Electrical and optical properties of indium tin oxide/epoxy composite film*

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The electrical and optical properties of the indium tin oxide (ITO)/epoxy composite exhibit dramatic variations as functions of the ITO composition and ITO particle size. Sharp increases in the conductivity in the vicinity of a critical volume fraction have been found within the framework of percolation theory. A conductive and insulating transition model is extracted by the ITO particle network in the SEM image, and verified by the resistivity dependence on the temperature. The dependence of the optical transmittance on the particle size was studied. Further decreasing the ITO particle size could further improve the percolation threshold and light transparency of the composite film.

Keywords: percolation effect, indium tin oxide/epoxy composite film, electrical state transition, optical transmittance

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1. Introduction

Electrically conductive polymer composites are widely used in the industrial applications due to the advantages of low cost, ease of molding, deflection, chemistry stable, temperature-activated switching feature and conductive performance adjustable in a wide range, and etc.[1,2] The resistivity of the composite increases suddenly by several orders of magnitude in a relatively narrow volume fraction range when it comes to a critical value. This phenomenon is known as the percolation effect, and the corresponding critical volume fraction of the conductive filler is called the percolation threshold (V_c).[3] The percolation effect has been found to be related to the dispersion state,[4] geometric shape,[5,6] particle size,[7] surface treatment,[8] filler bendability,[9] processing parameters and annealing treatment of the composites,[10,11] etc. Most conductive filling particles of the composites were usually prepared by opaque materials, such as metal,[12,13] metallic oxide,[14] carbon black,[15] and so on.

Printable optoelectronic devices have recently attracted substantial interest. Solution-based printable transparent materials with low resistivity and high transparency are imperative, because the main performances of printable optoelectronic devices are closely related to the electrical and optical properties of transparent electrodes. Ag NW percolating network was effectively embedded into the ITO NPs providing a conduction path, which led to a metallic conduction behavior of the ITO NPs/Ag NW/ITO NPs multilayer.[16]

In this paper, ITO particles, which were widely used in the light-emitting diode (LED) field as the transparent conductive layer, were utilized as the conductive filler to form ITO/epoxy transparent and conductive polymer composite film, which could modulate the current transport under the voltage-constant mode. The dependence of resistivity on the filler size and the volume fraction was studied as well as the corresponding optical transmittance. The physics mechanism of the sudden conductivity changing in the percolation region was explained and verified by the resistivity relationship with the temperature.

2. Experiments

Bulk ITO, which was purchased from NICOMO CO., LTD, was first ground for about 3 h into particles by hand. In order to obtain ITO particles with similar sizes, the ground particles were put into deionized water with ultrasonic dispersion for 10 min and then left in the suspension to stand for 30 min. The particles with smaller sizes would be on the top layer in the suspension, and then were filtered out. After repeating the above dispersion and filtering procedures five times in order to obtain particles with similar sizes, the filtered particles were baked on the hotplate for 10 min at a temperature of 100 °C. The particle sizes obtained in this experiment were around 1 μm and 3 μm, respectively, which were measured under the microscope. Then these ITO particles were stirred in the epoxy purchased from QINGDA-QS MATERIAL CO., LTD, at 80 °C for 20 min in order to make sure that ITO particles were dispersed uniformly to form the ITO particle matrix. The mixture of the ITO/epoxy composite was first painted by a brush on a glass slide to form a film with a size of 10 mm×10 mm×0.3 mm. The film was first cured for 4 h at 80 °C, and then cured for 8 h at 120 °C in an oven. To facilitate testing and reduce contact resistance, two copper sheets were preset inside the composite film before the curing

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process. A schematic diagram of the experimental set-up is shown in Fig. 1.

