Journal of Crystal Growth 436 (2016) 62–67

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

AlN thin film grown on different substrates by hydride vapor phase epitaxy

M.S. Sun [a,c], J.C. Zhang [a,b,*], J. Huang [a], J.F. Wang [a,b], K. Xu [a,b,*]

[a] Platform for Characterization and Test, Suzhou Institute of Nano-tech and Nano-bionics, CAS, Suzhou 215123, China
[b] Suzhou Nanowin Science and Technology Co, Ltd., Suzhou 215123, China
[c] School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Article history:
Received 17 September 2015
Received in revised form
20 November 2015
Accepted 30 November 2015
Communicated by T. Paskova
Available online 14 December 2015

Keywords:
A1. AlN
A1. AFM
A1. XRD
A3. HVPE

ABSTRACT

AlN thin films have been grown on GaN/sapphire templates, 6 H-SiC and sapphire by hydride vapor phase epitaxy. The influence of growth conditions and substrates on the crystal qualities and growth mode has been investigated by X-ray diffraction (XRD) and atomic force microscopy (AFM). The results showed that the low pressure was favorable for high-quality AlN thin film growth around 1000 °C. The full-width at half-maximum (FWHM) of (0002) XRD of 200-nm AlN thin film grown on GaN/sapphire, 6 H-SiC and sapphire are 220, 187 and 260 arc s, respectively. While the corresponding counterparts of (10-12) are 1300, 662 and 2650 arc s, respectively. Both suggested that low dislocation density in AlN grown on 6 H-SiC. The morphology of AlN thin film on sapphire showed islands without coalescence initially, and then changed to be coalescent with atomic steps at 1200 nm. However, those for samples on 6 H-SiC and GaN/sapphire showed smooth surface with clear atomic steps at thickness of 200 nm. The result indicated different growth modes of AlN on different substrates. It was believed that the different lattice mismatchs between AlN and substrates led to the different crystal qualities and growth modes.

1. Introduction

AlN and AlGaN alloys have superior physical and chemical properties, such as wide direct bandgap, high melting point, higher temperature stability and good chemical stability and so on, which make them technologically important. As one of important applications based on these materials, deep ultraviolet light-emitting diodes (UV LED) are expected to be used in many fields, such as solid-state lighting, sterilization, medicine, and biochemistry. So more and more efforts have been devoted to this device and great progress has been made [1–5]. Despite the progress, the external quantum efficiency is still very low for LEDs with emission below 300 nm [6]. The reasons are complicated, including the weak confinement of carriers and the low hole-injection efficiency [7]. However, the most serious problem was the high defect level in the materials grown on foreign substrates, which limited both efficiency and reliability of the devices. The possible best approach for reducing the defect density is the use of low-defect AlN substrate or AlN template. Some methods have been tried to grow AlN with low dislocation densities, such as physical vapor transport [8–10] and solution growth [11–13] and metalorganic chemical vapor deposition [14,15].

However, it is rather difficult to obtain large diameter and the optical transparency will be decreased significantly due to the presence of Al vacancies, substitutional impurities (carbon, oxygen) and their complexes. Another promising approach for preparing large-diameter and thick AlN layer with good optical properties is hydride vapor phase epitaxy (HVPE) [16–18]. 2 in. freestanding AlN substrate with thickness of 50 μm has been fabricated by growing thick AlN on 6 H-SiC by HVPE and removal of 6 H-SiC substrate using reactive ion etching [19]. Kumagai et al. reported high quality freestanding AlN substrate with good optical transparency above 208.1 nm grown at 1450 °C [20–23]. However, it is still difficult to grow high-quality AlN films due to the limitation of migration of Al atoms on the surface, which resulting in rough surface and poor quality. In order to increase the migration ability of Al atoms, high temperature (generally above 1400°) [24–27] are required. However, the reaction chamber of HVPE system was generally made of quartz, which cannot survive at such high temperature. Therefore, it is better to get high-quality AlN material performed on conventional HVPE system. Since the considerable size of native AlN substrates is not available currently, thin AlN templates on foreign substrates are good choice for heteroepitaxial deposition of AlN based devices.

---

* Corresponding authors at: Platform for Characterization and Test, Suzhou Institute of Nano-tech and Nano-bionics, CAS, Suzhou 215123, China.
E-mail addresses: jczhang2010@sinano.ac.cn (J.C. Zhang), kxu2006@sinano.ac.cn (K. Xu).

http://dx.doi.org/10.1016/j.jcrysgro.2015.11.040

2. Experiment details

AlN growth was carried out on home-made horizontal HVPE. The growth system equipped with hot wall quartz tube reactor and a resistive furnace. (0001) GaN/(0001) sapphire template, (0001) 6 H-SiC and (0001) Sapphire were used as substrates for the AlN growth. The growth temperature was from 950° to 1050° and the growth pressure was changed from 100 to 760 Torr. The influence of V/III ratio has been investigated and the optimized value of 90 was chosen for all the growth. HCl and Ammonia were used as input active gases. Before AlN deposition, HCl flowed over Al source to form gaseous aluminum chlorides at 550°. The mixture of H_2 and N_2 (mixed ratio of 1:1) were used as carrier gas.

The characterization of the surface was performed by atomic force microscopy (AFM) measurements in tapping mode using a Veeco Dimension 3100. The crystal quality of AlN template was characterized by high-resolution X-ray diffraction (HR-XRD) on a Bruker D8 Discover. The thickness was measured by a scanning electron microscope (SEM) on Quanta400FEG.

