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Band gap energy and bowing parameter of In-rich InAlN films grown by magnetron sputtering

Hong He [a,b], Yongge Cao [a,c,*], Renli Fu [b], Wang Guo [a], Zhi Huang [a], Meili Wang [a], Changgang Huang [a], Jiquan Huang [a], Hai Wang [a]

[a] Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China
[b] College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, PR China
[c] School of Materials Science and Engineering, Northwestern Polytechnical University, YouYi West Road 127#, XiAn 710072, Shanxi Province, PR China

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ABSTRACT

The crystal structure, band gap energy and bowing parameter of In-rich $In_xAl_{1-x}N$ ($0.7 < x < 1.0$) films grown by magnetron sputtering were investigated. Band gap energies of $In_xAl_{1-x}N$ films were obtained from absorption spectra. Band gap tailing due to compositional fluctuation in the films was observed. The band gap of the as-grown InN measured by optical absorption method is 1.34 eV, which is larger than the reported 0.7 eV for pure InN prepared by molecular beam epitaxy (MBE) method. This could be explained by the Burstein–Moss effect under carrier concentration of 10^{20} cm^{-3} of our sputtered films. The bowing parameter of 3.68 eV is obtained for our $In_xAl_{1-x}N$ film which is consistent with the previous experimental reports and theoretical calculations.

1. Introduction

InAlN has an adjustable band gap varying widely from 0.7 eV of InN to 6.2 eV of AlN depending on the In (or Al) content [1,2]. For this merit, it has become increasingly important in optoelectronic and electronic devices, such as thermoelectric device, ultraviolet photodiode, field effect transistor, Bragg mirror, especially in solar cell application [3–6]. InAlN and InN as light absorption layers have played crucial role in nitrides based full spectrum multi-junction solar cells [4–6]. Their promising application for solar cells is due to following reasons: (i) The band gap adjustability of InAlN in the range of ultraviolet spectra is better than that of InGaN, which makes it especially valuable in outer space; (ii) the high In content InAlN alloys, with band gap energy range of 0.7–2.4 eV, are very important in InAlN-based solar cells to match with the solar spectrum.

The band gap energy of InAlN film depending on the composition is crucial for its further applications as mentioned above. However, there has been uncertainty as the band gap of InAlN reported in a large part of the literature because these studies had been carried out by different processing methods before the confirmation of 0.7 eV [1] for band gap energy of InN. In addition, InAlN has been less investigated compared to InGaN and AlGaN, because it is difficult to avoid phase separation during the InAlN film growth process for most of the methods [7]. The low temperature and non thermal equilibrium magnetron sputtering is more preferable for overcoming the thermal stability and phase separation difficulties in high quality InAlN growth than other growth techniques, such as metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) etc. [8,9]. At the same time, this technique is versatile in preparing highly crystallized large area films economically, which is beneficial for lowering the cost of solar cells. The band gap energy of InAlN is closely related to the growth methods and resultant film qualities. Therefore, it is highly desirable to reinvestigate the band gap properties of InAlN films prepared by magnetron sputtering.

In this paper, we present an investigation of the band gap properties of high In content $In_xAl_{1-x}N$ films prepared by magnetron sputtering. In-rich $In_xAl_{1-x}N$ ($0.7 < x < 1$) films were fabricated by radio frequency (rf) magnetron sputtering technique.

* Corresponding author. Tel.: +86 591 83721039; fax: +86 591 83721039.
E-mail addresses: caoyongge@fjirsm.ac.cn (Y. Cao), renlifu@nuaa.edu.cn (R. Fu).

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The crystal structure, film morphology and optical properties of these films were investigated. The optical band gap and bowing parameter depending on the indium composition were estimated.

2. Experimental procedure

All $In_xAl_{1-x}N$ films were deposited by rf magnetron sputtering process. Aluminum (99.999%) and indium (99.99%) 2 in. plates were used as sputtering targets. A mixture gas of Ar (99.999%) and N_2 (99.999%) (Ar:N_2 = 3:1) was used as working gas and nitrogen source. The gas flow rate was set at 20 sccm and the gas pressure in the chamber was kept at 0.5 Pa. Before film deposition, the chamber was evacuated to 10^{-5} Pa by a turbo molecular pump and the targets were pre-sputtered for 20 min in order to remove possible contamination. Quartz glass was used as the substrate after degreasing by ultrasonic bath in acetone, alcohol and de-ionized water for 10 min sequentially. After moving into the chamber, it was further cleaned by sputtering for 3 min. The substrate placed upon the targets was heated and rotated. The substrate temperature was set from room temperature to 500 °C for InAlN, 450 °C for InN and 700 °C for AlN deposition respectively. For all InAlN samples, the In and Al targets were sputtered spontaneously. The radio frequency powder for indium target was set at 50 W and that for aluminum was varied from 80 W to 160 W in order to obtain different composition. After film deposition, the samples were in situ annealed at the growth temperature for 30 min.

The crystal structure of the films was examined by conventional X-ray diffraction (XRD, DMAX2500, RIGAKU, Japan). The surface morphology of the films was observed by atomic force microscopy (AFM, Nanoscope NS3A-02, Veeco, USA). The optical transmittance and reflectance spectra of the films (about 200 nm) deposited on quartz glass substrates were measured on an UV–vis spectrophotometer (Lambda 900, PerkinElmer, USA) in the wavelength range of 190–1400 nm. The carrier concentration of film with about 2000 nm thickness was obtained by Hall measurements on a HL55WIN Hall System.

