

Influence of the Heating Rate on the Microstructure and on Macroscopic Properties of Sol-Gel SnO₂ : Sb Coatings

J. PÜTZ, D. GANZ, G. GASPARRO AND M.A. AEGERTER

Institut für Neue Materialien—INM, Department of Coating Technology, Im Stadtwald, D-66123 Saarbrücken

Abstract. Sol-gel dip-coated films of transparent conducting antimony-doped tin oxide (SnO₂ : Sb) have been heat treated with heating rates varying from 0.2 to 4300 K/s using either a furnace or cw CO₂ laser irradiation. The final sintering temperature of 540°C was maintained for up to 15 min. The sheet resistance of the coatings decreases with increasing heating rate. A decrease of the sheet resistance with the sintering time at constant temperature can be observed for low heating rates but the final values are higher than those obtained with higher heating rates. It is assumed that the densification of the coatings is determined by a competition between the nucleation at low temperatures and the growth of the crystallites at high temperatures. The microstructure of the coatings has been investigated by high resolution TEM cross-sections, X-ray diffraction, and Rutherford back scattering (RBS) and has been correlated to the resulting electrical properties measured by 4 point technique. Different mechanisms of heating arise with the furnace and the cw CO₂ laser.

Keywords: SnO₂ : Sb, transparent conducting coating, sol-gel process, sintering, heating rate

1. Introduction

Transparent conducting coatings like antimony-doped tin oxide (ATO) are widely used as a basic component in optoelectronic applications [1]. Compared to SnO₂ : Sb coatings prepared by vapor deposition techniques [2, 3], sol-gel based films heat treated in a conventional furnace have resistivities which are at least one order of magnitude higher [4, 5]. To some extent this can be attributed to the microstructure of the sol-gel films, i.e., the smaller crystallite size and their high porosity of up to 50–60% [5]. These structural differences can be explained by a competition between nucleation and crystal growth occurring in the early stages of heat treatment as was observed during the rapid thermal annealing (RTA) of TiO₂ [6] and ZrO₂ [7].

In this paper it is shown for single layers of sol-gel SnO₂ : Sb that the thermal treatment of the films and, especially the initial heating rate, substantially influences its film microstructure and therefore determines the electrical properties of the films. The heating rates were varied over a large scale (0.2–4300 K/s) surpassing those typically achieved with rapid thermal annealing [6].

2. Experimental

Single layer SnO₂ : Sb films were dip coated from 0.5 M ethanolic solution of SnCl₂(OAc)₂ with 5 mol% SbCl₃ onto fused silica substrates. The films were treated in a furnace with a heating rate of 0.2 K/s or by cw CO₂ laser irradiation [8] with heating rates ranging from 8 to 4300 K/s, respectively. While the highest rates have been performed in a fast scanning mode [8], heating rates from 8 to 500 K/s were realized with a single laser spot by adjusting the power density of the beam [9]. The time τ_r to reach the final sintering temperature of 540°C was used to calculate the average heating rate for the laser treated samples. The substrate temperature was determined using a calibrated fast pyrometer [10]. After the initial heating ramp the temperature was kept constant for a period τ_s of up to 15 min leading to a total sintering time of $\tau_t = \tau_r + \tau_s$.

In another series of measurements the samples have been put directly into the preheated furnace at $T_s = 540^\circ\text{C}$. For these samples the corresponding heating rate could not be determined but it is estimated to be about 1 K/s. Hence, a distinction between the ramp and sintering phase is not possible.

HRTEM cross-sections, X-ray diffraction, and Rutherford back scattering have been used to investigate the morphology of the samples. The sheet resistance has been obtained from 4 point measurements. The film thickness was determined with a surface profiler (Tencor P10).

