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Preparation and Characterization of Sol-Gel $Zn_kIn_2O_{k+3}$ Transparent Conducting Thin Films

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Abstract

The objective of this research was to study properties of several $Zn_kIn_2O_{k+3}$ thin films prepared by a sol-gel process. The precursors, zinc-acetate and indium-nitrate, were mixed in different ratios using 2,4-pentanedione as a solvent. Due to the instability of the k=5 solution, this research focuses on the properties of $Zn_3In_2O_6$ (k=3) thin films. Films, deposited on vitreous silica substrates, were fired at different temperatures, and characterized by SEM, EDS, and X-ray diffraction. The films fired at different temperatures have about 80% transmittance in the visible region. The minimum resistivity in the order of 1 Ω-cm is of the film fired at 600°C in H_2/N_2. This value, which is higher than the optimum value for transparent conducting oxides, is probably due to the reaction between the films and the substrates, forming Zn_2SiO_4.

Introduction

Due to their fundamental band gap, transparent conductors exhibit high ultraviolet absorption while they show infrared reflection of about 90%, in addition to their high electrical conductivity. Their unique properties make them useful for a large number of applications such as solar cells, flat plate collector technologies, thin-film gas sensors, most electrochromic devices, and liquid crystal display (LCD). (Palmer, *et al.* 1998; Jarzebski, 1982).

Among the compounds used to produce transparent conductors, Sn-doped indium oxide or ITO is the most widely used. However, it is strongly absorbing in the range of 1.0-1.5 μm, which is in the working range of contacts for surface emitting lasers (Phillips, *et al.* 1995; Minami, *et al.* 1996). Compounds in the In_2O_3-ZnO system, expressed as $Zn_kIn_2O_{k+3}$, have shown good electrical conductivity and transparency. For example, thin films of $Zn_kIn_2O_{k+3}$, deposited by sputtering techniques, have a conductivity as high as 3,000 S/cm and transmittance above 95% (Minami, *et al.* 1996) (compared to ITO's conductivity of 1000-1500 S/cm and transmittance of 85-90%).

In this work, $Zn_kIn_2O_{k+3}$ films were prepared by using the sol-gel method, and characterized in terms of electrical conductivity, optical properties, surface morphology, and phase analysis. Films fired at different temperatures and under different atmospheres were compared in terms of these characteristics.

Experimental Approach

Solution Preparation

Precursors used in this study were zinc-acetate and indium-nitrate. These two precursors were mixed in a stoichiometric ratio based on 1/250 mole of ZnO. Two mole ratios of In to Zn were prepared, which were 2:3 (k=3) and 2:5 (k=5). As a solvent, 2,4-pentanedione was used to make solutions with a concentration of 0.46 mole per liter. All the solutions were mixed by refluxing at 150°C for 24 hours.

Film Preparation and Characterization

Solutions were aged for 24 hours at room temperature before film deposition because discontinuous films would be obtained if the spin coating was done immediately after the solutions cooled down. After aging, k=5 solution precipitated; therefore, only k=3 films would be prepared and characterized.

The substrates used in this study were vitreous silica slides. Films were prepared on the substrates by using a spin coater at 1,500 rpm for 30 seconds. In the process of making a film, after spin coating a layer, the film was dried at about 250°C for 15-20 minutes, and was then cooled down before depositing another layer until reaching three layers.

Characterization of films fired for an hour at increasing temperatures (600 900 1,100 and 1,200°C) in air includes;

- surface morphology by SEM
- elemental and phase analysis by EDS and XRD
- transparency (also of films fired in reducing atmosphere*) by UV-Vis and FT-IR spectrometers
- electrical resistance (also of films fired in reducing atmosphere*) by four-point probe.

*all films were fired at 500°C for an hour in $4\%H_2/96\%N_2$, and they are called by the temperatures when fired in air.

Results and Discussion

Surface Morphology

SEM micrograph of dried film on a vitreous silica substrate is shown in Figure 1. It is apparent that the film starts to crinkle after it is dried, which is probably due to the thermal mismatch between the film and substrate.

Film Composition and Phase Analysis

By EDS, all the films on vitreous silica substrates fired at increasing temperatures have the same elements; Zn, In, Si from the substrates, and Au and Pd from the SEM preparation process, as shown in Figure 3.

