Influence of annealing on the structural, optical and electrical properties of indium oxide films deposited on c-sapphire substrate*

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Indium oxide (In_2O_3) films were prepared on Al_2O_3 (0001) substrates at 700 °C by metal-organic chemical vapor deposition (MOCVD). Then the samples were annealed at 800 °C, 900 °C and 1 000 °C, respectively. The X-ray diffraction (XRD) analysis reveals that the samples were polycrystalline films before and after annealing treatment. Triangle or quadrangle grains can be observed, and the corner angle of the grains becomes smooth after annealing. The highest Hall mobility is obtained for the sample annealed at 900 °C with the value about 24.74 $cm^2 \cdot V^{-1} \cdot s^{-1}$. The average transmittance for the films in the visible range is over 90%. The optical band gaps of the samples are about 3.73 eV, 3.71 eV, 3.70 eV and 3.69 eV corresponding to the In_2O_3 films deposited at 700 °C and annealed at 800 °C, 900 °C and 1 000 °C, respectively.

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Indium oxide (In_2O_3) is one of promising alternative materials used as transparent conductive oxides due to the very good electrical conductivity, optical transmittance in the visible (vis) region and physical and chemical stability[1-5]. In_2O_3 films can be prepared using different methods, such as spray pyrolysis[6], sol gel technique[7], magnetron sputtering[8], chemical vapor deposition (CVD)[9] and pulsed laser deposition (PLD)[10]. Among these methods, metal-organic chemical vapor deposition (MOCVD) technique has many advantages, such as easy control of deposition rate and high throughput for commercial availability. There have been many reports on In_2O_3 films prepared by MOCVD method. Kong et al[11] investigated the domain structure and optical properties of In_2O_3 films on MgO (100) substrate prepared by MOCVD, and a multiple domain structure was found inside the In_2O_3 film. Yang et al[12] grew In_2O_3 thin films on α-Al_2O_3 substrates by MOCVD, and a single and sharp ultraviolet (UV) photoluminescence (PL) peak near 337 nm was observed at room temperature (RT). Li et al[13] deposited In_2O_3 thin films on MgO (110) substrates by MOCVD, and the average transmittance of the prepared films in the visible range was over 95%. In this paper, the In_2O_3 films were deposited on c-Al_2O_3 substrates by MOCVD, and the effects of annealing on the structural, optical and electrical properties of the films are investigated in detail.

The In_2O_3 films were deposited on Al_2O_3 (0001) substrates (double-face polished, with thickness of 0.5 mm) using a high vacuum MOCVD system. The sapphire substrates were cleaned in organic cleaner and deionized water with ultrasonic irradiation for 20 min, respectively. Then the substrates were dried with compressed nitrogen (N_2) and placed into the reaction chamber. Commercially available trimethylindium ($In(CH_3)_3$, 6N in purity) was used as organometallic (OM) source and store up in a stainless steel bubbler. The OM bubbler was maintained at a temperature of 20 °C with a pressure of 8.00×10^4 Pa. The OM source was transported into the reactor by ultrahigh purity N_2 (9N). High purity O_2 (5N) was used as oxidant and injected into the reactor with ultrahigh purity N_2 (9N) from a separate delivery line. During the deposition, the molar flow rates of $In(CH_3)_3$ and O_2 were kept at 2.58×10^{-6} mol/min and 6.5×10^{-3} mol/min, respectively, with the substrate temperature kept at 700 °C, growth pressure at 2.67×10^3 Pa and growth time for 360 min. Then the samples were annealed at 800 °C, 900 °C and 1 000 °C for 30 min in the atmosphere ambient, respec-

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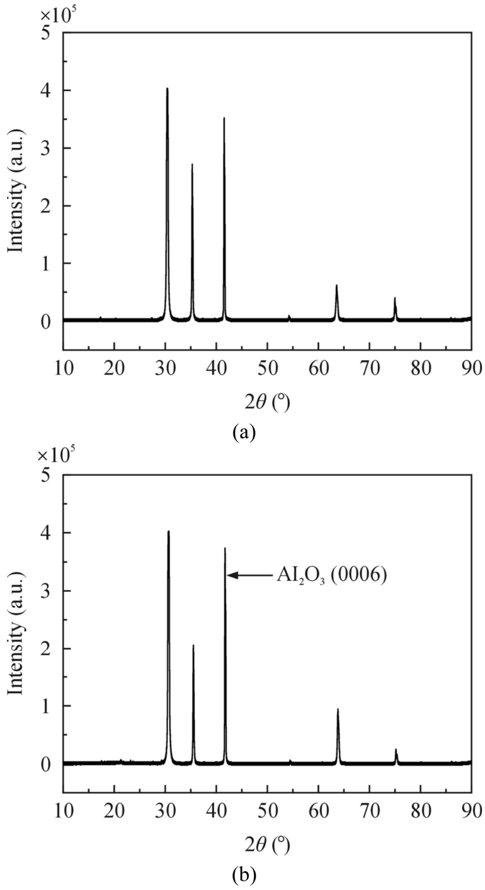
The structural properties of the samples were characterized and analyzed by a D/MAX-2500XRD X-ray diffractometer (XRD) with Cu Kα1 radiation (λ=0.154 06 nm). The surface morphology was examined using a JSM-6700F scanning electron microscope (SEM). The Hall mobility and carrier concentration of the film were performed with the East changing ET9000 Hall measurement system in vacuum (<10 Pa). The optical transmittance spectra were determined by the Shimadzu TV-1900 double-beam UV-vis-NIR spectrophotometer.

