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Reduction of Resistivity and Haze in Two Coating Layer of Indium Tin Oxide Doped Phosphorous on Glass

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In this research work, transparent conductive films produced by a series of steps comprising two coating layer having low haze of less than 3 %. The first coating layer obtained by dissolving indium compound and a tin compound in an organic, then coated on a glass substrate. The second was a coated substrate with conductive indium tin oxide and a phosphorous film. A calcinations step was carried out in which the coated substrate is calcinated at a temperature of 400 ºC or higher. Two tin layers causes excellent properties as strong adhesive strength to a substrate, increasing transmittance and low sheet resistance comparing to single indium-thin oxide layer. A series of two layer film thickness have been deposited on glass substrate and the effect of film thickness on the structural, electronically and optical properties have been investigated. The total film thickness is 500 nm to 50 µm. The transmittance of two layer coating is more than 83 % at a wavelength of 510 nm and the lowest resistance of 138 Ω sq^{-1} obtained.

Key Words: Indium-tin oxide, Phosphorous, Transparent, Glass.

INTRODUCTION

Transparent conductive films are used as crystal serving display element for an information terminal in a computer, a portable telephone, *etc*. Indium tin oxide (ITO) is mostly used as the raw material for such film. However, there is a demand for production of conductive film of lower resistance to realize a more high speed and finer display element. There are several coating methods such as spin coating[1], sol-gel[2-5], dip-coating[6], spraying[7], sputtering deposition process[8-11] and chemical vapour deposition[12] and each method has its own advantages and disadvantages. However the requirements and the need for highly conductive or/ and transparent coating cost are the main subject to select one of these method.

Indium oxide coating, specially doped, for example, with fluorine or indium- tin oxide coating on glass known to have a high visible light transmission and good electrical conductivity[7,8,12]. Tin doped indium oxide coating deposited by reactive sputtering are widely used as heat able coating, for example on aircraft windscreen. Indium tin oxide is widely used for solar-control industry and for low emissivity. Solar-control term describing the property of regulating amount of solar heat energy

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which is allowed to pass through a glass article into an enclosed space such as a property of an articles surface wherein the absorption and emission of mid-range infrared radiation is suppressed, making the surface a mid-range infrared reflector and thereby reducing heat flux.

By suppressing solar heat gain, interior space of building and automobile are kept cooler, allowing a reduction in air conditioning requirements and costs. The coating material could be various kind of metal oxide.

In this research work we report that the transparent conductive two layer films fabricated on soda lime glass substrate by both spraying and dip-coating techniques. The first layer was an indium oxide coating, doped with tin oxide and second layer consist of indium-tin oxide doped with phosphorous.

EXPERIMENTAL

The glass plates cleaned with distilled water, soap, ethanol and diluted acid accordingly. Indium chloride is dissolved in acetyl acetone and in another solution tin is added in concentrated nitric acid and the reaction carried out in the presence of acetyl acetone. The above two solutions mixed so that the amount of tin became 8 % by weight based on the total amount of indium.

Subsequencely, a glass substrate previously washed and cleaned sufficiently is dipped in the coating solution placed in a tank maintained at room temperature. Then the glass substrate coated with the coating solution is drawn up at a constant rate (5 to 15 cm/min). The calcinations procedure has been done above 400 ºC in an oven.

In another method, solution of indium-tin oxide mixed with 15 mL methanol and sprayed on the prepared glass by a glass nebulizer and was put on a preheated oven to 600 ºC. After heating for 10 min, remove from the oven and immediately sprayed with a fine mist of tin chloride solution for the second time and returned to the oven. For the second layer, indium - tin oxide solution doped with various amount of phosphorous is sprayed.

The resistance measured by a multimeter, model "Sanwa- JP-120" and the film thickness measured by Plymus BX60 Optical Microscope and Auger Electron Spectroscopy ‘HPI-610’. The optical characteristics of the indium tin oxide thin films were measured, using UV-Vis spectrometer in a wavelength of 400-800 nm.

