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The electrical and optical properties of thin layers of nano-sized antimony doped tinoxide particles

M. J. VAN BOMMEL, W. A. GROEN, H. A. M. VAN HAL, W. C. KEUR,
T. N. M. BERNARDS
*Philips Research Laboratories Eindhoven, Prof. Holstlaan 4, 5656 AA Eindhoven,
The Netherlands
E-mail: bommel@natlab.research.philips.com*

For the use in anti-static films on glass or polymeric substrates, transparent conductive layers can be prepared by spinning an aqueous suspension of nano-sized antimony-doped tinoxide (ATO) particles. These layers have a resistivity which is substantially higher than that of homogeneous ATO layers which are deposited by physical vapour deposition techniques. By curing the films to temperatures up to 700 °C, the resistivity of the particle layer can be decreased by two or three decades. Because the nano-sized particles are prepared by a low-temperature process a different mechanism can contribute to this decrease in resistivity. Possible effects which may influence the conductivity are sintering of the particles, change of the bulk material and the presence of an insulating layer at the outside of the particles. This decrease can be explained by the presence of an insulating antimony-rich layer on the outside of the particles, the thickness of which is reduced when the layer is cured. At temperatures above 350 °C, sintering of the particles also highly influences the decrease in resistivity. At temperatures above 700 °C, the resistivity is increased due to segregation of the antimony to the surface of the particle.

1. Introduction

There is a growing interest in the technical application of transparent and conductive elements in all kinds of optical switching devices and display devices such as electrochromic systems, solar cells and liquid crystal displays. Only a few materials exhibit both optical transparency to visible radiation and high electrical conductivity. Thin films of tin doped indiumoxide (ITO), fluor doped tinoxide (FTO) or antimony doped tinoxide (ATO) are widely used in these applications [1]. By sputtering or other physical vapour deposition techniques, resistivities of $2 \times 10^{-4}\ \Omega \cdot \text{cm}$ are generally obtained for ITO layers, and values of a decade higher are obtained for the doped tinoxides. For a number of industrial applications the wet-chemical deposition of transparent conductive films would be highly favourable, because the cost of processing the transparent conductive layers is low. However, little is known about the wet-chemical deposition of these transparent thin films. When using metal organic precursors in general for ITO, specific resistance values are found of $7 \times 10^{-3}\ \Omega \cdot \text{cm}$ [2, 3]. For some applications, a limitation to the use of the wet-chemical processing of these conductive materials is the temperature at which the layers need to be cured in order to obtain well conducting films [4]. Curing temperatures above 400 to 500 °C are necessary to transfer the precursors into films with conductivities which approach the intrinsic values. A different approach would be to use conductive particles. By spinning of a suspension of transparent conductive particles, a coating can be obtained with the desired optical and electrical properties. For use of this coating, there are strict requirements with respect to the particle size. In order to prevent the film from appearing dull, the particles used in the layer must not scatter light. This requirement restricts the use of particles to those with a size of less than 50 nm. The advantage of this approach would be that transparent conductive films can be prepared without the need of a firing step. This would allow an easy deposition of a transparent conductive film on polymeric substrates. In this paper the optical and electrical properties of a coating of nano-sized ATO particles are evaluated.

For a good understanding of the behaviour of the ATO particle layer, some background of the conductivity mechanism of ATO is necessary. SnO_2 is an n-type semiconductor having doubly ionised oxygen vacancies as the predominant mechanism of conduction. It has been suggested that Sn^{4+} in SnO_2 can be partially replaced by Sb^{5+} [5].

The limit in the intrinsic performance of transparent conductive oxides has been ascribed to impurity scattering, which limits the mobility of the charge carriers [6]. Grain boundary scattering has been found to be the dominant scattering mechanism at room temperature for undoped SnO_2 and low-level doped ATO [7].

TABLE I Chemical analysis of ATO suspension in water

Element	Concentration (mg/ml)
Sn	89 ± 3
Sb	14.8 ± 0.4
Cl	$(3.5 \pm 1) \times 10^{-6}$
Na	$(5.2 \pm 1) \times 10^{-6}$

2. Experimental

Transparent conductive layers were prepared by spinning an aqueous suspension of nano-sized ATO particles. The particles were prepared by a co-precipitation of $SnCl_4$ and $SbCl_5$, followed by a hydrothermal processing step.

