NANOSCALE CRYSTALLIZATION PROCESS IN ATO SOL-GEL FILMS USING EXCIMER LASER ANNEALING

V. S. Teodorescu^a, C. Ghica^a, C. S. Sandu^a, A. V. Maraloiu^a, Marie-Genevieve Blanchin^b, B. Canut^b, J. A. Roger^b

^a National Institute for Material Physics, P.O.Box Mg-7, Bucharest-Magurele, R-77125, Romania

^bLaboratoire de Physique de la Matière Condensée et Nanostructures, UMR CNRS 5586, Université Claude Bernard Lyon1, 69622 Villeurbanne, France

Excimer laser annealing has been successfully used to crystallize the SnO₂: Sb (ATO) solgel films deposited on Pyrex substrate. This technique allows confining the heating in the film thickness, without affecting the substrate, due to very short absorption length of the UV radiation. Semi-quantitative data about the crystal growth rate depending of laser fluence and number of laser pulses have been obtained. The ablation laser fluence threshold value was estimated by an optical method on the base of the edge Fresnel diffraction pattern observation. The crystallization process has been studied in detail using XTEM imaging. A mechanism of the laser crystallization process is proposed on the base of the statistical quantitative data of growth of the crystallite grain of the ATO oxide film induced by laser annealing.

1. Introduction

Antimony doped tin oxide ATO (SnO2:Sb) is a transparent conducting oxide (TCO) [1] with very good structural and chemical stability and good electrical conductivity allowing to be used in many applications, mainly in the form of thin films. One of the ways to produce ATO homogeneous thin films on large surfaces and low cost is the sol-gel route. Different film thicknesses can be obtained by muli-layer deposition technique. To become a transparent conductor oxide, the sol-gel ATO deposited film must be dried in order to eliminate the solvent and than densified and crystallized by thermal annealing at about 500°C. Classical thermal annealing (CTA) in conventional furnace or rapid thermal annealing (RTA) are the common methods used for this process. However, such procedures can be used only for film deposited on heat resistant substrates like inorganic materials.

In the case of polymer substrates, the heating must be confined in the film volume in order to prevent the damage of substrate structure. A solution of this problem is to use the ultraviolet (UV) laser radiation to induce film crystallization. Absorption of light by transparent conducting oxides (TCO) is very large in the UV range and therefore excimer lasers are appropriate to anneal TCO films. Several reports on the use of UV laser radiation for the TCO films crystallization have been reported in the last decade [2,3]. Also, excimer lasers with large homogeneous beams are now available [4].

We have already reported successful results to obtain crystallized ATO sol-gel films with good electrical conductivity [4-9]. In the present paper we present details about laser irradiation process and new nanoscale measurements on the crystal growth process.

2. Experimental

Single layers of SnO_2 :Sb (23%) film were deposited by dip coating on Pyrex glass [5-7] and dried for 5h at 200°C in order to completely remove the solvent. Normally, the sol-gel films are dried at 100°C or 150°C for 30 minutes. In the case of laser annealing, it is better to increase the drying time and temperature, in order to avoid the destruction of the film due to the explosive evaporation of the solvent traces, remaining in the film matrix.

After annealing at 200°C, the film structure is quasi amorphous, non electrically conductive, having some crystalline grain nuclei with dimensions in the range of 2 to 3 nm. At this stage, our films have a thickness between 180 and 200 nm, depending on the deposition conditions.

An ArF excimer laser ($\lambda = 193$ nm and $\tau = 17$ ns FWHM) and a KrF excimer laser ($\lambda = 248$ nm) were used for these experiments. The experimental set-up is showed in Figure1. A simple and efficient optical method was used to determine the laser pulse action on the film. A copper grid, normally used for TEM specimens, was used as a mask on the film surface, as it can be seen in Fig, 1. The optical inspection of the film surface after the laser shot reveals some traces of the laser pulse action at the edges of the square holes of the grid. (see Fig, 2a). A high optical magnification shows that in fact these traces represent patterns of edge Fresnel diffraction (see Fig, 2b). Atomic Force Microscopy (AFM) performed on such pattern (see Fig, 3) reveals a real relief on the film, with valleys in positions of the maxima of the diffraction pattern. Such experiment was useful to evaluate the threshold value for the necessary laser fluence to induce modification of the film structure. The advantage to use Fresnel diffraction pattern is the large gradient in the laser fluence in the diffraction pattern, which assures an excellent optical contrast, even for very small modifications appearing on the film surface.



