Effect of high-temperature annealing on AlN thin film grown by metalorganic chemical vapor deposition*

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The effect of high-temperature annealing on AlN thin film grown by metalorganic chemical vapor deposition was investigated using atomic force microscopy, Raman spectroscopy, and deep ultra-violet photoluminescence (PL) with the excitation wavelength as short as ∼ 177 nm. Annealing experiments were carried out in either N_2 or vacuum atmosphere with the annealing temperature ranging from 1200 °C to 1600 °C. It is found that surface roughness reduced and compressive strain increased with the annealing temperature increasing in both annealing atmospheres. As to optical properties, a band-edge emission peak at 6.036 eV and a very broad emission band peaking at about 4.7 eV were observed in the photoluminescence spectrum of the as-grown sample. After annealing, the intensity of the band-edge emission peak varied with the annealing temperature and atmosphere. It is also found that a much stronger emission band ranging from 2.5 eV to 4.2 eV is superimposed on the original spectra by annealing in either N_2 or vacuum atmosphere. We attribute these deep-level emission peaks to the V_{AL}–O_N complex in the AlN material.

Keywords: high-temperature annealing, AlN, optical properties

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1. Introduction

Wurtzite aluminum nitride (AlN) has generated tremendous interest because of its unique properties such as wide band gap (∼ 6.1 eV at low temperature[1]), high mechanical hardness, high thermal conductivity, low thermal expansion, large dielectric constant, and high resistance to chemicals and radiation. Its ultrahigh band-gap makes AlN an especially key material for applications in the solid-state light sources such as light-emitting diodes[2,3] and laser diodes,[4] operating in the deep ultraviolet spectral range. Recent technical achievements have enabled researchers to fabricate AlN films by a variety of methods (including metal-organic chemical vapor deposition (MOCVD),[5–8] molecular beam epitaxy (MBE),[9,10] and others[11,12]). However, the lattice mismatch between AlN film and the substrates produces a high density of misfit dislocations, which act as non-radiative recombination centers, reducing the performance of the devices. Post-growth annealing is often used to eliminate non-radiative defects and improve crystalline quality of semiconductors. Several investigations were already dedicated to the effects of annealing on the nitrides, but mainly about GaN[13,14] and $Al_xGa_{1-x}N$[15,16] with low Al composition x. Due to the lack of high-temperature annealing equipment and deep ultraviolet (UV) optical source, there has been little research about the effect of high-temperature annealing on the optical properties of AlN. To our knowledge, the highest annealing temperature ever reported in the literature is below 1400 °C and no band-edge emission peak has ever been reported in annealing experiments.[11,17,18] Therefore, it is necessary to experimentally study the effects of high-temperature annealing on AlN.

In this paper, atomic force microscopy (AFM), Raman spectroscopy, and deep UV photoluminescence (PL) were employed to monitor the surface morphology, misfit stress, and luminescence properties of the as-grown and thermally annealed MOCVD epitaxial AlN sample in different atmosphere conditions and at relatively high temperatures (up to 1600 °C). By means of our home-made spectroscopic system with excitation wavelength down to the deep UV range (∼ 177 nm), a significant improvement in the band-edge transition of the AlN sample was experimentally observed after annealing in N_2 atmosphere at 1400 °C. Furthermore, an impurity-related emission energy band in the AlN sample was investigated and is discussed here.

2. Experiment

The AlN samples studied were grown on c-plane sapphire substrate with MOCVD. Trimethyl aluminum and ammonia were used as Al and nitrogen sources respectively. First, a 25-nm AlN buffer was deposited at 535 °C on the sapphire substrate. Then, the substrate temperature was increased to 1080 °C for the epitaxial growth of AlN hetero-epilayer of about 2 μm.

A low-pressure hot wall chemical vapor deposition (CVD) furnace was used for the thermal annealing experi-

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ment. Three different annealing temperatures (1200, 1400, and 1600 °C) were used and the ramp-up rate of temperature was about 150 °C/min. The annealing time was 20 min for all the annealing experiments. Two different annealing atmosphere conditions were used: nitrogen atmosphere and vacuum atmosphere. The surface morphology of the AlN epitaxial layer was examined by AFM in contact mode; Raman spectra were performed at room temperature, collected from the top surface of the samples in the backscattering geometry with the 514.5-nm line of Ar^+ laser as the excitation source. The photoluminescence measurements were carried out in our home-made deep UV laser spectroscopy system by employing a frequency-quadrupled Ti:sapphire laser as excitation source, providing an excitation wavelength of about 177 nm with the 76-MHz repetition rate. The sample was attached onto the cold finger of a closed-cycle helium refrigerator. The emission spectra from the sample were collected by a pair of parabolic aluminum mirrors and directed to a monochromator, a photomultiplier was mounted to detect the luminescence signal and then a photon counter was used to record the emission intensity. The focused spot diameter was less than 100 μm and the spectra resolution was about 3 meV at 6 eV.