The particle size distribution of this suspension was measured using a Shimadzu SF4. The mean particle size was about 15 nm and no particles were found with a size larger than 50 nm. For an additional proof of the size of the particles, transmission electron microcope (TEM) recordings were made with a Philips CM30 TEM.

The chemical composition of the ATO material was analysed using Inductive Coupled Plasma Emission Spectroscopy (Philips ICP-ES). Cations present in the suspension were determined using ionchromatography. The result of the analysis is given in Table I. The level of impurities (as for instance Na and Cl) is very low.

The ATO suspension we used had a solid contents of 12 wt % and was de-agglomerated by an ultrasonic treatment (Branson) before use. The films were prepared by spinning the suspension and fired at different temperatures. To prevent contamination with alkali quartz substrates were used. With this procedure, layers are obtained with a thickness of about 330 nm. In order to obtain thicker layers the suspension was either concentrated or three layers, were deposited on top of each other. This last procedure resulted in a final layer thickness of about 1 mm. The thickness was determined with a Tencor Alfa step. In the text it is indicated which procedure was used when thick layers are being discussed. The layers were extensively dried in a vacuum stove at a temperature of 150 °C.

Part of the suspension was dried and used for the determination of the specific surface. The specific surface area of the powders heated at different temperatures in air was determined using the BET method at 78 K with Krypton as adsorption gas [8, 9].

The electrical measurements of the layers at temperatures above room temperature were carried out in a custom-made apparatus [10]. Room temperature electrical measurements were made with a four-point probe. Optical properties were characterised using a Perkin Elmer Lamda 19 spectrophotometer. The transmission was recorded at the wavelengths between 200 and 2500 nm.

3. Results

For the preparation of clear layers it is necessary to use a suspension without large agglomerates. For colloidal suspensions the pH will have an enormous effect on the stability of the sol. To get more insight into the influence of the pH on the stability of the suspension, the Zeta potential of the system was determined. In Fig. 1 the Zeta potential of the aqueous ATO suspension is given as a function of the pH. In this and other figures, lines are included for the readers convenience which connect the measured data points. This figure shows that it is necessary to use a pH above 4 in order to obtain a stable suspension. The suspension used for the deposition of the layers had a pH of about 7. In our experiments no additional agents were added to the suspension to increase the stability.

