

Laser Sintering of SnO₂ : Sb Sol-Gel Coatings

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Abstract. Sb doped sol-gel SnO₂ single layers (thickness ≈ 100 nm) were prepared from alcoholic solution and deposited via a dip coating process on fused silica substrates. The coatings have been sintered at a typical rate of 10–15 cm²/s by CO₂ laser irradiation. The laser spot was scanned in one direction at a speed of 15,000 cm/s and the sample was moved in a perpendicular one at a speed up to 250 mm/s. The temperature of the topmost 10 μ m layer was monitored by a fast pyrometer (μ s resolution). The following properties of the coatings have been determined: the electrical resistivity ρ , the carrier density n , and mobility μ , the structure, the thickness, the mesoscopic and micromorphology and the density. The sintering by CO₂ laser radiation is mainly a thermal driven process. At $T \approx 500^\circ\text{C}$ it allows to obtain coatings with a smaller resistivity ($6.8 \times 10^{-3} \Omega \text{ cm}$) than those produced by conventional furnace firing ($\rho_{\text{el}} \approx 2.9 \times 10^{-2} \Omega \text{ cm}$). The results are discussed in terms of particle size and packing density.

Keywords: sol-gel, thin film, SnO₂ : Sb, transparent conducting coatings, laser densification, electrical properties, morphology

1. Introduction

The sol-gel process enables homogeneous oxide films to be obtained using the dip or spin coating technique. The coatings are usually dried and fired in two separate processes in a furnace [1, 2]. The high temperature needed for the densification of the coatings, usually $\approx 500^\circ\text{C}$, and the repetition of the deposition and thermal processes necessary to produce thick coatings are drawbacks as the major speed-limiting factor of the coating process is the substrate/coating cooling rate.

During the last decade several attempts have been made to overcome these disadvantages by using electromagnetic radiation (EM) such as UV, visible or IR radiation as a densification energy source. In this process the EM radiation is absorbed either in the film or the substrate and converted locally into heat. Several authors densified films by scanning a low power laser spot at low speed (up to 2 cm/s) across the surface, resulting in a surface firing speed of 0.2 cm²/s [3–8].

This work presents data on the densification of electronic conductive transparent sol-gel SnO₂ : Sb

(5 mol%) films fired at high speed (up to 15 cm²/s) by a CO₂ cw laser. Comparison between laser fired and conventionally furnace fired coatings is also addressed.

2. Experimental

Sb doped sol-gel SnO₂ : Sb films were prepared from alcoholic solution and deposited via a dip coating process (one layer only) with a drawing speed of 5 mm/s on 5×2 cm² fused silica substrates. The thickness of the coatings dried at 25°C, measured with a Tencor P 10 Surface Profiler, was 158 nm for all samples. The preparation procedure of the sols [9] and the description of the laser setup [10] is given elsewhere. Some of the samples were fired in a furnace in air at 550°C for 15 min and the others were subjected to CO₂ laser densification reaching the same temperature.

The local temperature of the coatings is monitored by a fast pyrometer measuring in the spectral range of 7.3 to 9.3 μ m with a detector rise time of 3 μ s and a spatial resolution $d_{\text{spot}} = 0.5$ mm.

In the *fast scan* mode the laser beam is focused onto a rotating 14 plane mirrors polygon scanner and

