Int. J. High Techology Ceramics **3** (1987) 309–319

Microstructure and Conductivity of Short Duration Sintered Tin Oxide Ceramics

Heikki Torvela and Seppo Leppävuori

Microelectronics Laboratory, Department of Electrical Engineering,
University of Oulu, SF-90570 Oulu, Finland

SUMMARY

Microstructure and conductance of pure tin oxide specimens were investigated. For the manufacture of the material, 10-min sintering at peak temperatures of 500–1300°C was used.

It was noticed that the microstructural characteristics for the material sintered at 1300°C were remarkably different from the materials sintered at lower temperatures. Both the average particle size and the average pore size were essentially larger in this material. Specific surface area was correspondingly smaller. As for the sintering process, electron micrographs together with pore size measurements support the view that pores are coarsening within a framework of coalesced particles.

Conductance measurements showed pronounced non-ohmic behaviour at low test temperatures. On the basis of this non-ohmic conductance it was considered that in the materials studied, energy barriers rather than necks with open current paths control the current. The results were interpreted as the dependence of current on voltage based on the model of chain-like barrier combinations. It was also concluded that significant energy barriers do not appear at all of the particle boundary surfaces.

Results obtained in this work can be utilized in the development of working models of semiconductor gas sensors. On the basis of the results it can also be concluded that in gas sensors manufactured from tin oxide, suitable additional oxides might need to be used so as to control the growth of contact areas between the particles.

1 INTRODUCTION

In the manufacture of tin oxide (SnO_2) ceramic gas sensors, short sintering times can be utilized so as to maintain the microstructure typical of that at

Int. J. High Technology Ceramics 0267-3762/87/$03·50

the early stage of sintering. This structure is likely to be porous, with a large specific surface area which can effectively interact with the gas atmosphere. Prolonging the sintering time normally tends to reduce porosity as well as specific surface area.

Sintering temperature is another important parameter. It has a very pronounced effect on the microstructural characteristics of sintered ceramics. In a study[1] of the sintering of tin oxide, the specific surface area was found to decrease from $24{\cdot}5\,m^2/g$ to $1\,m^2/g$ when the sintering temperature was raised from 600 to 1300°C in 1 h sintering. The average pore size increased from $0{\cdot}03\,\mu m$ to $0{\cdot}7\,\mu m$ in the same experiment. On the other hand, prolonging the sintering time from 1 to 10 h had only a minor effect on the pore size distribution.

In order to develop suitable properties in gas sensor materials the ability to control the microstructure is one essential aspect. In addition to the particle, pore and surface features, electrical characteristics of the material are also influenced by the microstructure developed during the course of sintering. Different models for current flow in sensing materials have been put forward to explain the current control affected by the surface.[2,3] The two principal models are the 'necking' and the 'energy barrier' models. In the case of the necking model, the control of current by the atmosphere is thought to operate perpendicular to the direction of the current around current channels formed between particles during sintering. The width of the current channel is determined by the thickness of the surface depletion layer which, in turn, is affected by gas reactions with surface oxygen. In the energy barrier model the current is believed to pass across energy barriers caused by surface charges at boundary surfaces between particles. Current control is affected by the change of the barrier energy when the gas reacts with surface oxygen.

In a constant atmosphere such as dry air the necking model will show ohmic dependence of current on applied voltage. In the case of energy barrier control there may be a deviation from ohmic behaviour, especially at low test temperatures.

Energy barriers are modified when external voltage V is applied. Assuming that this voltage is divided into fractions of average value fV that are effective at surface energy barriers between particles, there is a reduction of barrier energy by the amount $efV/2$ in the direction of the electron flow and an increase by the same amount in the opposite direction, e being the electronic charge. On the basis of thermal activation the current I is then[3]

$$I \propto \exp(-eV_s/kT)\sinh(efV/2kT) \tag{1}$$

where eV_s is the barrier energy without external voltage, k is the Boltzmann constant, T is the absolute temperature, and f is the average particle diameter divided by the distance of the measuring electrodes of the specimen.