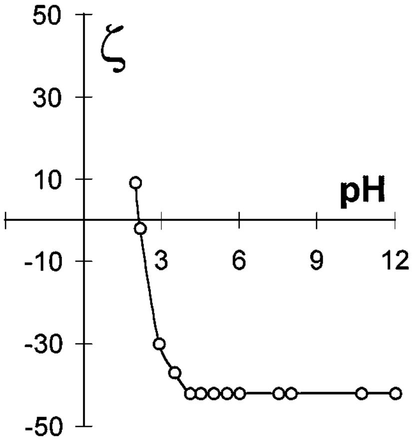


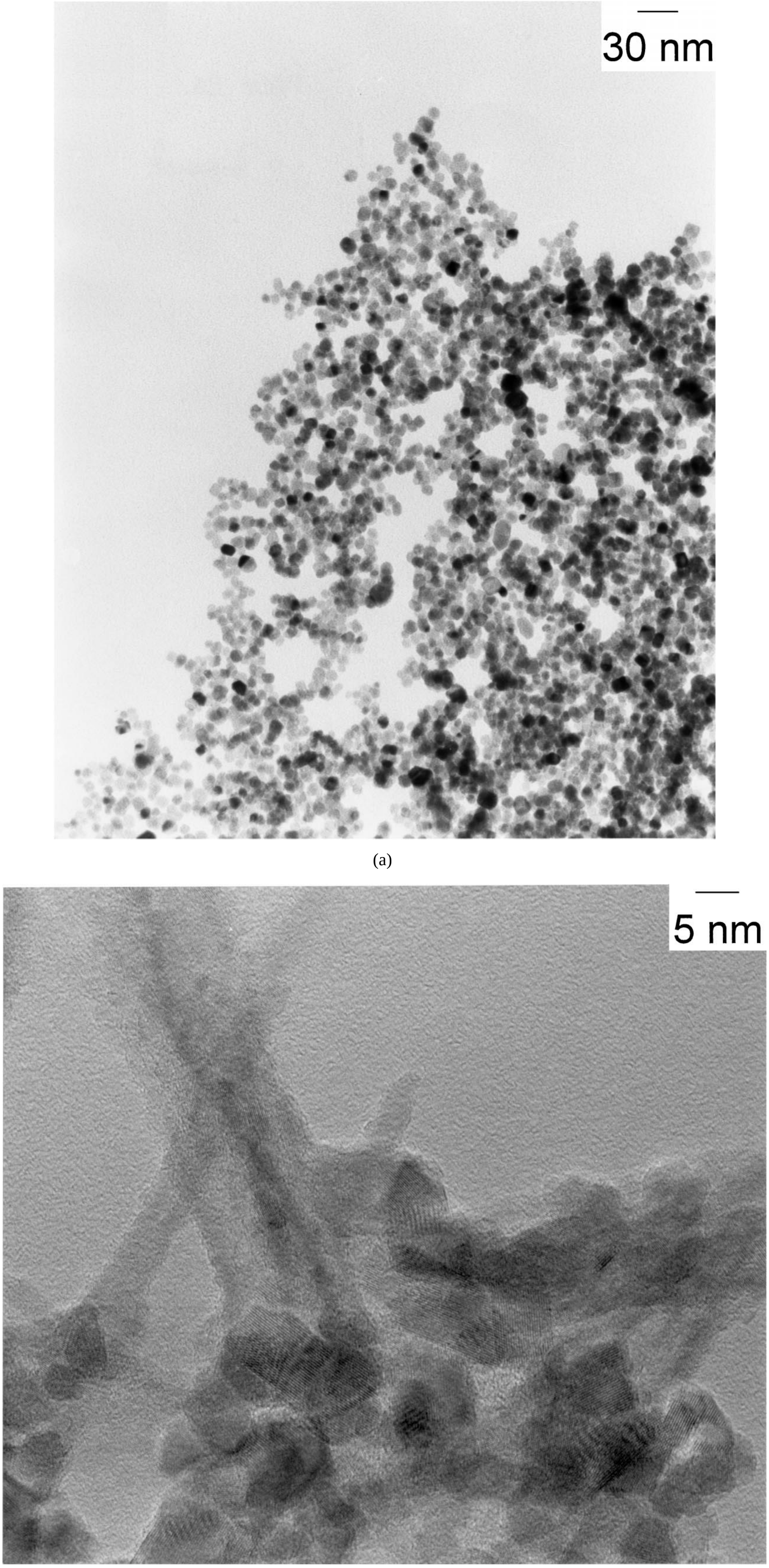
Figure 1 Zeta potential determinations (in mV) of ATO particles in an aqueous suspension as a function of pH.

In Fig. 2a, a TEM photograph is given of the ATO particles. This graph clearly shows that the system is almost monodispersed, with a particle size of about 20 nm, and that no particles are found with a particle size larger than 50 nm. In order to determine whether the particles where crystalline, some HResTEM photographs were made (Fig. 2b). In this photograph some of the ATO particles show the presence of lattice fringes, indicating the crystallinity of the particle. The layers prepared from the suspension were optically transparent and did not show any scattering.

When using a suspension with a solid contents higher than 15%, a deviation of a linear relation of the thickness of the layer and the solid contents is found. This deviation is attributed to a drastic increase in the viscosity of the solution at these high values for the solid contents. In Fig. 3 this effect is illustrated. When spinning is used as deposition technique, the film thickness is proportional to the square root of the viscosity. Thus, when the viscosity increases, thicker layers can be found.

In Fig. 4 the resistance of the ATO particle layer is given as a function of the solid contents of the suspension. Below 2.5 wt %, no significant contribution of the ATO particles to the conductivity can be observed. These layers, which are made from a suspension with a low solid contents, show a wide scattering in resistance values. The resistance is highly influenced by the humidity of the atmosphere. For this system, no effective contribution to the conductivity is found from the ATO layer. Therefore, the percolation threshold for the ATO suspension should be found in between a solid contents range of 2.5–3.5 wt %.

