Fast CO_2 laser firing of sol-gel SnO_2:Sb coatings

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In recent years the coating technology based on the sol-gel process has revealed a great reliability in industrial application. In this method the films are usually prepared by dip or spin coating and afterwards are dried and fired in two separate processes using a furnace [1, 2]. The main advantages of these techniques compared to other coating technologies such as sputtering, physical vapour deposition (PVD) or chemical vapour deposition (CVD) is that no vacuum installation is needed and that it is possible to produce very homogeneous films at a reasonable price even at large scale. A further benefit is the great variety of oxide materials that can be produced. Drawbacks are the high temperature needed for the densification of the coatings, usually around 500 °C 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. For flat-glass coating, the maximum attainable cooling rate is the speed-limiting factor of the coating process.

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.

Taylor *et al.* [3] successfully densified silica films prepared with TEOS sol using a CO_2 or a Nd:YAG laser. In the last case, as the films were transparent at the laser emission wavelength, they had to be covered with a metallic layer to get significant optical absorption in order to generate heat. Later Zaugg *et al.* [4] formed waveguides and Birnie *et al.* [5] multilayer interference filters by laser densification of sol-gel films. In these the authors have also used a furnace to dry the samples before the laser firing and only a small area has been densified by scanning a low power laser spot at low speed (up to 2 cm s^{-1}) across the surface, resulting in a low surface firing speed of 0.2 cm^2 s^{-1} [6]. Arfsten and colleagues [7, 8] have also claimed that large area flat-glass plates coated with thin sol-gel TiO_2 films can be densified directly by CO_2 laser radiation, with densities comparable to those obtained in the conventional oven process but in a much faster time scale. The restriction of the heated substrate zone to a depth of about 10% of the beam radius kept the bulk glass substrate temperature below 80 °C. Other laser techniques have been reported for large scale coating for example Alunovic *et al.* [9] for the formation of oxide ceramics by pulsed laser deposition (PLD) and Hopfe *et al.* [10] for the preparation of TiC or SiC films by laser assisted chemical vapour deposition (LCVD). The direct formation of dense films from a liquid running on different substrates by laser assisted photo deposition [11] and laser enhanced plating [12] have also been reported. However, these last techniques require either a vacuum or a certain atmosphere to work properly, increasing the production costs.

In this work we present preliminary data to fire large substrates at high firing speeds (10–15 cm^2 s^{-1}) using a Rofin Sinar 700 W cw CO_2 ($TEM_{0,1^*}$ mode) laser model RS 700 SM. The process has been applied to electronic conductive transparent sol-gel SnO_2:Sb (5 mol%) films. Comparison between laser fired and conventionally furnace fired coatings is also addressed.

The 10.6 μm light beam is guided by a mirror system into a clean room class 10 000 where it can be sent to two experimental stations built by BIAS Company (Bremen, Germany) (Fig. 1). For security purpose the laser beam is confined in tubes and both stations are located in closed cabins. In the first one (left side of Fig. 1) an optical device transforms the

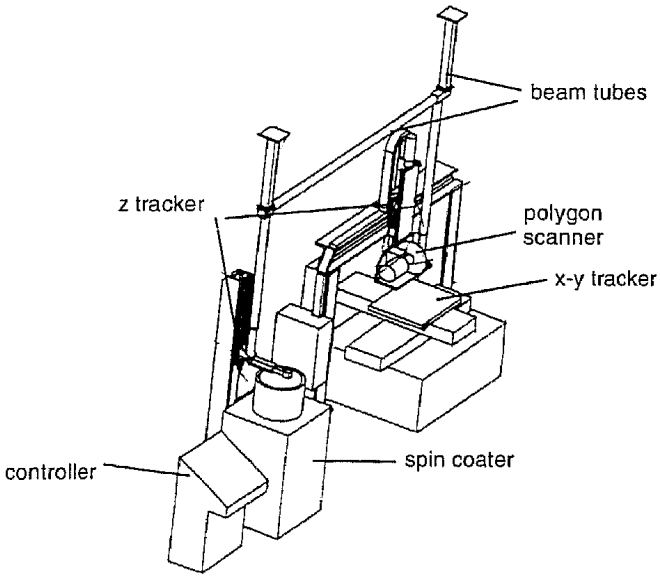

Figure 1 Overview of the experimental stations. Left side: station allowing densification of 9 × 9 cm^2 samples with uniform beam cross section (spot mode); right side: large scale laser firing station (slow and fast scan modes).

