Effect of GaN Buffer Layers on Deposition of AlN Films by DC Reactive Magnetron Sputtering

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Abstract：AlN films were prepared by DC reactive magnetron sputtering, and the effects of deposition conditions and GaN buffer layers on their qualities were also investigated. The crystal structure and surface morphology of films were characterized by X-ray diffractometer（XRD）and scanning electron microscopy（SEM）. The XRD results show that low pressure, short target-to-substrate distance and appropriate N_2 partial pressure can facilitate the（002）preferential orientation AlN films. With the increase of deposition time the full width half maximum of（002）diffraction peak for the films deposited on 50-nm-thick GaN buffer layers decreases drastically, but it was nearly unchanged for AlN films deposited on 1-μm-thick GaN films. The SEM measurements reveal that the grain size distribution of AlN film deposited on 1-μm-thick GaN films is much uniformer than on 50-nm-thick GaN buffer layers in the early stages of deposition, and with the increase of deposition time their grain size distributions can nearly reach the same.

Key words：AlN；GaN buffer layer；crystal structure；grain size

GaN 缓冲层对直流反应磁控溅射 AlN 薄膜的影响

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摘要：通过直流磁控反应溅射制备了氮化铝（AlN）薄膜，研究了沉积条件与氮化镓（GaN）缓冲层对薄膜质量的影响。利用 X-射线衍射仪（XRD）和扫描电镜（SEM）表征了 AlN 薄膜的晶体结构和表面形貌。XRD 研究结果表明，低工作压强、短靶距和适当的氮气偏压有利于（002）择优取向的 AlN 薄膜沉积。随着沉积时间的增加，沉积在 50 nm 厚的 GaN 缓冲层上的 AlN 薄膜的（002）面的衍射峰的半高宽急剧减小，而沉积在 1 μm 厚的 GaN 薄膜上的 AlN 薄膜的（002）面的衍射峰的半高宽几乎不变。SEM 测试结果表明：在沉积的初期，沉积在 1 μm 厚的 GaN 薄膜上的 AlN 薄膜的（002）面的晶粒大小分布比沉积在 50 nm 厚的 GaN 缓冲层上的 AlN 薄膜的均匀，而随着沉积时间的增加，它们的晶粒大小分布几乎趋向一致。

1 Introduction

In recent years, AlN has attracted more attentions due to its outstanding physical and chemical properties. AlN, a direct transition type semiconductor with a wurtzite crystal structure, has wide band gap, low electron affinity, high longitude sound velocity, high refractive index, high thermal conductivity, high thermal stability and high breakdown voltage[1-2]. These properties reveal that AlN has great potential applications in the fabrication of high frequency surface acoustic wave devices, field emission devices and magnetic devices, as well as in the package of high temperature and high power electronic devices[2]. In order to realize these devices, it is necessary to obtain high quality of polycrystal or preferential AlN films, as the polycrystal or preferential AlN films are enough to satisfy these needs. A series of methods such as ion beam sputtering (IBS), chemical vapor deposition (CVD), pulsed laser deposition (PLD) and reactive magnetron sputtering, have been empolyed to prepare AlN films on different substrates[3]. Reactive magnetron sputtering, however, presents many advantages over other methods in preparing AlN films. It can not only be compatible with microelectronic process due to low growth temperatures, but also can prepare AlN films at high growth rate and low cost. Although the great progress has been done by reactive magnetron sputtering, the film quality is still paid many attentions by researchers[4-6]. On the other hand, buffer layers are widely used to improve the quality of Ⅲ-nitrides films grown by metal organic vapor phase epitaxy (MOVPE)[1-2]. The buffer layers can not only supply more nucleation sites for the growth of Ⅲ-nitrides films, but also can decrease the lattice and thermal expansion coefficients between substrates and the films. However, to the best of our knowledge there are still few works concerning the effects of buffer layers on the deposition of AlN films by reactive magnetron sputtering.

In this work, AlN films were deposited on c-plane sapphire, GaN buffer layers and GaN films by DC reactive magnetron sputtering. The effects of GaN buffers on their crystalline structure and surface morphology have been studied in details with various analytical instruments, and the mechanism was also investigated.