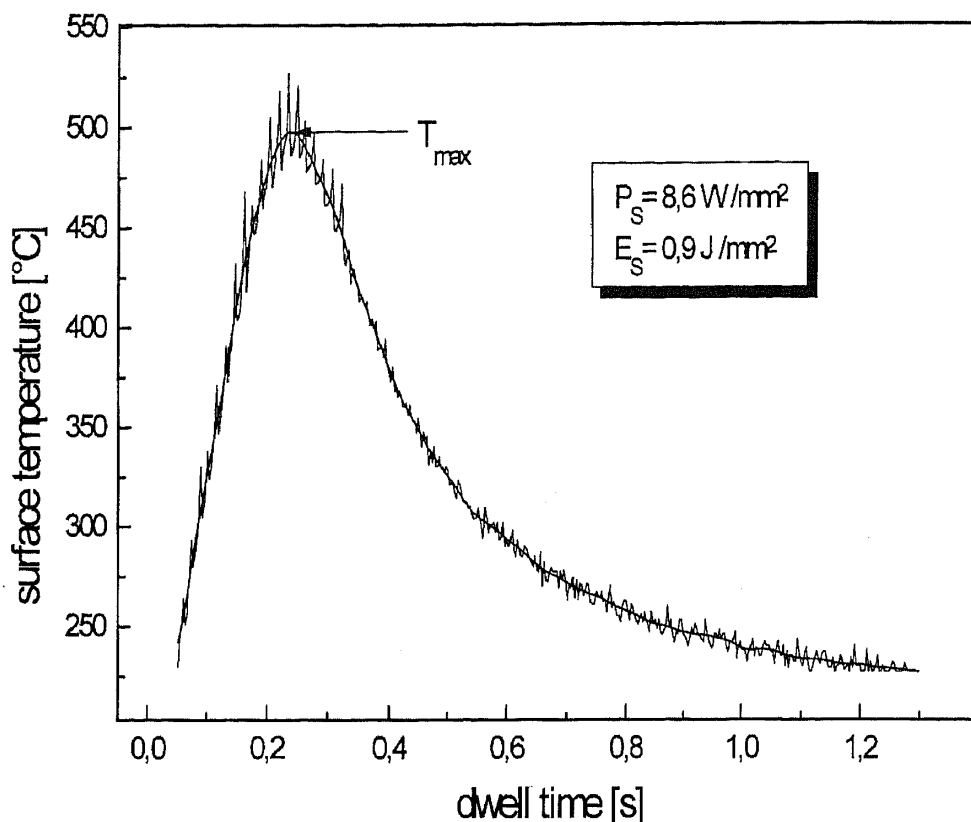


Figure 1. Typical surface temperature recorded during a fast scan mode. The smooth line is a Fast Fourier Transform of the data drawn to better determine T_{\max} .

scanned in the y direction at a very high speed (up to $\approx 20,000$ cm/s) resulting in a laser streak as small as 0.1 mm in width. This streak can be moved along a perpendicular direction at a speed up to 250 mm/s. In this way, areas can be densified at a typical rate of 10–15 cm²/s, a much larger value than those previously reported [11]. The focused beam integral output power delivers up to 560 kW/cm² to the samples.

The coatings have been characterized by several methods. The electrical properties of the coatings (resistivity ρ , carrier density n , electron mobility μ , and sheet resistance R) have been determined using a van der Pauw-Hall equipment (MMR Technology). The coating structure has been determined by X-ray diffraction (XRD) at glancing incidence using a Siemens D500 equipment and a high resolution transmission electron microscope (HRTEM, Philips CM 200 FEG). The surface morphology of the films has been observed by scanning electron microscopy (SEM) (JEOL 6400 F). The coating thickness was measured with a surface profiler (Tencor P10) and the density by X-ray total reflection (XTR) and Rutherford back scattering (RBS).

3. Results and Discussion

The typical time variation of the temperature measured at a fixed spot during the laser firing is shown in Fig. 1. It exhibits spikes which are due to the many passages of the laser along the y direction as the substrate moves along the x direction. The effective surface temperature maximum (T_{\max}) of the samples was defined as the maximum of the temperature curve smoothed by a fast Fourier transform (Fig. 1). Temperatures T_{\max} as high as 1000°C were obtained.

In Fig. 2 the resistivity is depicted as a function of the effective surface temperature T_{\max} for different laser power densities I_{st} . It decreases with increasing temperature for all laser power densities until $\approx 400^\circ\text{C}$ and then increases rapidly at higher temperatures with a slope that increases with the power density. For $I_{\text{st}} = 5$ W/mm² the resistivity reaches a minimum value $\rho_{\text{el}} \approx 8 \times 10^{-3}$ Ω cm at about 500°C. For $I_{\text{st}} = 15$ W/mm² the minimum is $\rho_{\text{el}} \approx 6.8 \times 10^{-3}$ Ω cm and lies at $T_{\max} = 375^\circ\text{C}$. The corresponding resistivity of the furnace fired coatings gradually decreases with temperature to a minimum value $\rho_{\text{el}} \approx 9 \times 10^{-3}$ Ω cm at 700°C (Fig. 2).

