LOW TEMPERATURE GROWTH OF SMOOTH INDIUM TIN OXIDE FILMS BY ULTRAVIOLET ASSISTED PULSED LASER DEPOSITION

V. Craciun, C. Chiritescu[a], F. Kelly, R. K. Singh

Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA
[a]Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Thin indium tin oxide (ITO) films were grown on Si substrates held at temperatures 50 ^{o}C up to 150 ^{o}C by conventional and *in situ* ultraviolet-assisted pulsed laser deposition (UVPLD) techniques. Atomic force microscopy and x-ray reflectivity techniques were employed to characterize the surface morphology of the ITO films on both microscopic and macroscopic scales. Roughness values (R_{ms}) below 0.5 nm were routinely achieved on films grown by the UVPLD technique.

1. Introduction

Indium tin oxide (ITO) is one of the most widely-used transparent conducting oxides for optoelectronic devices, flat panel displays, and sensors, as it combines good electrical conductivity with high transparency in the visible range. There are important applications for ITO thin films, such as anode contacts in organic light-emitting diodes or coating of flexible polymer substrates used in ultralight mobile display panels where a low processing temperature is very important.

Various types of sputtering techniques were shown to allow for the deposition of good quality ITO films even at room temperature [1-4]. However, the surface roughness of these films is often rather high [3-5]. A significant decrease of the roughness values over those measured for sputtered films, without compromising their electrical and optical properties, has been reported for films grown at room temperature (RT) using the pulsed laser deposition (PLD) technique [5-7]. Ultraviolet (UV) irradiation during thin film deposition by sol-gel [8, 9], sputtering [10], or laser ablation [11] was shown to result in an improvement of crystallinity and surface morphology. By using an *in situ* ultraviolet-assisted PLD technique (UVPLD) for the growth of ITO films, we obtained even smaller roughness values for films grown from 50 to 150 ^{o}C that are reported here.

2. Experiment

The ITO films were grown in a PLD system that employs an excimer laser (KrF, $\lambda = 248$ nm, fluence ~2 J/cm^2, repetition rate 5 Hz) to ablate ITO targets (99.99% purity, 10 % weight SnO$_2$). The oxygen pressure during deposition was set at 10 mTorr, the optimum value for our target-substrate distance of 10.5 cm [12, 13]. A low pressure Hg lamp, which allows for UV irradiation of the substrate during the laser ablation-growth process and molecular oxygen photodissociation, was fitted into the PLD system and located just below the target. Films were deposited onto (100) Si wafers that received an RCA cleaning followed by a dip in diluted HF, rinse in DI water and blow dry by high purity N$_2$. The thickness and optical properties of films were investigated by spectroscopic ellipsometry (VASE, Woollam Co.) at 70° incidence. The surface morphology was investigated by

atomic force microscopy (AFM) at a microscopic scale and by x-ray reflectivity (XRR) at a macroscopic scale. The fitting of the acquired XRR spectra with the aid of the Wingixa software installed in the Philips X'Pert MRD instrument also provided values for the interfacial roughness, thickness and density of the films.

3. Results

The crystalline structure, chemical composition and optical and electrical properties of films grown in our deposition system by conventional PLD and UVPLD were reported elsewhere [12, 13]. Films deposited at room temperature were amorphous, highly transparent and exhibited resistivity values lower than 4×10^{-4} Ωcm. The electrical resistivity decreased with increasing substrate temperature. Films deposited at a substrate temperature of 150 ^{o}C also exhibited crystallinity, with the average crystallite sizes of around 10 nm.

In Fig. 1 the refractive index and extinction coefficient values of films deposited by PLD (25.2 nm thick) and UVPLD (25.1 nm thick) at 50 ^{o}C are shown. These results were obtained by modeling the acquired ellipsometry data by a structure consisting of a single layer of ITO onto Si and starting with the ITO n and k reference values. One can note that the resulting films optical constants were quite close to the reference values, more so for the UVPLD grown film.
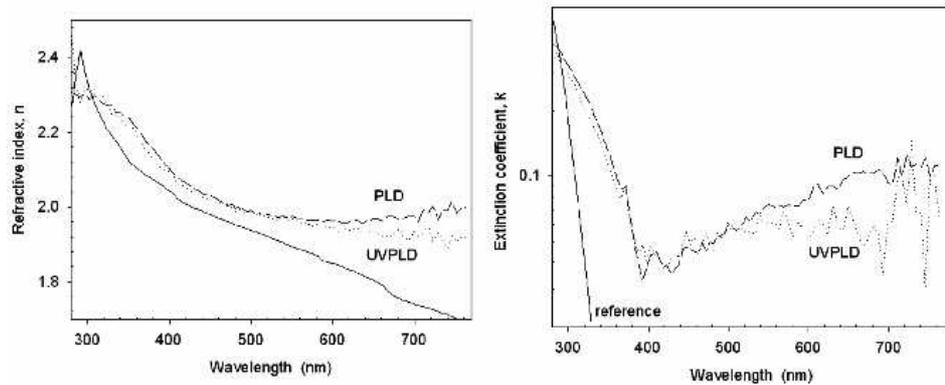