This model of the dependence of current on voltage is based on the assumption of linear chains of energy barriers. It presents a near linear dependence of current on voltage if $efV/2kT \leq 1/2$ or $fV \leq kT/e$. Otherwise non-ohmic behaviour can occur.

This study was conducted in order to elucidate the microstructure that is formed during the early stages of sintering of tin oxide gas sensor ceramics at different sintering temperatures. It was also intended to determine the mechanism of current control in these material structures. This was achieved by measuring the dependence of current on voltage at several temperatures. The current control mechanism is connected with surface gas reactions and related to the gas sensing properties of the material. The results can be utilized in the development of working models of semiconductor gas sensors.

2 EXPERIMENTAL PROCEDURE

2.1 Sample preparation

Pro analysis tin oxide powder was used as the starting material. The average particle diameter was 0·15 μm and the main impurities, antimony, arsenic and lead, together amounted to approximately 0·05 wt%. The powder was die-pressed at a pressure of 100 MPa using 0·5 wt % of polyvinyl alcohol as a binder. When producing specimens for electrical measurements, platinum wire electrodes of 0·3 mm diameter were partly imbedded in the material before pressing (Fig. 1). The form and dimensions of the specimens are also shown in Fig. 1. Specimens for pore size and surface area measurements were 10 mm in diameter and 15 mm in length. The sintering of the pressed specimens was carried out at temperatures of 500, 600, 700, 800, 900, 1000, 1100 and 1300°C and the sintering time was 10 min. Heating and cooling rates were 10°C/min.

2.2 Microstructure studies

Microstructure was characterized using scanning electron microscopy. Mercury-penetration porosimetry was used to characterize the porosity in the sintered specimens. In addition to the usual pore size distribution, the mean pore size and the specific pore surface area were calculated from Hg penetration. The mean pore size was defined as the pore size at which half of the total pore volume was intruded. Specific surface area values obtained by the Hg-penetration method have earlier been found to agree with the results of the more common BET method is similar material to within 10%.[1] The

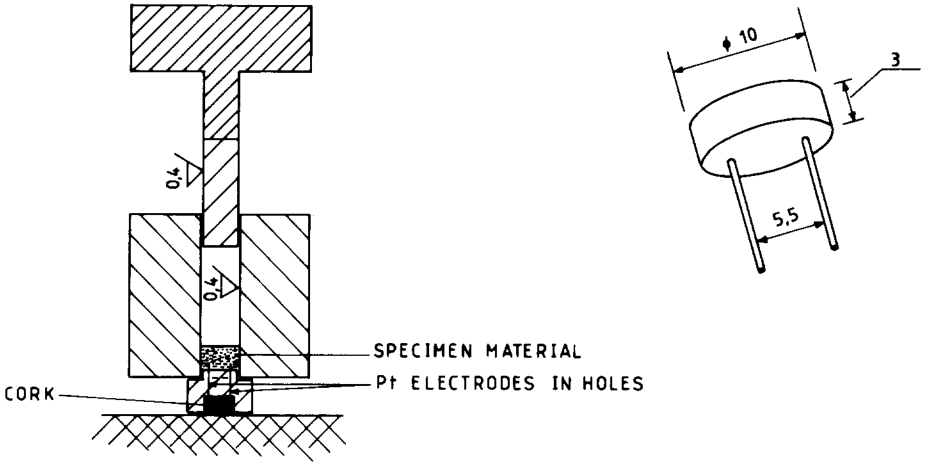


Fig. 1. Cross-sectional view of the die used for the forming of the specimens and the form and dimensions (in mm) of a sintered specimen.

BET method utilizes the adsorption of nitrogen on the surface and the measurement of the amount of nitrogen adsorbed.

2.3 Electrical measurements

Current as a function of applied voltage was measured at temperatures of 85, 200, 290, 385 and 470°C. The measurements were made in an atmosphere of synthetic air in order to eliminate the effect caused by impurities and especially by variations in humidity. Voltage was changed in steps of 0·1 V from 0·1 to 1 V and in steps of 1 V from 1 to 15 V.