3. Results and discussion

Figure 1 shows the surface morphologies of the as-grown and annealed AlN films in N_2 atmosphere at 1200, 1400, and 1600 °C, respectively. It can be seen that the as-grown surface presents granular worm-like nanostructures. After annealing at 1200 °C, no significant change in the surface morphology can be observed, as shown in Fig. 1(b). With increasing annealing temperature, the crystalline grains in the AlN layer become apparently larger and larger, giving rise to a remarkably smooth surface at 1400 °C (as can be seen in Fig. 1(c)). The surface morphology continues to become smoother at 1600 °C, while a small crack can be observed at the same time with naked eyes. The appearance of the cracks may be due to the stress developed in the film during the annealing treatment, which will be discussed later.

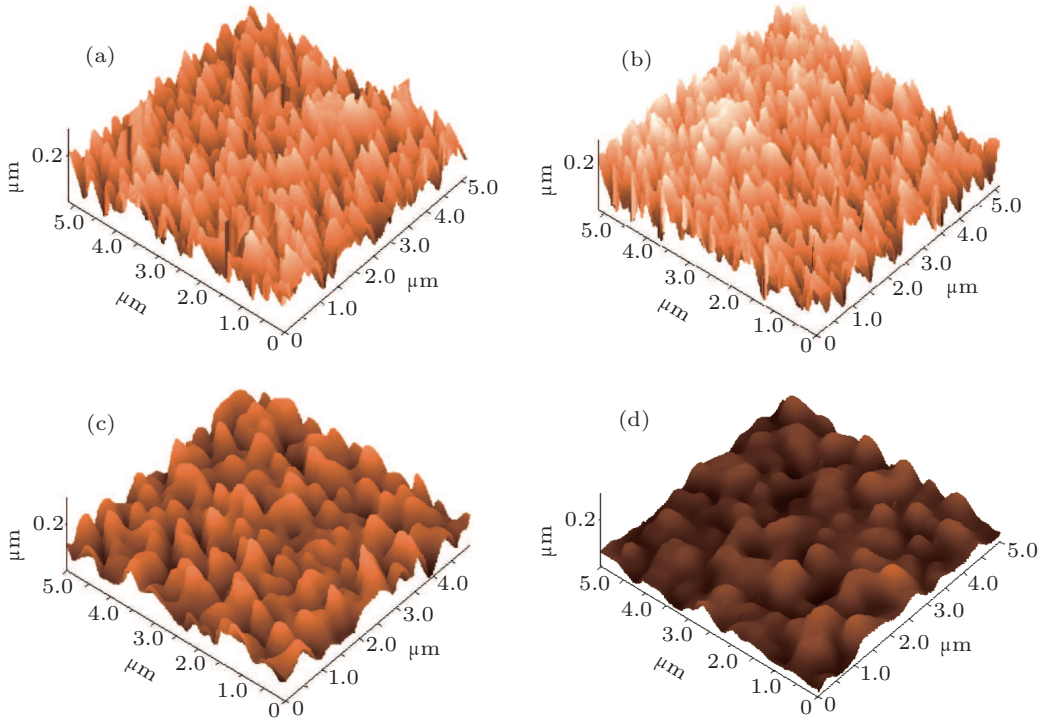


Fig. 1. (color online) 5 μm×5 μm AFM images of the AlN as-grown sample (a) and samples annealed in N_2 atmosphere at (b) 1200 °C, (c) 1400 °C, and (d) 1600 °C respectively.

From the change in surface morphology, it can be inferred that, in annealing process, the AlN film has undergone surface reconstruction during which the smaller grains in the epilayer merged into bigger ones. Figure 2 plots the evolution of the AlN surface root mean square (RMS) with the increase of annealing temperature under both N_2 and vacuum atmospheres. It can be seen from the figure that for N_2 annealing atmosphere, the surface roughness of the samples decreases from 51.5 nm (as grown) down to 36.0 nm (1400 °C annealing), and further down to 20.8 nm (1600 °C annealing). In contrast, the effect of vacuum annealing on surface roughness is much milder; as can be seen from the figure, the RMS decreases

from 49.4 nm (as grown) to 40.5 nm (1400 °C annealing). The AFM results indicate that thermal annealing acts to monotonically reduce surface roughness with increasing temperature for both N_2 and vacuum atmospheres.