3. Results and discussion

3.1. AlN film grown on GaN/sapphire substrate

Fig. 1(a) showed the (0002) XRD of 200-nm AlN thin film grown on GaN/sapphire under different growth pressures varied from 100 to 760 Torr which the growth temperature was 1000°. The width of AlN XRD pattern broadened as the pressure increased. It was difficult to observed the AlN peak when the growth pressure was 760 Torr. The dependence of the full-width at half-maximum (FWHM) of (0002) and (10-12) rocking curves on growth pressures was shown in Fig. 1(b). Obviously, the crystal quality of AlN thin films increases as the decrease of growth pressure.

Fig. 2 showed the AFM image of AlN film grown under different pressures which the growth temperature was 1000°. At low pressure (as shown in Fig. 2(a)), atomic steps were clearly observed. The morphology changed to be rougher and atomic steps disappeared as the increase of pressure, which indicated that the growth changed from 2-dimensional (2D) to 3-dimensional (3D) mode. It was believed that the decrease of growth pressure not only favored the decrease of pre-reaction in the vapor circumstance, but also contributed to the increase of Al migration on the growth front.

The influence of growth temperature on the crystal quality of AlN thin film was studied. Fig. 3(a) showed the dependence of the FWHM values of (0002) XRD rocking curve on growth temperature which the growth pressure was 100 Torr. The FWHM value decreased to a minimum value at 1000°. From the cross-sectional SEM measurements (Fig. 3(b)) of the sample grown at 1050°, it can be seen that the GaN was already decomposed. It is believed that the decomposition of the GaN resulted in the decrease of crystal quality of AlN.

Fig. 4 showed the AFM image of AlN film grown under different temperatures which the growth pressure was 100 Torr. At low temperature of 900°, the growth of AlN was in 3D mode as shown in Fig. 4(a), which is attributed to the low mobility of Al adatom. As the temperature increased, the mobility of Al adatom increased, which resulted in the growing up and coalescence of AlN islands (Fig. 4(b)–(d)). The atomic steps can be observed when the growth temperature was 1000°, suggesting the change of growth mode from 3D to 2D mode. However, the GaN was decomposed at 1050° which led to the cracks on the surface.

3.2. AlN film grown on 6 H-SiC substrate

The AlN grown on 6 H-SiC was performed at 1000° and 100 Torr. The thickness of AlN was about 200 nm. Fig. 5(a) showed (0002) XRD $2\theta/\omega$ scan. The sharp AlN (0002) diffraction peak existed besides 6 H-SiC (0006). The FWHMs of (0002) and (10-12) rocking curves were 187 and 662 arc s (Fig. 5(b) and(c)), respectively, indicating the good crystalline quality.

Fig. 6(a) and (b) showed the SEM and AFM images of the AlN. The AlN grown on 6 H-SiC showed smooth surface and atomic steps. The high quality of AlN was believed to be due to the small lattice mismatch of AlN and 6 H-SiC.

3.3. AlN film grown on sapphire substrate

Different thickness of AlN films were grown on the sapphire at 1000° and 100 Torr. Fig. 7(a) shows the dependence of FWHM of (0002) and (10-12) XRD rocking curves on AlN thickness. The FWHMs of both diffractions decreased monotonically as the thickness increases. At the thickness of 200 nm, the FWHM of (0002) and (10-12) are 260 and 2650 arc s, respectively. However, when the thickness increased to 1200 nm, the FWHMs of (0002) and (10-12) deceased to 47 and 1130 arc s, respectively. Fig. 7 (b) was the (0002) XRD $2\theta/\omega$ scan. The sharp AlN (0002) diffraction peak existed around 36.02° besides that of sapphire.

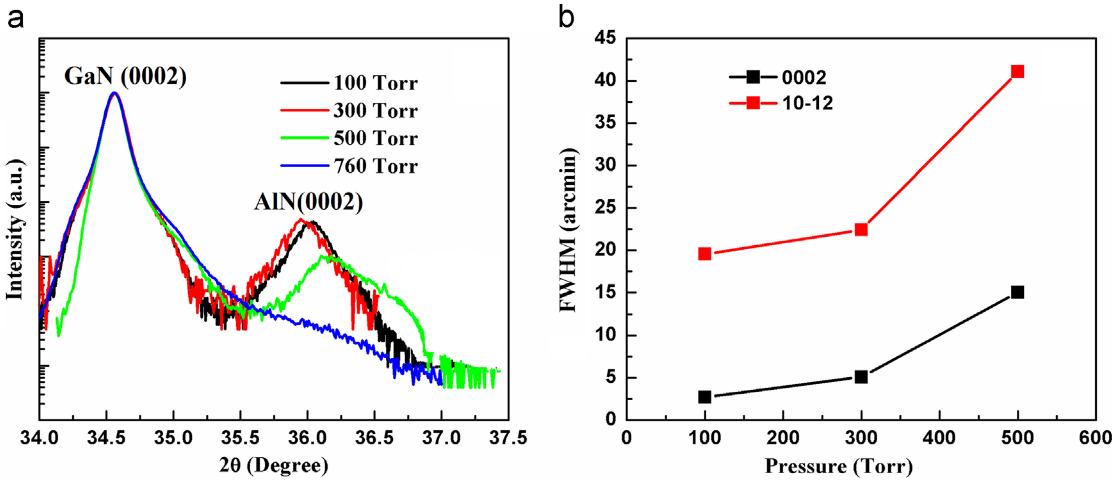

Fig. 1. (a) XRD patterns of AlN thin film under different pressures and (b) the dependence of (0002) and (10-12) FWHM on growth pressures.