The effect of the temperature on the resistivity of a layer of ATO particles deposited on a quartz substrate is



(a)

(b)

Figure 2 (a) Transmission electron micrograph of ATO suspension and (b) high resolution transmission electron micrograph of ATO suspension.

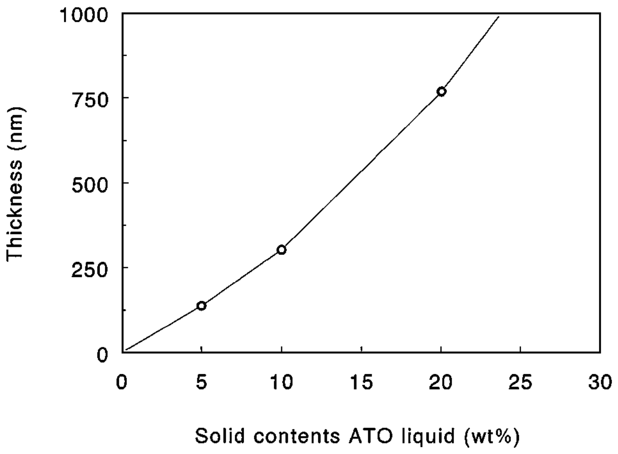


Figure 3 Thickness of ATO particle layer on a quartz substrate as a function of solid contents of the suspension used for the deposition of the layer. The layers were spin-coated at 1000 rpm and were fired at 450 °C for one hour.

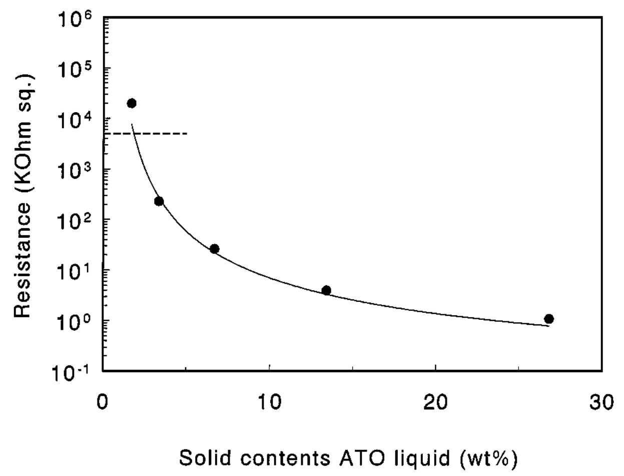


Figure 4 Electrical measurements of ATO particle layer on a quartz substrate measured as a function of solid contents of the suspension used for the deposition of the layer. The layers were spin-coated at 1000 rpm and were fired at 450 °C for one hour. The dashed line indicates the resistance of the non-coated substrate.

TABLE II Resistance of ATO particle layer fired at different temperatures

Temperature (°C)	R at T (Ω)	R at 25 °C after T (Ω)
25		5×10^5
300	2.5×10^4	9×10^3
400	7.5×10^3	2.5×10^3
500	5×10^3	9×10^2
600	9×10^2	6.5×10^2
700	2.5×10^2	1×10^2

given in Fig. 5. The heating cycle which was used consisted of a linear heating to a set temperature, maintain this temperature for one hour, cooling to room temperature, and heating to the next temperature, which was set 100° above the previous set temperature. This was repeated until a final set temperature of 700 °C was reached.

The electrical measurements show an irreversible decrease of the resistance as a function of increasing firing temperature. After the sample was heated, the resistance at room temperature was substantially lower than it was for the sample before the temperature step. This is also illustrated in Table II.

To evaluate the optical properties, the transmission was measured of samples which were fired in air at different temperatures. The results of the optical measurements are given in Fig. 6. This figure shows a significant shift of the plasma edge to higher wavelengths with increasing temperature. A shift to higher wavelengths of the plasma frequency indicates a reduction of the number of charge carriers in the material [11]. Additionally, the optical bandgap is expected to increase with increasing doping level because the conduction band is filled starting from the bottom. However, in the inset of Fig. 6 it can be seen that the wavelength of the bandgap hardly changes with increasing temperature.

