

Laser firing of transparent conducting SnO₂ sol–gel coatings

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Abstract

Sb doped sol–gel SnO₂ films were prepared from 0.5 M alcoholic solution of SnCl₂(OAc)₂ doped with 5 mol% SbCl₃ and deposited via a dip coating process on fused silica substrates. The coatings have been fired by CO₂ laser irradiation by means of a 700 W cw CO₂ laser using a *fast scan* mode in which the laser beam is scanned by a high speed rotating polygon scanner ($\omega_{\max} = 8800$ rpm) in one direction and the sample is moved perpendicularly at a speed up to 250 mm/s. Areas can be densified at a typical rate of ≈ 12 cm²/s. The properties of the coatings have been measured by several methods: their sheet resistance, R_{\square} , has been measured using a four-probe technique, the structure of the coatings has been determined by X-ray diffraction at grazing incidence, their thickness by a surface profiler and their morphology by transmission electron microscopy. The thickness of the coatings, the crystallite size and the sheet resistance are determined by thermal driven processes. The coatings are made of dense aggregates of spherical shaped crystallites. The smallest resistivity obtained for a 100 nm thick coating is $\rho = 6 \times 10^{-3} \Omega \text{ cm}$ a value that is three times lower than that obtained with conventionally heat treated samples.

1. Introduction

Coating technology based on the sol–gel process has already revealed a great reliability in industrial application [1,2]. In this method the films are usually prepared by dip or spin coating and then are dried and fired in two separate processes using a furnace. The main advantages of these techniques compared to sputtering, physical vapour deposition (PVD) or chemical vapour deposition (CVD) processes is that no vacuum installation is needed and that it is possible to produce homogeneous films (on a nanometer scale) at a reasonable cost even at large scale [1]. A great variety of oxide materials can be produced [2]. Drawbacks are the high temperature needed for the densification of the coatings, usually around 500°C

[1,2] and if several layers are needed, as for instance to produce interference filters or to increase the coating thickness, the substrate has to be heated up and cooled down between each coating [1,2]. For glass coating, the cooling rate is the speed limiting factor of the coating process.

During the past decade several attempts have been made to overcome these disadvantages by using electromagnetic radiation (EM) such as ultra violet (UV), visible or infra red (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 [3].

2. Experimental

Sb doped sol–gel SnO₂ films were prepared from 0.5 M alcoholic solution of SnCl₂(OAc)₂ and de-

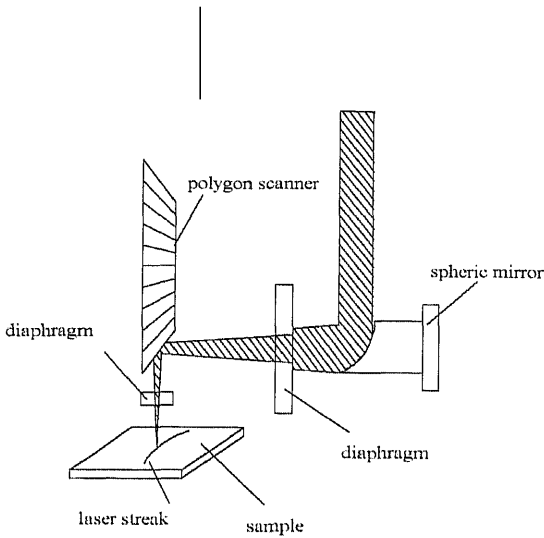


Fig. 1. Scheme of the fast scan mode laser firing of coatings.

posited via a dip coating process (one layer only) with a withdrawing speed of 5 mm/s on 5×2 cm² fused silica substrates. The thickness of the coatings dried 3 h at 25°C measured with a surface profiler (Tencor P10) was 158 ± 7 nm for all samples. The preparation procedure of the sols is published elsewhere [4,7]. The sintering has been realised by CO₂ laser cw irradiation (Rofin Sinar model RS 700 SM). The 10.6 μm light beam (TEM_{01*} mode) is guided by a mirror system into a clean room class 10,000 where it can be sent to two experimental stations [5]. The results presented in this paper were obtained

using a fast scan mode in which the laser beam is deflected by a rotating 14 plane mirrors polygon scanner and scanned in the y direction at a very high speed (typically $\approx 20,000$ cm/s) resulting in a laser streak as small as 0.4 mm in width (Fig. 1). The sample is placed on a stone table which is moved along the x direction at a speed up to 250 mm/s. Scan length, scan speed and repetition rate are programmable. In this way, areas can be densified at a typical rate of 10 to 15 cm²/s, a much larger value than those previously reported [6]. The laser power and energy densities, P_S and E_S , respectively for the fast scan mode are defined as follows:

