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Growth of In_2O_3 thin films on silicon by the metalorganic chemical vapor deposition method

Nam Ho Kim, Ju Hyun Myung, Hyoun Woo Kim[*], and **Chongmu Lee**

School of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

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We have deposited indium oxide (In_2O_3) films on silicon substrates by the metal organic chemical vapor deposition (MOCVD). We have investigated the effect of substrate temperature on growth and structural properties of films in the range of 200–300 °C. The films had a preferred orientation along [111] direction, with the X-ray diffraction (XRD) full width at half-maximum (FWHM) of less than 0.4°.

1 Introduction

Since indium oxide (In_2O_3) is a transparent semiconducting oxide material which is an n-type semiconductor with a wide band gap, it has recently attracted great interests as a material for photovoltaic devices, electro-optical devices, and sensor of oxidizing gases [1–6].

For the production of In_2O_3 films, various synthetic methods such as evaporation [7, 8], sputtering [9–12], spray pyrolysis [13–16], atomic layer deposition [17], thermal oxidation [18], ion assisted deposition [19], pulsed laser deposition [20–22], ultrasonic spray chemical vapor deposition (CVD) [23], and metalorganic CVD (MOCVD) [24–26] have been studied.

MOCVD is supposed to be one of the simplest techniques for the growth of high-quality films, with an advantage of producing uniform, reproducible, and adherent films. Also, the employment of silicon (Si) substrate needs to be studied not only because there are not many reports on growth using the Si substrate, but also because it will pave the way for integration of future devices with developed Si integrated circuit technology. Accordingly, in this paper, we demonstrate the deposition of In_2O_3 films on Si substrate using a simple reaction of a triethylindium (TEI) and oxygen (O_2) mixture. In order to investigate the possibility of obtaining the oriented In_2O_3 films at low temperatures, we have varied the substrate temperature in the range 200–300 °C.

2 Experimental

The In_2O_3 films were deposited in a vertical MOCVD on Si substrate with (001) orientation. Schematic representation of the MOCVD reactor used in our experiments was previously reported [27]. TEI and O_2 have been used, respectively, as indium and oxygen sources. High-purity Ar, used as the carrier gas, passed through the TEI bubbler and saturated with TEI vapor to the reactor. The TEI bubbler was maintained at the temperature of 35 °C. The substrate was cleaned with organic solvents and dried before

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[*] Corresponding author: e-mail: hwkim@inha.ac.kr, Phone: +82 32 860 7544, Fax: +82 32 862 5546

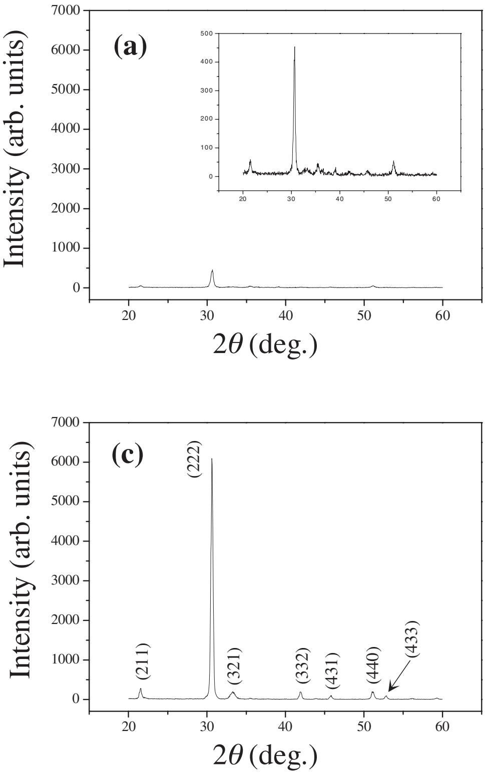

Fig. 1 XRD patterns of In_2O_3 deposits on Si substrates at a substrate temperature of a) 200 °C, b) 250 °C, and c) 300 °C. The inset shows the enlarge-ment of the XRD patterns.

loading into the system. The In_2O_3 film was synthesized by supplying O_2 and Ar carrier gases, respectively, with the flow rate of 5 standard cubic centimeters per minute (sccm) and 20 sccm. The substrate temperature has been varied in the range 200–300 °C with the deposition time of 20 minutes.