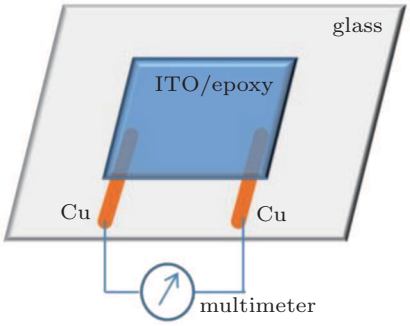


Fig. 1. (color online) Experimental set-up schematic of the ITO/epoxy composite film.

The electrical resistivity ρ of the ITO/epoxy composite was calculated according to $\rho = RS/l$, in which S is the area and l is the thickness of the film. The resistance R was measured by a Keithley 4200 under the direct current mode. All the samples were put in the oven for the temperature dependence measurement. In order to ensure the accuracy of the experimental results, the data were obtained after the temperature stayed constant for at least 20 min. The temperature was monitored by a thermometer, which was put just under the sample. Five samples were prepared for each experimental condition and each sample was measured five times.

3. Results and discussion

Figure 2 shows the resistivity of ITO/epoxy composite film as a function of ITO volume fraction for the particle sizes of 1 μm and 3 μm at room temperature. The resistivity increases 2 to 3 orders of magnitude within a 4% volume fraction change, which demonstrates a typical percolation effect. The experimental data scatter is relatively large but repeats very well when the resistivity is below 100 Ω·cm. Moreover, the experiment data are well fitted by the classical percolation equation[17]

$$\rho = \frac{\rho_0}{(V - V_c)/t}, \tag{1}$$

where ρ_0 is proportionality constant, V is the volume fraction of ITO, V_c is the percolation threshold, and t is the dc transport critical exponent. The fitting data of V_c are 13.6% and 29.9% for the ITO particle sizes of 1 μm and 3 μm, respectively. Each fitting curve could be divided into three parts, as shown in Fig. 2. For Part I, the resistivity of the composite is lower than 100 Ω·cm, which exhibits as a conductor. For Part III, the resistivity is as high as 10^8 Ω·cm and it exhibits insulating characteristics. However, for Part II, the resistivity drastically changes from 10^2 Ω·cm to 10^8 Ω·cm in a short range of the volume fraction. The electrical property of the composite film transits from a conductive to an insulating state.

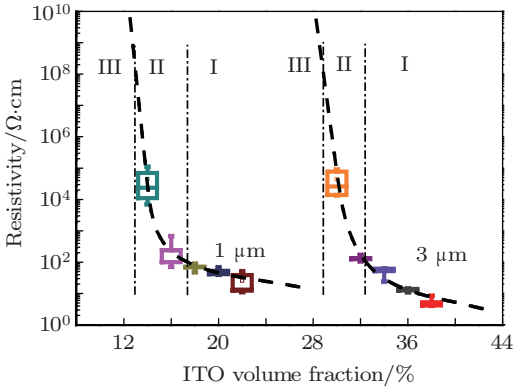


Fig. 2. (color online) Dependence of the resistivity of ITO/epoxy composite film at room temperature on the volume fraction of ITO particles with the sizes of 1 μm and 3 μm. The dashed lines are the fitting results for the experimental data as shown in scattered dots.

