第33卷 第2期 发 光 学 报 Vol. 33 No. 2
2012年2月 CHINESE JOURNAL OF LUMINESCENCE Feb., 2012

Article ID: 1000-7032(2012)02-0227-06

Deposition of AlN Films on Nitrided Sapphire Substrates by Reactive DC Magnetron Sputtering

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Abstract: Aluminum nitride (AlN) films were prepared successfully on sapphire and nitrided sapphire substrates by reactive DC magnetron sputtering. The effect of nitridation of sapphire substrate on the growth of AlN films was studied. The films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and optical absorption spectrum. XRD patterns of AlN films exhibited a strong preferential *c*-axis orientation, and nitridation of sapphire substrate could improve the crystal quality of AlN films and also decrease the residual stress of films. But AFM results revealed that the grain size distribution of films deposited on nitrided sapphire substrates was not more homogenous than that of films deposited on sapphire substrates, and optical absorption results also showed nitridation of sapphire substrate nearly had no effect on the optical behavior of AlN films.

Key words: crystal structure; optical absorption; surface morphology
CLC number: O76 **Document code:** A **DOI:** 10.3788/fgxb20123302.0227

直流反应磁控溅射在氮化的蓝宝石衬底上制备 AlN 薄膜

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摘要: 通过直流磁控反应溅射装置,在蓝宝石(0001)衬底和氮化的蓝宝石(0001)衬底上成功制备了氮化铝(AlN)薄膜。利用X射线衍射仪、原子力学显微镜和双光束扫描分光计,研究了蓝宝石氮化对AlN薄膜结构、应力、晶粒尺寸、形貌和光学性质的影响。X射线衍射研究表明:制备的AlN薄膜具有较强的(0002)择优取向,蓝宝石衬底的氮化不仅能够改善AlN结晶质量,而且还可以减少薄膜的残余应力。但是,原子力学显微镜结果表明:在蓝宝石衬底上制备的AlN薄膜的晶粒大小分布比在氮化的蓝宝石衬底上制备的AlN薄膜的晶粒大小分布更加均匀。我们认为,蓝宝石衬底在氮化的过程中形成的AlN具有过多的位错和缺陷,正是这些位错和缺陷造成了在氮化的蓝宝石衬底上制备的AlN薄膜的晶粒大小分布的不均匀性。吸收光谱显示:蓝宝石衬底的氮化并没有对AlN薄膜的光学性质产生明显的改善。

收稿日期: 2011-09-02; **修订日期:** 2011-10-08
基金项目: 国家自然科学基金(51072196,51072195)资助项目
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关 键 词: 晶体结构; 光吸收; 表面形貌

1 Introduction

In recent years, AlN has attracted a lot of interest due to its outstanding physical and chemical properties. AlN is a direct transition type semiconductor with a band gap of 6.14 eV at room temperature (RT), it shows high breakdown voltage, ultra fast longitude sound velocity and high thermal stability, resulting a broad of applications on insulating layers, high frequency surface acoustic wave devices and high temperature electronic and optoelectronic devices[1-2]. A series of methods such as molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD), ion beam sputtering (IBS), pulsed laser deposition (PLD) and reactive magnetron sputtering (RMS), have been used to prepare AlN films on different substrates[2-4]. Among them, RMS presents many advantages over the other methods in preparing AlN films[1]. RMS is compatible with microelectronic process due to low growth temperatures. On the other hand, the RMS system is a simple apparatus, AlN films can be prepared at high growth rate and low cost. At 1971, Duchene fabricate AlN films by RMS and studied its properties[5]. Since then enormous efforts have been devoted to fabricating AlN films on different substrates by RMS and studying its properties, the effects of growth conditions on its properties[6-7]. Recently, Yao *et al.* successfully fabricated the single domain AlN films on (111) $SrTiO_3$ substrate by reactive RF magnetron sputtering[8], and Duquenne *et al.* also synthesized the thick single crystalline AlN films by reactive DC magnetron sputtering at low temperature on AlGaN/GaN layer grown on (0001) sapphire substrate by MOCVD[9]. These reports indicate that high quality AlN films can be prepared by RMS.