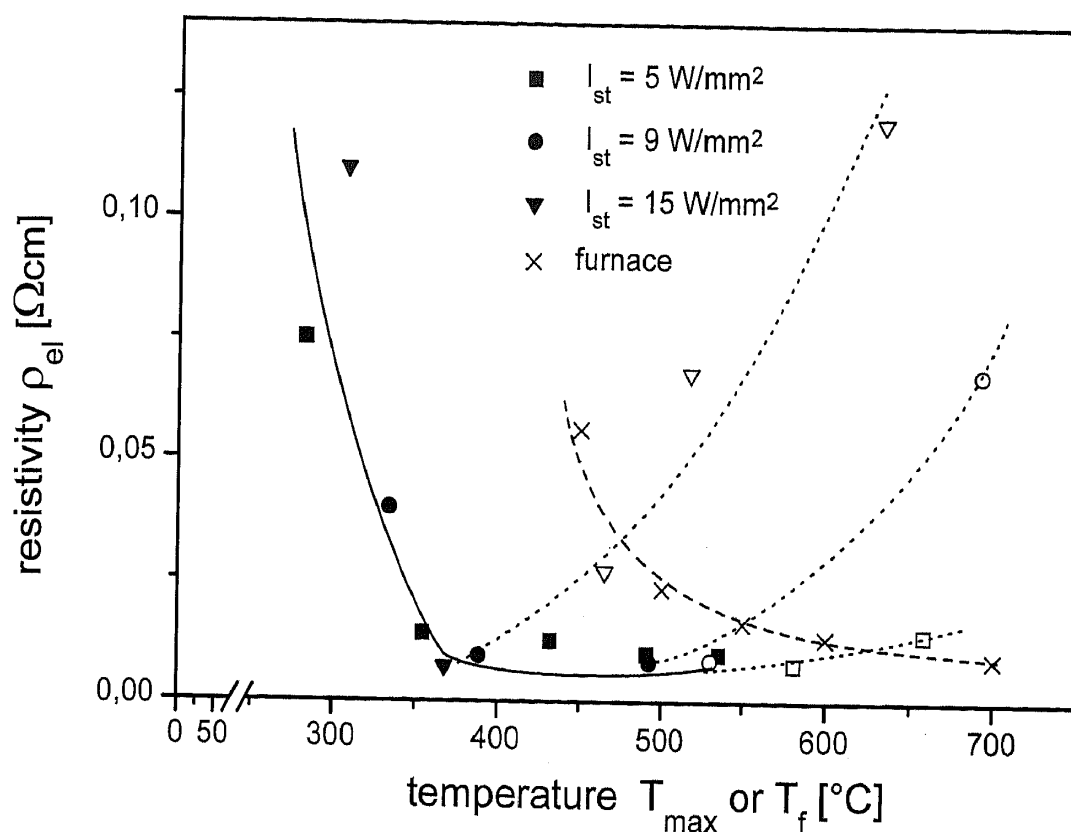


Figure 2. Variation of the resistivity ρ_{ei} vs. the sintering temperature. The lines drawn are guides for the eye.

This behavior can be understood by analyzing the temperature dependence of the carrier density n and the electron mobility μ . The carrier density increases monotonically with T_{max} (Fig. 3) and saturates at a temperature of 600°C at a value of $n \approx 3 \times 10^{20} \text{ cm}^{-3}$ for all heat treatment processes. For the laser treated samples the slope of the curves increases with power density. As the temperature increases the network formation due to chemical reactions occurring in the coatings increases, which leads to an increase of the carrier concentration. However at 600°C all chemical reactions are completed so that the carrier density cannot be increased any longer and reaches a maximum value ($n \approx 3 \times 10^{20} \text{ cm}^{-3}$).

The electron mobility (Fig. 4) shows a behavior complementary to that of the resistivity. It increases with increasing temperature for all laser power densities up to a certain temperature and then decreases. This decrease is faster the greater the power density is. Each curve has a maximum at a different temperature.

