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六方氮化硼成核层减小MOCVD外延生长氮化铝薄膜的应力及裂纹

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摘 要:利用单层六方BN材料(hexagonal BN:hBN)作为成核层,用金属有机物化学气相沉积法生长AlN薄膜,得到应力小裂纹少的外延材料。实验中,对hBN材料进行人为表面化学修饰,以增加hBN的缺陷和后续AlN生长的成核中心。对比分析了有无hBN成核层时生长的AlN薄膜质量,证实了hBN有助于减少AlN外延层中的裂纹,空气孔隙及应力。研究了V/III生长参数对AlN薄膜表面形貌、晶体质量和应力的影响,得到合适的生长窗口,获得完全无应力的氮化铝外延层,且其位错密度与蓝宝石上生长的氮化铝相当.

关键词:AlN薄膜;六方氮化硼;MOCVD;缺陷;应力
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Suppression of Stress and Cracks in the Epitaxy of AlN by MOCVD Through a Hexagonal BN Nucleation Layer

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Abstract: Monolayer hexagonal BN (hBN) material served as the nucleation layer in AlN epilayer by metal-organic chemical vapor deposition. Through this method both the stress and the cracks in AlN films were greatly suppressed. The monolayer hBN material was treated with artificial surface chemical modification to increase the defects in hBN and the nucleation sites for the subsequent AlN growth. We analyzed the quality of AlN materials with/without the hBN nucleation layer. The results show the hBN

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layer can help decrease the cracks, air voids and stress in AlN films. Meanwhile, the impacts of different V/III ratios on the surface morphology, the crystal quality and the stress in AlN films were studied. An optimized V/III-ratio range was obtained. Under the optimized growth condition, the stress in the AlN layer with the hBN nucleation layer can be eliminated completely, and the crystal quality of the AlN films with a hBN nucleation layer was comparable with that of AlN directly grown on sapphire.

Key words: AlN films; Hexagonal BN; MOCVD; Defect; Stress

OCIS Codes: 160.2100; 160.4236; 180.5655; 230.0250

0 Introduction

Deep-Ultraviolet Light Emitting Diodes (DUV LEDs) have wide applications in water purification, sensing, polymerization solidification and so on[1-2]. AlN materials as promising base materials for AlGaN-based DUV LEDs have gained interest recently[3-5]. Thus, the residual stress issues associated with the heteroepitaxy of high-quality crystals on foreign substrates deriving from the lattice and thermal mismatch still limit the device performance[6-8]. Several approaches have been introduced to resolve the above mentioned major issues[9-11]. Among various methods, buffer-assisted method is perceived as a major breakthrough[12]. The low-temperature (LT) AlN thin films served as the traditional buffer layers. However, after using LT-AlN buffer some stress still exists in the AlN epilayer due to the inevitable mismatch between AlN and foreign substrates.

Two-Dimensional (2D) material as a nucleation layer of III-nitride devices has attracted more and more attentions in LEDs field owing to the van der Waals interaction between 2D material and epitaxial layers[13-15]. It's a promising method to realize the free-standing structures of the LEDs[16-17]. Among various 2D materials, hexagonal BN (hBN) layer possesses advantages as a release layer to transfer LEDs to some unconventional substrates including metal, glass, flexible substrates and so on[18-19]. In recent years, InGaN-based visible LEDs have been successfully transferred by the aid of hBN[18-19]. Moreover, it has been proved the residual strain can be completely eliminated using the hBN layer[20]. However, AlGaN-based deep ultraviolet LEDs using a hBN nucleation layer have seldom been reported. It's deserving to clarify the effects of hBN used in the epitaxy of AlN materials and further realize the application of hBN layer in AlGaN-based deep ultraviolet LEDs. Here we report the AlN epitaxial layers on sapphire with an overlying hBN nucleation layer under different growth conditions. The effects of hBN nucleation layer on the crystal quality and stress conditions in AlN films were investigated.

1 Experiment

The monolayer hBN materials on the surface of copper foil were synthesized in a Low-Pressure Chemical Vapor Deposition (LPCVD) chamber with a two-heating-zone system[21]. Borazane was chosen as the precursor and H_2 gas accompanied the decomposition gases of borazane into the chamber whose temperature was set to 1 000 ℃. The as-grown hBN layer was transferred from Cu foil onto *c*-plane sapphire substrate by a PMMA-based wet chemical etching process[22]. Then the hBN layer was treated with O_2 plasma to help the nucleation of AlN materials.