Fig. 1. Schematic of the experimental set-up used for laser irradiation of the dried ATO sol-gel films. The copper TEM grid mask is used only in the case of experiments for the optical determination of the ablation threshold value of the laser fluence. The grid has a thickness of 50 µm and square holes with size of 100 µm.

The traces of the laser beam appear after multi-pulse laser irradiation at a fluence of about 20 mJ/cm², but they are easily seen also after a single laser pulse with 45 mJ/cm² laser fluence. As explained latter, the laser pulse results in a complex process in which ablation, densification and crystallization processes are involved.

The structure of the film before and after laser irradiation has been investigated by crosssection transmission electron microscopy (XTEM) using a high resolution Topcon B002 instrument. Specimens for cross section electron microscopy study have been obtained by the conventional procedure: cutting, face-to-face gluing, mechanical thinning and final ion milling in a Gatan system.



Fig. 2. Optical images of the ATO sol-gel film after two laser pulses (193 nm) with a fluence of 45 mJ/cm² through a copper TEM grid mask. A- low magnification image; B - higher optical magnification image revealing the Fresnel diffraction pattern located at the square hole edges of the grid mask.



Fig, 3. AFM image and profile measurement of the Fresnel pattern on the ATO film. This measurement reveals a real relief of this pattern, which is produced by a combination of ablation and densification effects of the laser pulse irradiation.

5.88

8.82

11.76

14.7 µ

2.94

3. Results and discussion

The structure of the films was analyzed by XTEM observations just after the first or the second laser pulse. Fig, 4 shows such a film after the second laser pulse. Two features are evident. A relief is formed on the film surface having a wave aspect. It is also evident that the top part of the film is densified. In the densified top zone, the crystallites size is increased to about 5 to 6 nm compared to 2 or 3 nm crystallite nucleus in the bottom part of the film. The relief is formed by a complex combination of ablation and densification process. The initial thickness of the dried film is about 200 nm and after two laser pulses the thickness is reduced to about 185 nm. This film shows already some electrical conductivity.



Fig. 4. XTEM image of an ATO sol-gel film dried at 200 °C and irradiated with 2 pulses of 45 mJ/cm² with the 193 nm excimer laser radiation. Surface relief and top part densification is evident.

The surface film topography is modified from the first laser pulse and changes from pulse to pulse due to the interference between the incident and the scattered pulsed laser beam. The surface relief changes from a simple to a chaotic structure under the multiple laser pulse irradiation [10]. In this way, a complex quasiperiodic structure develops on the film surface as can be seen in the XTEM image shown in Fig. 4. Some sub-harmonic periods of about 50 and 100 nm in length can be observed.

After 10 laser pulses with 45 mJ/cm² fluence (193 nm), the film thickness is reduced to about 150 nm, as it can be seen in Fig. 5. The top layer of the film (T- zone), with a thickness of about 50 nm, exhibits crystallites with diameter from 30 to 40 nm and is the main crystallized region of the film. The middle region (M-zone) is a thermally affected zone and here the crystallization takes place due to heat diffusion in the film. In this region, about 40 nm wide, the crystallite diameter varies continuously from 30 to 3 nm. The bottom part (B-zone) of the film, about 60 nm in thickness, is not affected and has practically the same structure as the non irradiated film.



Fig. 5. XTEM image of an ATO sol-gel thin film irradiated with 30 laser pulses with a fluence of 45 mJ/cm² (λ =193 nm).

A detailed evaluation of such structures resulted after different laser irradiation experiments were presented in our previous papers [8,9]. Some news data are now available using systematic statistic measurements. For this purpose a new series of measurements were performed using a new method. An example of this method is shown in Figure 6.



Fig. 6. XTEM image of a sol-gel ATO film after irradiation with 100 pulses at a fluence of 62mJ/cm2 ($\lambda = 248 \text{ nm}$). The film thickness was divided in levels of equal thickness, where the average grain size was determined.

