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Effects of deposition temperatures and annealing conditions on the microstructural, electrical and optical properties of polycrystalline Al-doped ZnO thin films

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ABSTRACT

Al-doped ZnO (AZO, ZnO:Al_2O_3 = 98:2 wt%) films are deposited on different substrates by an RF magnetron sputtering and subsequently annealed at three different conditions to investigate the microstructural, electrical, and optical properties. X-ray diffraction and scanning electron microscope results show that all the samples are polycrystalline and the samples rapid-thermal-annealed at 900 °C in an N_2 ambient contain larger grains compared to the furnace-annealed samples. It is shown that the sample deposited at room temperature on the sapphire gives a resistivity of 5.57×10^{-4} Ω cm when furnace-annealed at 500 °C in a mixture of N_2:H_2 (9:1). It is also shown that the Hall mobility vs. carrier concentration (μ–n) relation is divided into two groups, depending on the annealing conditions, namely, either rapid-thermal annealing or furnace annealing. The relations are described in terms of either grain boundary scattering or ionized impurity scattering mechanism. In addition, the samples produce fairly high transmittance of 91–96.99% across the wavelength region of 400–1100 nm. The optical bandgaps of the samples increase with increasing carrier concentration.

1. Introduction

Transparent conducting oxides (TCOs) are of considerable technological importance for their applications in various devices, such as flat-panel displays and thin-film solar cells, and so on [1–3]. In order for TCOs to contribute to the improvement of the performance of such devices, TCOs should have high transmittance as well as good electrical properties. Sn-doped In_2O_3 (ITO) is the most commonly used and investigated TCO [3,4]. However, indium is unstable in a reduced ambient and is facing exhaustion [5]. For this reason, hexagonal ZnO has attracted significant attention because of the possibility of replacing ITO. Several groups showed that group III elements-doped ZnO films produced fairly similar properties compared to those of ITO films [6–8]. For example, Minami et al. [7] reported that Al-doped ZnO (AZO) films exhibited a resistivity as low as 2×10^{-4} Ω cm and a visible transmittance of ∼85%. Park et al. [8] also reported on the growth of AZO films having a resistivity of 1.33×10^{-4} Ω cm and a visible transmittance of about 88%. To replace ITO films, however, the further improvement of the electrical and optical properties of AZO films is required. To achieve the goal, a wide variety of ways, such as the variation of deposition conditions and/or different deposition techniques, have been extensively investigated so far [9–12]. Among various deposition methods, radio frequency (RF) magnetron sputtering has been widely used because of the advantages, such as a low substrate temperature, the good adhesion and thickness uniformity of films, the good controllability and long-term stability of the process, and its relatively low cost [13]. Furthermore, it was shown that the electrical and optical properties of AZO films were improved when the films were post-deposition-annealed. For example, Lennon et al. [14], investigating the growth of AZO films on fused quartz substrates, showed that rapid-thermal-annealing at 350 °C for 30 min in a N_2 ambient caused reduction in the resistivity of the films, namely, it decreased from 3.79×10^{-3} to 7.19×10^{-4} Ω cm after annealing. The annealed samples showed an average transmittance of 86.9%. Kim et al. [15] deposited AZO films on sapphire substrates and then annealed them in a N_2 ambient at 900 °C for 3 min. The annealed samples produced a mobility of 65.5 cm^2/V s and a carrier concentration of 1.03×10^{20} cm^{-3}. Fang et al. [16] also investigated AZO films deposited on soda-lime glass substrates, which were annealed at temperatures above 400 °C for 2 h in vacuum <10^{-5} Torr. The 450 °C-annealed samples yielded a resistivity of 3.33×10^{-4} Ω cm and the 400 °C-annealed samples exhibited a visible transmittance of about 90%. Oh et al. [17] deposited AZO films on glass substrates and then annealed them for 1 h at 300 °C in a H_2 ambient. The annealed samples showed a resistiv-

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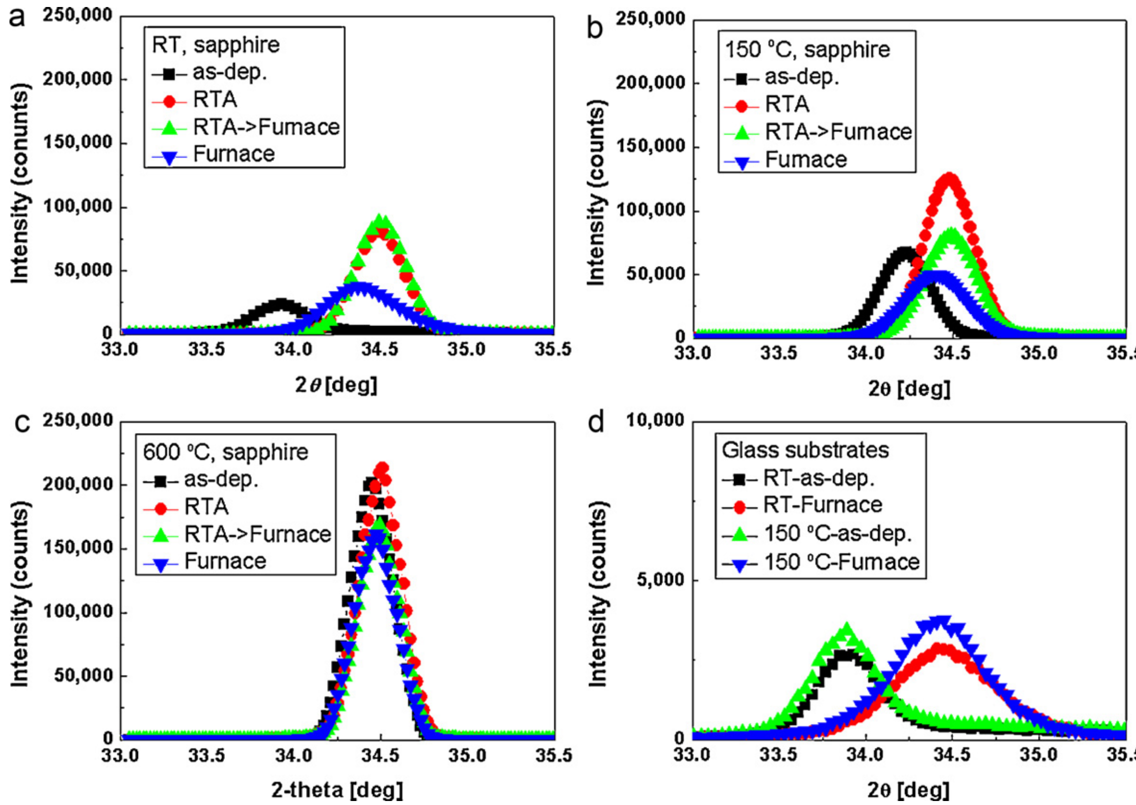