One possible mechanism which could be responsible for the decrease in resistance when the materials are heated to higher temperatures is the sintering of the

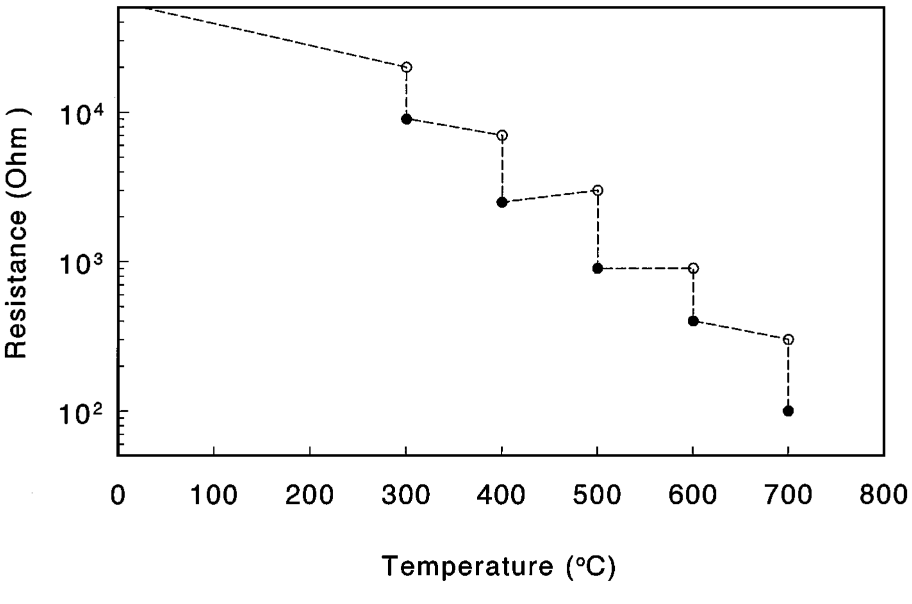


Figure 5 Electrical measurements of ATO particle layer on a quartz substrate measured as a function of the firing temperature. (○) are measurements made at the elevated temperature and (●) indicate the resistance when the sample is cooled to RT.

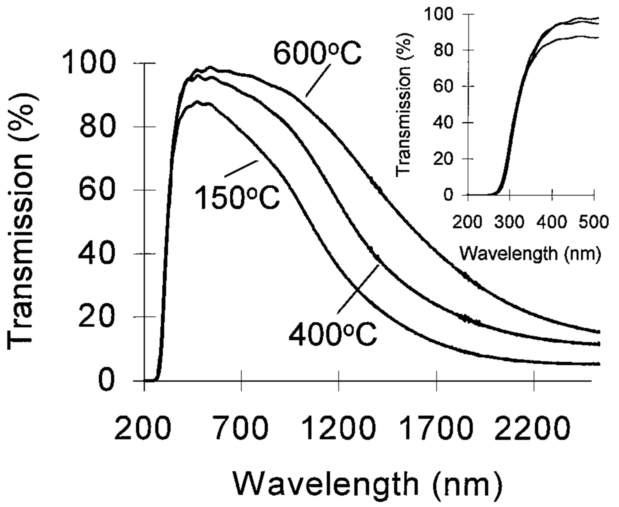


Figure 6 Optical transmission measurements of ATO particle layer on a quartz substrate in the wavelength range between 200 and 2500 nm. The inset shows the results on an enlargement scale for of the wavelengths between 200 and 500 nm.

particles, which results in a larger contact surface between the particles and thus in a decrease in the resistance. To gain insight into this behaviour, the specific surface area was determined of powder samples obtained from the suspension used and which were fired at different temperatures in air for 30 min. Sintering of the particles is accompanied by a decrease in the specific surface. The results of the measurements are given in Fig. 7. An almost constant specific surface was found for the samples fired up to 350 °C. In contrast, for the sample fired at 700 °C, a reduction of 50% in the specific surface was found. So, at least from temperatures above 350 °C, sintering of the particles will have an influence on the conductivity of the ATO layer. In addition, the resistivity of an ATO nano-particle layer was measured when fired at higher temperatures. The results, given in Fig. 8, first show a decrease in the resistance, as was also indicated in Fig. 5. However, when the sample is fired at temperatures above 700 °C, an increase in the resistance is observed.

