In wide studies X-ray diffraction (XRD) is a strict and widely used method to measure for crystallographic texture. However, a good film crystallographic texture per se is not a guarantee for high quality devices in many applications. For example, the stress is also important because it alters the energy band structure and influences the device performance. Raman scattering is widely used to detect the phonon vibrational properties and has been proven to be a practical method for studying stress of III–V semiconductor, including AlN. Most of the reports focused on the phonon mode in single crystal films [2–4], but there are few reports concerning the phonon mode of polycrystalline AlN films deposited by sputtering [8,9].

In this work the phonon modes of various polycrystalline AlN films deposited by RF (radio-frequency) reactive sputtering have been studied. XRD patterns and Raman spectra have been compared to find out the influence of the texture on the phonon mode in the films. Furthermore, the Raman-stress factor has been obtained by the energy shift of E2 (high) mode and the measured residual stress.

2. Experimental details

In this study, various thin AlN films were deposited using a RF reactive sputtering system (ANEIVA SPF-210F). The target was a 4-inch-diameter aluminum with 99.99% purity. The polished 1-inch-diameter Si

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target-to-substrate spacing</td>
<td>6 cm</td>
</tr>
<tr>
<td>Pressure</td>
<td>0.55 Pa</td>
</tr>
<tr>
<td>Ar flow rate</td>
<td>5 sccm</td>
</tr>
<tr>
<td>N2 flow rate</td>
<td>5 sccm</td>
</tr>
</tbody>
</table>
(001) was used as the substrate. The chamber was evacuated until the base pressure decrease to less than 3 × 10^{-5} Torr. High-purity argon was then introduced and pre-sputtered the target for 15 min before film deposition. The substrates were heated to 300 °C and kept at this temperature during the deposition process. The RF power was turned to 120 W to obtain various AlN films. The thicknesses of all films were controlled to about 1 μm. Other sputtering parameters were maintained at constant value in this study and summarized in Table 1.

The crystal structure and the orientation of the films were identified by XRD (BRUKER-AXS) at wavelength of 0.15418 nm (Cu Kα). The cross-sectional morphology of films was observed by field effect scanning electron microscope (FEI SIRION 200) under the operating voltage of 10 kV. The Raman measurement was performed at room temperature in the backscattering configuration at the film surface using the 488 nm line from Ar+ laser, and a double monochromator (Spex 1404) equipped with a charge coupled device detector was employed to analyze the scattered light. The profilometer (Veeco DekTak-6) was used to measure the radius of curvature of the substrate before and after the growth of the AlN films, from which we obtained the residual stress according to Stoney’s equation. Multiple measurements revealed good uniformity in the stress across the wafer.

### Table 1

<table>
<thead>
<tr>
<th>RF Power (W)</th>
<th>Intensity (arb. unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td></td>
</tr>
<tr>
<td>175</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Mode</th>
<th>Energy (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁ (TO)</td>
<td>120.2 ± 0.2</td>
</tr>
<tr>
<td>E₂ (high)</td>
<td>380.2 ± 0.2</td>
</tr>
<tr>
<td>E₁ (TO)</td>
<td>360.2 ± 0.2</td>
</tr>
<tr>
<td>A₁ (LO)</td>
<td>380.2 ± 0.2</td>
</tr>
<tr>
<td>E₁ (LO)</td>
<td>360.2 ± 0.2</td>
</tr>
</tbody>
</table>

### 3. Results and discussion

Fig. 1 displays the XRD patterns of AlN films prepared in four RF power levels. It is seen that the samples are all wurtzite hexagonal AlN structure. In the case of low RF power, two diffraction peaks are observed at 2θ around 33° and 36°, which correspond to the AlN (002) and (100) orientation, respectively. Increasing the RF power, the (002) peaks become stronger and sharper, while the (100) peaks become weaker. This means that the (002) texture of the AlN films is improved. The sample deposited at the RF power of 175 W exhibits a single and sharp (002) diffraction peak with the full-width at half maximum (FWHM) of 0.31°, which indicates preferred c axis orientation. By Scherrer’s formula, the calculated average gain size of the sample deposited at 175 W is about 27 nm. Highly parallel columnar crystals are observed from the cross-sectional morphology of the film (shown in Fig. 2). Fig. 3 shows the X-ray rocking curve of AlN films deposited at 120 W and 175 W. The FWHM value (10,64°) of the film deposited at 120 W is observed much larger than that of 175 W. The intensity of the rocking curve is also enhanced with increasing RF power. However, further increase of the RF power (higher than 175 W) fails to improve the (002) texture of the film. Generally, increase of the RF power not only enhances the sputtering yield, but also raises the kinetic energy of the particles in the plasma. As a result, the aluminum–nitride complex particles have sufficient kinetic energy to attach themselves to the substrate, hence providing the atoms with increased opportunities to move to the lowest energy state and to form a highly (002) oriented crystalline film structure. However, the substrates are strongly attacked when the RF power exceeds 175 W, resulting in surface damage and deterioration in the (002) texture [10].

According to the group theory, wurtzite AlN structure belongs to the space group $\Gamma_m^6 (\text{C}_6 \text{v} \text{mc})$ with two formula units per primitive cell. Theory analysis predicts the zone-center optical modes in the representation as $\Gamma=A_1+2B_1+E_1+2E_2$. The $A_1$, $E_1$, and two $E_2$ modes are Raman active, while the $B_1$ modes are inactive. Furthermore, the $A_1$ and $E_1$ modes are each split into the longitudinal optical (LO) and transverse optical (TO) components, thus creating the $A_1$ (LO, TO) and $E_1$ (LO, TO) modes [3]. The Raman phonon energy of the unstressed AlN film is summarized in Table 2.