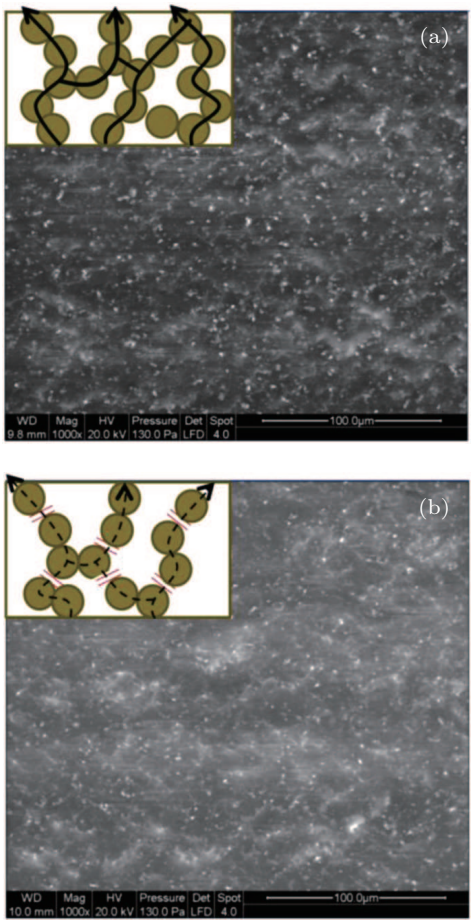


Fig. 3. (color online) SEM images (1000×) of the fracture surface of the ITO (1 μm)/epoxy composite with ITO volume fractions: (a) 20%, (b) 13.6%.

Figures 3(a) and 3(b) show the SEM images of the cross sectional ITO/epoxy composite film with the volume fractions of 20% and 13.6% for the particle size of 1 μm, respectively. The ITO particles, shown as white dots in the SEM image, are dispersed uniformly in the epoxy. Obviously, a big cluster of ITO particles cannot be found. Because ITO particles are conductive, the distribution of ITO particles can be extracted as a kind of network formed by the conductive particles which

spanned throughout the insulating epoxy. For the denser distribution as illustrated in Fig. 3(a), the distance between the adjacent ITO particles was close, even with some particles in contact with each other. The ITO particles could form several continuous conductive paths, which behave like a conductor corresponding to Part I in Fig. 2. Continuously increasing the volume fraction can increase the conductive area, and then decrease the resistivity. On the contrary, most ITO particles distribute in the epoxy individually, which indicates that the conductive paths are destroyed. The sample with a sparser volume fraction behaves like an insulator corresponding to Part III in Fig. 2. However, if the distance of two adjacent particles is not too large, the tunneling current can be generated under the electric field. The tunneling current increases exponentially as a function of the distance, which forms the electrical sudden transition from insulating to conductive state, corresponding to Part II in Fig. 2. The inset of Fig. 3 illustrates the conductive network formed by ITO particles. The distance between the two adjacent ITO particles plays an important role in generating the conductive path.

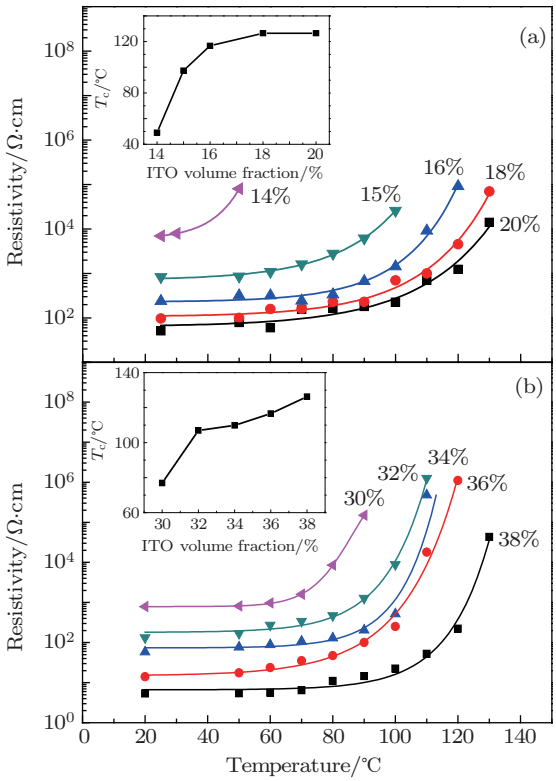


Fig. 4. (color online) Dependence of the resistivity on temperature with different volume fractions of the composite for the ITO particle sizes of (a) 1 μm and (b) 3 μm. The inset shows the T_c as a function of ITO volume fraction.