4. Discussion

An electrical conducting layer can be prepared by spinning an aqueous suspension of nano-sized ATO particles. The resistance of this layer is much higher than that of the theoretical resistance of a homogeneous ATO layer of the same thickness [1]. This can be explained in part by the small contact area between the particles. One of the issues in this study was the origin of the gradual decrease in resistance of the layer with increasing firing temperature, especially at lower temperatures (between 150 and 400 °C). One of the hypotheses was that this is caused by the sintering of the particles, since sintering results in a large contact surface between the particles and thus in a reduction of the resistance. However, the specific surface area determinations in the temperature interval between 100 and 350 °C were found to be almost constant. This indicates that hardly any change in the particle size occurs which is to expected when the particles would sinter. This in contrast to layers which are fired at temperatures above 350 °C. Above this temperature the specific surface starts to decrease indicating that sintering of the particles occurs.

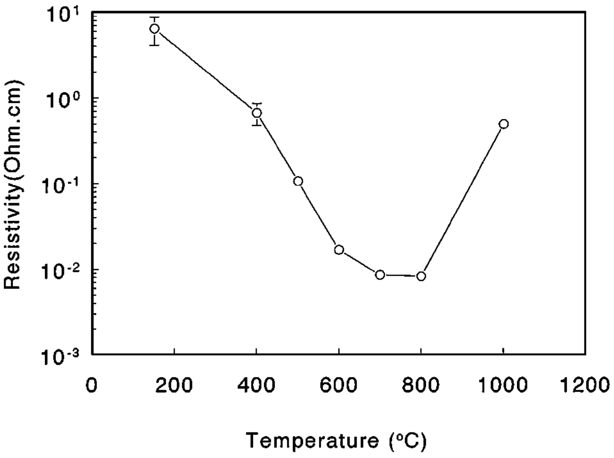


Figure 8 Resistivity of ATO particle layer on a quartz substrate measured as a function of the firing temperature. Measurements are made at RT.

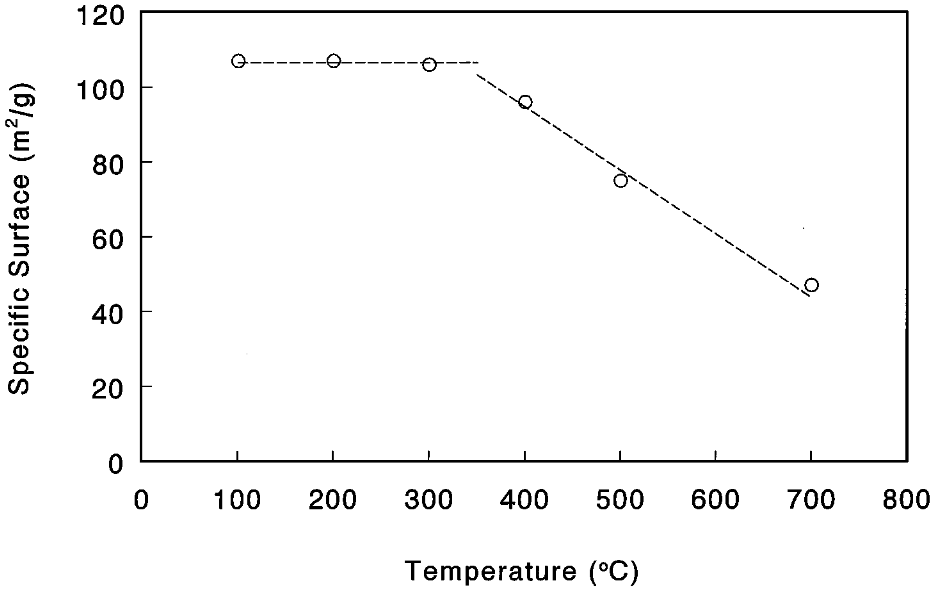


Figure 7 Specific surface determinations as a function of firing temperature of a powder sample of ATO particles.

