

Preparation of ATO Conductive Particles with Narrow Size Distribution

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II. EXPERIMENTAL SECTION

A. Materials

$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and SbCl_3 hexadecyltrimethylammonium bromide (CTAB) were all analytical grade and used without further treatment. The other chemicals were analytical grades and used as received.

B. Preparation of ATO conductive particles

The precursor preparation procedure of ATO with median diameter of $4.20 \mu\text{m}$ via chemical coprecipitation was as following[3]: 6.98 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.020 mol) was dissolved in 90 ml of HCl aqueous solution at pH of 2 and a concentrated acidic solution of SbCl_3 (0.365 g , 0.002 mol) was prepared by induction of SbCl_3 to concentrated HCl solution. Then the solution of SnCl_4 was heated up to 60°C under vigorous stirring, acidic solution of SbCl_3 was added dropwise to the above system in accompany with the addition of NaOH aqueous solution (5 g of NaOH was dissolved in about 20 ml water) to maintain the pH at about 2.0 and then 3 after 2 hour of reaction. When the stock solutions were added completely, the reaction system was allowed to settle for 3 h and separated by centrifuge at 5000 rpm . The solid was washed with distilled water until Cl^- could not be examined in the aqueous solution and then dried for 12 h at 80°C .

The procedure for precursor preparation of ATO with $1.11 \mu\text{m}$ median diameter was as following[10,12]: 0.365 g (0.002 mol) of SbCl_3 , 6.98 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.020 mol), 2 ml of H_2O and 8 ml of HCl were mixed in a flask, then 4.60 g of CTAB surfactant, 9.2 g of *n*-butyl alcohol and 90 ml of cyclohexane were added into this mixture under agitation until the transparent microemulsion A was obtained. 5 g of NaOH and 8 ml of H_2O were mixed in another flask, then equal amount of CTAB, *n*-butyl alcohol and cyclohexane as in microemulsion A were added to give the reverse microemulsion B. The microemulsion B was slowly added to microemulsion A at 60°C under quick agitation within 1h. The emulsion was then allowed to age for 24 h at the same temperature to obtain the precursor of ATO particles. The precipitates were then collected by centrifuge at 5000 rpm , washed with distilled water for several times until Cl^- could not be examined in the aqueous solution. Finally, the collected precipitates were dried in a vacuum oven at 80°C for 12 h .

The dried precursor was subsequently calcined at 700°C for 30 min to give the ATO particles.

Abstract—Antimony-doped tin oxide (ATO) particles were prepared via chemical coprecipitation and reverse emulsion. The size and size distribution of ATO particles were obviously decreased via reverse microemulsion method. At the relatively high yield the ATO particles were nearly spherical in shape, meanwhile the crystalline structure and excellent conductivity were reserved, which could satisfy the requirement as composite fillers, such as dielectric filler of polyimide film.

Keywords—ATO particle, Conductivity, Distribution, Reverse emulsion

I. INTRODUCTION

ANTIMONY-DOPED tin oxide (ATO) is an important transparent semiconductor oxide that has been extensively studied for its chemical, physical, electric and optical properties [1] for its utilization in solar cells[2]. Many methods, such as sol-gel or chemical precipitation[3], hydrothermal method[4], sputtering method [5], spray pyrolysis method[6], are performed to control the size as well as morphology of the semiconductor nanostructures with improved crystallinity because the above parameters are the key facts altering physicochemical properties of semiconductors[7]. But no study on the preparation of ATO via reverse emulsion is reported.

Reverse-microemulsion technique is one of the novel methods for synthesis of fine crystals, including calcium carbonate[8], zinc sulfide[9], titanium oxide[10] and silver[11] because of its simple experimental procedure and mild operating conditions. Its successful application in nanoparticle preparation is because the single droplet can act as a micro-reactor. Then, the crystal growth is limited or confined in the droplets, which are separated by the continuous phase[9].

In the present study, reverse emulsion is used to prepare ATO particles. At a relatively high yield the median diameter of the particle could be decreased to be $0.96 \mu\text{m}$ which determines its applications in a variety of industries, such as plastics, rubber and composite fillers.

This work was financially supported by the Fundamental Research Funds for the Central Universities (2010ZY46), national key laboratory of minerals (09B003), China, and City University of Hong Kong Strategic Research Grant (SRG, 7008009).

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C. Characterizations

The size distribution measurement of ATO was carried out by BT-9300H laser particle size analyzer. The crystal structure of the composites were measured by D/MAX 2000 X-ray diffraction with Cu K α -radiation ($\lambda=1.541806\text{\AA}$), The morphology of the particles was deduced by JEOL6301F SEM. The conductivity was tested by the universal meter VC9820A quantitatively. The conductive particles were fitted into a mould of organic glass, the universal meter VC9820A was used for testing the Ohmic resistance (R) of powders, the resistivity can be calculated from the equation: $\rho=RA/H$, where ρ is the resistivity of the powders (cm); R is the Ohmic resistance of testing; A is the area of the powder pole (cm^2); H is the height of the powder pole.