3 RESULTS AND DISCUSSION

3.1 Porosity and specific surface area

As can be seen from Fig. 2 the total volume of pores remains the same irrespective of the sintering temperature. The value is about $0{\cdot}12\,\mathrm{cm}^3/\mathrm{g}$, which is practically the same as the total pore volume measured after 1 h and 10 h sintering of a similar powder.[1] The average pore size remains the same ($0{\cdot}065\,\mu\mathrm{m}$) within the sintering temperature range of 500 to 700°C. It increases with temperature in the range 700 to 1100°C and becomes considerably larger at 1300°C. The values of the average pore sizes agree well with earlier measurements for materials sintered for 1 h.[1] At all sintering temperatures these values remain a little smaller in the case of 10 min sintering compared with 1 h sintering. The values of the specific surface area remain, correspondingly, somewhat larger. The average pore size values

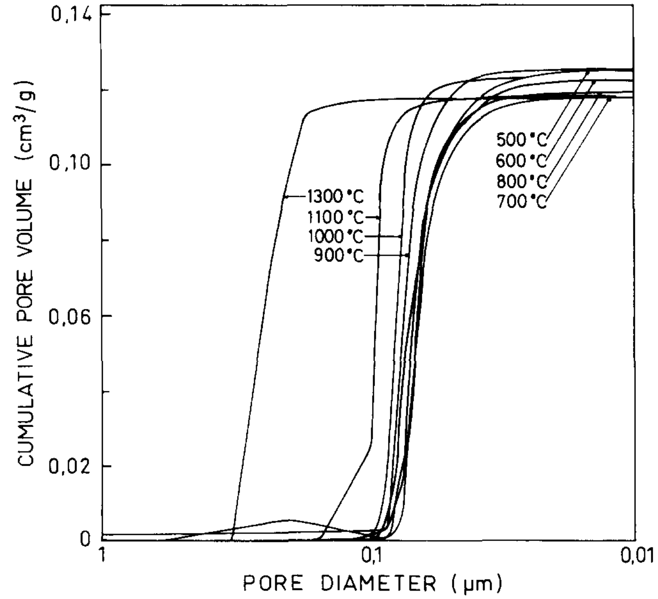


Fig. 2. Pore size distribution of tin oxide compacts sintered for 10 min at different temperatures.

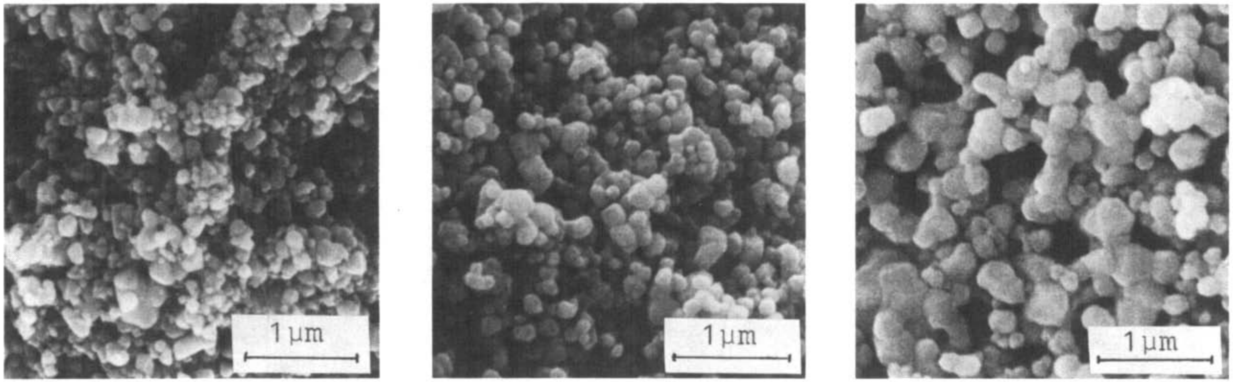
after 10 min sintering are shown in Table 1, together with corresponding values of the specific surface area.