Nitridation of substrate is widely used to improve the quality of III-nitrides film grown by MOCVD[1,10]. First, the material formed on the surface of substrate after the nitridation can supply more nucleation sites for the growth of III-nitrides film, which makes the film surface more flat. Second, this material can also decrease the lattice and thermal expansion coefficients between substrate and film. It is expected that the quality of AlN film deposited by RMS can be improved by nitridation of substrate.

In this paper, AlN films were deposited on sapphire and nitrided sapphire substrates by reactive DC magnetron sputtering. The effect of nitridation of sapphire substrate on the grain size, residual stress, surface morphology and optical properties of AlN films were studied in detail with various analytical instruments, and the mechanism was also investigated.

2 Experiments

AlN thin films were deposited on (0001) sapphire and nitrided (0001) sapphire substrates by reactive DC magnetron sputtering. The nitrided sapphire substrates used in our experiments were obtained by exposing (0001) sapphire substrates to NH_3 atmosphere for 30 min at 1 100 ℃. All substrates, however, were cleaned ultrasonically with acetone and alcohol for 15 min, respectively, and then rinsed thoroughly in deionized water. During the growth, the substrate temperature (34 ℃), working pressure (0.45 Pa), distance of the target to the substrate (3.5 cm), Ar/N_2 ratio (4:5) and DC power (60 W) were maintained constant.

The crystalline structure of AlN films was examined with an X-ray diffractometer (D8Focus, Bruker, Germany), and the surface morphology was observed by an AFM (multimode, Veeco, American). The optical properties of AlN films were characterized by a dual beam scanning spectrophotometer (UV-3101PC, Shmadzu, Japan).

3 Results and Discussion

Fig. 1 shows the XRD patterns of AlN films deposited on sapphire and nitrided sapphire substrates with different film thickness. From these figures, we observed that the AlN (0002) diffraction peak only appears at 2θ of 36.10° in the scan range of 30° to

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50°, implying that AlN films with strong preferential *c*-axis orientation were prepared successfully in our experiments. By comparing these two figures, two significant differences can be observed. First, the (0002) diffraction peak of films deposited on nitrided sapphire substrates seems asymmetry and tends to broaden at the low-angle side, which is more obvious with the increase of film thickness [Fig. 1(b)]. This feature can not been observed in the (0002) diffraction peak of films deposited on sapphire substrates as shown in Fig. 1(a). Second, the film thickness is smaller than 400 nm, the crystal quality of films deposited on nitrided sapphire substrates seems much poorer than that of films deposited on sapphire substrates, just judging from the full width at half maximum (FWHM) of the (0002) diffraction peak. But the crystal quality of films deposited on nitrided sapphire substrates seems to be improved greatly with the increase of film thickness, and last seems little higher than that of films deposited on sapphire substrates.

In order to study the effects of nitridation of sapphire substrate on the grain size and residual stress of AlN films, we used the Lorentz function to fit the (0002) diffraction peak of all films. Fig. 2 shows the representative results of films deposited on sapphire and nitrided sapphire substrates around the (0002) Bragg angle. In Fig. 2(a), the (0002) diffraction peak of films deposited on sapphire substrates can be fitted accurately by using a single Lorentz function. However, two Lorentz functions are necessary to fit accurately the asymmetric broadening of the (0002) diffraction peak of films deposited on nitrided sapphire substrates [Fig. 2(b)]. The most intense Lorentz function, called function A, presents a maximum at approximately the same Bragg angle as the Lorentz function used to fit the (0002) diffraction peak of films deposited on sapphire substrates. The second Lorentz function, called function B, is considerably less intense than function A, and its maximum is located at a Bragg angle less than function A.