AlN films were grown on sapphire substrates with/without hBN nucleation layer by a low-pressure vertical showerhead Metal-Organic Chemical Vapor Deposition (MOCVD). The structure schematic diagrams of the AlN films on the two substrates were shown in Fig.1. Trimethylaluminum (TMAl) and NH_3 were used as Al and N precursors. H_2 was chosen as the carrier gas. Prior to the AlN growth, the substrates were thermal cleaned at 1 000 ℃ in H_2 rich ambient for 2 minutes. A Low-Temperature (LT) AlN layer was deposited on the substrates at 650 ℃ for 5 minutes. Then the temperature rose to 1 200 ℃, high-temperature AlN films were grown for 1 hour with the V/III ratios of 500/750/1 000. The pressure was kept at about 50 torr during the whole growth process. The samples with two different substrates were under the same growth parameters.

The surface morphologies of the hBN and AlN materials were studied by Scanning Electron Microscopy (SEM) (HITACHI S-4 800) and tapping mode Atomic Force Microscopy (AFM) (Veeco D3100). The chemical compositions of hBN materials were characterized by JOBIN YVON-HORIBA HR800 Raman spectroscope using a 532 nm line of semiconductor laser at 1-mW power as the excitation source. The crystal quality of AlN was

analyzed by a Bede X-ray metrology double crystal high resolution X-ray diffraction rocking curves (XRCs). And Raman spectroscope was carried out to estimate the stress conditions in the AlN films.

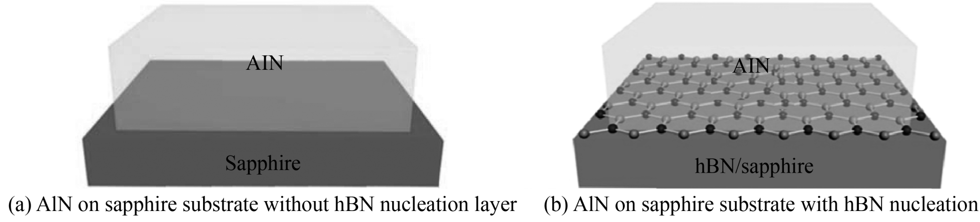

Fig.1 The structure schematic diagrams of theAlN films on the two substrates

2 Results and discussion

We transferred the hBN layer from Cu foil onto *c*-plane sapphire substrates and treated it with O_2 plasma. SEM and AFM were carried out to characterize the morphology of the as-transferred hBN. The hBN layer shows a continuous surface, as shown in Fig. 2(a). However, there are many nanoparticles formed because it was difficult to control the growth process of the hBN. They could influence the subsequent growth of AlN materials. As we can see in Fig.2(b), the AFM image is consistent with the SEM image, and the RMS roughness was 3.88 nm for (5×5) μm^2. The surface morphology of hBN layer and the number of nanoparticles almost remained unchanged even after the O_2 plasma treatment. The Raman spectra of hBN before and after the O_2 treatment were carried out to obtain their compositions and defect properties, as shown in Fig.2(c). In both of the samples, the Raman spectra feature peaks are at about 1 370 cm^{-1} and 1 600 cm^{-1} attributed to the vibration of B—N bonds and C = C bonds, respectively[23]. The peak intensity in 1 372 cm^{-1} in the spectrum of hBN after the O_2 plasma treatment is weaker and noisier owing to the defects caused by O_2 plasma treatment. These defects can serve as the nucleation site for the subsequent growth of AlN[24]. The peak in 1 600 cm^{-1} may be related to the impurity originating from the growth process of hBN in LPCVD. Except for the two peaks, another Raman feature peak at 1 500 cm^{-1} showed after the O_2 plasma treatment, which may be ascribed to the bind of O atoms in the atom structure of hBN. These changes of chemical properties from O_2 treatment could be favor of the nucleation of AlN[24].