3.2 Microstructure

The particle structure remains rather uniform during the initial stage of sintering (Fig. 3). The average particle size of specimens sintered at 500 to

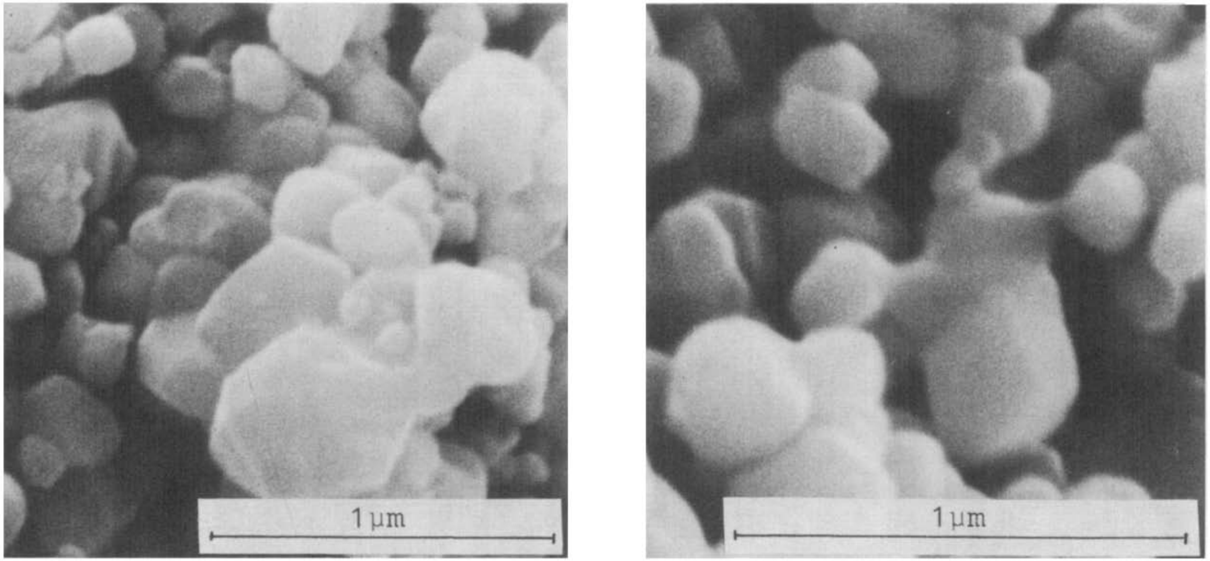
TABLE 1
Dependence of Average Pore Size and Specific Surface Area on Sintering Temperature for 10 min Sintering
(Values of specific surface area for 1 h sintering are given for comparison.[1])

Sintering temperature (°C)	*Average pore size (μm)*	*Specific surface area 10 min (m²/g)*	*Specific surface area 1 h (m²/g)*
500–700	0·065	8·9	7·98 (600°C)
800	0·070	8·3	
900	0·076	7·6	6·11
1 000	0·083	7·0	
1 100	0·095	6·1	3·96
1 300	0·25	2·5	1·17



(a) (b) (c)

Fig. 3. Microstructure of a fractured surface of SnO_2 sintered for 10 min at (a) 700°C, (b) 1100°C and (c) 1300°C.



(a)

(b)

Fig. 4. Typical shapes of particles and necks in SnO_2 sintered at 1300°C. Micrographs of the fractured surfaces.

1000°C is 0·15 μm, increases at 1100°C and is definitely larger (0·35 μm) in the material sintered at 1300°C. Particles appear to have sintered together significantly at 1300°C. The typical shape of particles was noticeably altered so that the touching surfaces look more plane-like (Fig. 4(a)). Coalesced particles seem to have formed a framework within which the pores have coarsened (Fig. 3(c)). Typical necks between particles in the structure are shown in Fig. 4(b). However, their fraction in the structure is very small. The coarsening of pores within the framework is in accordance with earlier measurements[1] and with results found in the literature.[4] The pore growth occurs with practically no change in the total pore volume and also with little or no shrinkage.

