The electrical and optical properties of ZnO:Al films prepared by ultrasonic spray pyrolysis

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초음파 분무법으로 제조한 ZnO:Al 박막의 전기 및 광학적 특성

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Abstract

Transparent conductive aluminum-doped ZnO (AZO) films were prepared by a ultrasonic spray pyrolysis method at the substrate temperature below 230℃. A vertical type hot wall furnace was used as a reactor in the deposition system. Zinc acetate dissolved in methanol was selected as a precursor. The substrate temperature was varied from 180℃ to 240℃. Aluminum (Al) was doped into ZnO films by incorporating anhydrous aluminum chloride ($AlCl_3$) in the zinc acetate solution. The proportion of the Al in the starting solution was varied from 0 wt % to 3.0 wt %. The crystallographic properties and surface morphologies of the films were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The resistivity of the films was measured by the Van der Pauw method, and the mobility and carrier concentration were obtained through the Hall effect measurements. Transmittance was measured in the visible region. The effects of substrate temperature and aluminum content in the starting solution on the structural and electrical properties of the AZO films are discussed.

1. Introduction

Transparent conductive films such as Sn-doped In_2O_3(ITO), SnO2 and ZnO have been widely studied for their practical applications as window materials in display, solar cells and various optoelectronic devices. Up to this time, ITO films have been generally used for the applications due to low resistivity and stable physical properties even though ITO is relatively expensive and unstable in an ambient of active hydrogen. Nowadays ZnO films have attracted much attention as the transparent conductive films because of their amenability to doping, low cost, non-toxicity and stability in the hydrogen atmosphere [1, 2]. Undoped and doped ZnO films can be prepared by various methods, e. g., spray pyrolysis [3-5], rf magnetron sputtering [6-8] and metalorganic chemical vapor deposition (MOCVD) [9, 10]. The ZnO target employed in the rf magnetron sputtering system and the alkylmetal compounds used as precursors in MOCVD are very expensive. Although the spray pyrolysis method has an advantage over the other growth methods in the cost of raw materials, it has a problem in the uniformity of the films grown. Recently, several researchers [11-13] have reported that ZnO films with c-axis orientation can be grown by ultrasonic spray pyrolysis (USP). The USP technique is considered to be a very useful method due to the simplicity of the apparatus and the low cost of the raw materials used. The USP method has an advantage in the uniformity of the films deposited over the conventional spray pyrolysis as well. The as deposited doped ZnO films grown by the pyrolysis methods including USP, however, have shown the resistivity ($\sim 10^{-2}\Omega$cm) to be much higher than that ($\sim 10^{-4}\Omega$cm) of rf magnetron sputtered doped ZnO films.

In this paper, we grew transparent conductive aluminum-doped ZnO (AZO) films by USP at the substrate temperature as low as 220℃. The structural and electrical properties of the AZO films are studied. The effects of substrate temperature and aluminum (Al) content in the starting solution on the structural and electrical properties of the AZO films are discussed. We try to find out the factors that hinder the AZO films from being improved in conductivity.

2. Experimental procedure

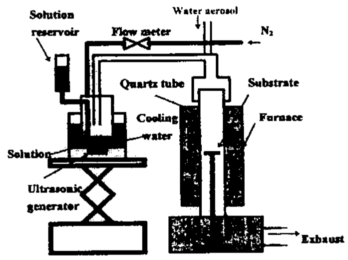

Fig. 1. Schematic diagram representing the ultrasonic spray pyrolysis apparatus.

Fig. 1 shows a schematic diagram of the USP apparatus that we developed. A vertical type hot wall furnace is used as the reactor in the deposition system. A hot wall reactor has an advantage over a cold wall reactor in that temperature control is easy. The reactor is 20 cm long and the substrates are placed at the center. In this pyrolysis process, zinc acetate dissolved in methanol was selected as a precursor. The concentration of zinc acetate in the methanol was 0.03 mol/ℓ. Aerosols of the solution produced by the ultrasonic generator are conveyed by nitrogen gas to the heated substrate that is placed at the center of the reactor. The flow rate of the carrier gas was 1 ℓ/min. Sodium glasses were used as substrates. The substrate temperature was varied from 180℃ to 240℃. We doped the ZnO films with Al by incorporating anhydrous aluminum chloride ($AlCl_3$) in the zinc acetate solution. The proportion of the Al in the starting solution was varied from 0 wt % to 3.0 wt %. At higher Al doping (above 4.0 wt %), the films tended to be powdery in nature. The film thickness was measured using an α-step (Tencor Instruments 500). The crystallographic properties of the films were analyzed by X-ray diffraction (XRD) using CuK_α radiation, and the scanning range was between 2θ=20 and 60°. The surface morphologies of the films were studied by scanning electron microscopy (SEM). The resistivity of the films was measured by the Van der Pauw method. The mobility and carrier concentration were obtained through the Hall effect measurements. The optical properties were studied by the measurements of transmittance in the visible region.

3. Results and discussion

It has been known [14] that an Al impurity doped into ZnO films can act as an effective donor as a result of substitutional introducing of Al^{3+} at the Zn^{2+} site generating one free carrier.

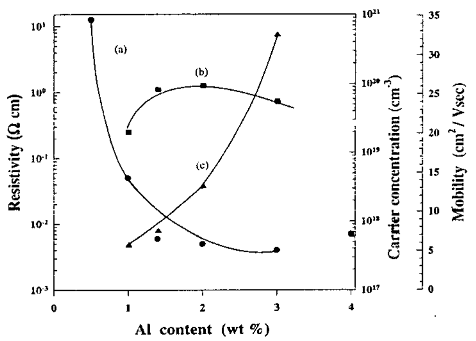

Fig. 2. (a) Resistivity, (b) carrier concentration and (c) Hall mobility as a function of Al content in the solution. All the samples were prepared at 230℃.