The average size of the ATO crystallites was determined making a statistic of the grain crystallites size at different level in the film thickness. For this purpose, the XTEM images was divided in levels with an approximate thickness of 20 nm, beginning from the substrate interface. For our films, this corresponds to a number of levels between 8 and 10.

The dimension of the crystallites was determined with an error of about 1 nm for the crystallites showing only a Bragg contrast. In some cases this error is only 0.35 nm if the analyzed crystallites show lattice fringes contrast of the (110) lattice planes of the SnO_2 structure.

Fig, 7 presents an example of statistical measurements. From such figure is possible to analyze systematically the dynamics of the crystalline growth and also the film thickness reduction.



Fig. 7. Average size of the SnO₂ crystallites, measured on levels at the same distance from the substrate. Laser irradiation was made with $\lambda = 248$ nm. Series 1. – dry non-irradiated film (about 180 nm in thickness); Series 2. – film irradiated with 100 pulses at a fluence of 62 mJ/cm² (thickness 165 nm); Series 3. – film irradiated with 10 pulses at a fluence of 94 mJ/cm² (thickness 145 nm); Series 4. – film irradiated with 100 pulses at a fluence of 94 mJ/cm² (thickness 125 nm).

Comparing the films morphologies in the XTEM images presented in Figs, 5 and 6, one feature looks very different. In Fig, 5, the top layer of the film shows big crystallites with an evident discontinuity of the crystallite size gradient between the T and M zones. In Figure 6, the gradient of the crystalline grain size is almost constant. The computer simulations of the temperature evolutions during the laser pulse action [11] suggest and sustain the idea that the surface top part of the film was melted in the case of the film in Fig, 5.

The main problem in the laser heating simulations is the value of the heat conductivity in the amorphous sol-gel dry layer. At present, no data are available about this value. Our result suggests that this value is at least two orders of magnitude lower than the corresponding value of the crystallized ATO structure. In this case, at the beginning of laser irradiation, the amorphous film structure acts like a thermal insulator. As a consequence the laser heating will be confined in the top part of the film in a zone corresponding to the radiation penetration depth. In this case, this top part can be easily melted at the beginning of the irradiation. A supplementary feature proving the presence of melting is the lower melting temperature effect, well known for the nano-size crystalline nuclei, which are formed at the beginning of irradiation. This effect can lower the melting temperature of the SnO2 structure (1898 K) [12] by several hundred degrees, in function of the crystallite size.

It is interesting to note that the ablation will be always present during laser annealing of the sol-gel film. Fig, 8 shows the material loss of the film due to the multi-pulse laser action on the ATO film. The experimental data show a logarithmic dependence of the material loss respective to the number of laser pulses in the irradiation series. As the laser fluence is constant, the only explanation of the lowering of the ablation process, is the increasing ablation threshold with increasing densification and crystallization of the film.



Fig. 8. Material loss due to the multipulse laser irradiation of the ATO sol-gel film at different fluences with the 193 nm radiation.

Fig. 9 reveals data about the average crystal growth rate, in function of the number of laser pulses at a given fluence. It is possible to see that in the middle zone (like M in Fig, 5) the growth rate look to have a logarithmic variation, but in the top part, the grain size remains almost constant.



Fig. 9. Average crystalline grain size in function of the number of laser pulses. Measurements are made for 193 nm laser radiations and 36 mJ/cm2 laser fluence. (T) top level of the film and (M) the middle level of the film.

Considering the exposed data, the crystallization process can be described in two situations.

1. In the first one, the laser fluence is over the threshold values for film surface melting.

The first and probably also the second laser pulse induces an important ablation of the film, but also a densification of the top part of the film thickness. The next pulses will melt the dense region of the surface in a depth of about 40 to 50 nm thickness which corresponds in fact to the radiation penetration depth. After solidification of the superficial melted layer, crystallites with dimensions of about 30 to 50 nm appear in this region. After about 10 pulses, the morphology of the cross section of the film is stabilized. The following pulses will melt and re-melt the surface top part of the film. The propagation of the heat in the film thickness will induces the crystallization and the crystal growth in the middle part of the film. Increasing the number of pulses, the crystallization front will penetrate all the film thickness. Finally, a gradient of the grain size in the film depth establishes.