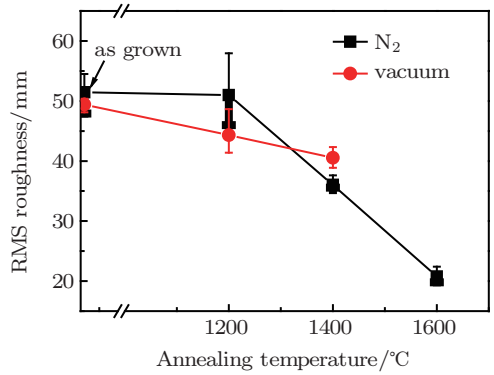


Fig. 2. (color online) Average RMS roughness as a function of the annealing temperature for AlN samples annealed for 20 min in either N_2 or vacuum atmosphere.

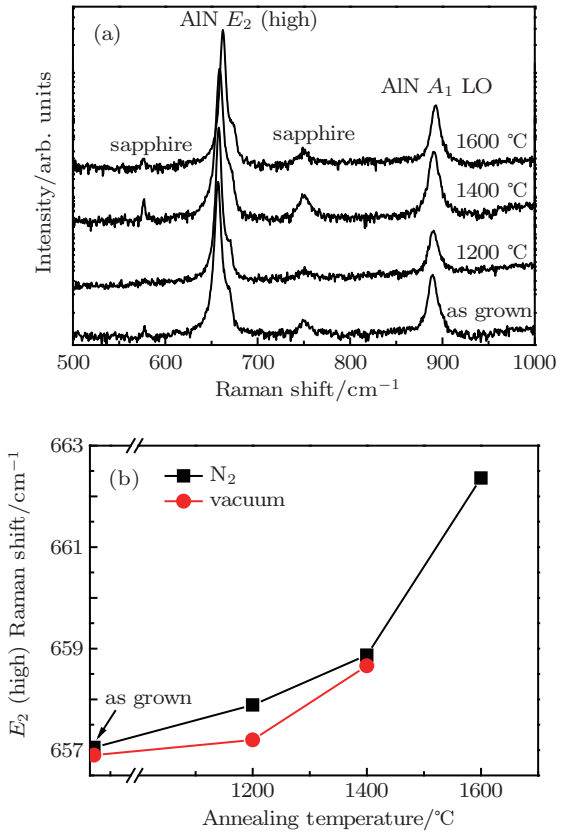


Fig. 3. (color online) (a) Raman spectra of the AlN samples annealed in N_2 atmosphere. (b) E_2 (high) phonon frequency shift in the AlN samples after annealing in both N_2 and vacuum.

Raman spectra of the as-grown and thermally annealed AlN samples in N_2 atmosphere are shown in Fig. 3(a) in the log coordinates. For the as-grown sample, the strongest Raman signal is that from the E_2 (high) phonon of AlN with the peak position at 657.1 cm^{-1}, which is identical to the data in Ref. [19]. In addition, a much weaker Raman-active mode A_1 (LO) is resolved at 890 cm^{-1}. The two sapphire substrate E_g modes are visible at 577 cm^{-1} and 749 cm^{-1} respectively. After high-temperature annealing, the Raman spectra remain almost unchanged except for a shift of the AlN E_2 (high) phonon frequency. Figure 3(b) shows the frequency of the AlN E_2 (high) phonon as a function of annealing temperature in either N_2 or vacuum atmosphere. As can be seen from the figure, the E_2 (high) phonon frequency moves to a higher wave number with the increase of annealing temperature. At 1600 °C and in N_2 atmosphere, the E_2 (high) phonon shifts by 5.3 cm^{-1} compared to the as-grown sample; while the corresponding shift in the vacuum annealed sample is slighter. The increase of E_2 (high) phonon frequency illustrates the increase of compressive stress in the annealed AlN sample, along with the modifications in the surface morphology.

Low temperature (7 K) PL measurements were performed on all the AlN samples in order to investigate the effect of thermal annealing on the optical properties, as depicted in Fig. 4. Note that all of the PL spectra were measured sequentially with the identical set-up conditions. The as-grown sample has a band-edge emission peak at 6.036 eV with the full width at half maximum (FWHM) of about 34 meV. According to the relevant data in the literature,[20,21] we attribute this peak to a free exciton transition in AlN. In addition to the band-edge luminescence, a relatively intense defect-related luminescence band centered at 4.7 eV is also observed. The drop at 3.5 eV in all spectra is due to the second-order diffraction of the excitation laser line; in order to avoid the disturbance, the laser was shut down at this energy position during the experiment. Several important observations can be made from the data presented in Fig. 4.