Figure 4 presents the dependence of the resistivity on the temperature with different volume fractions for the 1 μm and 3 μm ITO particles. The volume fraction selected at the beginning is higher than V_c, which indicates that the electrical state of all the samples is conductive. As shown in Fig. 4, all the resistivity increases with the temperature increasing slowly at the beginning, and then increases drastically in a narrow range of temperature when the temperature exceeds the transition temperature (T_c). This is caused by the different thermal expansion coefficients between ITO and epoxy. The thermal expansion coefficient of epoxy is larger than that of ITO particles, which results in the declination of the ITO volume fraction with temperature. When the ITO volume fraction dropped to the point of V_c, the resistivity increased sharply in a narrow range of temperature, which is further evidence of the percolation effect. All the T_c data are extracted and plotted in the inset of Fig. 4, which are selected as the extremum of the secondary differential of the curves as a function of the ITO volume fraction. The T_c increases with the volume fraction for both samples because a larger volume expansion is needed for samples with a higher volume fraction for dilution. The percolation effect cannot appear until the ITO volume fraction drops to the point of V_c.

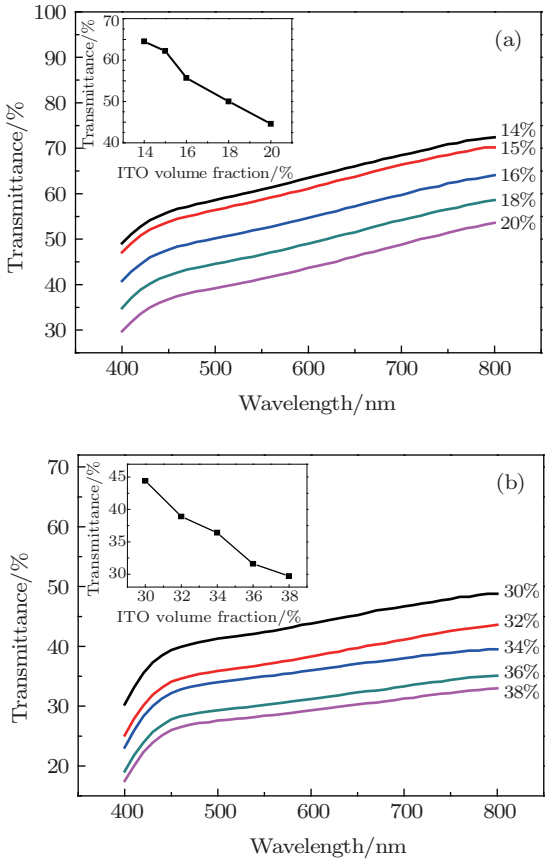


Fig. 5. (color online) Dependence of transmittance measurement results on the ITO volume fraction for the filler sizes of (a) 1 μm and (b) 3 μm. The insets are the transmittance at 620 nm with ITO volume fraction.

Figures 5(a) and 5(b) show the transmittance measurement results with ITO particle sizes of 1 μm and 3 μm, respectively. The thickness of the composite film is about 50 μm. All the transmittance curves increase with the wavelength. The transmittance of epoxy resin in the visible region is larger than 92%. The transmittance of the composite film decreases with

the ITO volume fraction, which is caused by the absorption of ITO particles.[18] The transmittance data at 620 nm are extracted and plotted in the inset of the Fig. 5. The maximum transmittance was 64.5% and 44.4% for the volume fraction of 14% with a filler size of 1 μm and of 30% with a filler size of 3 μm, respectively. The optical transmittance of ITO is directly related to the particle size. The transmittance increased 20% when the filler size decreases from 3 μm to 1 μm, which indicates that the transmittance can be enhanced with the decrease of the filler size.

4. Conclusion

The percolation effect of ITO/epoxy composite film was characterized with the ITO particle sizes of 1 μm and 3 μm. The electrical transition mechanism from the insulating to the conductive state in a short volume fraction range was explained according to the SEM images, which was then confirmed by the resistivity dependence on the temperature. The dependence of the optical transmittance on the particle size was studied. Further decreasing the ITO particle size could further improve the percolation threshold and optical transparency.

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