3. Results and Discussion

The variation of sheet resistance with the heating rate is given in Fig. 1 where the first values in each series corresponds to the ramp time τ_r . The sheet resistance decreases with increasing heating rate from about $5 \text{ k}\Omega_{\square}$ (0.2 K/s) to $800 \text{ k}\Omega_{\square}$ (4300 K/s). The influence of the sintering time τ_s on the sheet resistance depends on the heating rates. For high heating rates of 100 to 500 K/s the sheet resistance stays nearly constant in time whereas the sheet resistance for furnace fired samples with a heating rate of 0.2 K/s slightly decreases. The final sheet resistance therefore is dependent on the heating rate.

The variations in sheet resistance cannot be attributed to a change in film thickness (see Fig. 2) but arise from differences in the microstructure of the coatings. The initial thickness of the gel film of 158 nm

is reduced to about 140 nm for a heating rate of 0.2 K/s (furnace) and to 107 nm for a heating rate of 4300 K/s (laser treated sample). The furnace treated samples have a shrinkage of less than 10% indicating that the porous structure of the gel film is largely retained while the laser treated samples with a higher shrinkage of about 30% should have a denser structure. As the total mass of the films has to be the same, this can only reflect a large difference in the sintered film density which is confirmed by RBS density measurements. The densities are 3.2 and $4.8 \text{ g}\cdot\text{cm}^{-3}$ for the furnace and laser treated sample, respectively, which corresponds to porosities of 50 and 30%, respectively, assuming a theoretical density of $7.0 \text{ g}\cdot\text{cm}^{-3}$ for pure SnO_2 .

This difference in morphology is clearly seen in the HRTEM cross-sections of two samples both heat treated at 540°C at a rate of 0.2 and 2600 K/s, respectively (Figs. 3 and 4). For the furnace treated sample with the low heating rate (Fig. 3) a loose structure of small crystallites, intercepted by numerous pores, can be seen. In contrast, the laser treated sample (Fig. 4) is denser and consists of larger crystallites in a less porous structure [5].

A similar trend of densification with increasing heating rate is evidenced by the crystallographic grain size.