The XRD θ-2θ scans of the obtained In_2O_3 samples deposited on Al_2O_3 (0001) substrates are shown in Fig.1. Fig.1(a), (b), (c) and (d) correspond to the samples prepared at 700 °C and annealed at 800 °C, 900 °C and 1 000 °C, respectively. From Fig.1(a) and (b), besides the diffraction peak of Al_2O_3 (0006) at around 41.6°, four peaks corresponding to body centered cubic (bcc) structure In_2O_3 (222), (444) and In_2O_3 (400), (800) (JCPDS #06-0416) are clearly observed. As the annealed temperature increases to 900 °C and 1 000 °C, two another diffraction peaks corresponding to In_2O_3 (411) and (822) plan can be detected. The main In_2O_3 peaks are strong and sharp with a narrow full width at half maximum (*FWHM*), which means the crystal qualities of the samples are good. And the crystal qualities of the samples grew at 700 °C and annealed at 800 °C are better than those of samples annealed at 900 °C and 1 000 °C.



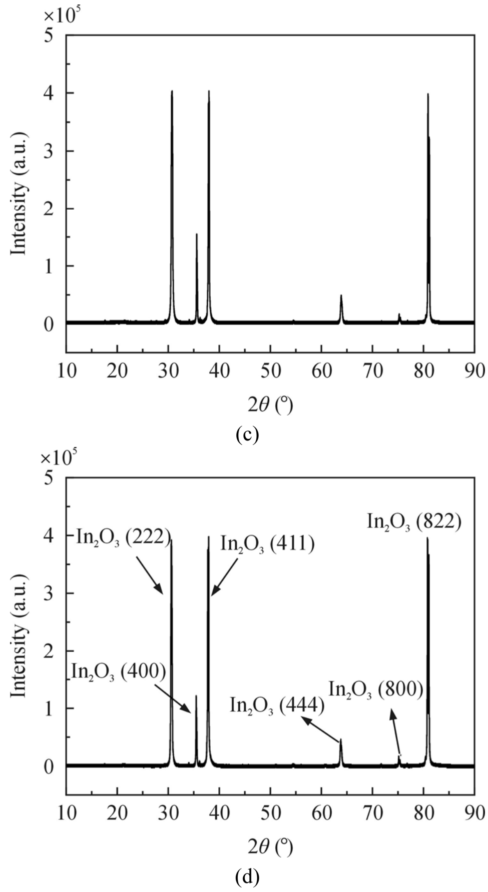


Fig.1 XRD θ-2θ scans of the In_2O_3 films (a) deposited at 700 °C and annealed at (b) 800 °C, (c) 900 °C and (d) 1 000 °C

Fig.2 shows the SEM images of the In_2O_3 films deposited at 700 °C and annealed at 800 °C, 900 °C and 1 000 °C. All the samples exhibit a compact surface with clear grains and well-defined grain boundaries, indicating good film crystallinity. Thus the polycrystalline structures were obtained. Before annealing, the grains present triangle or quadrangle morphologies as shown in Fig.2(a). After the annealing treatment, the corner angles of the grains become smooth, and as the annealing temperature increases to 1 000 °C, round grains can be observed. And the grain size becomes larger with the increase of annealing temperature.

Fig.3 shows the resistivity (ρ), Hall mobility (μ) and carrier concentration (n) of the In_2O_3 films as a function of the annealing temperatures. The resistivity of the sample prepared at 700 °C is about 1.6×10^{-2} Ω·cm. After annealing at 800 °C, the resistivity is increased to 1.4×10^{-1} Ω·cm, then as the increase of annealing temperature, the resistivity of the samples drops slightly. As the temperature increases from 700 °C to 900 °C, the carrier concentration is decreased from 2.08×10^{19} cm^{-3} to 1.97×10^{18} cm^{-3}, and then is increased slightly to 3.13×10^{18} cm^{-3}. The highest Hall mobility of the samples obtained from the sample annealed at 900 °C is about 24.74 cm^2·V^{-1}·s^{-1}.