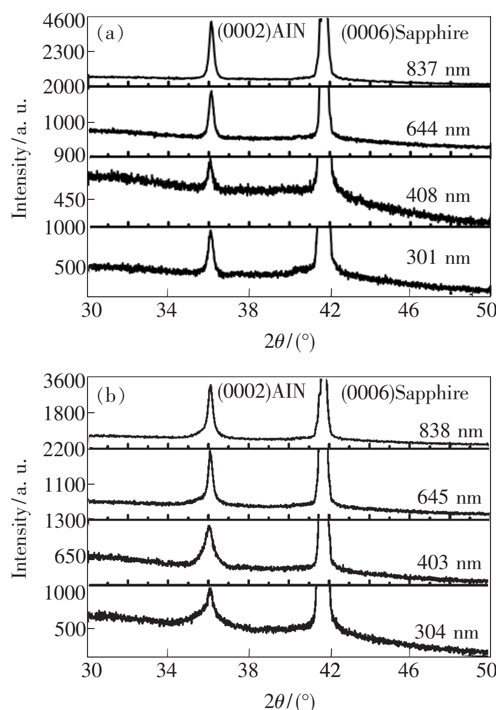

Fig. 1 XRD patterns of AlN films deposited on (a) sapphire and (b) nitrided sapphire substrates. The film thickness is indicated in patterns.

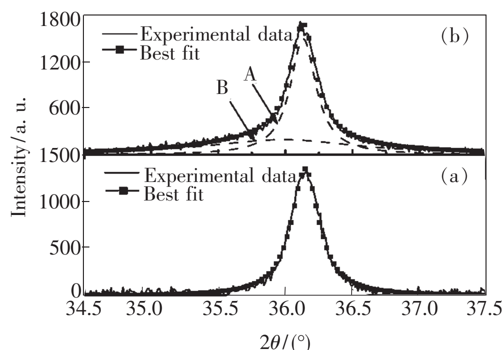

Fig. 2 The (0002) diffraction peak of AlN films deposited on (a) sapphire and (b) nitrided sapphire substrate. Film thickness is about 645 nm.

In order to study the origin of these two Lorentz functions, the XRD measurement for nitrided sapphire substrate was performed and the result is presented in Fig. 3. We find that an AlN layer is formed on the surface of sapphire substrate after the sapphire substrate is exposed in NH_3 atmosphere for 30 min at 1 100 ℃, and the FWHM of the (0002) diffraction peak is quite broad. The FWHM and maximum location of the (0002) diffraction peak of nitrided sapphire substrate and representative films deposited on nitrided sapphire substrates are shown in Table 2. It can be observed that the Lorentz function used to fit the (0002) diffraction peak of nitrided sapphire substrate nearly possesses the same

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FWHM and maximum location with the function B. So we can determine that the function B describes the (0002) diffraction peak of AlN layer formed on the surface of sapphire substrate after the nitridation prosess, and the other one describes the (0002) diffraction peak of AlN films deposited on nitrided sapphire substrates by reactive DC magnetron sputtering.

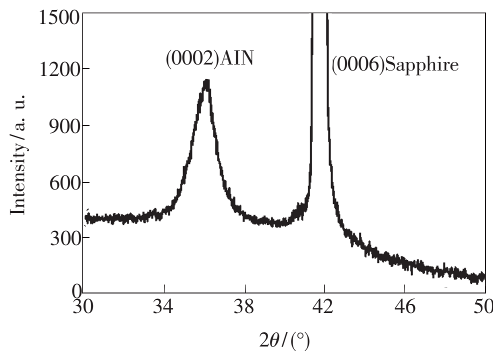

Fig. 3 The XRD pattern of nitrided sapphire substrate

Table 2 The FWHM and maximum location of Lorentz function using to fit the (0002) diffraction peak of (a) nitrided sapphire substrate and (b, c) AlN films deposited on nitrided sapphire substrate. (b) The function B, and (c) the function A. The film thickness is about 300 nm.