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TEM_{01*} mode of the laser into a $9 \times 9\ cm^2$ area of uniform intensity and deflects the beam onto a Convac spin coater. The beam integral output power delivers up to $8\ W\,cm^{-2}$ to the sample. This station works only in a spot mode and can produce densified films in a short time as the deposition and firing processes are integrated in one apparatus.

The second station (right side of Fig. 1) consists of a rotating polygon scanner which rotates at speed up to 8800 r.p.m. and a $50 \times 50\ cm^2$ x-y tracker stone table programmable with regard to scan length, scan speed and repetition rate. The beam is focused by an exchangeable parabolic mirror and the scan length and beam width are adjusted by moving the set of mirrors manually along the z direction. The local temperature of the coatings is monitored by a fast pyrometer measuring in the i.r. radiation spectral range of 7.3 to 9.3 μm with a detector rise time of 3 μs and a spatial resolution $d_{spot} = 0.5$ mm (CompoTherm, Syke, Germany). Two modes of operation are available. In the *slow scan* mode the laser beam is directly focused on the sample and the scanning is realized only by the x-y tracker which moves the sample (maximum lengths $x_0 = 600$ mm, $y_0 = 400$ mm) at velocities v_x and v_y which can be adjusted independently between $1-250\ mm\,s^{-1}$ (Fig. 2).

In the *fast scan* mode the laser beam is focused onto the rotating 14 plane mirrors polygon scanner. The laser spot is therefore scanned in the y direction at a very high speed (typically $\simeq 20\,000\ cm\,s^{-1}$) resulting in a laser streak as small as 0.1 mm in width (Fig. 3). This streak can be moved along the x direction at a speed up to $250\ mm\,s^{-1}$. In this way areas can be densified at a typical rate of $10-15\ cm^2\,s^{-1}$, a much larger value than those previously reported [13]. The focused beam integral output power delivers up to $560\ KW\,cm^{-2}$ to the samples.

Pure and Sb-doped sol-gel SnO_2 films were prepared from alcoholic solution and deposited via

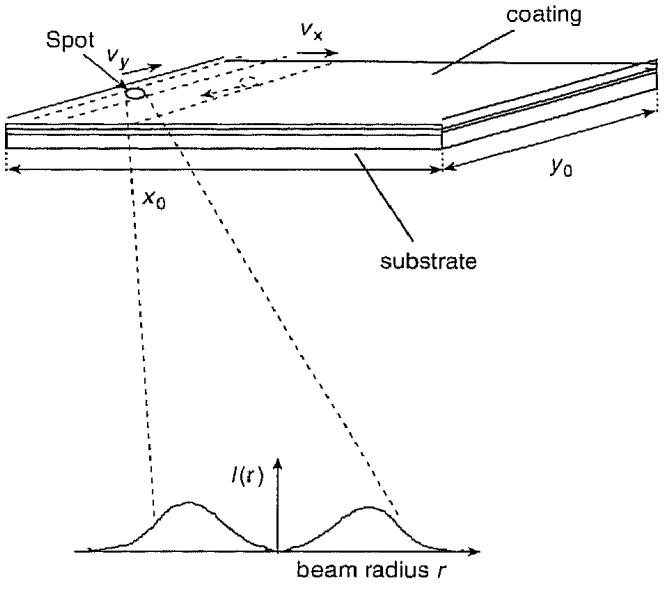

Figure 2 Scheme of the slow scan mode and radial distribution of the laser intensity TEM_{01*} mode.