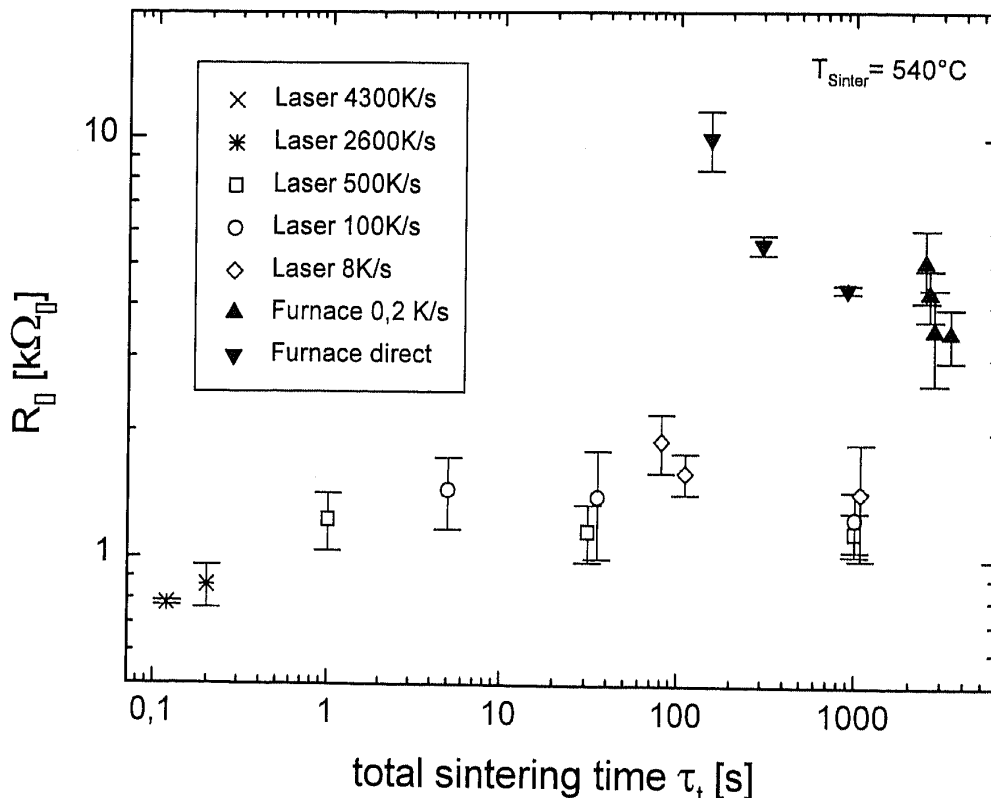


Figure 1. Sheet resistance of $\text{SnO}_2:\text{Sb}$ coatings prepared with different heating rates using either a furnace or a cw CO_2 laser at a final sintering temperature of 540°C .

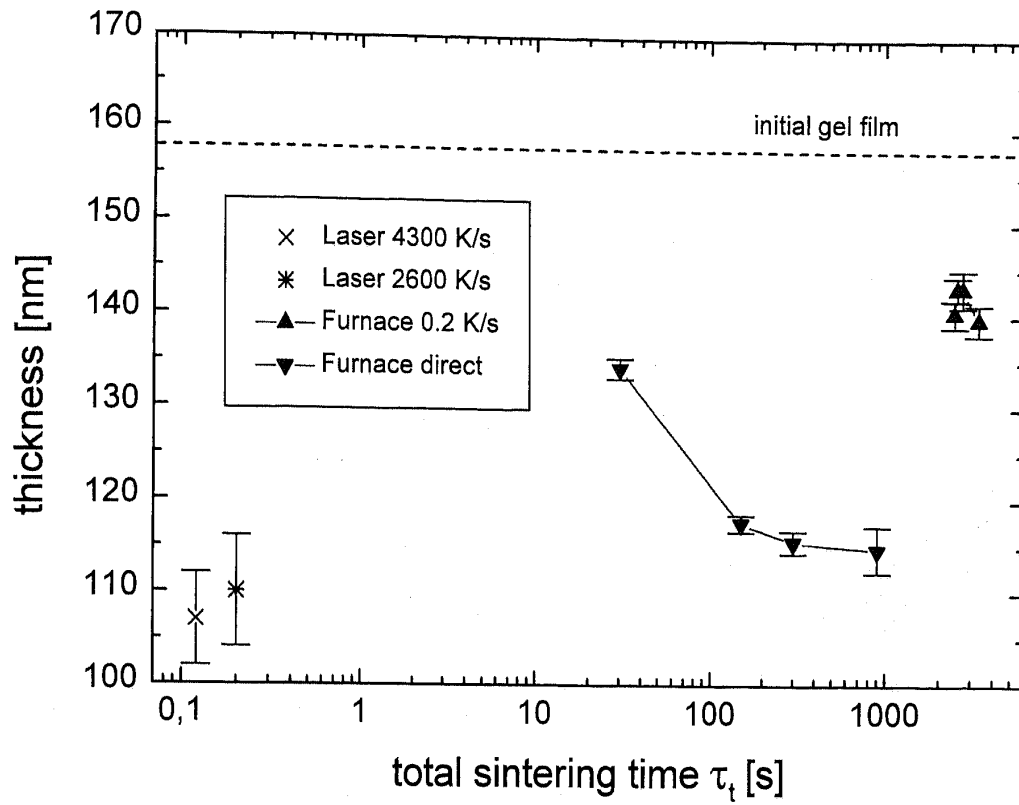


Figure 2. Film thickness of samples heat treated with different heating rates at a final sintering temperature of 540°C. The thickness of the initial gel film is 158 nm.