2 Experiments

The AlN films were deposited by DC reactive magnetron sputtering on c-plane sapphire, GaN buffer layers and GaN films. The GaN buffer layers and GaN films used in the experiments were grown on c-plane sapphire by MOVPE, and their thicknesses are 50 nm and 1 μm, respectively. Trimethylgallium (TMGa) and ammonia (NH$_3$) were used as the gallium (Ga) and nitrogen (N) sources, and the carrier gas was hydrogen (H$_2$). The 50-nm-thick GaN buffer layer was directly grown on sapphire substrate at 550 ℃ after the sapphire substrate was thermally cleaned in H$_2$ ambient for 10 min at 1 100 ℃. Two-step growth was carried out to grow the 1-μm-thick GaN film. A low temperature GaN buffer layer with 50 nm thickness was firstly grown on sapphire substrate at 550 ℃ after the sapphire substrate was thermally cleaned in H$_2$ ambient for 10 min at 1 100 ℃. Once the low temperature GaN buffer layer was grown well, the temperature was raised to 1 150 ℃ to grow the 1-μm-thick GaN film. Then, they were diced into 10 mm × 10 mm sizes. Before loading into the vacuum chamber to prepare the AlN films, all GaN buffer layers and GaN films were cleaned sequentially in ultrasonic baths with acetone, alcohol and deionized water for 15 min to remove any organic and inorganic surface contamination, and then dried thoroughly by using N$_2$ gas. The pressure in vacuum AlN films growth chamber kept 6.4 × 10^{-4} Pa. In order to remove atmosphere gas impurities and any previous target surface contamination, pure aluminum (Al) target (99.99%) was pre-sputtered for 15 min in an Ar atmosphere. During the growth,

the substrate temperature and DC power were maintained 34 ℃ and 60 W, respectively.

The crystal structure of AlN films was characterized by X-ray diffractometry (XRD) (D8Focus, Bruker, Germany). The scanning electron microscopy (SEM) (HTTACHI S-4800, Japan) was used to study the grain size and surface morphology of these films.

3   Results and Discussion

In order to obtain the optimized experimental parameters, AlN films are firstly deposited on sapphire substrates by adjusting various experimental parameters such as working pressure, target-to-substrate distance and N_2 partial pressure. The characterization of crystal quality for all films is performed by XRD, and the results are shown in Fig. 1.

Fig. 1 (a) showed the XRD patterns of AlN films deposited at various target-to-substrate distances. From the figure it can be observed that with the increase of the distance, the preferential orientation of AlN films can be transformed from the (002) orientation to the (100) orientation, and the film deposited at the distance of 2 cm has the smallest full width half maximum (FWHM) of (002) diffraction peak. The effects of working pressure and N_2 partial pressure on the crystal structure of AlN films are presented in Fig. 1(b, c). The results reveal that the low and high working pressure are respectively favorable to the (002) and (100) preferential growth, and either the shortage or excess of N_2 partial pressure can lead to bad crystal AlN films. These phenomena can be attributed to the following facts[7-8]. In the process of Al and N atoms bonding to AlN molecules, the valence electrons of Al and N atoms according to Pauling rule form four sp^3-hybridized orbitals respectively. The N atoms have three partially filled orbitals and one completely filled orbital, whereas the Al atoms have three partially filled orbitals and one empty orbital. Then the completely filled orbital of N atoms overlaps with the empty orbital of Al atoms to form the bond known as the B_2 bond along the *c*-axis in the hexagonal wurtzite AlN structure, and for the other three partially
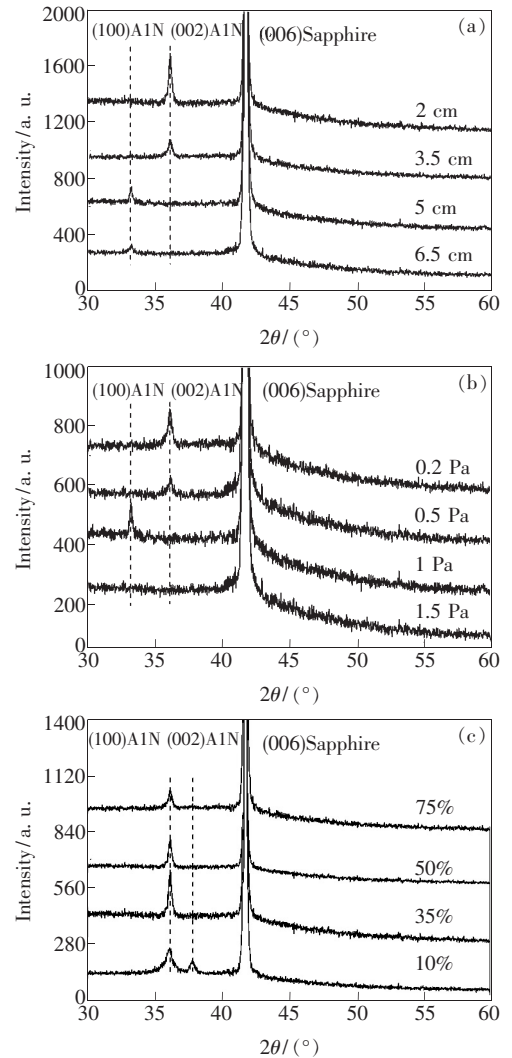