The behavior of μ for the samples heat treated in a furnace is different. The overall values are smaller and only slightly increase with the temperature.

The fact that the electron mobilities of all laser fired samples follow the same temperature dependence up to $\approx 420^\circ\text{C}$ is essentially due to the network formation. At

higher temperatures the crystallite size starts to increase (Fig. 5) leading to an increase of the mobility (Fig. 4).

The individual decrease for each power density is due to the formation of cracks by strong temperature gradients (Fig. 8). These cracks do not appear in furnace fired samples. The difference in the temperature dependence of the laser and furnace fired samples can be understood in terms of densification and crystal growth. The high heating rates (up to 7000 K/s) during laser firing cause a densification rather than a nucleation of the films [12]. The films are highly densified with a small number of nuclei. These nuclei grow larger as the temperature rises and the morphology of the layer is formed by large and densely packed crystallites (Figs. 6 and 7). This leads to a high electron mobility in the laser fired samples. In a furnace the coatings are fired at a low heating rate. This creates many nuclei and no significant densification. With rising temperature the large number of nuclei increases slightly resulting in a porous layer composed of small crystallites [12].

This was confirmed by Rutherford back scattering measurements [13] which gave a value of 4.8 and 3.2 g/cm³ for the samples fired at $T = 550^\circ\text{C}$ by laser and furnace respectively, and by the HRTEM analysis (Figs. 6 and 7).

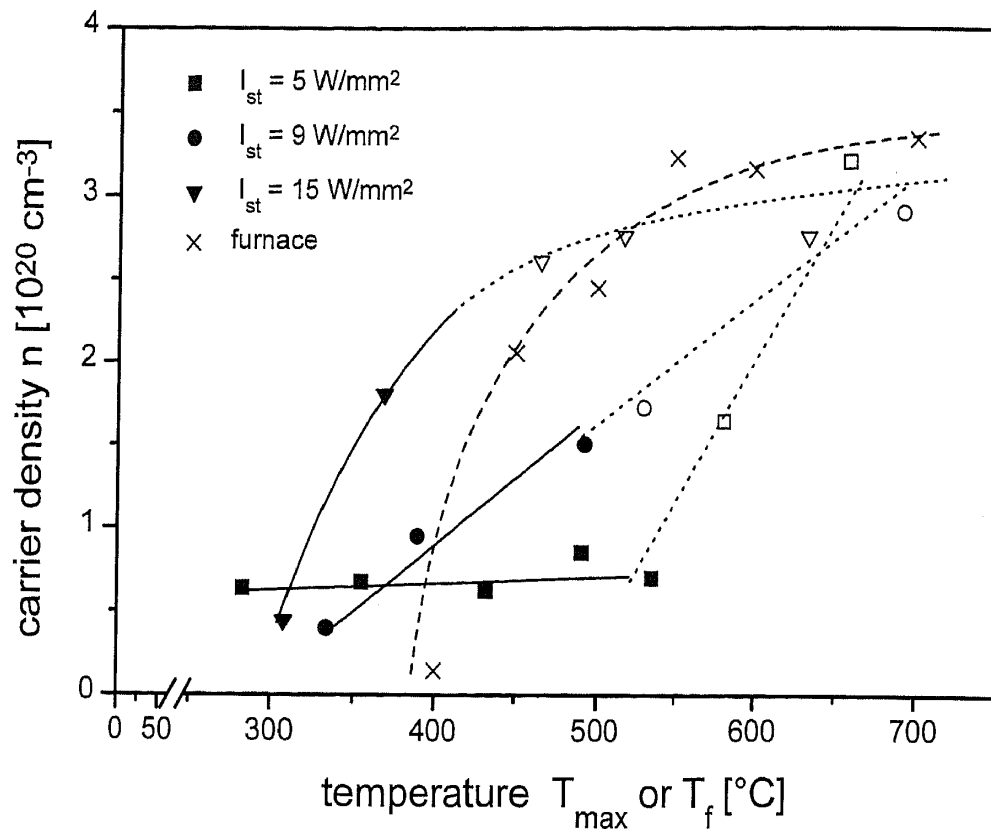


Figure 3. Variation of the carrier density n vs. the sintering temperature. The lines drawn are guides for the eye.

