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Preparation and characterization of $Al_{2x}In_{2-2x}O_3$ films deposited on MgO (1 0 0) by MOCVD

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ABSTRACT

The ternary $Al_{2x}In_{2-2x}O_3$ films with different compositions x[Al/(Al + In) atomic ratio] have been fabricated on the MgO (1 0 0) substrates by the metal organic chemical vapor deposition (MOCVD) method. The influence of different Al contents on the structural, optical and electrical properties of $Al_{2x}In_{2-2x}O_3$ films has been studied. The structural studies reveal a change from single crystalline structure of cubic In_2O_3 to amorphous as the Al content increases. The average transmittances of all samples in the visible range are over 80%. The optical band gap is observed to increase monotonically from 3.67 to 5.38 eV as the Al content increases from 0.1 to 0.9.

1. Introduction

Recently wide-band gap semiconductors have attracted much attention recently due to their potential applications in ultraviolet light emitters and detectors, solar cells and thin film transistors [1–3]. Semiconductors with wide band gap such as ZnO [4,5], In_2O_3 [6,7], SnO_2 [8], $Al_xGa_{1-x}N$ [9,10], and $Mg_xZn_{1-x}O$ [11,12] have been extensively investigated as the alternative building units for UV detectors. Tremendous advances have been achieved in the field of III-nitride based photonics and optoelectronics in the past several years [13–15] reflected by the recent Nobel Prize 2014. The recent development in AlInN alloys [16,17] and high Al-content AlGaN-based quantum wells with delta layers [18–21] have resulted in advances for deep UV optoelectronics. The $Al_xGa_{1-x}N$ and $Al_xIn_{1-x}N$ materials have induced considerable effort because their band gap can be modulated by changing their chemical composition of alloys. Therefore, modulation of the band gap is one of the major requirements for designing optoelectronic devices. However, the high preparation temperature and large lattice mismatch, as well as the oxygen impurity in $Al_xGa_{1-x}N$ behave as obstacles of the further development of $Al_xGa_{1-x}N$ based detectors. While for the $Al_xIn_{1-x}N$ material with a wider band gap range, aluminum and indium differ a lot in the nitriding process when using the MOCVD method, which limits the applications of this material. Furthermore, the indium convergence is still a hurdle to overcome in preparing the $Al_xIn_{1-x}N$ material. On the other hand, the oxide-based materials which are free of oxygen impurity problem show more stable properties compared with the nitride-based materials. $Mg_xZn_{1-x}O$ has been extensively studied in recent years. Nevertheless the phase separation is likely to occur with high Mg concentrations due to the different crystalline structures of ZnO and MgO. Therefore, a new ternary semiconductor material with the modulation of band gap in a larger range is urgently needed to meet the requirements of future ultraviolet photoelectric devices.

In_2O_3, with an optical band gap of 3.7 eV [22], is a very important transparent oxide semiconductor (TOS) material owing to its physically stability and chemically inertness which has been widely used in many fields such as photovoltaic devices and gas sensors [23,24]. However, the fundamental band gap of In_2O_3 is about 2.93 eV, which is determined by many experimental and theoretical investigations [25]. The direct optical transitions at Γ from the valence band maximum (VBM) to the conduction band minimum (CBM) are parity forbidden, so the first strong transitions occur from valence bands 0.81 eV below the VBM [26]. In contrast, Al_2O_3 with a larger band gap of 8.7 eV [27] is a deep-ultraviolet transparent oxide which is considered as a good passivation layer [28] in the fabrication of optoelectronic devices, and it has been used as a perfect substrate material for films growth [29,30]. However, it is rather difficult for Al_2O_3 to introduce shallow donor levels because the position of conduction band bottom is relatively high and the donor levels become deep levels. $Al_{2x}In_{2-2x}O_3$ is a new alloy material that could make the band gap modulation possible through the change of Al content. According to the theory of Hill [31], similar to $Mg_xZn_{1-x}O$, $Al_{2x}In_{2-2x}O_3$ can be seen as an alloy of Al_2O_3 and In_2O_3. The optical band gap of $Al_{2x}In_{2-2x}O_3$ can

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be tuned from 3.7 to 8.7 eV depending on the Al content x. However, to date almost no work has been done to investigate the $Al_{2x}In_{2-2x}O_3$ alloy films with tunable band gap depending on the composition. The lattice of the cubic structure MgO is not only matched with the lattice of indium oxide, but also with that of aluminum oxide. MgO with physically stability and chemically inertness is always used as substrates for the deposition of thin film materials [32,33]. Furthermore, owing to a wide band gap of 7.8 eV, MgO can be also employed as a good substrate for the growth of wide band gap semiconductors [34]. Therefore, MgO may be an appropriate substrate for the deposition of aluminum indium oxide films. In this paper, the $Al_{2x}In_{2-2x}O_3$ thin films were deposited on the MgO (1 0 0) substrates by the MOCVD technique. The structural, optical and electrical properties of the films have been investigated in detail.

2. Experimental

The $Al_{2x}In_{2-2x}O_3$ thin films with different compositions (x = 0.1–0.9) were prepared on the double-side polished MgO (1 0 0) wafers ($10 \times 10\,mm^2$) under high vacuum in a MOCVD reaction chamber. Prior to the film deposition, the substrates were ultrasonically cleaned with acetone, ethonal, and subsequently rinsed in de-ionized water and dried with a nitrogen gas stream. Trimethylaluminium and trimethylindium were used as the organometallic precursors. The OM vapors were transported into the reactor according to the defined atomic ratio x by ultra high purity nitrogen (9N) which was used as the carrier gas. High purity oxygen (5N) was injected as the reactive gas with a flow rate of 50 sccm (standard-state cubic centimeter per minute) using a separate delivery line into the reactor. The reactor pressure was kept at 20 Torr, and the substrate temperature was kept at 600 °C. The deposition time was 60 min.