Fig. 1   The XRD patterns of AlN films deposited on sapphires by adjusting various experimental parameters： (a) target-to-substrate distance, (b) working pressure, and (c) N_2 partial pressure.

filled orbitals of N and Al atoms each two of them respectively overlap with each other to form the other three equivalent bonds which are usually labeled as the B_1 bond in the hexagonal wurtzite AlN structure. The nature of the B_1 bond is more covalent, whereas the B_2 bond is more ionic. This indicates that the bond energy of B_2 bond is smaller than that of the B_1 bond. After observation of the hexagonal wurtzite structure it can be found that the (100) plane is only composed of the B_1 bond, whereas the (002) plane consists of not only the B_1 bond but also the B_2 bond. This indicates that the (002) plane in the hexagonal wurtzite structure possesses the lowest surface energy. Consequently, increasing the mobility

of particles absorbed on the substrate surface can facilitate the growth of (002) preferential orientation AlN films. In the experiments the energy of particles reaching the substrate surface becomes high with the decreased target-to-substrate distance due to less collision between these particles, *i. e.* the mobility of the particles can be enhanced with a decrease of the distance. Besides, the mean free path of the reactive particles becomes large with the decreased working pressure, and the particles reaching the substrate surface can experience less collision between these particles. This indicates that with the decrease of working pressure the energy of the particles reaching the substrate surface increase, and the mobility of these particles is enhanced. This is the reason that preferential orientation of AlN films can be transformed from the (100) plane to the (002) plane with the decreased working pressure or the target-to-substrate distance. Lastly, during the deposition of AlN films the shortage of N_2 partial pressure in the sputtering ambience can not only result in the nonstoichiometric AlN films but also generate nitrogen vacancies and Al interstitials in these AlN films, whereas too high N_2 partial pressure can also cause the compound formation on the target surface, which known as the target poisoning has the negative influence on the yield and energy of particles. Therefore, either the shortage or excess of N_2 partial pressure can lead to a bad crystal AlN films as shown in Fig. 1(c).

Fig. 2 (a, b) showed XRD patterns of AlN films deposited on 50-nm-thick GaN buffer layers and 1-μm-thick GaN films for different deposition times. In order to obtain differences between these films from the results of XRD, the Gauss function is used to fit the profile of (002) diffraction peaks, and the results are shown in Fig. 2(c). From the figure it can be clearly found that with an increase of deposition time the FWHM of AlN films deposited on 1-μm-thick GaN films is nearly constant. However, the FWHM of AlN films deposited on 50-nm-thick GaN buffer layers decreases drastically with the deposition time, and its value is nearly equal to the FWHM value of AlN films deposited on 1-μm-thick

GaN films for the sample of 30 min. It is known that the FWHM obtained from the result of XRD relates to finite crystallite sizes, stacking faults, microtwins, stresses, dislocations, concentration variations, which parameters have a strong dependence on the crystal quality of films[9]. This suggests that the crystal quality of the AlN films deposited on 50-nm-thick GaN buffer layers can be improved drastically with an increase of deposition time, whereas the crystal quality of the AlN films deposited on 1-μm-thick GaN films is nearly unchanged.

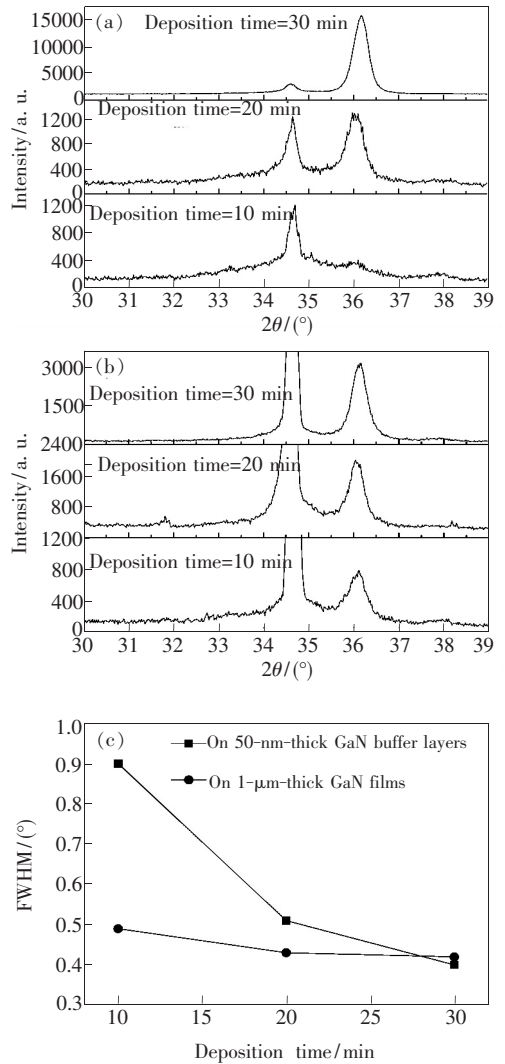In order to further identify the difference of AlN films deposited on GaN buffer layers and GaN films