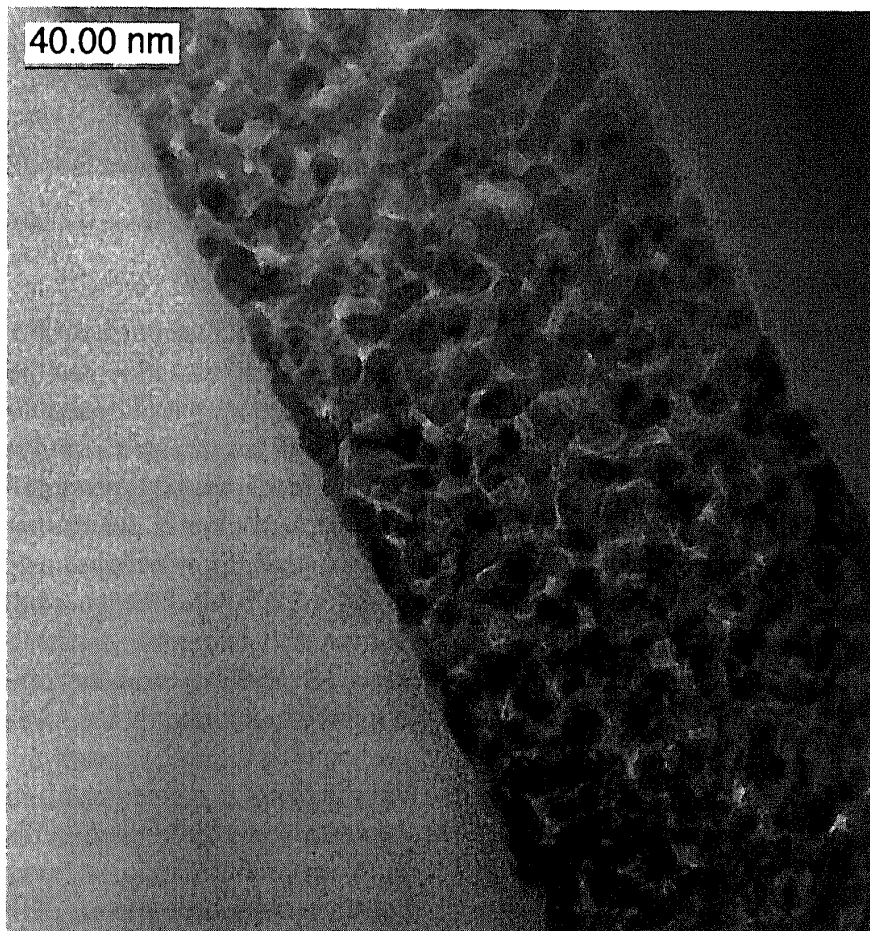


Figure 3. HRTEM cross-section of an SnO₂ : Sb coating heat treated in a furnace at a heating rate of 0.2 K/s.