3. Results and discussion

The XRD results show that the $In_xAl_{1-x}N$ films deposited on quartz glass substrates are all highly *c*-axis oriented, as shown in Fig. 1. No second phase was detected indicating phase separation does not occur. Only (0 0 2) diffraction peak of the wurtzite structure was observed indicating these films are grown along ⟨0 0 0 1⟩ direction. With different power ratio of Al target to that of

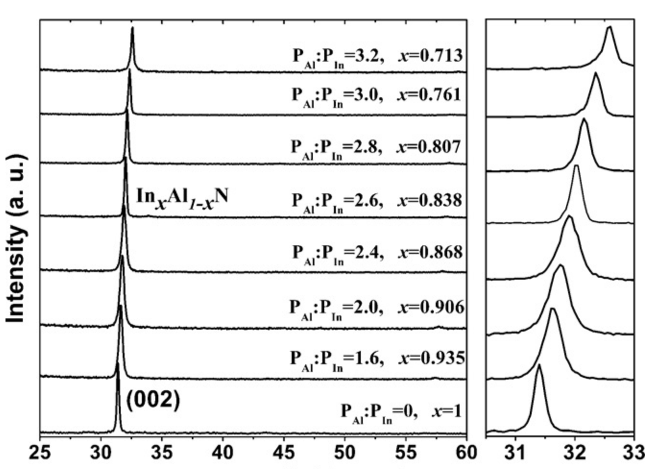

Fig. 1. XRD patterns of $In_xAl_{1-x}N$ films grown with different power ratio of Al target to In target (P_{Al}:P_{In}).

In target, films with different In composition were obtained. The diffraction peak shifts toward higher 2θ angle with the power ratio P_{Al}:P_{In} increasing from 0 to 3.2. Based on Vegard's law, the In molar content in these ternary alloy films was calculated. The In content decreases from 1.0 to 0.713 by increasing the target power ratio. We also examined the validity of Vegard's law in our high In content film since it was challenged recently. However, little difference was found and the error was within 3%. Therefore, we still consider the composition values calculated by Vegard's law being valid for our high In content $In_xAl_{1-x}N$ films.

The crystal structure and crystallinity quality of the InAlN films are quite related to the substrate temperature. In the experimental process, InAlN films were grown under different substrate temperatures varying from room temperature to 500 °C and compared by their XRD patterns. When the substrate temperature is below 300 °C, the diffraction peak form the (1 0 3) crystal plane shows up indicating the higher the substrate temperature is, the better the [0 0 0 1] orientation the film has. With increasing temperature, the crystallinity of the film increases presented by its (0 0 2) diffraction intensity increasing. However, the substrate temperature should be controlled. When it exceeds 500 °C, XRD peaks of In show up due to InN decomposition resulting in In particles in the film. In addition, substrate temperature rising may also induce surface roughing due to higher film growth rate. Therefore, we consider a substrate temperature of 500 °C to be preferable for InAlN film growth by rf sputtering method.

This highly textured structure of InAlN films was further confirmed by atomic force microscopy (AFM). The typical morphology of these films with different film thickness is shown in Fig. 2. The rod-like grains with hexagonal ends are observed perpendicular to the substrates. The pyramid-like grains indicate the crystal grain grew in the island growth mode. The root mean squared surface roughness obtained from a 3 μm × 3 μm scan area increases from 2.8 nm to 9.8 nm as the growth time increases from 1 h to 2 h. Our InAlN films prepared by magnetron sputtering would have potential in solar cell application as the highly oriented rod-like structures are good channels for charge carrier transport. Even though, the surface roughness should be controlled if these films are considered in further applications. An insertion of a buffer layer would obviously decrease the surface roughness. Yeh et al. [10] reported the effect of the AlN buffer layer on the InAlN films deposited on Corning glass by sputtering. The AlN buffer layer improves the crystallinity of the InAlN film and prevents the oxygen diffusion from the glass substrate into the film. Furthermore, the surface of InAlN film becomes smoother with an AlN buffer than that of the film deposited directly on glass substrate. This method proves to be excellent for improving the quality of InAlN films by sputtering, contents of which are also being carried out in our investigation, for example, the influences of the AlN buffer on the crystallinity, the optical properties and electronic properties of the InAlN films.

The optical properties of $In_xAl_{1-x}N$ were investigated by measuring the reflectance and transmittance spectra of about 200 nm thick films on UV–vis spectrophotometer. The typical results of $In_xAl_{1-x}N$ films with In content x = 0.94, 0.81, 0.74 are shown in Fig. 3. The transmittance spectra (Fig. 3(a)) clearly show that the absorption edge of $In_xAl_{1-x}N$ films shifts to shorter wavelength as the In content decreases. The absorption coefficients (α) were calculated from the absorption and transmittance spectra by the equation $\alpha = 1/d\ln[(1-R)/T]$, where d, R, T are the film thickness, reflectance and transmittance respectively [9]. The squared absorption coefficients (α^2) as a function of photon energy are plotted in Fig. 3(b). The band gap energy tailing of the absorption spectra (Urbach tail) [8–12] becomes obvious as In content decreases. This phenomenon is commonly observed in either single crystalline epitaxial or polycrystalline films of