RESULTS AND DISCUSSION

A method of producing indium tin oxide coated glass having low haze of less than 3 % and a low emissivity layer and a doped indium tin oxide coating having at least two layer has been achieved. One of these layers being a solar absorbing comprising indium-tin oxide and another layer being a low emissivity layer comprising indium-tin oxide containing a dopant of phosphorous. Wherein the thickness of solar absorbing layer is from 300 to 800 nm and the thickness of low emissitivity layer is from 250 to 900 nm. Ethyltrifloroacetoacetate, butyric acid or HF was used as a haze reducing additive.

Fig. 1 shows the transmittance of the thin films at the wavelength of 400 to 800 nm which is visible range. The air was used as reference. Transmittance more than 83 % obtained which shows a good optical properties. This is in agreement with the result reported by Seki and his co-worker[13].

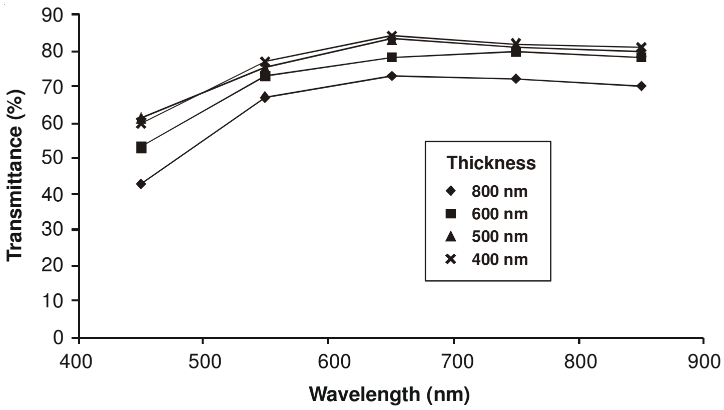

Fig. 1. Transmittance of thin film at various wavelengths

It is known that indium tin oxide material is tetravalent, each Sn^{4+} replacing In^{3+} substitutionally, thereby, donating a free electron for the conductivity in the process. So, the indium tin oxide materials retain the cubic In_2O_3 structure up to solid solubility limit of SnO_2 in In_2O_3[14,15]. Because of high solubility of tin oxide in indium oxide, enable a high concentration of charge carried to be achieved. Thus a tin doped indium oxide coating is formed on the hot glass surface. The indium tin oxide coating may be formed as first layer on the substrate, then indium tin oxide doped phosphorous could be formed on the top of previously formed coating layer.

However, a source of phosphorous as incorporated in the solution, directed onto the hot glass surface to form phosphorous doped indium-tin oxide coating causes further resistivity reduction.

In this work, electrical resistance was measured with four-point probe method. It was shown that the resistance of sample directly related to heat treatment of the procedure. Higher heat treatment show lower resistance, but temperature more than 650 ºC causes a deformation of the glass. Two layer thin film including indium tin oxide doped 0.6 wt% phosphorous as second layer decreases the resistance. The optical transmittance of this film show a lower value than of single indium tin oxide layer.

Fig. 2 shows that the phosphorous doping ratio of indium tin oxide plays an important role on electrical resistivity. Notably, the carrier density of indium tin oxide increase almost linearly with increasing phosphorous doping ratio up to 0.6 % and then saturates at higher doping concentration. Thus it is implied that the phosphorous doping amount of indium tin oxide used in this study optimized in terms of maximum electrical conductivity.