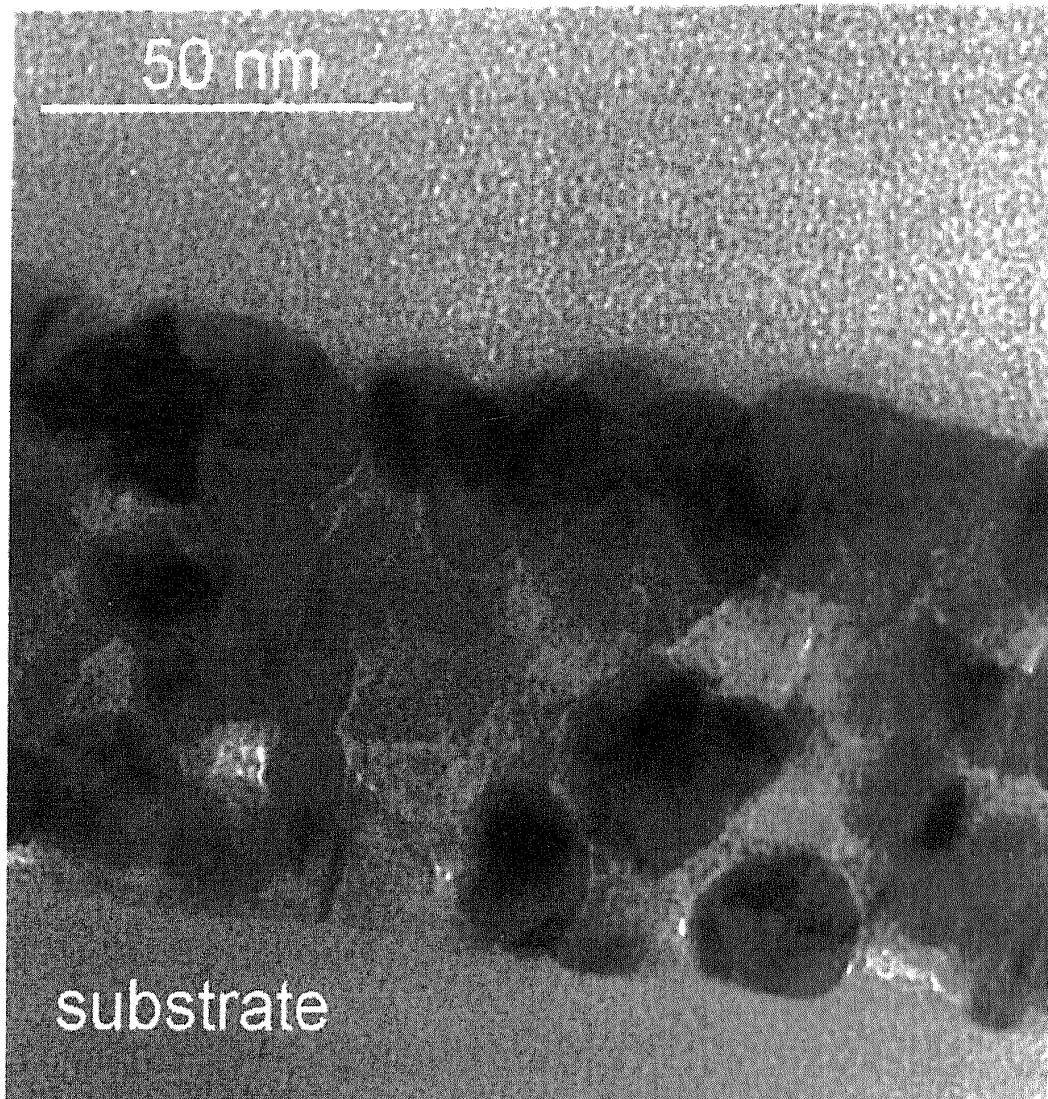


Figure 4. HRTEM cross-section of an SnO₂:Sb single layer heat treated with a cw CO₂ laser and a heating rate of 2600 K/s.

The furnace treated samples typically have crystallite sizes of 5–6 nm whereas higher heating rates lead to crystallites of 8 nm (2600 K/s) and 12 nm (4300 K/s). The crystal structure of all investigated samples corresponds to natural cassiterite.

The results lead to the conclusion that a competition between nucleation and crystal growth is responsible for the differences in the densities. At lower temperatures a nucleation process takes place whereas at higher temperatures crystallite growth can be observed [11]. Low heating rates favor the formation of numerous nuclei. By the use of high heating rates this nucleation process is passed through very quickly leading to few nuclei that can grow more easily because of shorter diffusion pathways.

The series of samples fired in a pre-heated furnace shows a different behavior, with a higher decrease in sheet resistance from 800 to 4.4 kΩ_□ after 15 min

(Fig. 1). The final thickness of the film is 115 nm (Fig. 2) which is smaller than that of the slowly heated furnace samples but only slightly higher than that obtained with laser treated samples. This higher densification in a pre-heated furnace compared to more slowly furnace fired films is due to the formation of a dense surface layer [5], which is shown in Fig. 5.