3.3 Dependence of current on voltage

The results of the measurements of specimen current as a function of applied voltage are plotted in Fig. 5 for the test temperature range of 200 to 470°C. As can be seen, the curvature of the graphs decreases as the test temperature increases, and the dependence of current on voltage seems to approach ohmic dependence at high test temperatures. There are some differences, however, between different specimens that could be attributed to the different microstructures of the materials. It can be seen from Fig. 5 that the dependence of current on voltage in the range 0·1 to 15 V at test temperatures 200 to 470°C is nearest to ohmic behaviour in the case of the specimen sintered at 1300°C. This material also clearly shows different microstructural characteristics.

The non-ohmic conductance found in this study is different from the results obtained with thick film sensors and Taguchi gas sensors,[5] which show ohmic behaviour. This is probably due to additives in those sensors that control the growth of the contact points between particles with the resultant microstructure being different.

In the material sintered at 1300°C the dependence of current on voltage measured at 85°C is that predicted by eqn (1) if the particle diameter is assumed to be 6 μm on average (Fig. 6(a)). This is far larger than the actual particle size which is 0·35 μm. One explanation for this discrepancy could be that there is not a significant energy barrier at every boundary surface of the particles. Fitting the measurement results obtained at 200°C with eqn (1) requires the apparent value of 15 μm for the average particle diameter. This is an apparently conflicting result as particle boundaries with energy barriers are not likely to be essentially less at 200°C than at 85°C. The discrepancy could be caused by there being energy barriers of different heights in the supposed linear chain. At elevated temperatures the effect of the applied voltage could be more pronounced at the larger energy walls, making the energy barriers apparently fewer.