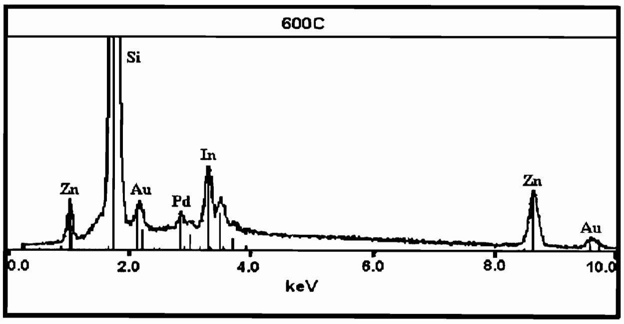
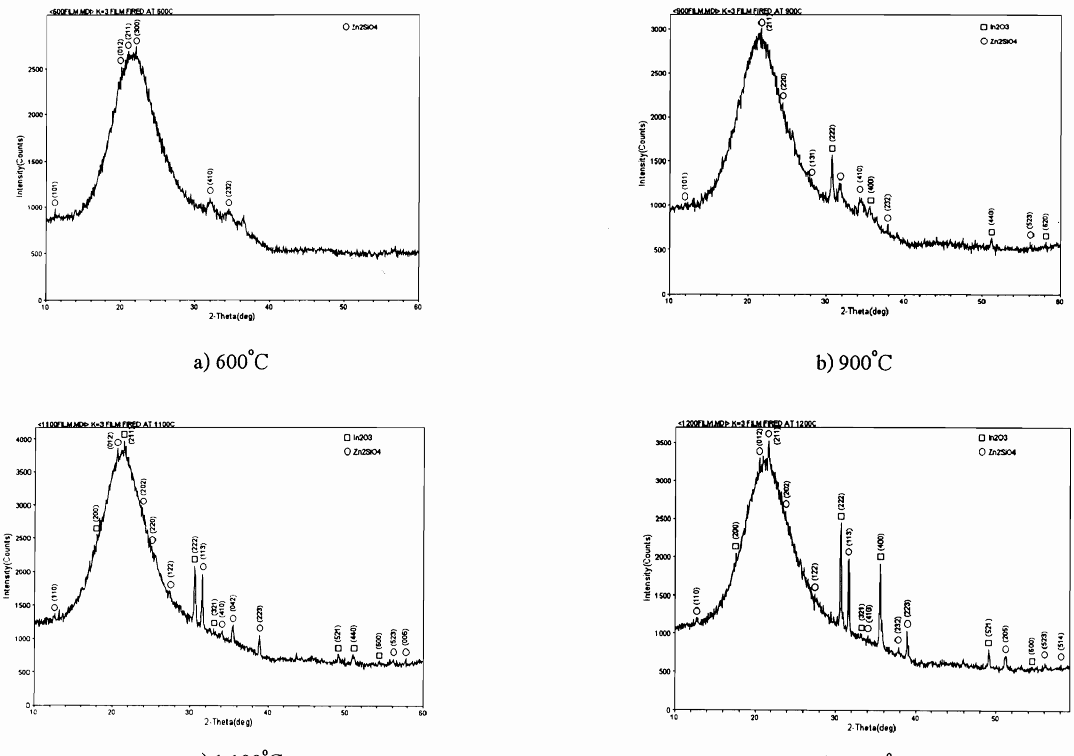


Figure 3 EDS spectra of k=3 films fired at 600 900 1,100 and 1,200°C in air

Phase analysis by x-ray diffraction is shown in Figure 4. The result agrees with that from the SEM. At 600°C, only poorly crystallized Zn_2SiO_4 is present. At 900°C, the film presents a small amount of poorly crystallized In_2O_3 and Zn_2SiO_4. After being fired at 1,100 and 1,200°C, more In_2O_3 and Zn_2SiO_4 crystallize progressively and with a better crystallinity.



a) 600°C

b) 900°C

c) 1,100°C

d) 1,200°C

Figure 4 X-ray profiles of k=3 films fired at increasing temperatures in air

Optical Properties

UV-Vis spectra of films on vitreous silica substrates fired in air and in reducing atmosphere are shown in Figure 5 and 6 respectively. These films have good transparency in the visible region with a transmittance of about 80%, which is comparable to films made by other processes.

In the wavelength of 300-400 nm, there is a hump in each spectrum. From SEM micrographs, the size of the cracks varies from 0-0.4 μm (0-400 nm). It appears that these humps are the result of increased transmittance through the cracks.