An explanation for this could be different mechanisms of heating for pre-heated and slow furnace firing, respectively, and for CO₂ laser treatment. For the low heating rates in the furnace a uniform temperature profile through the sample can be assumed. The slow increase in temperature allows for a complete escape of volatile compounds during film formation. The structure of the coatings is homogeneous and porous, reflecting the loose structure of the gel film. The film is formed by the aggregation of small crystallites, which results in a high sheet resistance, due to a large number

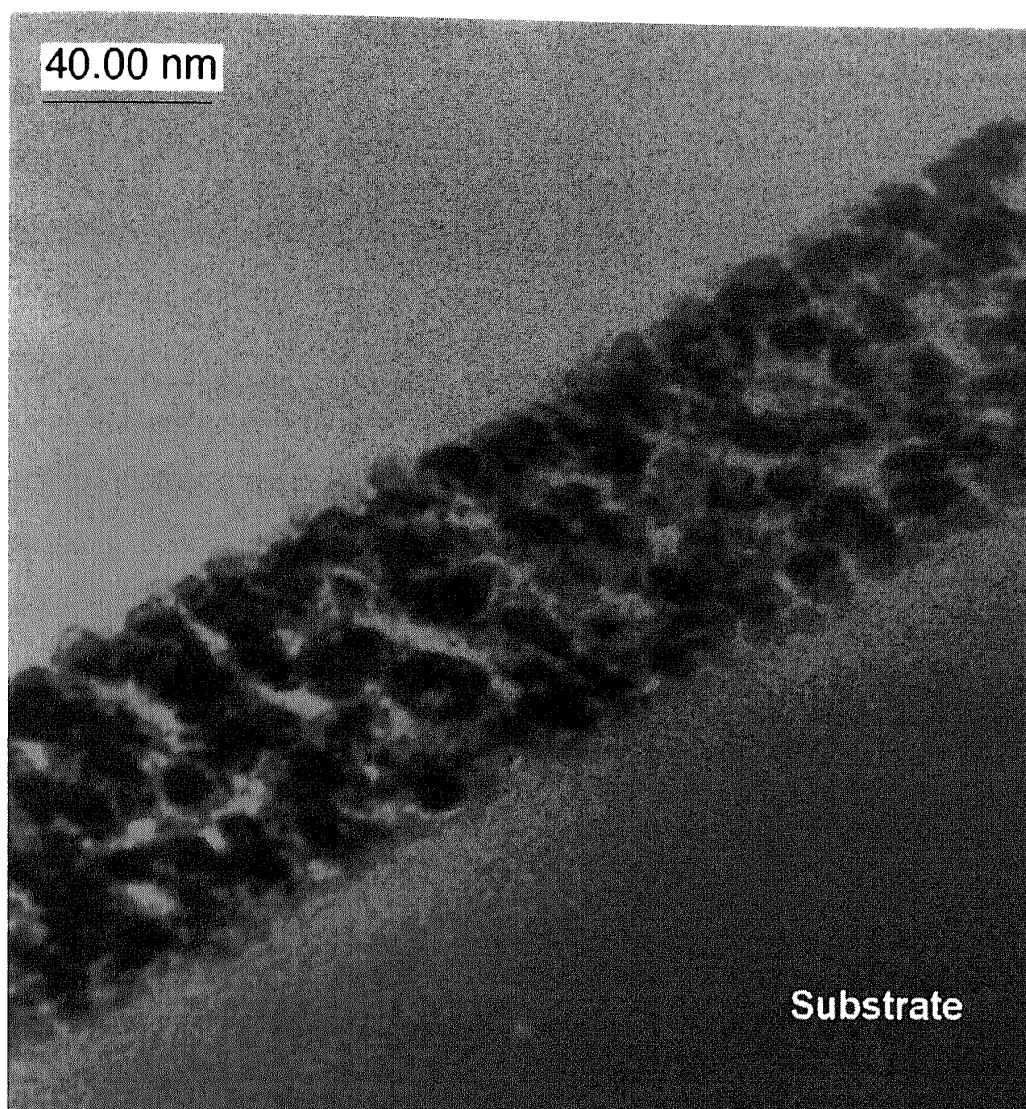


Figure 5. HRTEM cross-section of a SnO_2 :Sb coating prepared by firing in a pre-heated furnace with a heating rate of ca. 1–2 K/s.

of grain boundaries. With pre-heated furnace firing (rate ~ 1 K/s) the heat has to be conducted from the film surface to the substrate. The upper film surface is heated quickly leading to a thin dense layer which seals the film bulk. Thus, the evaporation of residues from the gel film is impeded and further heating is retarded as the conductive surface layer reflects heat radiation and the sample has to be heated mainly by heat conduction. As a consequence the film bulk exhibits a structure similar to that observed with slow furnace firing. The sheet resistance in both films is about the same as the crystallite sizes are similar, but for the pre-heated furnace fired sample this is obtained with a lower film thickness. This implies a higher overall density for these films.