Kinds	FWHM/(°)	Maximum location/(°)
(a)	1.398	35.981
(b)	1.395	35.983
(c)	0.243	36.130

Fig. 4 plots the grain size and residual stress deduced from the above analysis as a function of film thickness. It can be observed that the residual stress of films deposited on sapphire substrates is higher than that of films deposited on nitrided sapphire substrates, and the grain size of crystallites of films deposited on nitrided sapphire substrates is bigger than that of films deposited on sapphire substrates. These results suggest that the nitridation of sapphire substrate can improve the crystal quality of AlN films and also decrease the residual stress of films. It is worth to note that the grain size and residual stress of films deposited on sapphire and nitrided sapphire substrates show different trends with the increase of film thickness. As shown in Fig. 4, the grain size and residual stress of films deposited on sapphire substrates increase with film thickness, indicating that the crystal quality of films deposited on sapphire substrates improved gradually with the film thickness. However, the grain size and residual stress of films deposited on nitrided sapphire substrates increase with the film thickness. This suggests that the crystal quality of films deposited on nitrided sapphire substrates nearly holds the line with an increase of film thickness.

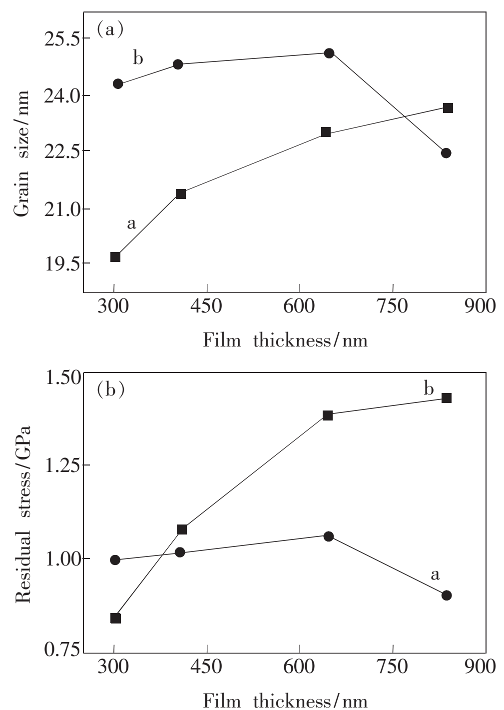

Fig. 4 The grain size and residual stress of films deposited on (a) sapphire and (b) nitrided sapphire substrates as a function of film thickness. The grain size of films is obtained by formula[4]: $\langle D_3 \rangle_v = \lambda/(W\cos\theta)$, where $\langle D_3 \rangle_v$ is the grain size of crystallites, W is the FWHM of the (0002) diffraction peak, θ is the Bragg angle and λ is the wavelength of Cu Kα (0.154 18 nm). The residual stress of films is obtained by formula[11]: $\sigma = [C_{13} - 0.5(C_{11} + C_{12})C_{33}/C_{13}]\varepsilon$, where σ is the residual stress, $C_{i,j}$ is the elastic constants and ε is the strain.

To further study the effects of nitridation of sapphire substrate on the growth of RMS AlN films, AFM operating in contact mode was used to study the surface morphology of films and the representative results are shown in Fig. 5. It can be observed

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that the grain size distribution of films deposited on sapphire substrates is more homogenous than the films deposited on nitrided sapphire substrates, and the grain size of crystallites of films deposited on nitrided sapphire substrates is bigger than the films deposited on sapphire substrates (Fig. 6a). This difference between films may be attributed to the fact that the AlN layer formed on the surface of sapphire substrate after the nitridation process has a lot of defects or dislocations, which can be proved by the XRD result of nitrided sapphire substrate (Fig. 3). The free energy of crystallites grown on these defects or dislocations is lower than that of crystallites grown on normal sites as the defects or dislocations benefit the relaxation of stress[12]. These crystallites would be expected to grow more rapidly, resulting in small crystallites in vicinity donating their atoms to these larger crystallites. That may be why the grain size of crystallites of films deposited on nitrided sapphire substrates is bigger than that of films deposited on sapphire substrates, and the residual stress of films deposited on nitrided sapphire substrates is smaller than that of films deposited on sapphire substrates.