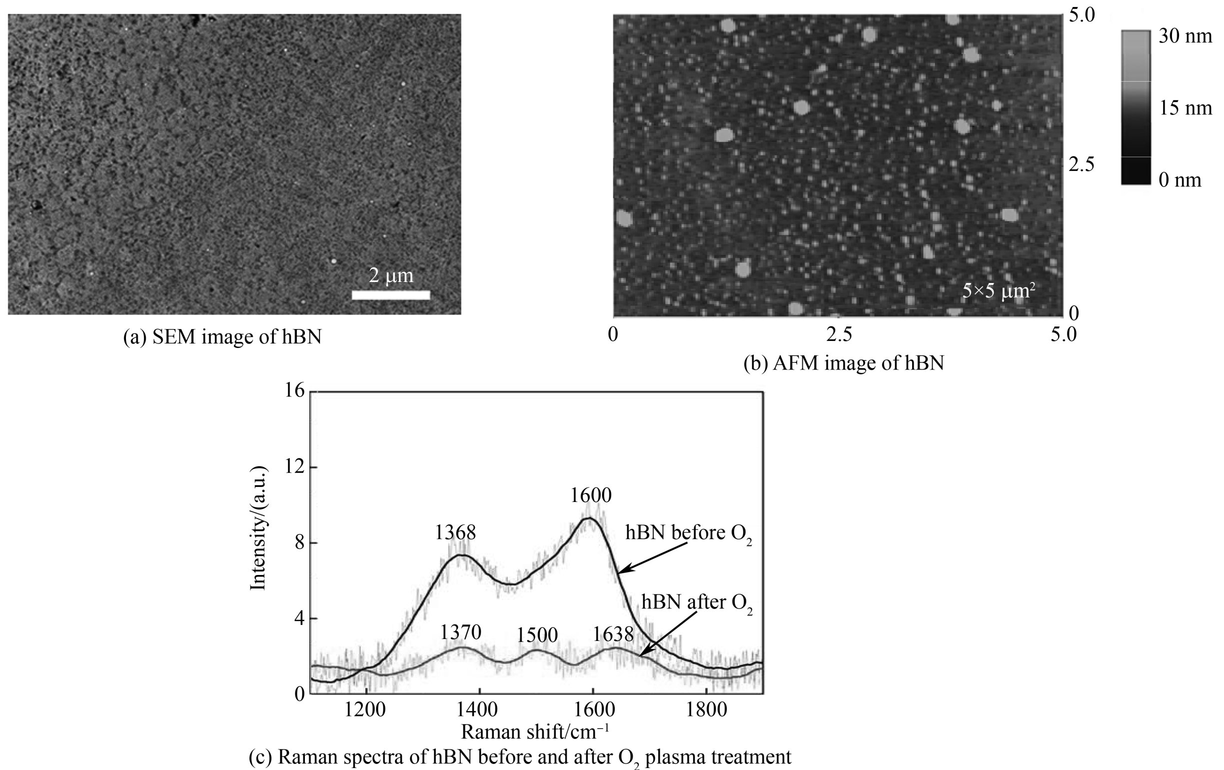

Fig.2 The morphology and chemical compositions of hBN materials on sapphire substrates

AlN films with thickness of 1.5 μm were grown on the substrates with/without the hBN nucleation layer. Figure 3 shows the SEM results of AlN grown on the two substrates with the same V/III ratio of 500. SEM image of AlN directly grown on sapphire presents dense cracks on the surface resulting from the lattice mismatch and thermal mismatch between AlN and sapphire, as shown in Fig.3(a). The number of cracks in the AlN films with the hBN nucleation layer is much less than that in AlN directly on sapphire due to the weak interaction between hBN and AlN, as shown in Fig.3(b). However, there are still several cracks on the surface of AlN on hBN/sapphire. These cracks may ascribe to the damage of O_2 plasma treatment on hBN materials, which may cause the exposure of some sapphire regions. Furthermore, the stress in AlN due to the mismatch between AlN and sapphire in the exposed region formed. There are many black pits on the surface of the AlN on hBN/sapphire, which are AlN polycrystal regions resulting from some nanoparticles on the hBN layer, as above mentioned. To further characterize the quality of the AlN films, SEM images with smaller scale were obtained. The voids can be observed clearly in AlN films on sapphire, while the AlN films on hBN/sapphire exhibit a smooth surface, as shown in Fig.3(c) and Fig.3(d). The SEM results have revealed that hBN may be in favor of the nucleation of AlN materials and high-quality AlN epilayer could further be achieved on hBN/sapphire. Additionally, the hBN interlayer could release strain stress in the AlN films and suppress cracks.