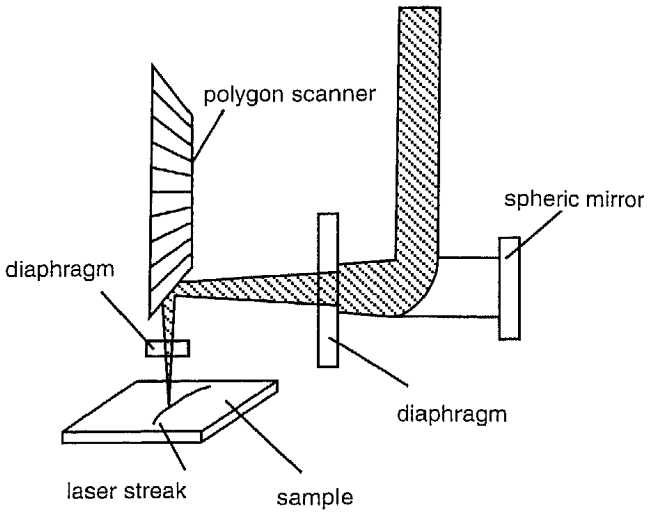

Figure 3 Illustration of the fast scan mode.

a dip coating process (one layer only) on $5 \times 2\ cm^2$ fused silica substrate with a drawing speed of $5\ mm\,s^{-1}$. The thickness of the gels dried at 25 °C was 158 nm for all samples. The preparation procedure of the sols will be published elsewhere [14]. Part of the samples were fired in a furnace in air at 550 °C for 15 min and the other submitted to CO_2 laser densification using the *fast scan* mode. The laser power density was varied between 0.8 and $1.3\ KW\,cm^{-2}$ with an energy density ranging from $40-200\ J\,cm^{-2}$, the values refer to the area of the laser streak.

The electrical properties of the coatings (resistivity (ρ), carrier density (n), electron mobility (μ), and sheet resistance (R)) have been measured using a 4 points technique with a MMR van der Pauw-Hall measurement equipment. The results obtained for a single dip-coated layer are presented in Table I. Large difference have been observed between the two sets of samples. The laser fired samples show a 4 times lower resistivity and a much higher carrier density and mobility than the corresponding values obtained with furnace heat treated samples.

Fig. 4 shows a comparison of the scanning electron microscopy (SEM JEOL 6400 F) surface morphology of the same Sb-doped SnO_2 coating either laser fired (Fig. 4a) or conventionally heat-treated (Fig. 4b). The laser fired samples present a smooth surface with small cracks while the furnace fired samples show a rougher surface with morphological structures of about 30 nm in size. The X-ray

TABLE I Comparison between the layer thickness d (nm), resistivity ρ (Ω cm), carrier density n (cm^{-3}), electronic mobility μ ($cm^2\,V^{-1}\,s^{-1}$) and sheet resistance R (Ω) of SnO_2:Sb coatings (dip coated single layer) obtained by laser densification ($P_s = 1.3\ kW\,cm^{-2}$, $E_s = 61\ J\,cm^{-2}$) or conventionally fired at 550 °C during 15 min

Property	Laser	Furnace
d (nm)	120	110
ρ (Ω cm)	3.2×10^{-3}	1.5×10^{-2}
n (cm^{-3})	7.3×10^{20}	2×10^{20}
μ ($cm^2\,V^{-1}\,s^{-1}$)	3.2	1.7
$R_\square$ ($\Omega_\square$)	250	1300