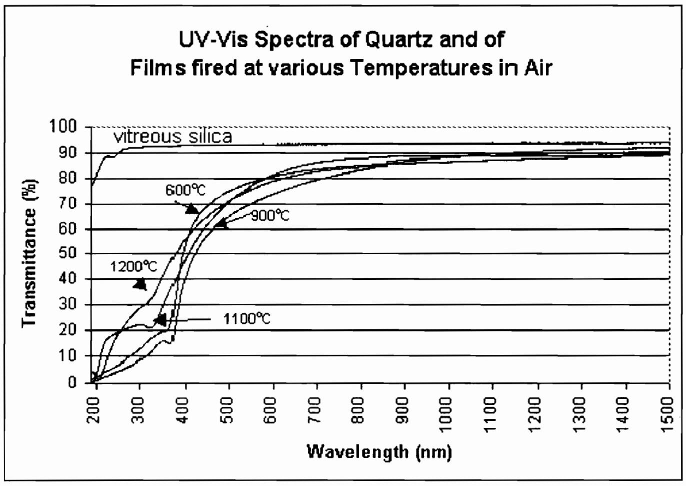


Figure 5 UV-Vis spectra of k=3 films fired at increasing temperatures in air compared with the spectrum of vitreous silica substrate

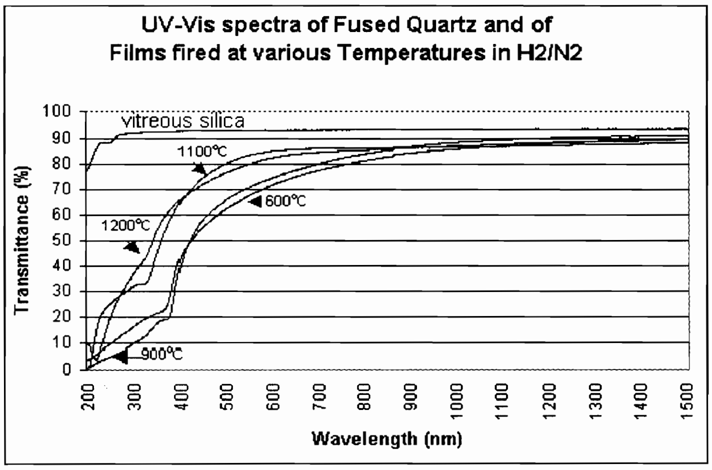


Figure 6 UV-Vis spectra of k=3 films fired at increasing temperatures in reducing atmosphere compared with the spectrum of vitreous silica substrate

FT-IR spectra of films fired at increasing temperatures in air and in reducing atmosphere are shown in Figure 7 and 8, respectively. The spectra of films fired in air are the same as the spectrum of vitreous silica substrate (Figure 9) with a transmittance of about 90%. The primary absorption band at about 2,730 nm. is due to Si-OH bonds in the vitreous silica substrate. Overtones at about 3,770 and 4,420 nm. are from the ombination of Si-OH frequencies with fundamental Si-O vibrations. The spectra of films fired in H_2/N_2 are also the same as that of vitreous silica substrate, but exhibit a spike at the wavelength of about 4,250 nm. The spike gradually develops as temperature increases, and is due to carbon dioxide in air.