Another possible origin of the effect of the decrease in resistivity is the increased concentration of the dope level in the tinoxide host material. On basis of the Drude theory, an increase in the dope level would result in an increase of the bandgap wavelength (Burnstein shift). The optical measurements, however, indicate the opposite. From the curves as given in the inset in Fig. 6, which is an enlargement of the optical curves in the wavelength range from 250–500 nm, hardly any change in the bandgap is observed. Also the shift of the plasma edge is an indication for a decreased concentration of the charge carriers. The plasma edge increases from about 1100 nm when fired at 150 °C to about 1600 nm when fired at 600 °C. So, although for the layers a reduction of the resistance is found with increasing temperature, the optical measurements indicate a reduction of the number of charge carriers. This indicates that the mobility of the electron through the grains of the particles, and thus the particle to particle transport, will be the dominant mechanism for the conductivity of our ATO layer.

The possible explanation of the effects observed in the electrical and optical measurements is given by the following model. For the preparation of good-conducting homogeneous ATO layers an optimal dope level of antimony of about 3% has been found [12, 13]. From the chemical analysis as given in Table I it can be found that in our experiments an ATO material with a molar Sb : Sn ratio of $(16.5 \pm 0.7)\%$ was used. Therefore, in the ATO material an excess amount of antimony is present. As a consequence of our preparation procedure, the antimony is probably preferentially located at the outside of the ATO particles, in a non-conductive modification. The antimony plays an important role in the particle size of the final ATO particles when using the given preparation process. This phenomenon has also been found by Behr *et al.* [14]. They found for SnO_2 a strong dependency of the particle size on the amount and nature of the doping level. In order to obtain a conductive Sb doped SnO_2 the antimony should be incorporated in the SnO_2 lattice. It can be expected that only a small quantity of the available antimony will be incorporated in the lattice. This amount of antimony will be dependent on the total amount of antimony present (and mainly located at the outside of the particles). So, there will be an equilibrium between the amount of antimony in the SnO_2 lattice and the antimony present and located at the outside of the particle. This equilibrium will be strongly depending on the process parameters as the temperature at which the material has been processed. Additionally, because we used a hydrothermal process to prepare our particles it can be expected that the outside layer of the particles will not be completely transferred into an oxidic system. Many hydroxy groups may still be present at the surface [15]. As a consequence the conductive bulk will be encapsulated by an insulating layer.

By an additional firing process, the antimony is diffused into the tinoxide lattice of the bulk, which is at a substantially lower dope level than the 16.5 mol % as found by the analysis. The insides of the particles consist of bulk antimony-doped tinoxide material. The optical properties of the ATO particle layer are mainly determined by the bulk ATO material. Due to the incorporation of the extra antimony, the resistance of the bulk increases when the dope level exceeds the optimal value of 3% [7, 16]. A higher doping level first results in a decrease in the mobility of the charge carriers. Finally, it also results in a decrease in the concentration of the charge carriers [12]. This seems to be in contradiction with our experimental observation that the resistance gradually decreases. However, due to a reduction of the antimony compound and the amount of hydroxy groups present on the outside of the particles, a less well-insulating layer will surround the good conducting bulk material and therefore will result in a decrease in the resistance.

At firing temperatures above 350 °C, a decrease in the specific surface area is found. This indicates that sintering of the particles occurs. Due to the sintering, a better contact of the particles is obtained and a lower resistance of the layer is found. Firing of the layers above 800 °C results in a decrease in the conductivity compared to layers fired at 700 °C (see Fig. 8). This effect can be attributed to the segregation of the antimony to the outside of the particle with increasing firing temperature [17]. The antimony-rich surface layer results in a decrease in the mobility of the charge carriers through the layer and thus in an increase in the resistance of the layer. The competition between the sintering on the layer on the one hand and the formation of the antimony-rich layer by segregation on the other hand ultimately determines the shape of the resistance temperature curve. In addition when the ATO layer is fired at temperatures above 700 °C, due to the sintering of the layers, stresses are induced in the particle layer which ultimately lead to a cracking of the layer. This, of course, has a negative effect on the mobility of the charge carriers and thus on the conductivity of the layer.

Generally, it can be assumed that the grain boundaries of the particles play a dominant role in the conduction mechanism of the ATO particle layer. Mobility of the free charge carriers is highly reduced at the grain boundaries of the ATO particles. Additionally, due to our processing the presence of hydroxy group may influence the electrical properties of the ATO material. In the literature it has been described that hydroxy groups can also be present in the bulk [18]. More investigations are necessary to elucidate the influence of these hydroxy groups on the resistivity.

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