In contrast, the laser treated samples are mainly heated from the substrate side as the gel film practically does not absorb at $10.6 \mu\text{m}$. The sintering of

the films proceeds from the substrate towards the film surface. As the transport of heat through the thin film is fast and hence the heating is high, the low number of nuclei that is formed in this time allows a growth of larger crystallites. This leads to a homogeneous structure with a higher density and consequently to a better sheet resistance due to a reduced number of grain boundaries.

4. Conclusions

Heat treatment of SnO_2 :Sb thin films with different heating rates from 0.2 to 4300 K/s at a sintering temperature of 540°C has shown that the heating rate decisively determines the film morphology. It is proposed that this is caused by a competition between nucleation at lower temperatures and the growth of the formed nuclei at higher temperatures. Whereas slowly heated

samples present a porous structure of small crystallites, the laser samples are denser and consist of significantly larger crystallites with few pores. The porosity and the limited crystallite size of sol-gel processed SnO₂:Sb thin films can therefore be overcome if heating rates in the order of 10⁴ K/s, which can only be obtained by high power laser irradiation are closer. In this way a sheet resistance as low as 250 Ω□ in 120 nm thick coatings (resistivity of 3 × 10⁻³ Ω · cm) [5] has been obtained. Due to the high energy density and the fact that CO₂ laser irradiation, unlike rapid thermal annealing, can heat glass substrates directly, this method seems favorable for the investigation of sintering processes with heating rates in the range from 0.1 to 10⁴ K/s.

Acknowledgments

Dr. Th. Krajewski is gratefully acknowledged for the preparation of the HRTEM cross-sectional images and C. Battaglin for the RBS measurements performed at the Department of Physics of the University of Padova.

References

1. K.L. Chopra, S. Major, and D.K. Pandya, *Thin Solid Films* **102**, 1 (1983).
2. H.S. Randhawa, M.D. Matthews, and R.F. Bunshah, *Thin Solid Films* **83**, 267 (1981).
3. E. Shanti, V. Dutta, A. Banerjee, and K.L. Chopra, *J. Appl. Phys.* **51**, 6243 (1980).
4. C. Terrier, J.P. Chatelon, R. Berjoan, and J.A. Roger, *Thin Solid Films* **263**, 37 (1995).
5. G. Gasparro, D. Ganz, J. Pütz, and M.A. Aegerter, in *Proc. of 1st International Conference on Coatings on Glass, ICCG (1996)* (Saarbrücken, Germany, 1996), to be published in *J. Non-Cryst. Solids* (1997).
6. J.L. Keddie and E.P. Giannelis, *J. Am. Ceram. Soc.* **74**, 2669 (1991).
7. R. Pascual, M. Sayer, C.V.R.V. Kumar, and L. Zou, *J. Appl. Phys.* **70**, 2348 (1991).
8. D. Ganz, G. Gasparro, A. Reich, and M.A. Aegerter, in *Proc. of PacRim 2* (Cairns, Australia, 1996), to be published.
9. D. Ganz, G. Gasparro, J. Otto, A. Reich, N.J. Arfsten, and M.A. Aegerter, *J. Mater. Sci. Lett.* (1997), in press.
10. D. Ganz, A. Reich, and M.A. Aegerter, in *Proc. of 1st International Conference on Coatings on Glass, ICCG (1996)* (Saarbrücken, Germany, 1996), to be published in *J. Non-Cryst. Solids*, (1997).
11. M. Avrami, *J. Chem. Phys.* **9**, 177 (1941).