$$P_S = P/A_{\text{streak}} \text{ [W/mm}^2\text{]}, \quad (1)$$

$$E_S = P_S w/v_x \text{ [J/mm}^2\text{]}, \quad (2)$$

where P denotes the laser power (W) and $A_{\text{streak}} = wL_y$ the laser streak area where w is the width of the streak (mm) (typically 0.5 mm) and L_y the scan length (mm) (typically 91 mm). v_x denotes the speed of the table in the x direction (mm/s). The focused beam integral output power delivers up to 560 kW/cm² to the samples. The surface temperature of the coatings is monitored by a fast pyrometer measuring in the spectral range of 7.3 to 9.3 μm with a detector rise time of 3 μs and a spatial resolution $d_{\text{spot}} = 0.5$ mm (CompoTherm, Syke, Germany). In

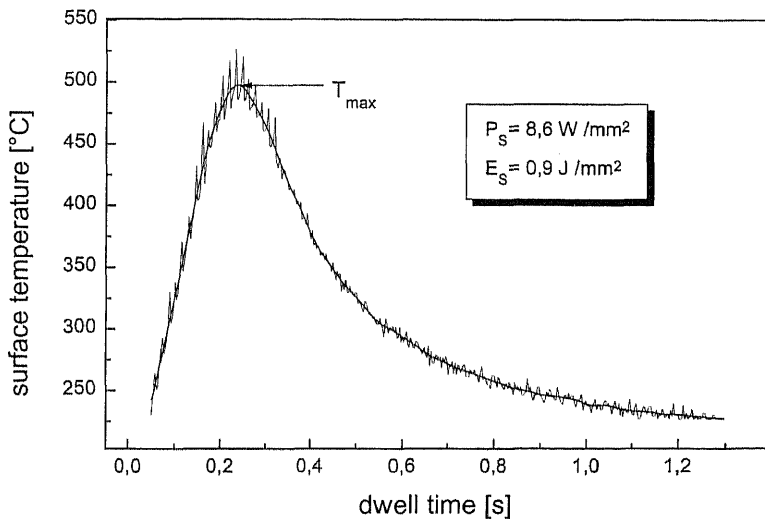


Fig. 2. Typical surface temperature recorded during a fast scan mode. The smooth line is a Fast Fourier Transform of the data drawn to better determine T_{max} .

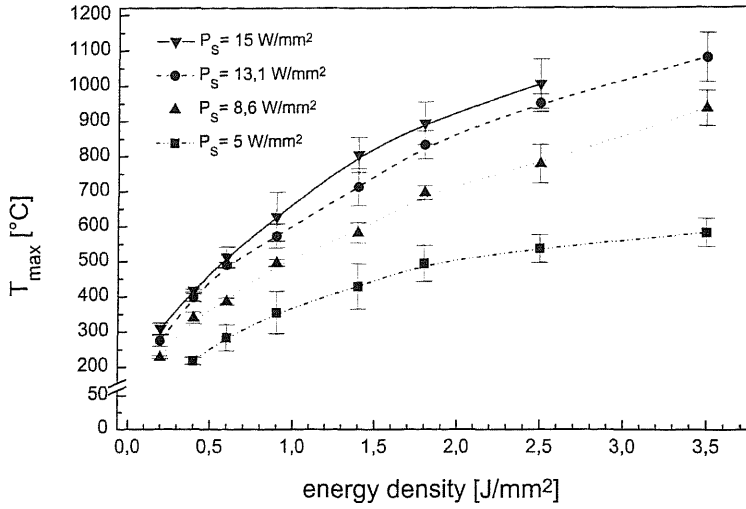


Fig. 3. T_{max} versus laser energy density for various laser power densities. The lines drawn through the points are to guide the eye.

this spectral range the IR radiation is absorbed in a 10 μm thick layer. Therefore the measured temperature corresponds to the glass surface and is an important value for the densification of the coating. The pyrometer was calibrated against a black body.

The coatings have been measured by several methods. Their electrical properties (sheet resistance (R_{\square})) have been measured using a four-probe technique. The structure of the coatings have been determined by X-ray diffraction (XRD) (Siemens D500) at glancing incidence and the films thickness by a surface profiler (Tencor P10). The morphology of

the coatings has been analysed by transmission electron microscopy (Philips CM 200 FEG).