In order to study the structural properties of deposited In_2O_3 film, we used a scanning electron microscopy (SEM, Hitachi, S-4200) and an X-ray diffraction (XRD, Philips, X'pert MPD, $CuK_{\alpha 1}$ ($\lambda = 0.15405$ nm)). The growth rate was determined by dividing the film thickness by the deposition time, with a unit of micrometers (μm) per hour (hr).

3 Results and discussion

Figure 1 shows the XRD patterns of deposits on Si substrates at substrate temperatures in the range of 200–300 °C. The θ–2θ scan data from the deposits at 250–300 °C exhibit main peak at 30.58°, corresponding to (222) diffraction peak of cubic bixbyite In_2O_3 phase (JCPDS 44-1087), in addition to the strong peak at 69°, corresponding to the (004) peak of Si substrate (not shown here). Figure 1a indicates that although the deposit prepared at 200 °C does not show a strong In_2O_3 diffraction peak compared to those prepared at 250–300 °C, a In_2O_3 (222) peak of low intensity appears. The (222) diffraction peaks from the deposits are relatively strong compared to the neighbouring diffraction peaks, which means a preferred orientation along the [111] direction.

Figure 2 indicates that the full width at half-maximum (FWHM) of the (222) diffraction peak at a substrate temperature of 200, 250, and 300 °C, respectively, are 0.3940, 0.3521, and 0.3380, revealing that the FWHM of the (222) diffraction peak is less than 0.4° and decreases with increasing substrate temperature in the range of 200–300 °C. Since the FWHM of the (222) diffraction peak is inversely proportional to the grain size of the film, we suppose that the grain size of the In_2O_3 thin film increases by

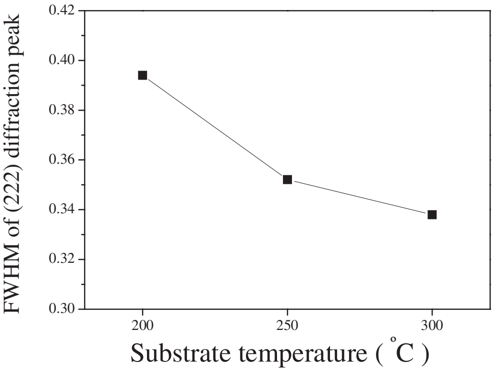

Fig. 2 FWHM of the (222) diffraction peak at a substrate temperature of 200 °C, 250 °C, and 300 °C.

increasing the substrate temperature in the range of 200–300 °C. In order to evaluate the mean grain size (D) of the films based on the XRD results, we adopted the Scherrer formula [28] $D = 0.9\lambda/(B \cos \theta)$, where λ, B, θ were X-ray wavelength (0.15405 nm), the FWHM of In_2O_3 (222) diffraction peak, and the Bragg diffraction angle, respectively. The mean grain sizes of the films are calculated to be 21.0, 23.4, and 24.4 nm, respectively, at a substrate temperature of 200, 250, and 300 °C.

Figure 3 shows the cross-sectional SEM images at substrate temperatures of 200, 250, and 300 °C. According to SEM images, we reveal that the thicknesses of the films grown at 200, 250, and 300 °C, respectively, are in the range of 290–320 nm, 660–840 nm, and 1740–2190 nm.

The variation of the growth rate with substrate temperature is shown in the Arrhenius plot of Fig. 4. The average growth rate increases with increasing the substrate temperature, from 0.92 μm/h at 200 °C