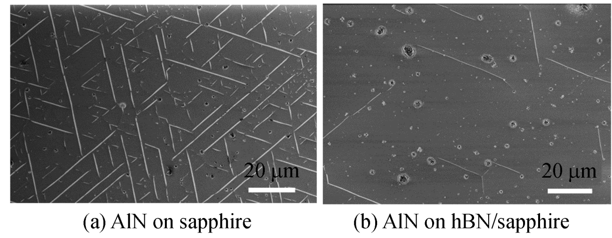

Fig.3 The SEM images of AlN on sapphire and hBN/sapphire with the V/III ratio of 500

Then we investigated the effect of V/III ratios on the quality of AlN on hBN/sapphire. As we can see in Fig.4, the RMS and the voids number of AlN films increased as the V/III ratios increased. What's more, when the V/III ratios are in the range of 500-750, the atom steps can be seen clearly. However, when the V/III ratios rose to 1 000, the atom steps are blurry while the porous structure becomes apparent, which indicate the AlN grains can't merge completely. The results indicate the V/III ratios have

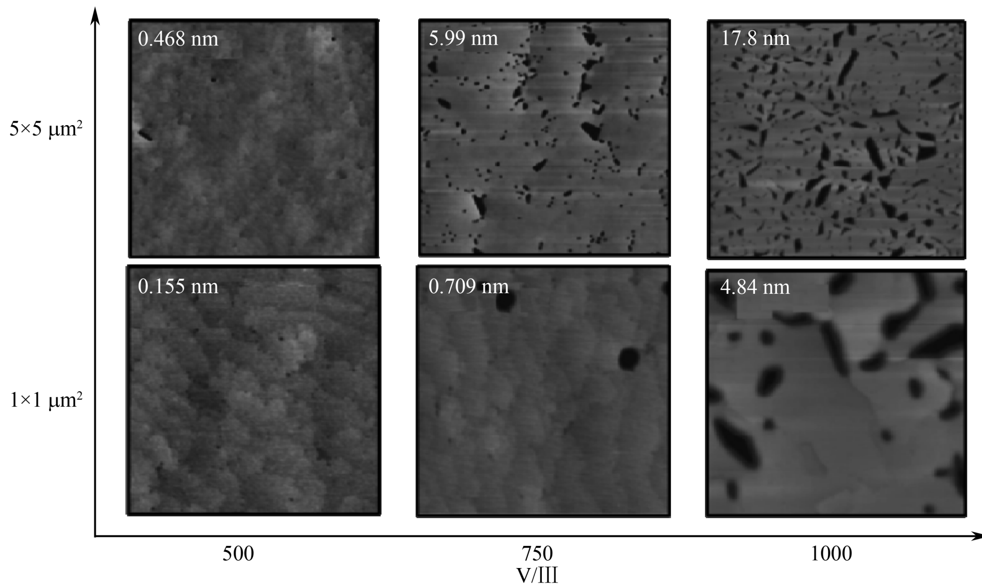

Fig.4 AFM images of AlN on hBN/sapphire with different V/III ratios (the white number is the RMS value)

impact on the merging of AlN islands. So we must control the V/III ratios in the range of 500～750 to achieve high-quality AlN films.

The threading dislocation density (TDD) including mix (screw＋edge) and edge dislocations is the most important property for the performance of DUV LEDs[25]. We estimated the FWHM values of (0002) and $(10\bar{1}2)$ reflections of XRCs for the 6 samples to evaluate the densities of screw dislocations and edge dislocations, respectively. As shown in Fig.5, the TDD of AlN on hBN/sapphire was comparable to that of

AlN on sapphire when the V/III ratio was in the range of 500-750, which is consistent[3] with the AFM images. The crystal quality of AlN on hBN/sapphire decreased as the V/III ratios were greater than 750. Among these samples, the best one was under the V/III ratio of 750. The XRCs FWHM values of (0002) and $(10\bar{1}2)$ reflections in this sample were 951 arcsec and 1 459 arcsec, respectively. As estimated from the XRD FWHMs, the densities of screw and edge dislocations are about 1.97×10^{9} cm^{-2} and 1.99×10^{10} cm^{-2}, respectively[26]. The result shows the AlN on hBN/sapphire achieved in our experiment is promising to be used as the base materials for DUV LEDs.