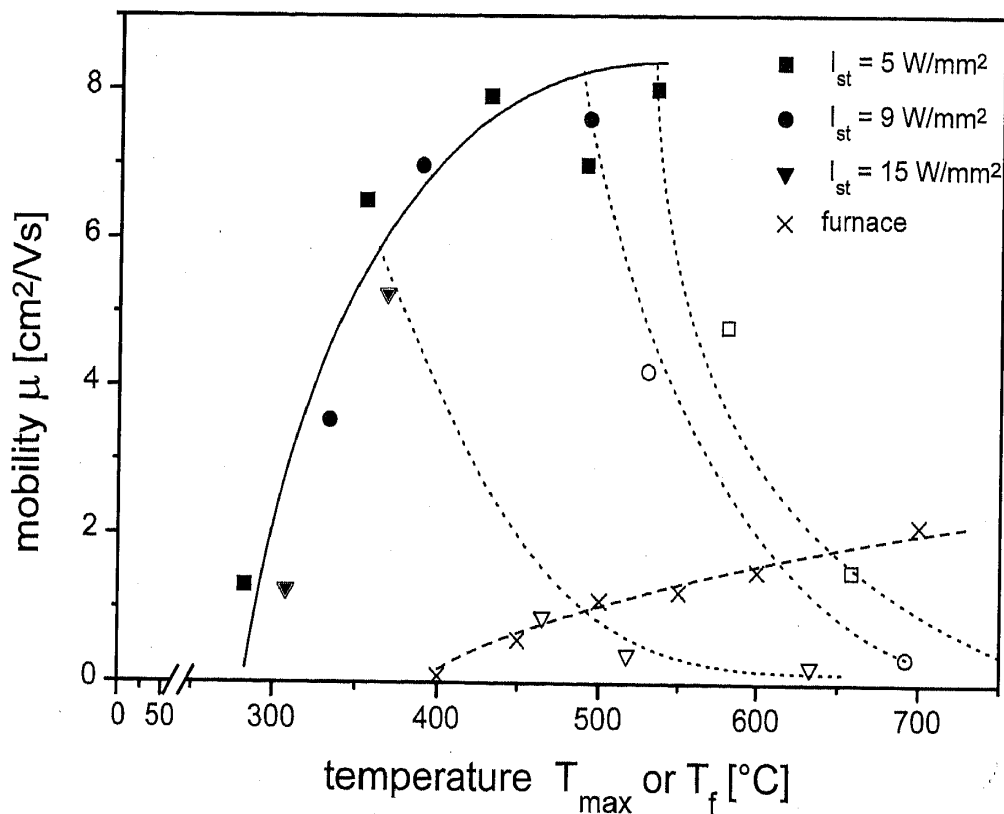


Figure 4. Variation of the electron mobility μ vs. the sintering temperature. The lines drawn are guides for the eye.

