SOLUTION PROCESSED HIGHLY CONDUCTIVE TRANSPARENT ELECTRODES

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ABSTRACT

We have successfully demonstrated highly transparent and conductive, antimony doped tin oxide (ATO) films based on a fabrication process using the sol-gel method. Three distinctive advancements have been accomplished: (1) solution-processed ATO films for low-cost, wide range applications; (2) highly transparent films of more than 95% transmittance in the visible light spectrum; and (3) high conductivity of over 20,000S/m. As such, this process opens up a new class of micro/nano fabrication process for making transparent and conductive electrodes in various systems, such as transparent electronics and displays.

INTRODUCTION

There are growing interests in the fields of transparent conductive oxides (TCOs) and semiconductors since they have excellent properties in both the electrical conductivity and optical transparency in the visible light spectrum [1]. As such, they have been key elements in many state-of-art opto-electronic devices such as solar cells, displays and electrochromic windows [2].

Transparent conducting materials are only attainable when a material has large energy band gap so that visible light can pass through. On the other hand, it also needs to have high concentration of carriers with decent mobility for good electrical conductivity [3]. In general, trade-offs between the transmittance and carrier concentration decide the suitability of conducting materials. For example, large amount of free carriers can result in high plasma frequency absorption in the visible light range to make the material opaque. As such, there are very few material candidates to meet the properties of both transparency and conductivity.

There are two types of metal oxides for TCOs: pure metal oxides and compound metal oxides such as: indium oxide (In₂O₃), tin oxide (SnO₂), and zinc oxide (ZnO). Their energy band gaps are greater than 3.1eV [4] such that they are transparent to the visible light. They also have high concentrations of intrinsic free carriers from the oxygen vacancies and defects. However, these pure metal oxides films are not suitable for practical usages due to their high electrical resistivity and instability [5]. In most cases, extrinsic dopants are added for better properties in opto-electronic applications. For example, the widely used TCO is tin doped indium oxide (ITO) due to their good optical transmittance and electrical conductivity deposited by the dc-magnetron sputtering deposition method [3]. However, ITO has several drawbacks for outdoor systems such as digital signs, smart windows and automobile displays. First, indium is an expensive rare earth material [6]. Second, it is not stable under the high temperature and humid environments [7]. Third, vacuum based processes are expensive for large-scale processes. As such, various research labs have been looking into new oxide materials to replace ITO and low-cost deposition processes [8].

Previously, J. Hu et al demonstrated fluorine-doped ZnO films by using atmospheric pressure chemical vapor deposition to make high quantum efficiency TCO films for solar cell applications [9]. J. M. McGraw et al presented Cd₃SnO₄ films by the pulsed laser depositions for thermo-voltaic plasma filter applications [10]. D. J. Seo et al deposited In₃O₈ : Mo (IMO) films on glass substrates by using the spray pyrolysis method [11]. Among various TCO materials, antimony doped tin oxide (ATO) thin films have attracted a lot of interests due to their outstanding properties in thermal, chemical stability and mechanical durability [13, 14]. Among various deposition methods, chemical solution deposition has lately become a subject of interest due to their ease of fabrication, scalability, and the potential to lower device-manufacturing costs [15].

ATO thin films and solution-processed method have been previously reported without detailed studies. This work report results on high quality ATO film depositions with detailed material characterizations.

CONCEPT

Figure 1 shows the conceptual process flow for the solution processed ATO thin films. The choice of the precursor depends on many factors, including solvent, formulation, and the specific processing routes. Chloride salts are one of the most commonly used materials in TCO precursors due to their low price and availability. As such, Tin (II) chloride dehydration (SnCl₂·2H₂O) and antimony (III) chloride (SbCl₃) were chosen as the starting materials as shown in Figure 1(A). The coating solution was formulated by adding solvent and other additives with the precursors as the intermediate state called “alkoxides”, which are compounds with formula shown in Figure 1(B). Two chemical reactions, “hydrolysis” and “condensation”, were involved in the solution formulation and the coating process was then carried out. Among various coating techniques such as printing, spray coating and spin coating, we chose the spin coating process due to simplicity and reproducibility. A procedure of multiple coating was conducted on top of a glass substrate to increase the thickness of high quality thin films. Afterwards, the prototype samples were thermally annealed to decompose the precursors and remove organic residues in order to control the electronic carrier concentration. Figure 1(C) shows three fabricated TCO samples placed on top of the printed UC seal to
show their transparency using different ambient gases of N₂, O₂ and air during the annealing process. These optical photos demonstrate that these films are all transparent as the light can penetrate them.