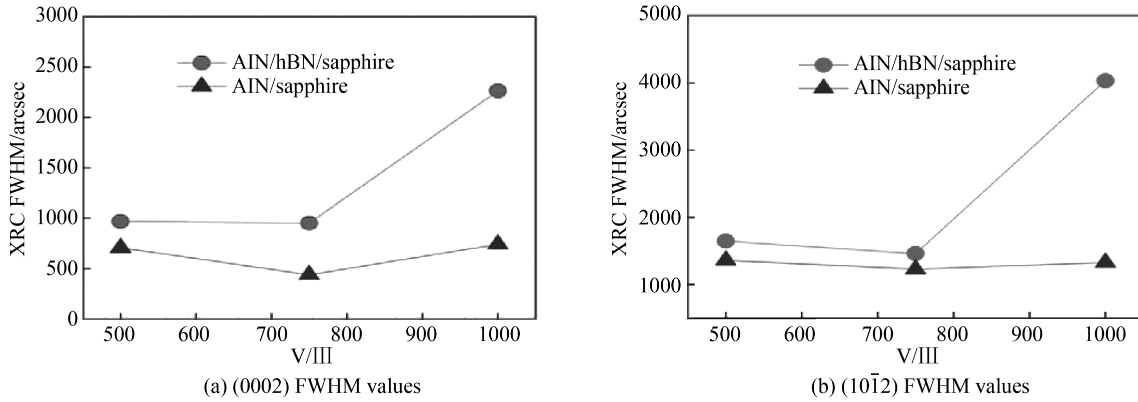

Fig.5 The FWHM values of X-ray rocking curves (XRCs) of (0002) and $(10\bar{1}2)$ diffractions for AlN films on hBN/sapphire and sapphire with different V/III ratios

To further analyze the residual stress conditions in AlN films, we investigated the Raman spectra of the as-grown AlN films. The E_2 (high) Raman shift values for AlN films on hBN/sapphire and sapphire with different V/III ratios are shown in Fig.6. The tensile stress derives from the coalescence process, which proves the complete merging of AlN grains on the two substrates[3]. The tensile stress in AlN films grown on hBN/sapphire are much less than the tensile stress in AlN films on sapphire when the V/III ratios were in the range of 500-750. Therefore, the results confirm hBN nucleation layer can suppress the residual stress in AlN films, which is consistent with the SEM images. In addition, we have found the stress can be completely removed in AlN films with a hBN nucleation layer when the V/III ratio was 750. It's promising to overcome the crack issues and electric leakage of DUV LEDs in the future.

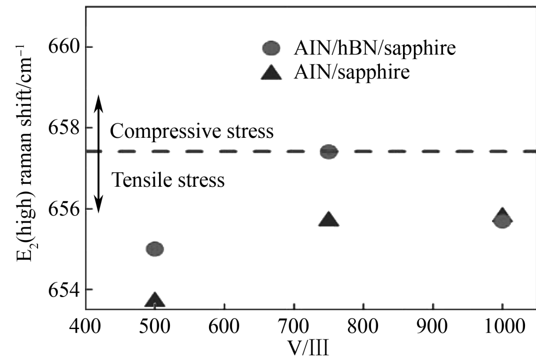

Fig.6 The E_2 (high) Raman shift values for AlN films on hBN/sapphire and sapphire with different V/III ratios

3 Conclusion

Our study suggests that the hBN nucleation layer can suppress the stress and decrease cracks in AlN films resulting from lattice mismatch between sapphire and AlN in appropriate growth conditions. We found the V/III ratios had crucial impact on the merging of AlN grains on hBN/sapphire. The RMS of AlN on hBN/sapphire increased as the V/III ratios increased. The crystal quality of AlN on hBN/sapphire decreased as V/III ratios were greater than 750. Thus, we achieved high-quality AlN films on hBN/sapphire under the V/III ratio of 750. Its crystal quality was comparable with that of AlN on sapphire, but no residual stress remained. Moreover, AlN materials with lower stress and less cracks can provide excellent foundation for developing efficient deep ultraviolet optoelectronics.

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