The crystal structure of the obtained films was analyzed by the X-ray diffraction (XRD) technique using a Bruker D8 Advance X-ray diffractometer with Cu Kα1 radiation. The surface morphology was examined by a FEI Nova NanoSEM 450 field emission scanning electron microscope (FE-SEM). The high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) measurements were performed with a Tecnai F30 transmission electron microscope operated at 300 kV on the cross-sectional samples to study the microstructure of the films. The cross-sectional samples were prepared specially to get a very thin area (1–2 nm) which is electron transparent. The chemical composition of the films was examined by the energy dispersive X-ray (EDX) analysis instrument which is attached to the Tecnai F30 TEM. A TU-1901 double-beam UV–vis–NIR spectrophotometer was used to measure the optical transmittance spectra of the films in the wavelength range of 200–800 nm.

3. Results and discussion

Fig. 1 shows the X-ray patterns of the as-deposited $Al_{2x}In_{2-2x}O_3$ films with different Al contents. It can be seen that only the diffraction peaks corresponding to In_2O_3 (2 2 2) and (4 4 4) reflections are observed apart from the substrate MgO (2 0 0) peak ($2\theta = 42.7°$) for the samples with Al contents of $x = 0.2$ and 0.3 indicating a bixbyite In_2O_3 structure with a single orientation along the (1 1 1) direction is obtained. For the sample with Al content of $x = 0.5$, no other diffraction peak is detected from the XRD patterns except for the substrate peak, implying an amorphous structure is obtained. Since the Al content for this sample is the same as In content, the interaction effect between In_2O_3 and Al_2O_3 phases makes it difficult to form any crystalline structure. As x increases further to 0.7 and 0.8, a very weak diffraction peak located at $2\theta = 20.9°$ emerges. This peak does not show up in the depicted XRD patterns of the samples with high In contents, so the weak diffraction peak is speculated to belong to Al_2O_3. Since the deposition temperature is 600 °C which is the proper temperature for the growth of η phase Al_2O_3, this weak peak located at $2\theta = 20.9°$ may be corresponding to the η-Al_2O_3 (0 0 4) reflection. Yet the intensity of this Al_2O_3 peak is fairly weak and the full width at half maximum (FWHM) of this peak is relatively large, which implies that the grain size of these films is smaller than that of the other samples with lower x values and the crystallization quality degrades apparently. All these results imply that the Al content significantly affects the structure of $Al_{2x}In_{2-2x}O_3$ thin films.

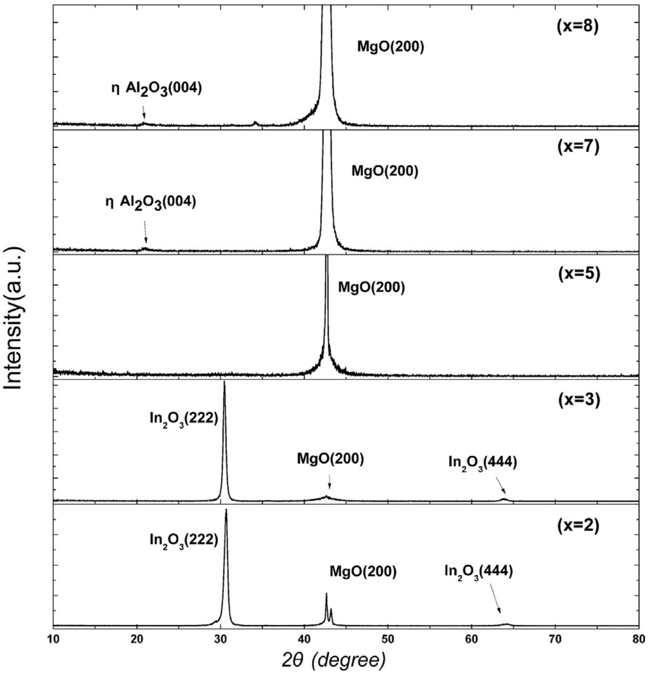

Fig. 1. X-ray diffraction diagram of the $Al_{2x}In_{2-2x}O_3$ films with different Al content.

Typical SEM micrographs of the $Al_{2x}In_{2-2x}O_3$ films with different Al contents are displayed in Fig. 2. Fig. 2(a)–(c) are corresponding to the films with x values of 0.1, 0.5 and 0.9, respectively. From Fig. 2(a), it can be seen that the surface of the film with Al content of $x = 0.1$ is covered by a striking array of square-shaped grains with obvious grain boundaries. Since the composition of this film is of high In content, the morphology of this film is similar to that of cubic bixbyite In_2O_3 [35]. While in Fig. 2(b), a smooth surface with ill-defined grain formation is observed which can be attributed to the amorphous nature of the film with $x = 0.5$ in accord with the XRD result. A densely packed surface with a compact structure can be seen in Fig. 2(c) with few pinholes and microcracks detected. No obvious crystalline grain is observed for the film with high Al content which is due to the difficulty to form a good crystal structure for the Al_2O_3 material at such a low temperature. From the SEM results, we can infer that the films with low x values have good crystalline texture. As x increases to 0.5 and higher, the structure of films becomes amorphous or microcrystalline.

Fig. 3 shows the cross-sectional transmission electron microscopy (XTEM) images and SAED pattern of the as-deposited $Al_{2x}In_{2-2x}O_3$ sample with $x = 0.2$. Fig. 3(a) exhibits the low magnification transmission electron microscopy image of this sample, from which the thickness of the film can be estimated to be 171 nm and a clear interface between the $Al_{0.4}In_{1.6}O_3$ film and the MgO substrate is observed. Fig. 3(b) shows the HRTEM image of the