3. Results

A scheme of the set-up of the fast scan mode laser firing is shown in Fig. 1. A typical time variation of the temperature measured at a fixed spot at the substrates surface during an experiment is shown in Fig. 2. A graph of the maximum temperature, T_{max} , as defined in Fig. 2, is shown in Fig. 3 for four

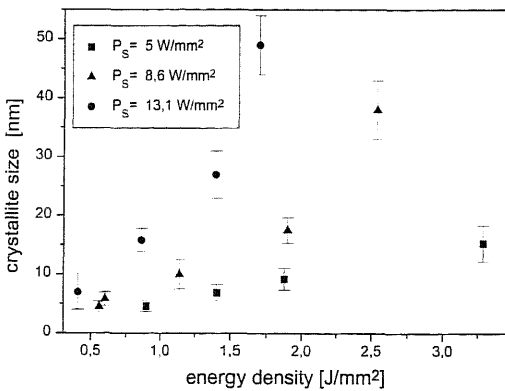


Fig. 4. Crystallite size versus energy density for three different power.

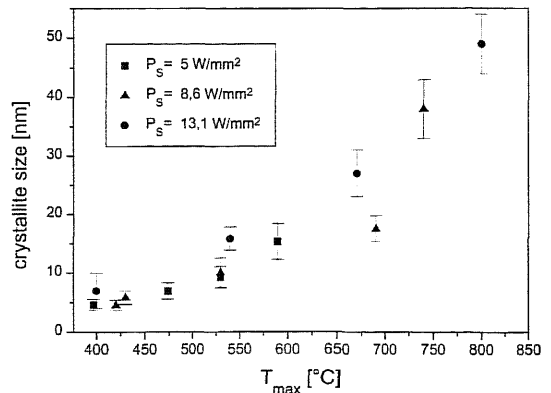


Fig. 5. Temperature dependence of the crystallite size.

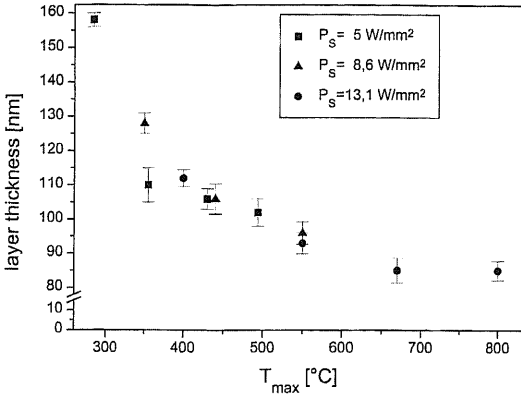


Fig. 6. Layer thickness versus T_{max} .

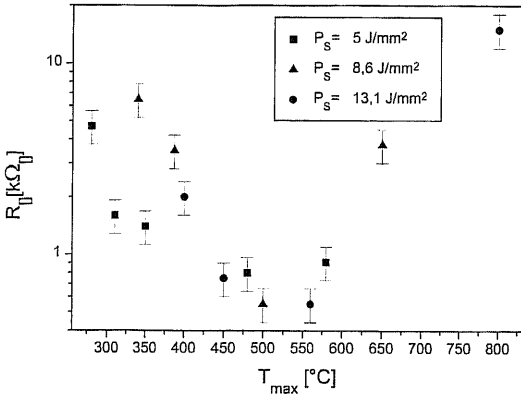


Fig. 7. Variation of the sheet resistance, R_s versus the laser energy density, E_s .

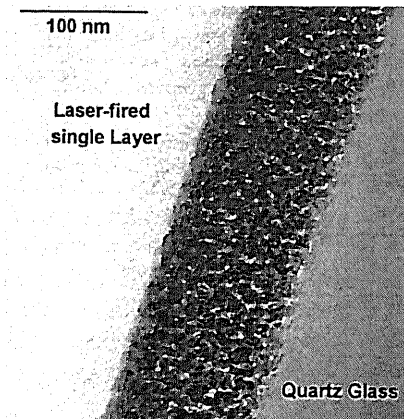


Fig. 8. TEM cross-section of a $\text{SnO}_2:\text{Sb}$ coating sintered in a furnace.