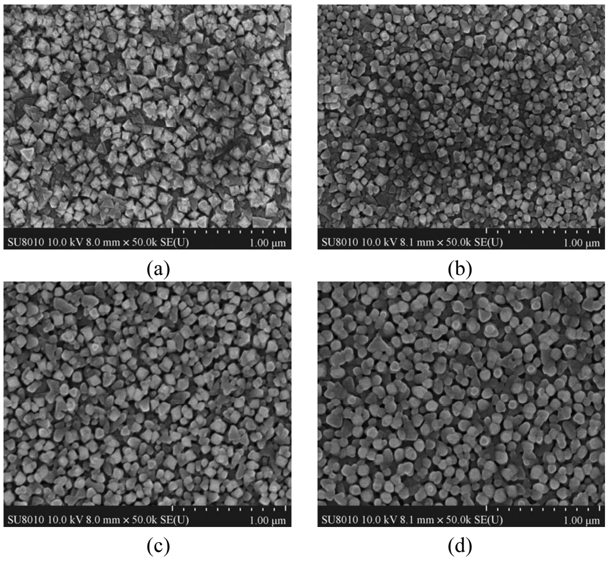


Fig.2 SEM images of the In_2O_3 films (a) deposited at 700 °C and annealed at (b) 800 °C, (c) 900 °C and (d) 1 000 °C

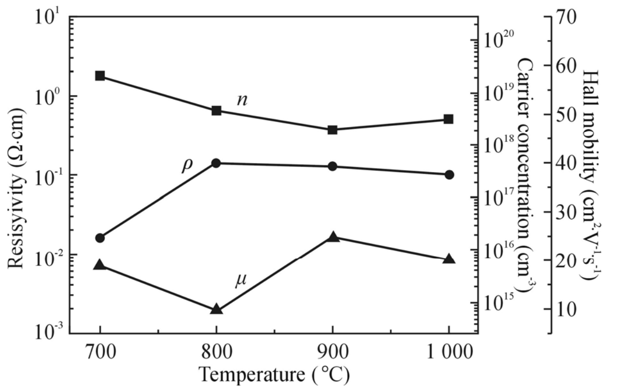


Fig.3 Resistivity (ρ), carrier concentration (n) and Hall mobility (μ) of the In_2O_3 films as a function of annealing temperatures

Fig.4 shows the optical transmittance spectra of the deposited samples as a function of wavelength in the range of 200—800 nm. The average transmittance of the In_2O_3 films grown at 700 °C and annealed at 800 °C, 900 °C and 1 000 °C in the visible range are about 94.3%, 94.3%, 93.9% and 90.6%, respectively. For direct transition semiconductors, the absorption coefficient (α) and optical band gap (E_g) are related by

$$\alpha hv=A(hv-E_g)^{1/2}, \quad (1)$$

where E_g is defined as the energy corresponding to the onset of significant optical absorption[14,15], h is the Planck's constant, v is the frequency of the incident photon, and A is a material dependent constant. So the optical band gap of the films can be estimated by plotting $(\alpha hv)^2$ versus hv and extrapolating the straight-line portion of the plot to the x-axis. As shown in Fig.5, the optical band gaps of the samples are about 3.73 eV, 3.71 eV, 3.70 eV and 3.69 eV corresponding to the In_2O_3 films deposited at 700 °C and annealed at 800 °C, 900 °C and 1 000 °C, respectively. As the temperature increases, the optical band gaps of the samples narrows down.

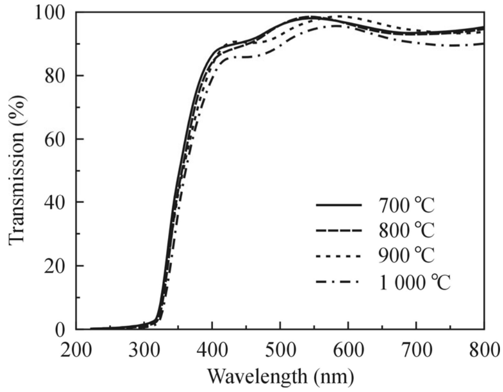


Fig.4 The optical transmittance spectra of the In_2O_3 films deposited at 700 °C and annealed at 800 °C, 900 °C and 1 000 °C in the range of 200—800 nm

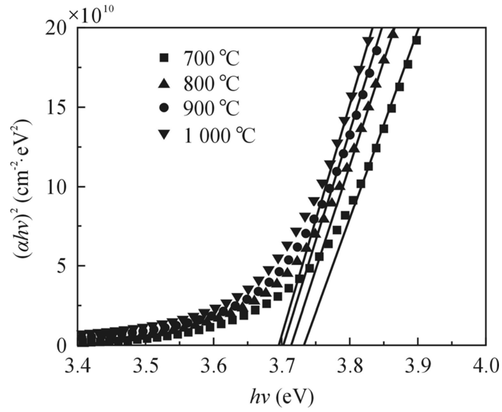


Fig.5 The plot of $(\alpha hv)^2$ versus hv for the In_2O_3 films deposited at 700 °C and annealed at 800 °C, 900 °C and 1 000 °C

In_2O_3 films were deposited on Al_2O_3 (0001) substrates by MOCVD method. The structural, optical and electrical properties as well as the surface morphology of the samples can be affected by annealing treatment. The highest Hall mobility of the samples is obtained for the sample annealed at 900 °C with the value of about 24.74 $cm^2 \cdot V^{-1} \cdot s^{-1}$. The absolute average transmittance of the obtained films in the visible range exceeds 90%, and the optical band gaps of the samples are about 3.73 eV, 3.71 eV, 3.70 eV and 3.69 eV corresponding to the films deposited at 700 °C and annealed at 800 °C, 900 °C and 1 000 °C, respectively.

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