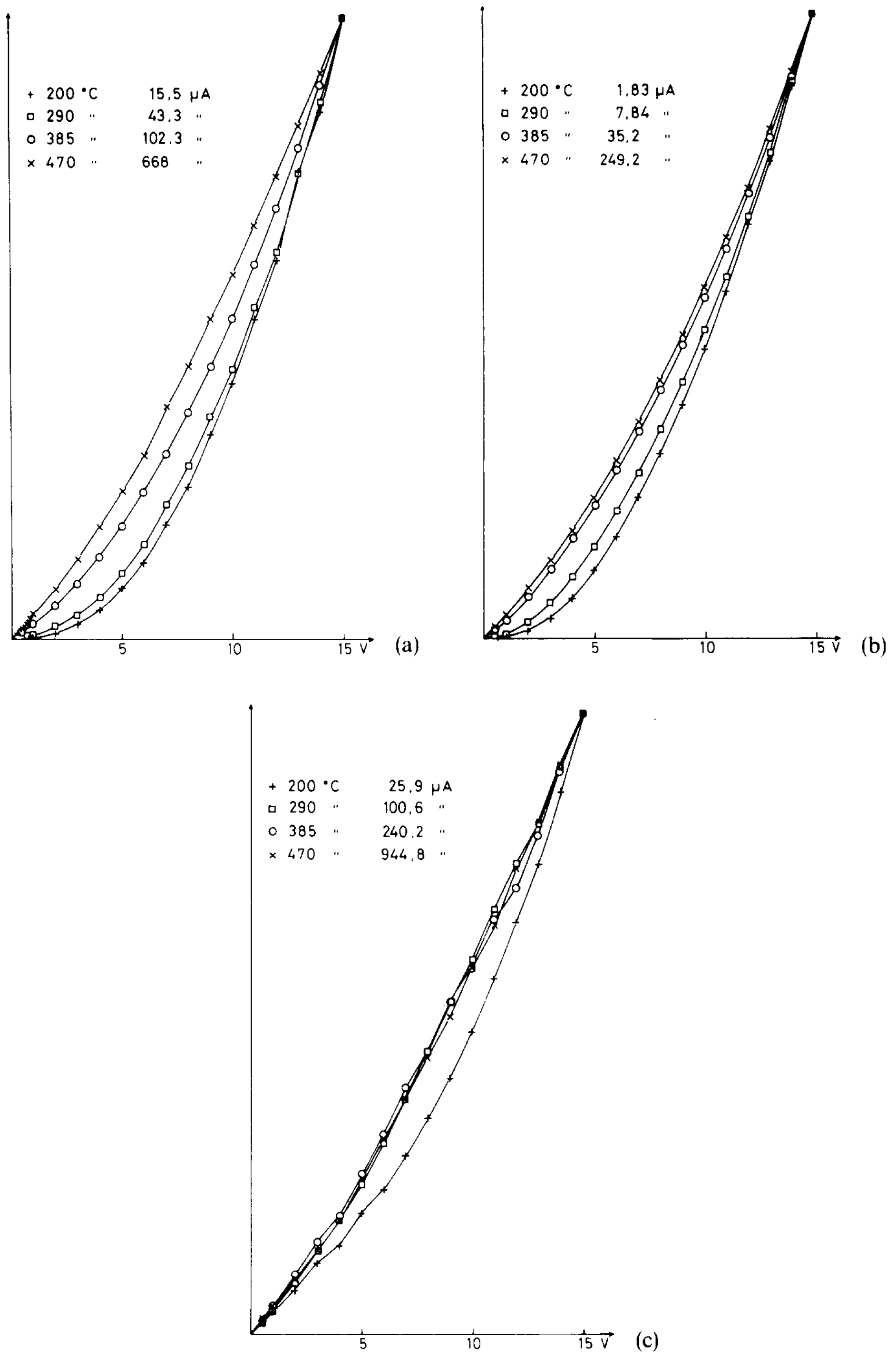
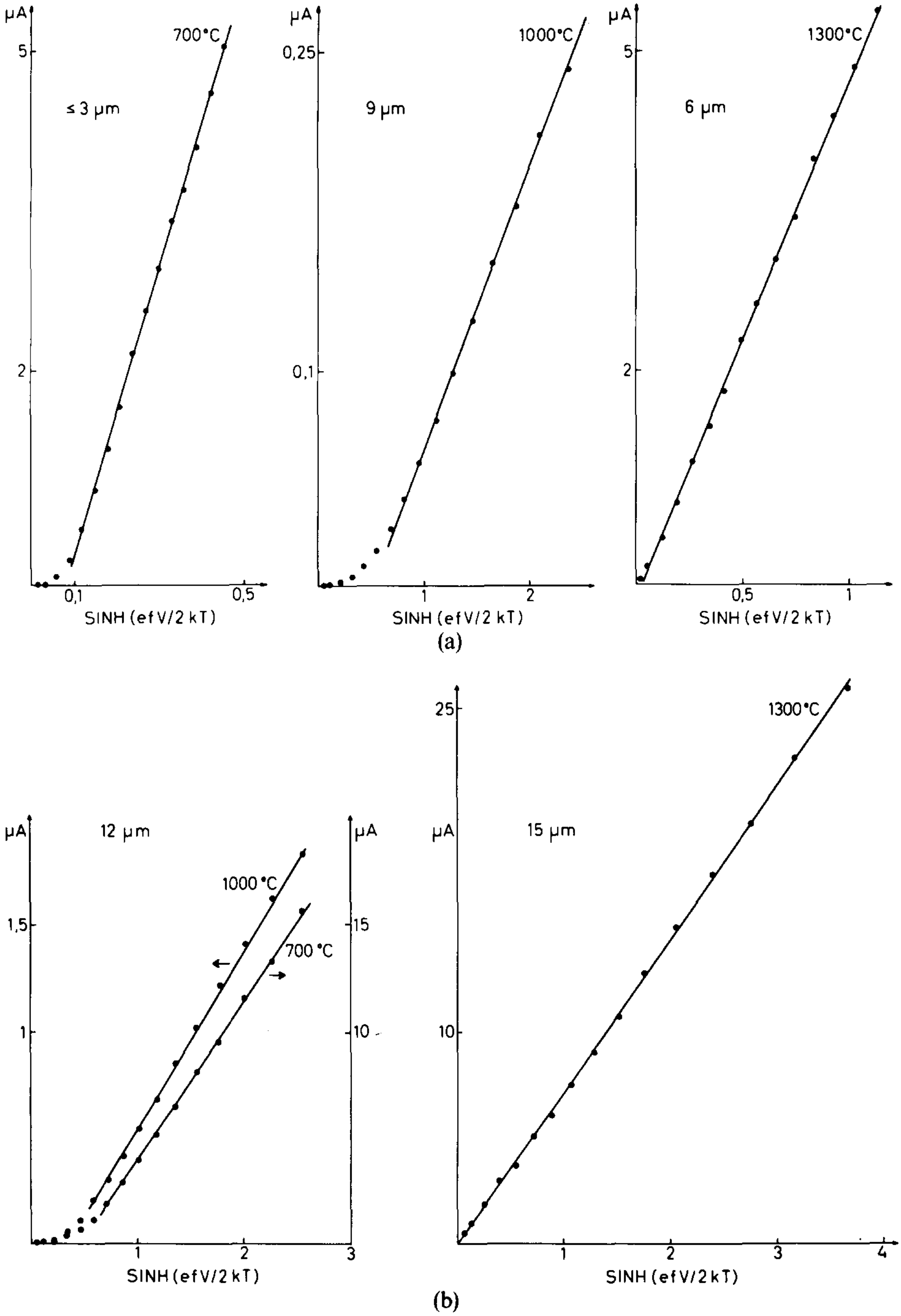