III. RESULTS AND DISCUSSION

A. Preparation of ATO particles

ATO particle was prepared by first formation of ATO precursor and then calcination. Chemical coprecipitation and reverse emulsion were carried out to prepare ATO precursor. Just as shown in Table 1, the concentration of SnCl_4 , type of base and its addition rate were studied in the chemical method. The size distribution curves of the ATO were shown in Fig.1 (d,e,f). The size and size distribution of ATO particles became small and narrow when reaction rate was decreased by decreasing the concentration of reactant and base addition rate,

TABLE I
PREPARATION OF ATO PARTICLES VIA DIFFERENT METHODS

Methods	Concentration ^a [mol/L]	Base addition rate [drops/min]	Base used	Median diameter [μm]	Yield [%]
Chemical coprecipitation	0.14	60	NaOH	4.20	99.8
	0.07	30	NaOH	2.47	99.5
	0.035	15	$\text{NH}_3\cdot\text{H}_2\text{O}$	1.89	66.5
Reverse emulsion ^b	0.006	15	NaOH	1.30	80.4
	0.013	15	NaOH	1.11	78.3
	0.019	15	NaOH	0.96	63.3

^aConcentration of SnCl_4 in chemical coprecipitation method and apparent concentration of CTAB in reverse emulsion method.

^bThe ratios of oil to aqueous solution and CTAB to n-butyl alcohol were 1/10 and 1/12.5 respectively.

changing the type of base. However, the particle distribution still could not satisfy the requirement as dielectric filler since unhomogeneous composites could form easily, so reverse emulsion method was used. Fig. 1(a,b,c) displayed the particle distribution curves. The particle size and size distribution decreased obviously. The diameter of 96% of ATO particle with the median diameter of 0.96 was lower than $2.0\mu\text{m}$. It should be pointed out that nanometer ATO particles could be prepared by further decreasing the concentration of reactant and increasing the surfactant via reverse microemulsion, but the apparent concentration of reactant and yield were very low and could not

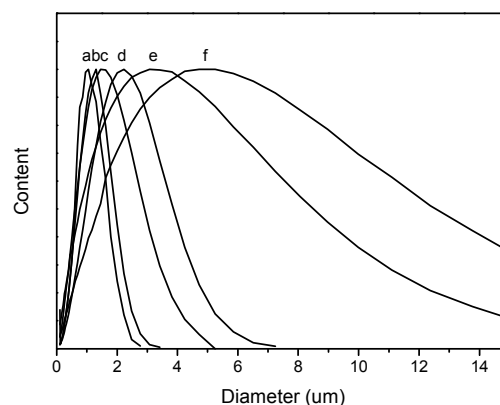


Fig. 1 Size and size distribution curve of ATO prepared by different methods.

satisfy the quantity requirement as composite filler[13]. So further experiment for preparation nanometer ATO via reverse emulsion was not been carried out.

B. Morphology of ATO conductive particles

Fig.2 (a,b) showed the morphology of ATO particles prepared by reverse microemulsion method where the particles were nearly spherical in shape and most of the particles were aggregates of small ones connected by loose packing, which may result from the dehydration in calcination and the instability of the microemulsion due to the ionic strength change in the micro-reactor in the reaction process.

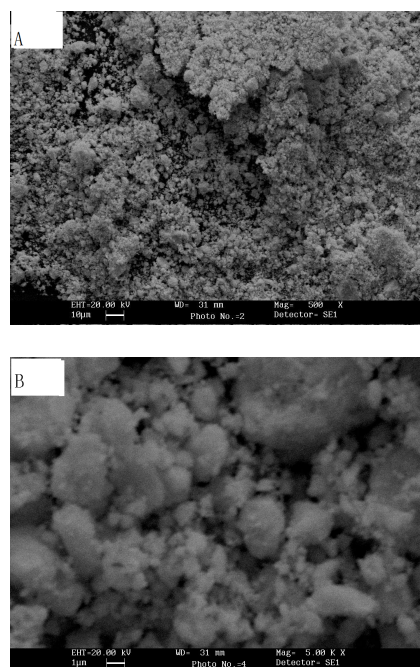


Fig. 2 General(a) and magnified (b) SEM photographs of ATO prepared by reverse emulsion.

C. Structure of ATO particles

In the XRD pattern of ATO particles, the specific peaks of tin oxide (SnO_2) at $2\theta=26.59^\circ$, 33.95° , 51.80° were obvious showing the formation of crystalline structure. But the intensity of these peaks was not large enough indicating the crystalline structure was not perfect due to the substitution of Sn^{4+} by Sb^{3+} or Sb^{5+} which was consistent with the report[3,4].

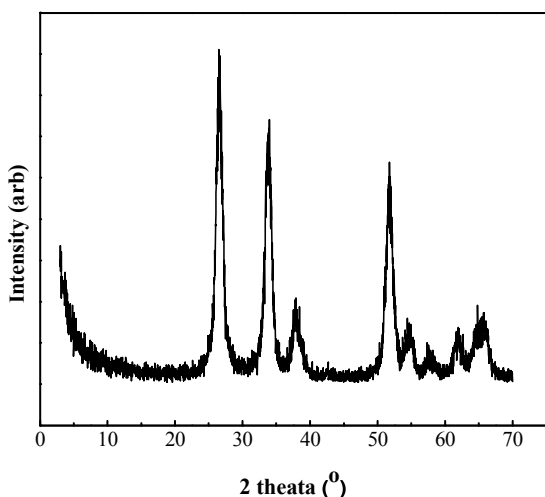


Fig. 3 XRD pattern of ATO particles prepared by reverse microemulsion

D. Conductivity of the particles

Since the successful doping of antimony in SnO_2 , the ATO particles showed excellent conductivity. The resistivity of the particles reached $86 \Omega \cdot \text{cm}$. The dielectric constant of ATO/polyimide was improved 100 grades as ATO with the median diameter of $1.11 \mu\text{m}$ was introduced in polyimide films as filler.

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