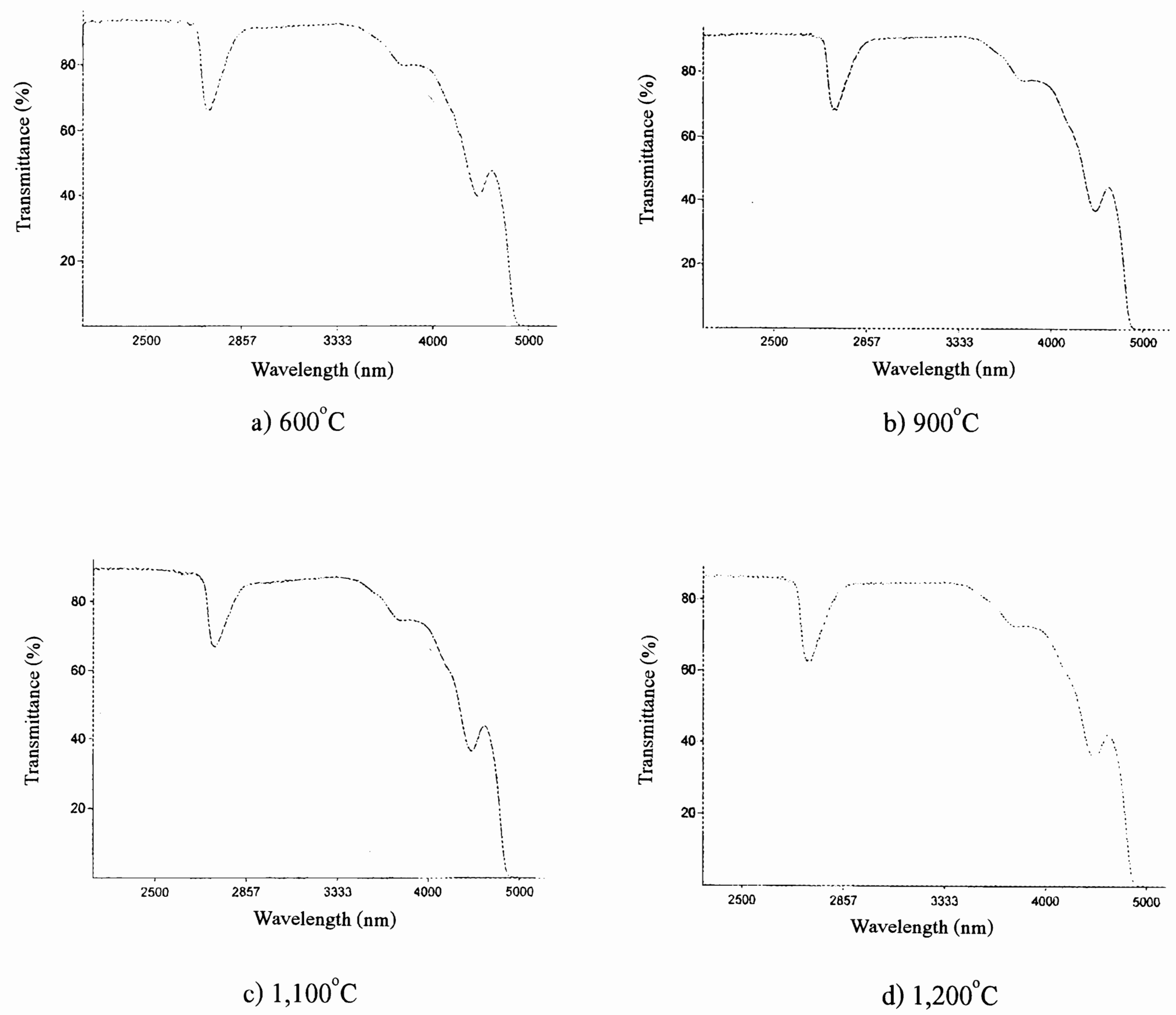
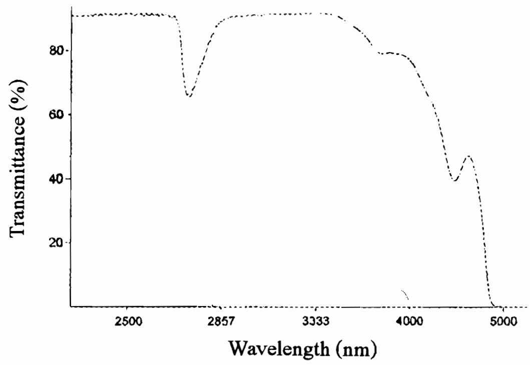
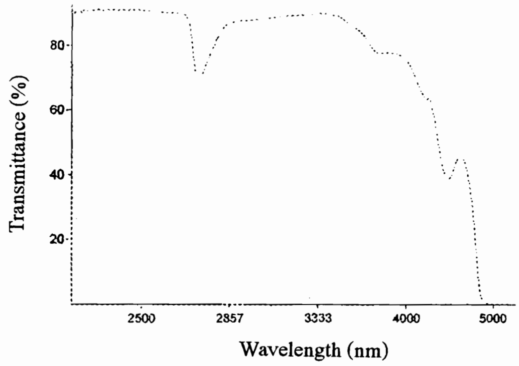


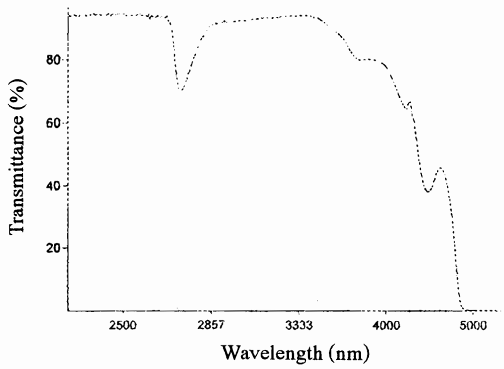
Figure 7 FT-IR spectra of k=3 films fired at increasing temperatures in air