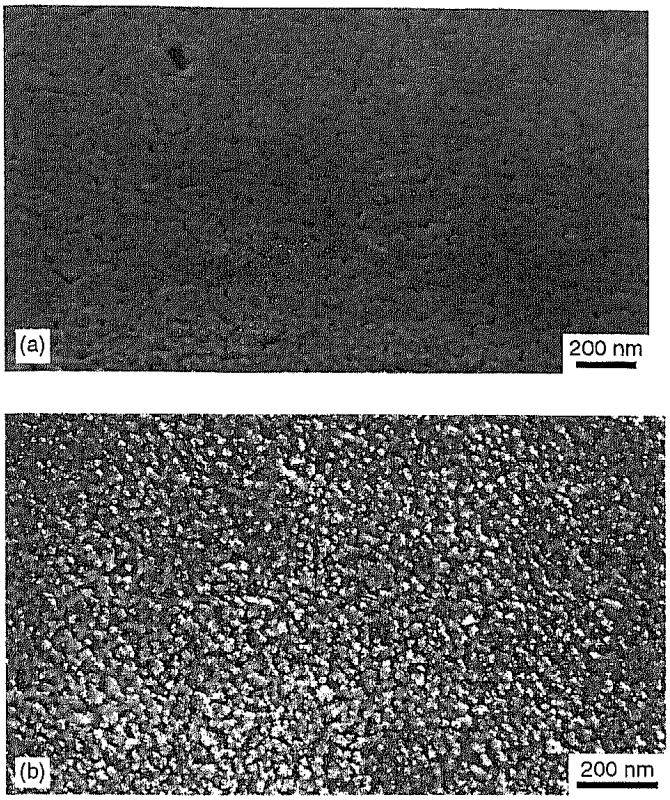

Figure 4 SEM micrographs of (a) a laser fired single SnO_2:Sb layer ($P_s = 1.3$ kW cm^{-2}, $E_s = 60$ J cm^{-2}); (b) furnace fired single SnO_2:Sb layer, heat treated at 550 °C for 15 min.

diffraction patterns (XRD) of these samples measured with a Siemens D500 equipment reveal that both densification processes lead to coatings having the same Cassiterite crystalline structure (Fig. 5). The size of the crystallites determined by the Debye-Scherrer method is about 10 nm and 16 ± 1.5 nm for the furnace and laser densified samples respectively. At constant laser power density $P_s = 1.3$ kW cm^{-2}, the size of the particles was found to increase with the energy density from 6 to 45 nm when E_s increases from 40 J cm^{-2} to 200 J cm^{-2} respectively.

The values of the electric parameters are still not as good as those obtained with coatings obtained by spray pyrolysis [15] or sputtering [16]. However, they are much better than the best values obtained for a single dip- or spin-coated layer of the same thickness heat-treated in air in a conventional furnace but the optical appearance of the laser fired coatings are excellent. The laser process parameters P_s and E_s used here have not been yet optimized and further improvement is expected. This preliminary study shows that *direct* CO_2 laser densification is a promising process which allows a fast homogeneous densification of large sol-gel coatings at a rate as high as 15 cm^2 s^{-1}. As for TiO_2 coating Arfsten, [8], homogeneous and smooth films are obtained by line scanning and the average size of the crystallites can be smaller than those obtained in the oven process. Structured films should be easily obtained by using mask techniques and washing off the undensified film.

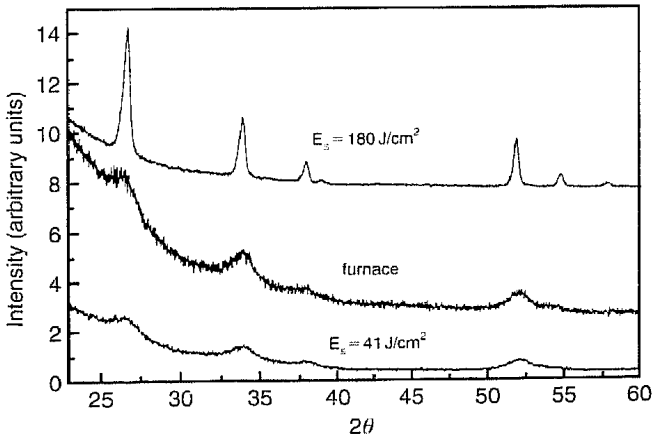

Figure 5 Glancing incident XRD spectra of laser and furnace fired single layered SnO_2:Sb coatings.

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