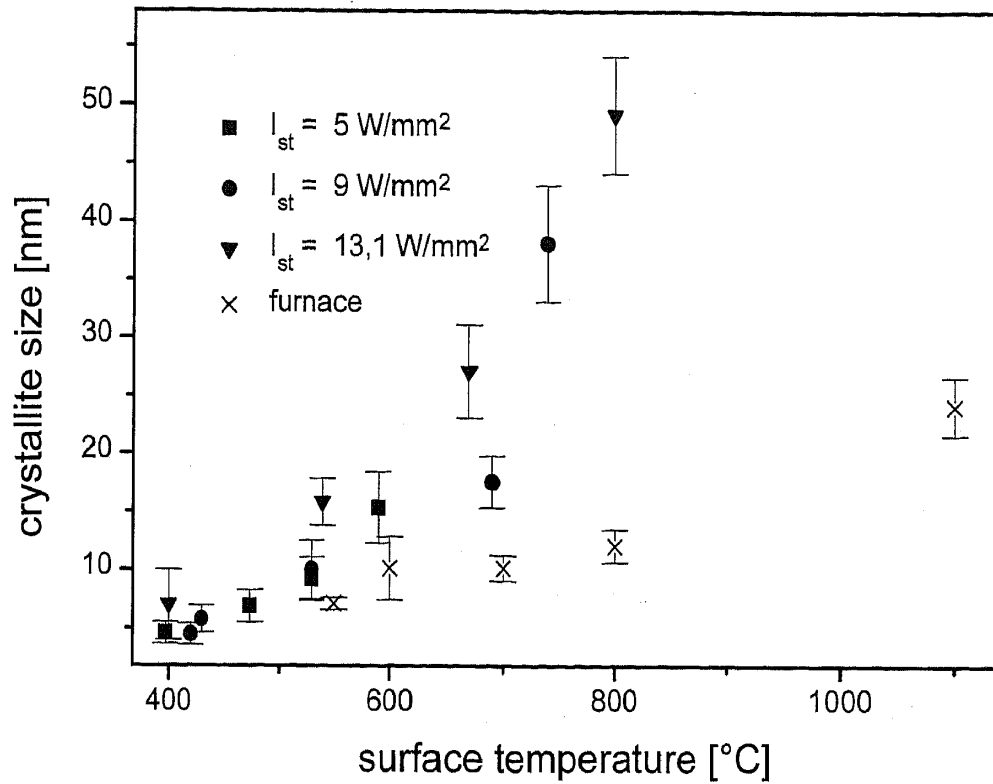


Figure 5. Temperature dependence of the crystallite size.

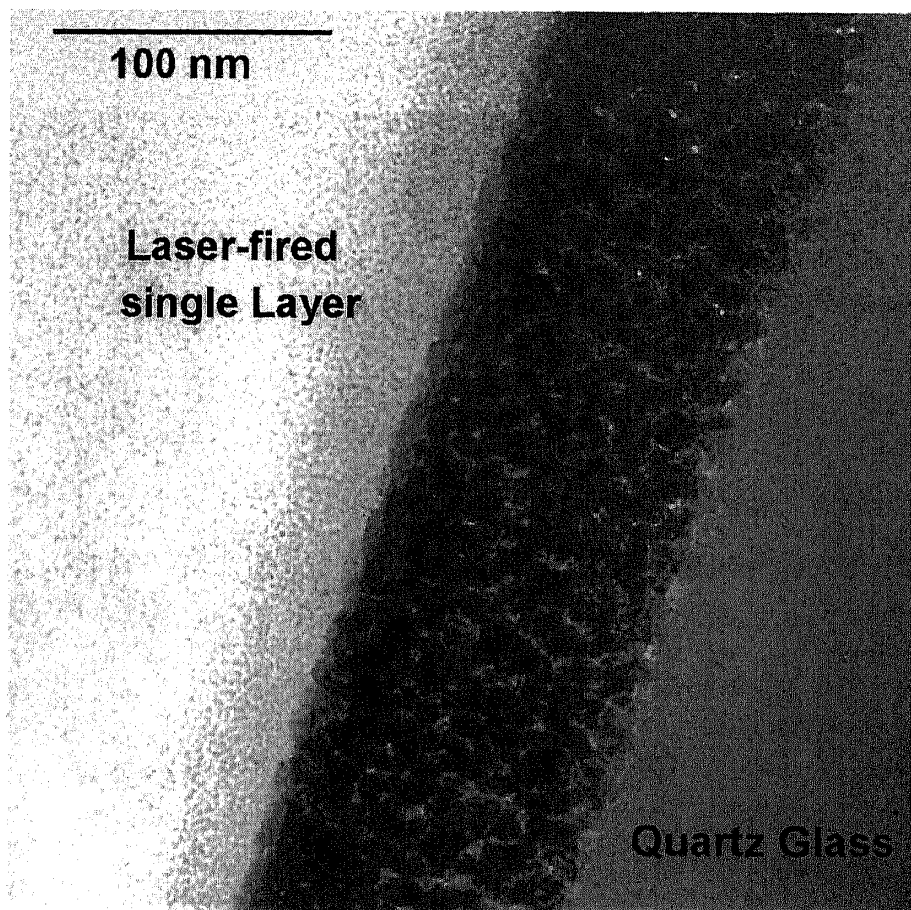


Figure 6. HRTEM cross section of a $\text{SnO}_2:\text{Sb}$ coating sintered at 380°C , $I = 9 \text{ W/mm}^2$.