Fig. 2 The XRD patterns of AlN films deposited on (a) 50-nm-thick GaN buffer layers, and (b) 1-μm-thick GaN films for different deposition time. (c) The FWHM of (002) diffraction peak of AlN films versus the deposition time.

the SEM were used to carry out the characterization of the films, and the results are shown in Fig. 3. It can be observed that the grain size distribution of AlN films deposited on 1-μm-thick GaN films is greatly uniformer than on 50-nm-thick GaN buffer layers in the early stages of deposition (for the deposition time of 10 min), and in the last stages of deposition (for the deposition time of 30 min) their grain size distributions are nearly the same. This suggests that with the increase of deposition time the grain size distribution of AlN films deposited on 50-nm-thick GaN buffer layers becomes uniform, and last their grain size can reach the same distribution to the grain size of AlN films deposited on 1-μm-thick GaN films. The great difference in the grain size distribution between the AlN films deposited on 1-μm-thick GaN films and 50-nm-thick GaN buffer layers can be attributed to the following factors. It is known that the film growth is related with not only the growth conditions but also the substrates. The 50-nm-thick GaN buffer layer consists of mixed cubic and hexagonal GaN with a high-degree-of stacking disorder and rough morphology, whereas the 1-μm-thick GaN film is only composed of hexagonal GaN with a low-degree-of stacking disorder and smooth morphology[10-12]. This indicates that the AlN nucleation distribution on the 50-nm-thick GaN buffer layer is very uneven in the early stages of deposition, and some amorphous AlN nuclei can even be easily formed. This is the reason why grain size distribution and crystal quality of AlN films deposited on 50-nm-thick GaN buffer layers is relatively uneven and low in the early stages of deposition. As shown in Fig. 3(a, b) and Fig. 2(c), with the increase of deposition time the nuclei with (002) preferred orientation can grow quickly and last cover the amorphous nuclei. Consequently, the crystal quality of AlN films deposited on 50-nm-thick GaN buffer layers can be improved drastically with the increase of deposition time, and last their grain size distribution and crystal quality are nearly the same to AlN films deposited on 1-μm-thick GaN films as shown in Fig. 3(c, d) and Fig. 2(c).
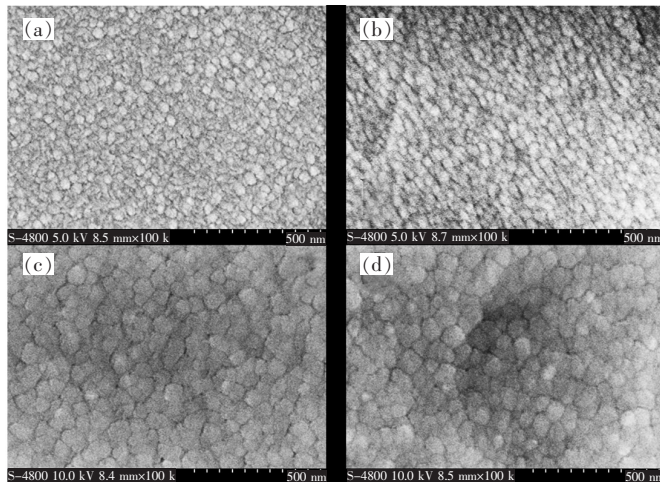

Fig. 3　The typical SEM images of AlN films deposited on (a, c) 50-nm-thick GaN buffer layers and (b, d) 1-μm-thick GaN films for deposition time of (a, b)10 min and (c, d) 30 min

4　Conclusion

In summary, the AlN films with the (002) preferential orientation were successfully prepared by DC reactive magnetron sputtering, and the effects of deposition conditions and GaN buffer layers on their quality were studied. Their crystal structure and surface morphology were characterized in details by XRD and SEM. The XRD results show that low working pressure, short target-to-substrate distance and appropriate N_2 partial pressure can facilitate the deposition of (002) preferential orientation AlN films. With the increase of deposition time, the FWHM of (002) diffraction peak for the

films deposited on 50-nm-thick GaN buffer layers decreases drastically, and it is nearly unchanged for AlN films deposited on 1-μm-thick GaN films. The SEM measurements reveal that the grain size distribution of AlN film deposited on 1-μm-thick GaN films is greatly uniformer than on 50-nm-thick GaN buffer layers in the early stages of deposition, and with an increase of deposition time their grain size distributions can nearly reach the same.

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