Fig. 2 shows how the resistivity, carrier concentration and mobility of AZO films are related to Al content in the starting solution. All the samples were prepared at the substrate temperature of 230℃. The resistivity decreases drastically to ~ 5.0 x 10^{-3}Ωcm for the AZO prepared with the 1.4 wt % solution. Any further increase of the Al content in the solution does not show a remarkable decrease in the resistivity of the AZO films. The carrier concentration for AZO films is between $10^{19}cm^{-3}$ and $10^{20}cm^{-3}$, which is lower than that [8] of the AZO films prepared by rf magnetron sputtering by an order of 10. As Al content in the solution increases, the carrier concentration also increases and reaches a maximum value of ~9.5 x $10^{19}cm^{-3}$ for a 2.0 wt % solution. On the other hand, the carrier concentration decreases to ~5.8 x $10^{19}cm^{-3}$ for a 3.0 wt % solution. The above behavior of the carrier concentration can be explained by the segregation of Al. When Al atoms are added to ZnO, excess Al atoms above a certain critical concentration in the ZnO films are segregated into the grain boundaries in the form of Al_2O_3. The mobility increases as the Al content in the AZO film increases. The increase of the mobility is due to the enlarged grains by adding Al into the ZnO films, which is the main factor in lowering the resistivity of AZO.

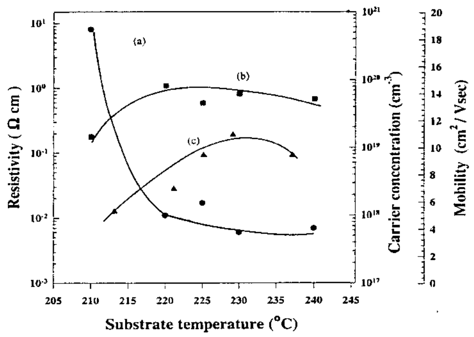

Fig. 3. (a) Resistivity, (b) carrier concentration and (c) Hall mobility dependence on substrate temperature. All the samples were prepared from the 1.4 wt % solution.

Fig. 3 shows the variations of the resistivity, carrier concentration and mobility with respect to the substrate temperature for AZO films prepared from the 1.4 wt % solution. The resistivity of the AZO films decreases rapidly at the substrate temperature of 220℃, which is due to the increase of the carrier concentration and the mobility. However the carrier concentration decreases a little bit beyond the substrate temperature of 220℃. Above 220℃, we think, the concentration of Al atoms in the aerosol decrease before the Al atoms arrive at the substrate due to the high temperature of the reactor.

AZO films are expected to have a high transmittance due to the increased grain size. Fig. 4 shows the optical transmittance of the AZO films prepared from solutions having different Al contents at the substrate temperature of 230℃. The optical transmittance is between 80 % and 95 % in the visible range for all the samples. The optical transmittance of AZO films deposited at different temperatures is shown in Fig. 5. As the substrate temperature increased above 240℃, the AZO films became brownish in appearance resulting in the reduction of the transparency. The optical energy band gap obtained from Fig. 4 and Fig. 5 was ~3.3 eV, and a noticeable shift in energy band gap (blueshift) was not observed.

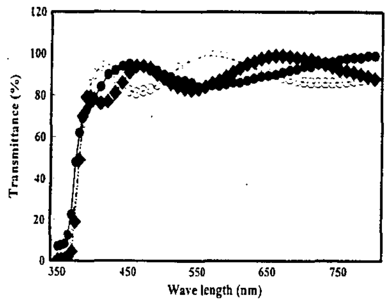

Fig. 4. Transmission spectra for the 300 nm-thick AZO films prepared from the 0.1 (●), 1.0 (◆) and 3.0 (○) wt % solution at 230℃.

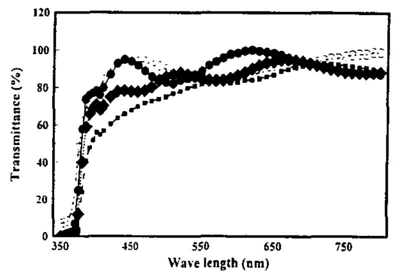

Fig. 5. Transmission spectra for the 300 nm-thick AZO films prepared from the 1.4 wt % solution at 210 (●), 220 (◆), 230 (○) and 240 (■) C.

4. Conclusions

Highly conductive and transparent aluminum -doped ZnO (AZO) films were prepared by ultrasonic spray pyrolysis at low substrate temperatures below 230℃. Zinc acetate dissolved in methanol was used as a precursor. Aluminum (Al) was doped into ZnO films by incorporating anhydrous aluminum chloride ($AlCl_3$) in the zinc acetate solution. Al doping lead to increase in the grain size with a disk-like hexagonal structure. The grain size increased as the substrate temperature increased, also. Samples with the resistivity of ~5.0 x $10^{-3}\Omega$ were prepared by using the 3.0 wt % (Al) solution at the substrate temperature of 230℃. The carrier concentration for AZO films was between 10^{19} cm^{-3} and 10^{20} cm^{-3}. The increased mobility, which is due to the enlarged grains by adding Al into the ZnO films, is considered to be the main factor in lowering the resistivity of AZO films. The optical transmittance was between 80 % and 95 % in the visible range and the optical energy band gap was ~3.3 eV for all the samples.

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