The Raman spectra of the samples are shown in Fig. 4. All samples exhibit two major peaks around 660 cm⁻¹ and 610 cm⁻¹, which...
correspond to the $E_2$ (high) mode and the $A_1$ (TO) mode. The Raman spectrum of the substrate was also measured, but the silicon modes are not detected because the AlN films may be thick enough (> 1 μm). With the increase of RF power, the $A_1$ (TO) peak is found to weaken and the $E_2$ (high) peak becomes narrow. The spectrum for the film deposited at 175 W has the smallest $A_1$ (TO) peak and the narrowest $E_2$ (high) peak. The peak positions, FWHM and integrated area of the spectrum of each sample are compared. The degree of (002) orientation vibration in polycrystalline AlN films, the XRD pattern and the Raman spectrum of each sample are compared. The degree of (002) orientation resulting from the appearance of other orientation, the $A_1$ (TO) mode is enhanced and $R_{E2/A1}$ goes down. Generally, the $c$ axis of the wurtzite unit cell is defined as $z$ direction, and $x$ and $y$ are perpendicular to $c$ [2]. According to the rule of Raman scattering [2,3], the $E_2$ (high) vibrational mode is allowed by an electric field perpendicular to $z$ direction, while the $A_1$ (TO) mode is allowed by an electric field parallel to $z$ direction. The direction of propagation of laser light is parallel to the $c$ axis and the backscattering geometry is equivalent to $z$ (xy) in the grains with perfect (002) orientation. So the $E_2$ (high) mode is allowed and the $A_1$ (TO) mode is forbidden. However, for the grains with other orientations, the electric field has components parallel and perpendicular to the $c$ axis, which excite both of the $E_2$ (high) and the $A_1$ (TO) mode. Therefore the deterioration of (002) orientation and the appearance of other orientations lead to the enhancement of $A_1$ (TO) mode in the films as shown in Fig. 5.

Additionally, the broadening of the Raman peaks is the result of the phonon scattering caused by small grains, point defects, interfaces, and stress gradients [8]. In this experiment, we can reasonably assume that there is no strong stress gradients present in the films. The FWHM of $E_2$ (high) peaks measured in Fig. 4 varied from 13.5 to 39.7 cm$^{-1}$, which are intermediate between the 3 cm$^{-1}$ reported by Kuball et al. [11] for the highest quality AlN bulk crystals and the 50 cm$^{-1}$ reported by Perlin et al. [12] for highly defective crystals. It is well known that the crystal quality of the films can be described by the FWHM of the rocking curve of the films. Fig. 6 shows the FWHM of the $E_2$ (high) peaks as the function of the FWHM of the (002) peaks in the XRD patterns.

Fig. 6. The FWHM of the $E_2$ (high) peaks as the function of the FWHM of the (002) peaks in the XRD patterns.
atoms from the target hit the film with higher energy. This process, called atomic peening, in which atoms are attracted to the substrate, results in compressive residual stress \([13-15]\). At low RF power, the occurrence of tensile stress is suggested to be due to the existence of numerous grain boundaries \([16]\). The residual stress in the deposited film distorts the crystal unit cell, resulting in the variations on the energy of phonon vibration. Some authors \([2,8,11,17]\) have reported that the Raman peak spectra can be used to monitor the stress in the films. For the undoped AlN films under biaxial stress \((\sigma_8)\) perpendicular to the growth \(c\) axis, the shift in the phonon energy \((\Delta \omega)\) can be written as

\[\Delta \omega = k \sigma_8\]  

where \(k\) is the Raman-stress factor. Tensile (compressive) stress corresponds to \(\sigma_8 > 0 (\sigma_8 < 0)\).

Here we combine the energy shift of \(E_2\) (high) mode with the measured residual stress to obtain the Raman-stress factor. As shown in Fig. 8, the \(E_2\) (high) energy linearly decreases as the residual stress varied from compression (negative) to tensile (positive). The slope of the line provides the Raman-stress factor \(k\). The value is \(-4.1 \pm 0.3 \times 10^{-9} \text{ cm}^{-1}/\text{Pa}\), in accordance with the data reported in other papers \([2,8]\). The zero-stress energy obtained from these data \((657.6 \text{ cm}^{-1})\) is also in good agreement with the value listed in Table 2.

4. Conclusions

Raman spectra and XRD patterns were measured to study the influence of the texture on the phonon mode in polycrystalline AlN films. The \(E_2\) (high) mode and the \(A_1\) (TO) mode were observed in Raman scattering along the \(c\) axis. The orientation and the crystal quality of AlN films have a great impact on the phonon vibration. The deterioration of \((002)\) orientation and the appearance of other orientations lead to enhancement of \(A_1\) (TO) mode in the film. The broadening of the Raman peaks can be associated with degeneration of the crystal quality. Additionally, by combining the energy shift of \(E_2\) (high) mode with the measured residual stress, the Raman-stress factor of polycrystalline AlN films is found to be \(-4.1 \pm 0.3 \times 10^{-9} \text{ cm}^{-1}/\text{Pa}\) for \(E_2\) (high) phonon.

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References