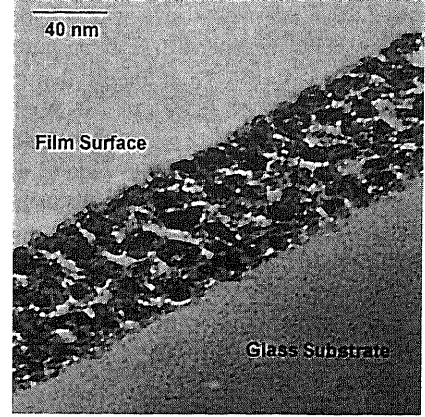


Fig. 9. TEM cross-section of a $\text{SnO}_2:\text{Sb}$ coating sintered by a CO_2 laser.

different laser power densities, P_s . The $\text{SnO}_2:\text{Sb}$ crystallite size calculated with the Debye–Scherer method [8] from grazing X-ray diffraction spectra is given in Figs. 4 and 5 for different laser firing conditions. Figs. 6 and 7 show the variation of the thickness and R_s respectively of a single layer $\text{SnO}_2:\text{Sb}$ as a function of the maximum temperature, T_{max} , for different laser power densities, P_s . Finally, typical TEM micrographs of cross-sections of a $\text{SnO}_2:\text{Sb}$ single layer sintered either in a furnace (Fig. 8) or by CO_2 laser irradiation Fig. 9 are shown.

4. Discussion

The typical time variation of the temperature measured at a fixed spot during the laser firing shown in Fig. 2 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 surface temperatures of the samples were defined as the maximum of the temperature curve (T_{max}) smoothed by a Fast Fourier Transform (Fig. 2). Its variation as a function of the laser energy density is shown in Fig. 3 for four different laser power densities. Temperatures as high as 1000°C were obtained.

Grazing angle X-ray diffraction patterns reveal that all laser treated samples crystallise in the cassiterite structure the same structure can be observed at samples conventionally fired in a furnace [4]. Contrary to SnO_2 coatings prepared by spray pyrolysis or sputtering technique the sol–gel made films are

not textured. The crystallite size was calculated by the Debye–Scherer method. For a given power density it increases with the laser energy density (Fig. 4). The crystallite growth is due to a thermal driven process since the size of the crystallites only depends on the temperature reached in the coating after the light absorption. It increases as the temperature rises (Fig. 5). There is however a temperature threshold. For temperatures less than 500°C all crystallites have the same size. The growth starts at about 530°C.

A similar scaling behaviour is observed for the layer thickness and the sheet resistance of the coatings. Fig. 6 shows the final thickness of the samples after fast scan laser firing as a function of the surface temperature for three different power densities. For all samples studied the thickness decreases with increasing temperature and this diminution is independent of the laser parameters.

R_{\square} varies with the laser power and energy density (Fig. 7). The samples dried at room temperature are insulating ($R_{\square} > 200 \text{ M}\Omega_{\square}$) and R_{\square} gradually decreases as the surface temperature increases. It passes through a minimum, $R_{\square}^{\text{min}} \approx 600 \Omega_{\square}$ (corresponding to $\rho \approx 6 \times 10^{-3} \Omega \text{ cm}$) and then increases. In conventionally heat treated samples the resistivity plotted against the temperature decreases monotonically and becomes invariant, $\rho = 9 \times 10^{-3} \Omega \text{ cm}$, at 700°C [7].

The decrease of the resistivity can be understood in terms of the morphology of the layers. Figs. 8 and 9 show that the layers consist of an aggregation of almost spherical shaped particles. In furnace treated samples where the resistivity is larger the packing density is smaller and the layer is more porous. Laser sintered layers which have smaller resistivities have a similar morphology but the shape of the particles and their packing density is higher [7]. The increase in the resistivity that is observed at a temperature of

about 575°C is not yet understood. It may be due to the presence of structural defects (cracks) or from valence change of Sb ions $\text{Sb}^{5+} \rightarrow \text{Sb}^{3+}$ resulting in a lower carrier density. A simultaneous growth of the pores and crystallites may also reduce the electronic mobility. Detailed measurements are underway to confirm these assumptions.

5. Conclusion

Sintering of a sol–gel $\text{SnO}_2:\text{Sb}$ coating by fast scan CO_2 laser irradiation has been demonstrated. The thickness of the coatings, the crystallite size and the sheet resistance are determined by thermal driven processes. The coatings are made of dense aggregates of spherical shaped crystallites. The minimum resistivity obtained until now is $\rho = 6 \times 10^{-3} \Omega \text{ cm}$ a value that is three times less than that obtained with conventionally heat treated samples.

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