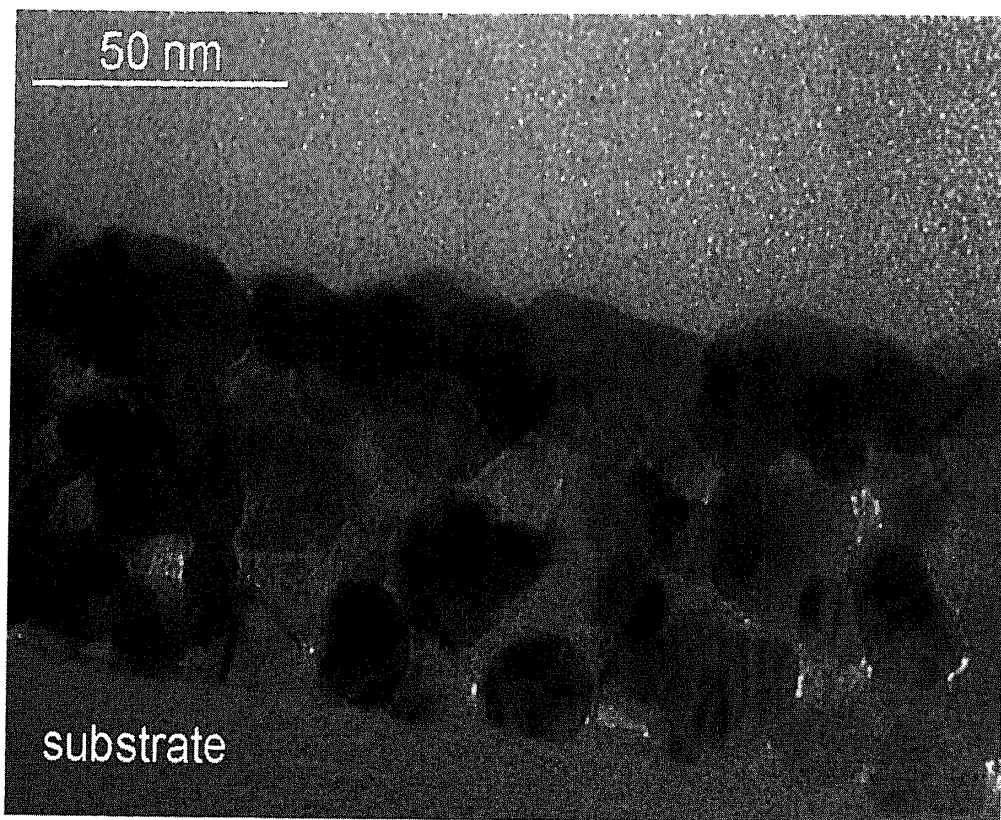


Figure 7. HRTEM cross section of a $\text{SnO}_2 : \text{Sb}$ coating sintered at 700°C , $I = 9 \text{ W/mm}^2$.



Figure 8. SEM micrograph of the surface of a $\text{SnO}_2 : \text{Sb}$ coating sintered at 700°C , $I = 9 \text{ W/mm}^2$.

4. Conclusion

Fast CO₂ laser sintering is mainly a temperature driven process. The important parameter is the effective maximum temperature. Laser firing produces denser layers with larger crystallites than those obtained by furnace firing at the same temperature. This sintering process leads to coatings that show lower resistivities than conventionally furnace fired ones. There exists a threshold for the appearance of cracks that depends on the laser power density, and which reduces the electron mobility and consequently increases the resistivity. CO₂ laser irradiation therefore appears to be an interesting way to sinter single layers of SnO₂:Sb conducting coatings. Sheet resistances as low as $R_{\square} = 780 \Omega_{\square}$ can be obtained at 500°C with a 100 nm thick coating.

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