**EXPERIMENT**

The solution process begins by mixing metal chloride precursors with ethanol. Tin (II) chloride dehydrate (SnCl₂·2H₂O, Sigma Aldrich) and antimony (III) chloride (SbCl₃, Sigma Aldrich) were dissolved separately in 10ml of ethanol. Coating solution is prepared by adding variable amount of 0.1M Antimony chloride solution to 10ml of 0.1M Tin chloride solution for controlling the dopant concentration. We prepared four types of molar ratio between Sn : Sb, 10:0.6, 10:0.8, 10:1 and 10:1.2 (6%~12% dopants concentration).

Before starting the spin coating of ATO solution, glass substrate cleaning and surface treatment using ozone plasma were performed to increase surface tension of the glass substrate. In order to make high quality ATO thin films, we introduced the multiple spin coating and solvent removal process. Each time, only 10 nm-thick layer at were coated and dried on top of a hotplate at 285°C to remove solvents. In this multiple spin coating process, subsequent spin coatings filled porosities left from the previous solvent drying process. By changing the number of the spin coating process, we prepared four different thicknesses of high quality ATO thin films of 60nm, 90nm, 120nm, 150nm, respectively.

During the annealing process, the ambient gases and temperatures in the thermal furnace (Thermo Electron Corp., model Lindberg/Blue M® three-zone tube) were studied during the thermal annealing process. We used three different gases (Air, O₂ and N₂) and four different temperatures (300°C, 400°C, 500°C and 600°C) to study the thermal annealing process.

To achieve high electrical conductivity and optical transparency, four key processing parameters have been investigated in the prototype ATO thin films processes with studies on surface morphology, crystallinity, electrical, and optical properties, respectively. The goal is to identify optimal processing parameters for high quality transparent ATO films.

**RESULTS AND DISCUSSION**

Figure 2 compares the SEM (LEO 1550 Schottky field emission SEM) images of ATO thin films using different ambient gases during the thermal annealing process: nitrogen, Air, and Oxygen. It is found that under the nitrogen environment, large particles of ~20nm in size can be seeing uniformly distributed on the surface. On the other hand, as the oxygen content increases, the particle size becomes smaller in the air and O₂ environments.

Figure 3 shows the optical transmittance spectra tests acquired from each prototype sample groups with different doping concentrations in (A); different thickness in (B); and different gases in the annealing process in (C). The base condition is 12% in doping concentration; 150nm in thickness; and oxygen as the annealing gas environment. It is found that all samples have very good transmittance with around 95% at 550nm, which is comparable to that of commercially available sputtered ITO thin films [16]. Furthermore, Figure 3C clearly shows that transmittance is related to the oxygen contents and the increase in oxygen contents in the ATO films results in the enhancement of transmittance.
Figure 3: Measured optical transmittance spectra of ATO thin films from 350 to 800nm: (A) comparison of different doping concentrations of 6, 8 and 10%; (B) comparison of different thickness of the ATO thin films of 60, 90, 120 and 150nm; (C) comparison of different ambient gases during the thermal annealing process in N₂, Air and O₂.

Figure 4: XRD measurement result of the 200nm-thick, 10% doping concentration ATO film annealed at 500°C in O₂ showing amorphous structure.

Figure 5: Conductivity/sheet resistance measurements of the 60 nm-thick, 10% doping concentration ATO films annealed at 500°C in N₂, Air, and O₂, respectively.

Figure 6: Electrical properties of the ATO (60nm) thin films annealed at 500°C in oxygen with different doping concentrations. It is found that the optical transmittance decreases with the increases of the doping concentration. This result is in good agreement with the classical dielectric theory, which explains the relationship between the carrier concentration and absorptivity of materials. Although higher free carrier concentration can result in the decrease of the optical transmittance of a few percentages, it is important to maintain high free carrier concentrations in the ATO thin films in order to gain good electrical conductivity. These results demonstrate that highly conductive and transparent ATO thin films can be processed using the sol-gel method even though their crystalline morphology is amorphous.

Table 1 summarizes the optical and electrical properties obtained from ATO samples using various deposition methods with different doping concentrations. Although the DC sputtered ATO samples showed the highest electrical conductivity, their optical transmittance was fairly poor (74%). As such, the solution processed ATO films could be further studied for potential applications.
CONCLUSION

This paper describes the design, fabrication and experimental characterization processes for the transparent ATO films. The solution-processed ATO thin films are introduced for outdoor opto-electronic applications where the conventional transparent films such as ITO have reliability issues. Highly transparent (~95%) and metallic (~20000 S/m) thin films have also been fabricated by using the solution-based process. A parametric study has been performed on four key process factors: doping concentration, thickness, ambient gases and temperatures, in order to achieve high electrical conductivity and transparency. Studies on the surface morphology, crystallinity, electrical, and optical properties of prototype ATO films have also been conducted. These investigation results provide useful information for future research directions, namely, to enhance the conductivity of the ATO films by improving the crystallinity. In summary, the ATO thin film fabrication process is simple, fast and effective for potential applications in the area of emerging opto-electronic devices.

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