(i) In N_2 atmosphere, the intensity of the AlN band-edge emission can be changed by thermal annealing above a certain temperature. As indicated in Fig. 4(b), the PL spectrum after 1200-°C annealing remains nearly the same as the as-grown sample; while the PL intensity increases by approximately a factor of 3 after 1400 °C in comparison to the as-deposited sample, which indicates an improvement in crystalline quality. Liu *et al.*[17] found that the density of threading dislocations can be reduced after annealing at a relatively high temperature, and the enhancement of PL intensity is related to the decrease in nonradiative defects. However, when the annealing temperature increases to 1600 °C, it is hard to see the band-edge emission peak. Therefore, it is reasonable to say that 1400 °C is the optimal annealing temperature to enhance the intensity of the AlN band-edge emission.

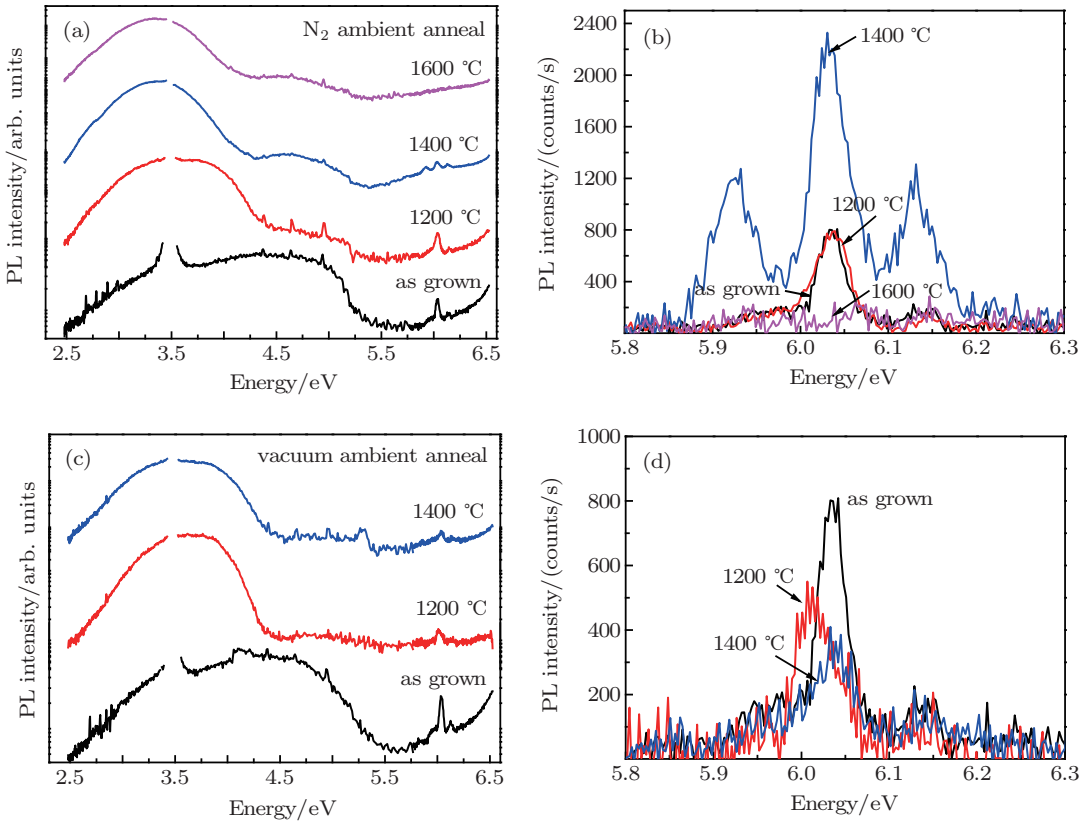


Fig. 4. (color online) Photoluminescence spectra of the AlN samples annealed at different temperatures recorded at ∼ 7 K: (a) annealed in N_2 atmosphere; (c) annealed in vacuum atmosphere. (b) and (d): Comparison of the band-edge PL spectra from as-grown, and thermally annealed AlN samples in the corresponding atmosphere; the background has been subtracted from the spectrum. And the 6.13-eV emission peak has been proven not to originate from our AlN sample.