2. In the second situation, the laser fluence is below the threshold value for inducing film surface melting. In this case we have the same effect of densification and ablation induced by several laser pulses at the beginning of the irradiation. The thermal effect induced in film by absorption of the radiation along the penetration depth will induce crystallization, gradually, in a much slower process, closer to a classic process. After a long series of pulses, the film will be crystallized in all its thickness. A gradient of the grain size will be also present, but smaller than in the first case.

It is interesting to note that the ablation will be always present. We have data to estimate that the ablation threshold value increases with the number of pulses. The experimental data show a logarithmic dependence of the material loss respective to the number of laser pulses in the irradiation series. As the laser fluence is constant, the only explanation is the lowering of the ablation process on the crystallized and densified surface of the film.

4. Conclusions

The crystallization of the sol-gel ATO thin films under excimer laser annealing shows two different mechanisms, depending on the fluence of the laser beam. One mechanism involves the melting of the top part of the film if the fluence exceeds the melting threshold value. The melting depth is close to the absorption depth of the laser radiation. The second mechanism is much closer to the crystallization mechanism working in the case of the RTA annealing, but it is much faster. A logarithmic law for the crystallite size growth as a function of the number of laser pulses can be established experimentally.

An optical method based on the observation of the Fresnel diffraction pattern was used in order to determine the minimum laser fluence which affects the film surface. The ablation threshold value for the laser fluence is very low for the first and the second laser pulse and it increases for the rest of the pulses. The densification of the film is important from the first and the second laser pulse action and it looks to be independent of crystallization. After crystallization of the top part of the film, the further densification is controlled only by the diffusion assisted crystallization process.

This study shows that excimer laser crystallization of the oxide sol-gel film can be conducted and controlled at the nanoscale level and can be applied successfully to the crystallization of the TCO film deposited by sol-gel on thermally sensitive substrates.

Acknowledgements

This work was supported by CEEX project (4/104) and Dolores project of Region Rhon-Alpes.

References

- [1] Transparent Conducting Oxides, MRS Bulletin, Volume 25, nr.8, 2000.
- [2] H. Imai, A. Tominaga, H. Hirashima, M. Toki, N. Asakuma, Journal of Applied Physics, 85, 1999, 203-207.
- [3] N. Asakuma, T. Fukui, M. Aizawa, M. Toki, H. Imai, H. Hirashima, Journal of Sol-Gel Science and Technology 19, 333-336 (2000).
- [4] M. Stehle, Journal of Non-Crystalline Solids 218, 218-222 (1997).
- [5] J. P. Chatelon, C. Terrier, M. G. Blanchin, J. Mugnier, J. A. Roger, Materials Science Forum 239-241, 81 – 86 (1997).
- [6] J. P. Chatelon, C. Terrier, J. A. Roger, Semicond. Sci. Technol. 14, 642-647 (1999).
- [7] C. S. Sandu, J. A. Roger, B. Canut, M. G. Blanchin, V. S. Teodorescu (2001) Radiation Effects and Defects in Solids 156, 129-134.
- [8] C. S. Sandu, V. S. Teodorescu, C. Ghica, P. Hoffmann, T. Bret, A. Brioude, M. G. Blanchin, J. A. Roger, B. Canut, M. Croitoru, Journal of Sol-Gel Science and Technology 28, 227-234 (2003).
- [9] C. S. Sandu, V. S. Teodorescu, C. Ghica, B. Canut, M. G. Blanchin, J. A. Roger, A. Brioude, T. Bret, P. Hoffmann, C. Garapon, Applied Surface Science 208-209, 382-387 (2003).
- [10] A. Barborica, I. N. Mihailescu, V. S. Teodorescu. Physical Review B, 49, 8385, 1994.
- [11] C. S. Sandu, Phd. Thesis, Lyon University, 2003.
- [12] R. West, Handbook of Chemistry and Physics, 72 th edition, 1991, CRC Press.