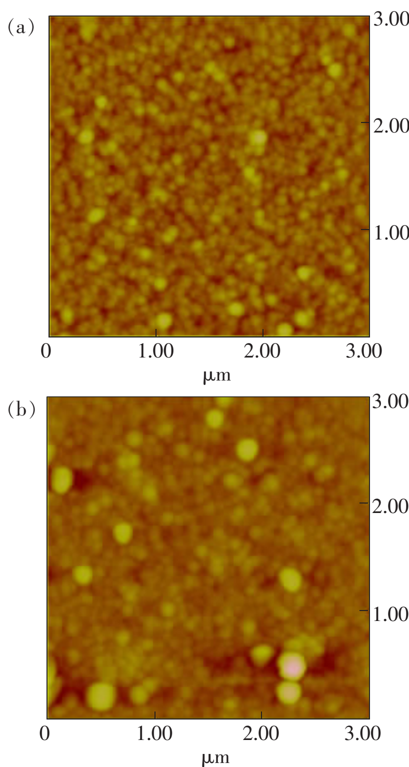

Fig. 5 The typical AFM images of AlN films deposited on (a) sapphire and (b) nitrided sapphire substrate. The filmthickness is about 645 nm.

The optical behavior of AlN films deposited on sapphire and nitrided sapphire substrates was determined by optical absorption spectrum, the results for films of about 300 nm are shown in Fig. 6. It can be observed that the films present excellent transparency, absorbing after 5.25 eV. We fitted optical absorption spectrum at the absorption edge and found the band gap of AlN films deposited on sapphire and nitrided sapphire substrates was 5.88 eV and 5.85 eV, respectively. This suggests that the band gap of our films is much smaller than that of normal AlN films (6.14 eV at RT). We calculated the variation of band gap, resulting from the tensile stress of films, and found that the effect of tensile stress on the band gap was too small to induce so great variation. We think the variation of band gap may origin from the defects such as grain boundaries or threading dislocations which may be determined mainly by deposition conditions such as the background pressure.

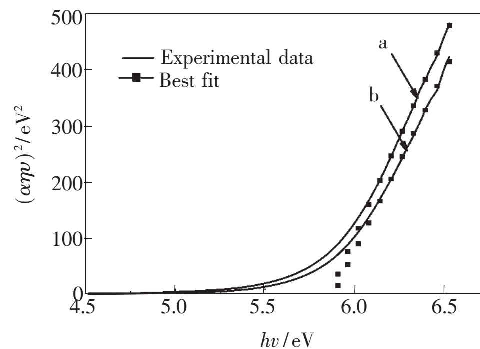

Fig. 6 The optical absorption spectra of AlN films deposited on (a) nitrided Sapphire and (b) sapphire substrate. The best fit was obtained by formula: $(\alpha h\nu)^2 = A(h\nu - E_g)$, where A is a constant, α is the absorption coefficient, $h\nu$ is the energy of excitation and E_g is the band gap energy.

4 Conclusion

In summary, AlN films were prepared successfully on sapphire and nitrided sapphire substrates by reactive DC magnetron sputtering. The effect of nitridation of sapphire substrate on the growth of AlN films was studied. From XRD studies, we found that all AlN films exhibited a strong preferential c-axis

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orientation, and nitridation of sapphire substrate could improve the crystal quality of AlN films and also decrease the residual stress of films. But AFM results revealed that the grain size distribution of films deposited on nitrided sapphire substrates was not more homogenous than that of films deposited on sapphire substrates, which many be attributed to the fact that the AlN layer formed on the surface of sapphire substrate after the nitridation process has a lot of defects or dislocations. Optical absorption results also showed nitridation of sapphire substrate nearly had no effect on the optical behavior of AlN films.

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