Fig. 5. Dependence of current on voltage of sintered SnO_2 samples at different test temperatures. Scales are linear and the current values are normalized so as to make the values at the measuring voltage of 15 V to coincide. This value of the current at each test temperature is indicated in the figure. The sintering temperatures of the specimens are: (a) 700°C, (b) 1000°C and (c) 1300°C.



(a)

(b)

Fig. 6. Dependence of current on voltage of sintered SnO_2 specimens measured at (a) 85°C and (b) 200°C. Sintering temperatures and the apparent particle diameters for fitting the curves are shown in the figure.

Values of specimen current vs. sinh $(efV/2kT)$ are plotted in Fig. 6 for test temperatures of 85 and 200°C. The apparent particle size used to fit the curves is also shown in the figure. The dependence between specimen current and voltage in the range 0·1–15 V follows eqn (1) only in the material sintered at 1300°C. For specimens sintered at 700 and 1000°C the model of current control based on linear chains of energy barriers appears inadequate at small voltages. In these specimens the particle size was significantly smaller than in that sintered at 1300°C. A more precise treatment of the effect of energy barriers should be based on examination of energy barrier networks instead of linear chains.

As an interpretation of the results it can be considered that energy barriers rather than necks with open current paths control the current in the pure tin oxide ceramic structure formed in short duration sintering. It can also be concluded that significant energy barriers do not appear at all of the particle boundary surfaces.

ACKNOWLEDGEMENTS

The work was supported by the Finnish Academy of Sciences and the Kemira Research Foundation.

REFERENCES

1. Torvela, H., Jaakola, T., Uusimäki, A. and Leppävuori, S., Processing characteristics of tin and tungsten oxides relevant to production of gas sensors, *J. Electronic Mat.*, **15** (1986) 7–11.
2. Morrison, S. R., Semiconducting gas sensors, *Sensors and Actuators*, **2** (1982) 329–41.
3. McAleer, J. F., Moseley, P. T., Tofield, B. C. and Williams, D. E., Factors affecting the performance of SnO_2 as a gas sensor, *Proc. Brit. Ceramic Soc.*, **36** (1985) 89–105.
4. Whittemore, O. J., Jr, Pore morphology in ceramic processing, *Mat. Sci. Res.*, **11** (1978) 125–33.
5. Lantto, V., Romppainen, P. and Leppävuori, S., A study of the temperature dependence of the barrier energy in porous tin dioxide, Paper submitted to *Sensors and Actuators*.

Received 25 April 1987; accepted 12 October 1987