Fig. 1. XRD θ–2θ profiles of the samples deposited on sapphire substrates at (a) RT, (b) 150 °C, (c) 600 °C, and (d) on the glass substrates deposited at RT and 150 °C.

ity of 8.30×10^{-4} Ω cm and a visible transmittance of ~90%. Kim et al. [10] intentionally added Zn during the deposition of AZO (ZAZO) films at various temperatures, which were then annealed at different conditions. They showed that the ZAZO films yielded somewhat comparable electrical, optical and structural properties to those of AZO films deposited at optimum temperature. However, there are few works describing the effects of deposition temperatures combined with post-deposition annealing conditions on the microstructural, electrical and optical properties of AZO films. Thus, in this work, we investigated the effects of deposition temperatures and annealing conditions on the microstructural, electrical and optical properties of Al-doped ZnO films deposited on different substrates using an RF magnetron sputtering system. It is shown that the mobility-carrier concentration (μ–n) relations of the samples depend on the annealing conditions used. The samples deposited on the sapphire substrates at room temperature exhibit a low resistivity of 5.57×10^{-4} Ω cm and an average transmittance of 96.99% across the 400–1100 nm region, when furnace-annealed at 500 °C in a mixture of N_2:H_2 (9:1) gases.

2. Experimental

Polycrystalline Al-doped ZnO films (600–700 nm thick) were deposited on Corning Eagle 2000 glass and *c*-plane sapphire substrates by a conventional RF magnetron sputtering system. A 2-inch ZnO target doped with Al (ZnO:Al_2O_3 = 98:2 wt%, 4N, LTS Chemical Co.) was used. The base pressure of a main chamber was maintained below 1×10^{-6} Torr. After cleaning, the substrates were loaded into the main chamber through a load-lock chamber. Pre-sputtering was performed for at least 5 min before commencing deposition. The substrate temperatures used were room temperature (RT), 150 or 600 °C, and other deposition parameters were fixed for all the samples, namely an Ar:O_2 working gas ratio of 16:1, a working pressure of 10 mTorr, and a RF power of 120 W. For the glass substrate, the samples were deposited only at RT and 150 °C. The samples were annealed under three different conditions. First, the samples were annealed at 900 °C for 1 min in a N_2 ambient in a rapid-thermal-anneal (RTA) system. Second, the samples were annealed by a two-step process, namely, first RTAed at 900 °C and then tube-furnace-annealed in a mixture of N_2:H_2 gases (9:1) at 500 °C for 1–2 h. Third, the samples were annealed in a tube furnace in a mixture of N_2:H_2 (9:1) at 500 °C for 1–2 h. The samples deposited on the glass substrates were only furnace-annealed because the Eagle 2000 glass substrates can be softened above 660 °C. Hall measurements were performed using Ecopia HMS-3000 system equipped with a permanent magnet of 0.55 T. Transmittance spectra (300–1100 nm) were measured using a Shimadzu UV-1800 spectrophotometer. X-ray diffraction (XRD) θ–2θ measurements were performed using a PANalytical X'pert Pro system equipped with a Cu Kα target. The thicknesses and the microstructures of the samples were characterized by a high resolution FE-scanning electron microscope (SEM)(Hitachi S-4800).

3. Results

Fig. 1 shows the XRD θ–2θ profiles for AZO films deposited on different substrates as a function of the substrate temperature and subsequent annealing conditions. All the samples showed only intense (0 0 2) peaks, indicating the polycrystalline nature. The peak intensities of the samples on the sapphire substrates that were either RTAed or two-step annealed are stronger than those of the as-deposited and furnace-annealed samples. The samples deposited on the sapphire substrates at 600 °C show the most intense peak, while the samples deposited on the glass substrates exhibit the lowest intensity. Measurements showed that the samples deposited at 600 °C showed larger grains than those of the samples deposited at RT or 150 °C. It is noted that upon annealing, the peaks of the as-deposited samples shift toward the higher