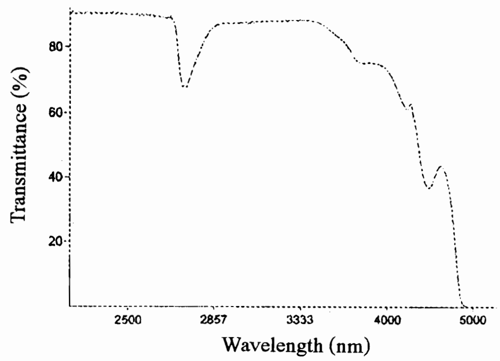
a) 600°C



b) 900°C



c) 1,100°C



d) 1,200°C

Figure 8 FT-IR spectra of k=3 films fired at increasing temperatures in reducing atmosphere

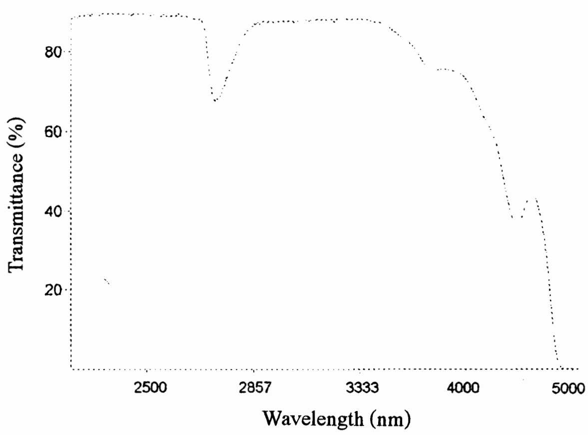


Figure 9 FT-IR spectrum of vitreous silica substrate

Electrical Properties

Electrical properties of films, with thickness between 150 and 350 nm measured by using a profilometer and fired at different temperatures under different atmospheres, are shown in Table1.

A way to improve electrical property of transparent conducting oxides is to control the oxygen partial pressure during firing. In this experiment, films were fired in $4\%H_2/96\%N_2$ at 500°C for an hour to introduce oxygen vacancies. As shown in Table 1, the sheet resistance of the 600°C film fired in reducing atmosphere is about two orders of magnitude lower than that of the same film fired in air. In addition, 900°C film fired in reducing atmosphere has sheet resistance roughly an order of magnitude lower than that of the same film fired in air.

The minimum resistivity in the order of 1 Ω-cm is obtained from the film fired at 600°C in reducing atmosphere. This value is about four orders of magnitude higher than the minimum resistivity (between 0.3 and 3.9×10^{-4} Ω-cm) of films prepared by other processes. This is due to the formation of the silicate, Zn_2SiO_4, a resistive phase, according to the x-ray profiles.

Table 1 Electrical properties of k=3 films on vitreous silica substrates

Firing temp. and atmosphere	Resistance, R (Ω)	Sheet resistance, ρ_s (Ω/□)	Resistivity, ρ (Ω-cm) at a thickness of	
			1.5×10^{-5} cm	3.5×10^{-5} cm
600°C/air	9.0×10^{5}	3.84×10^{6}	58	130
600°C/H_2/N_2	9.9×10^{3}	4.29×10^{4}	0.64	1.50
900°C/air	1.1×10^{6}	4.70×10^{6}	71	160
900°C/ H_2/N_2	3.2×10^{4}	1.36×10^{5}	2.0	4.8
1100°C/air	R>2.0×10^{7} at an input current less than nanoamperes			
1100°C/ H_2/N_2				
1200°C/air				
1200°C/ H_2/N_2				

Conclusion

1. Multiphase thin films were produced by the sol-gel method using zinc-acetate and indium-nitrate as precursors and refluxing as mixing process. The solution was unstable, so care must be taken to avoid precipitation.

2. All films have good transmittance at about 80% in the visible region, which is comparable to ITO and $Zn_kIn_2O_{k+3}$ films prepared by other processes. Nonetheless, the minimum resistivity, belonging to the film fired t 600°C in $4\%H_2/96\%N_2$, is about four orders of magnitude higher than that of ITO and $Zn_kIn_2O_{k+3}$ films prepared by other processes. This could be due to the formation of Zn_2SiO_4, a resistive phase.

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