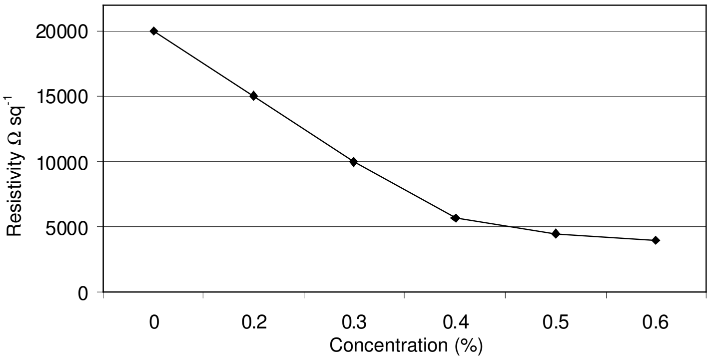

Fig. 2. Effect of phosphorous concentration on resisitivity

The thickness of the indium tin oxide thin film was controlled with the dipping rate on minute. For the second layer, phosphorous with the concentration of 0.2, 0.4 and 0.6 wt % was added to indium tin oxide solution, respectively. After fabrication, optical transmittance and electrical properties of the thin film according the film thickness and phosphorous added are characterized. Fig. 3 shows the relationship between the thickness and the resistivity. It was also found that thickness less than 100 nm causes an increase in resistivity.

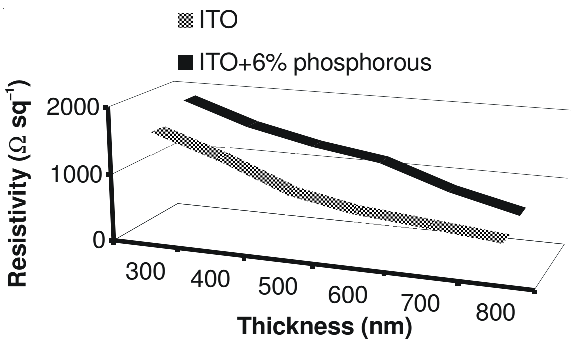

Fig. 3. Effect of thickness on resistivity

Fig. 4 shows the image of the film annealed at 600 ºC for 1.5 h. A few cracks on photographs could be seen. It might be that the coated glass was taken out at high temperature into room atmosphere condition. This experiments shows that the resistance of indium tin oxide and indium tin oxide doped phosphorous enhanced and the optical properties of the film decrease due to these cracks.

Conclusion

The present research found that two layer coating composed of a film of indium tin oxide containing a small amount of phosphorous shows a lower resistivity and can be used as an excellent transparent conductive film.

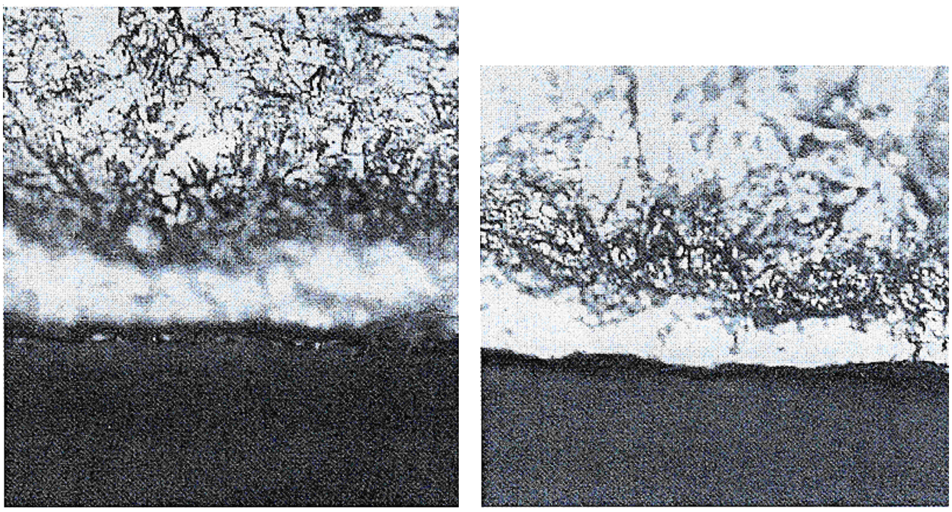

Fig. 4. Photograhphs of indium tin oxide and indium tin oxide doped phosphorous thin films with 600 nm thickness annealed at 600 °C (Left = indium tin oxide, Right= indium tin oxide doped phosphorus 6 %)

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