(ii) The effect of vacuum atmosphere annealing on the PL spectrum of the AlN epilayer is obviously different from that of N_2 atmosphere annealing. As shown in Fig. 4(d), the decrease of the emission intensity at 6.036 eV in the PL spectrum after 1200-°C annealing is evident as compared to that of the as-grown sample. The band-edge intensity is further reduced after 1400-°C annealing. This suggests that vacuum annealing did not improve the AlN band-edge emission intensity at all. On the contrary, the PL spectrum is deteriorated by vacuum annealing. This may be due to the fact that N atoms evaporate from the AlN sample, and produce many more N vacancies within the AlN bulk.

(iii) A broad luminescence band with peak energy at 4.7 eV below the band gap is observed in the as-grown sample. This deep-level emission band covers a very wide energy range with the full width at half maximum (FWHM) more than 2 eV. After annealing, it is found that a much stronger emission band ranging from 2.5 eV to 4.2 eV superimposed on the original spectra either in N_2 or vacuum atmosphere. Furthermore, it is worth noting that the additional emission peak is detected at 3.75 eV at 1200-°C annealing in N_2 atmosphere; when the annealing temperature increases to 1600 °C, this emission peak energy shifts to lower energies centered at 3.35 eV. In comparison, the emission peak does not shift and remains at 3.74 eV in the vacuum annealing. We infer that the wide emission energy band should be associated with some unintentional impurities or intrinsic structural defects in our AlN samples. According to first principles calculations, the aluminum vacancy V_{AL} would be the dominating intrinsic defect in both the undoped and n-type AlN. With the presence of oxygen, extended clusters (V_{AL}–O_N) may form easily in AlN, as they are energetically favored over isolated V_{AL} and O_N.[22] Jiang *et al.*[23,24] reported that there are three different kinds of deep acceptor energy levels above the valence band in AlN, one of which is identified as an isolated $(V_{AL})^{3-}$, the other two are V_{AL}–O_N complexes with two-negative and one-negative charges. The recombination between shallow donors and these energy levels would result in three different transitions in low temperature peaking at 3.4, 3.9, and 4.7 eV, respectively. In the literature, others report[25–28] studying the ultraviolet spectra between 3 eV to 5 eV, and attribute the transition in this energy range to the (V_{AL}–O_N) complex. Based on the above research results and considering oxygen as the impurity commonly encountered in the AlN crystal, we infer that there should be some amount of oxygen unintentionally doped in the as-grown AlN sample, which, together with the Al vacancy, may form the complex (V_{AL}–O_N), resulting in the energy transition centered at 4.7 eV with a long low en-

ergy band tail, as experimentally observed in the PL spectrum. As the annealing temperature increases, some oxygen atoms may break away from the sample due to the thermal annealing, so a presence of (V_{AL}–O_N) complex with two negative charges becomes measurable, thus the corresponding emission peak appears at 3.75 eV after 1200-°C annealing in N_2 atmosphere. At 1400 °C and 1600 °C, the content of oxygen in AlN should be further reduced by annealing, and V_{AL} becomes the main acceptor in the AlN sample; therefore, the emission band shifted to 3.35 eV. According to the above discussion, the shift of the energy peak during annealing in N_2 atmosphere can be interpreted. However, in vacuum atmosphere, up to 1400 °C the emission peak remains at 3.74 eV. This phenomenon indicates that a certain content of oxygen remained in the annealed sample. The reason may be that the vacuum atmosphere had residual oxygen, so when the AlN sample was annealed, oxygen impurities were harder to get out of the AlN surface. Therefore, it can be deduced that a higher vacuum degree in annealing would shift the emission from the AlN to lower energy. More experimental investigations should be carried out to confirm our interpretation.

4. Conclusion

In summary, we have performed high temperature thermal annealing experiments on the AlN epilayers grown by MOCVD in both N_2 and vacuum atmospheres. It is found that the surface morphology, stress and optical properties of the AlN samples have changed obviously after annealing. With the annealing temperature increasing, the surface roughness reduced and the compressive stress became larger. In addition, annealing in N_2 atmosphere at 1400 °C for 20 min increased the band-edge luminescence intensity threefold; while no such an enhancement was observed in vacuum atmosphere annealing. Also, an impurity-related emission band at 4.7 eV below band edge was observed in the as-grown sample; while after annealing, it shifted to a lower energy position ranging from 2.5 eV to 4.2 eV. There is considerable evidence that these deep energy level emission bands are correlated with (V_{AL}–O_N) complex.

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