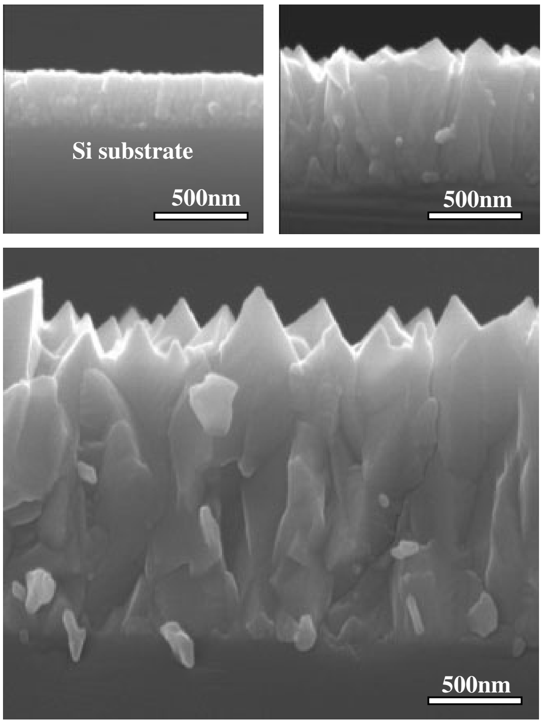

Fig. 3 Cross-sectional SEM images of In_2O_3 films at a substrate temperature of a) 200 °C, b) 250 °C, and c) 300 °C.

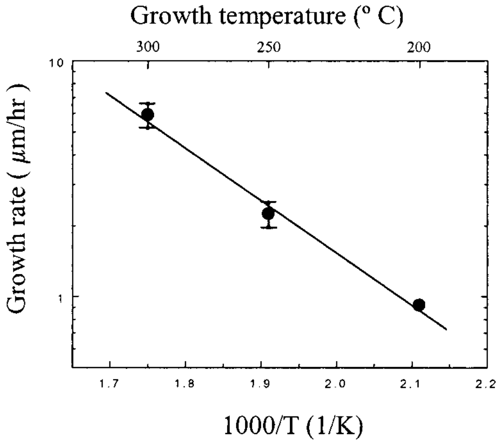

Fig. 4 Arrhenius plot of the growth rate versus reciprocal temperature. The error bars indicate the uncertainty in measuring film thickness due to surface roughness

to 5.9 μm/h at 300 °C. The activation energy at temperatures in the range of 200–300 °C is approximately 10.2 kcal/mol.

Figure 5 shows the plan-view SEM images of In_2O_3 thin films, indicating that the triangular-shaped grain structures appear on top of the film at substrate temperatures of 250–300 °C. We surmise that at higher temperature, the atoms have enough diffusion activation energy to occupy the correct site in the crystal lattice and thus grains with the energetically favored orientation will become larger. In Fig. 5b and 5c, the grain structures with smooth facets and a sharp tip are shown on the surface of the films. From the geometrical shapes of the grain structures and the XRD analysis (Fig. 1), we surmise that the tip direction normal to the triangular-shaped plane is along the [111] direction. The detailed role of temperature on the grain growth and orientation in the In_2O_3 thin film needs to be fully understood and more systematic study is necessary.

4 Conclusions

We have demonstrated the deposition of In_2O_3 thin films on Si substrates using the TEI as a precursor in the presence of oxygen. The growth rate of In_2O_3 thin films increases with increasing substrate temperature. The XRD results show that (222) orientation with the cubic structure dominates for the films deposited at 200–300 °C. The grain size and the FWHM of (222) XRD peak, respectively, increase and decrease, with increasing the substrate temperature. The production of In_2O_3 thin films on Si substrate using the simple MOCVD technique will shed light on the potential application of In_2O_3 films.

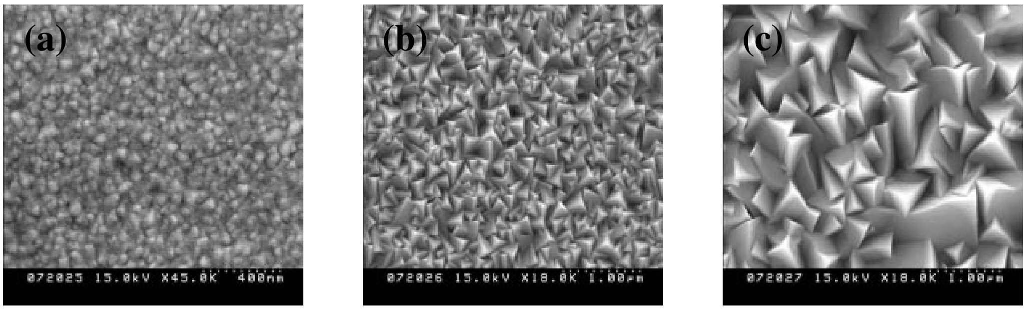

Fig. 5 Plan-view SEM images of In_2O_3 films at a substrate temperature of a) 200 °C, b) 250 °C, and c) 300 °C.

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