Fig. 1. Refractive index and extinction coefficient values of ITO films grown under
10 mTorr at 50 ^{o}C by PLD and UVPLD.

The films surface morphology was first investigated by AFM. Typical images obtained from films deposited at 100 ^{o}C by UVPLD and PLD are displayed in Fig. 2. The films were quite smooth, with an average root-mean-square roughness (R_{ms}) of around ~0.3 nm. These are very good values, comparable to the best one reported so far [5-7, 14, 15].
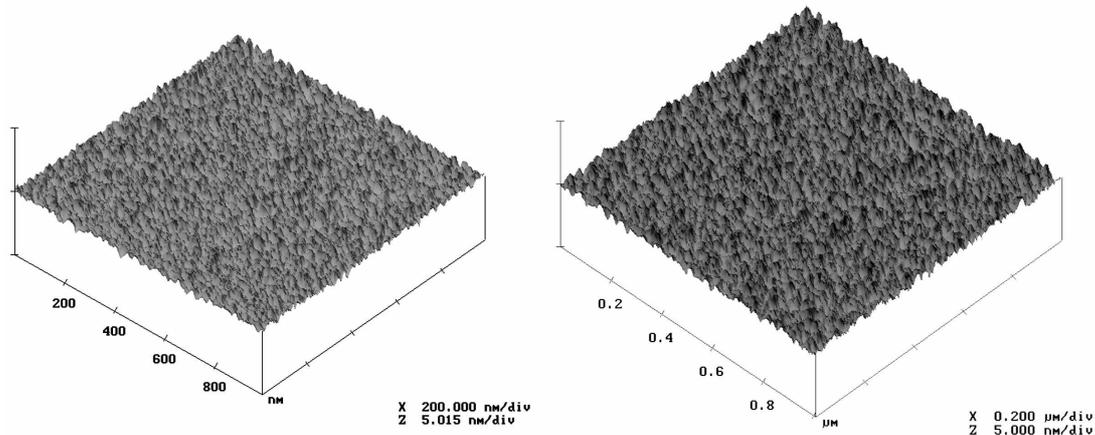

Fig. 2. AFM images (1 μm x 1μm) of ITO films grown on Si at 100 ^{o}C by UV-assisted and
conventional PLD. Please note the expanded z scale. The R_{ms} values were measured at
around 0.22 and 0.26 nm, respectively.

The R_{ms} values obtained by AFM characterize the surface morphology at a microscopic scale. To investigate the roughness at a macroscopic scale, XRR spectra were acquired from the deposited films. In order to obtain good fits for the acquired XRR spectra, the addition of an interfacial layer between the Si substrate and the deposited ITO layer was required. As shown in Fig. 3, the thickness of this layer was around 0.5-2 nm, depending on the deposition conditions, while its estimated density, which was always higher than 2.2 g/cm^3, the value corresponding to SiO_2 density [16], indicated some intermixing with the deposited ITO layer. It is worth mentioning that UVPLD grown samples exhibited a thinner interfacial layer that possessed both a lower density and roughness than those of interfacial layers formed on PLD grown samples. It was found that thin silicon oxide layers grown by low temperature UV-assisted oxidation exhibited physical and chemical properties much closer to those of standard SiO_2 layers than the native silicon oxide or oxide grown at similar temperatures [17, 18]. During the UVPLD process, the Si surface is rapidly covered by a high quality oxide layer which once formed acts as a diffusion barrier and significantly slows down further growth and mixing with the deposited ITO layer. This accounts for the lower density and roughness values of the interfacial layer obtained from the fitting program of the acquired XRR spectra.
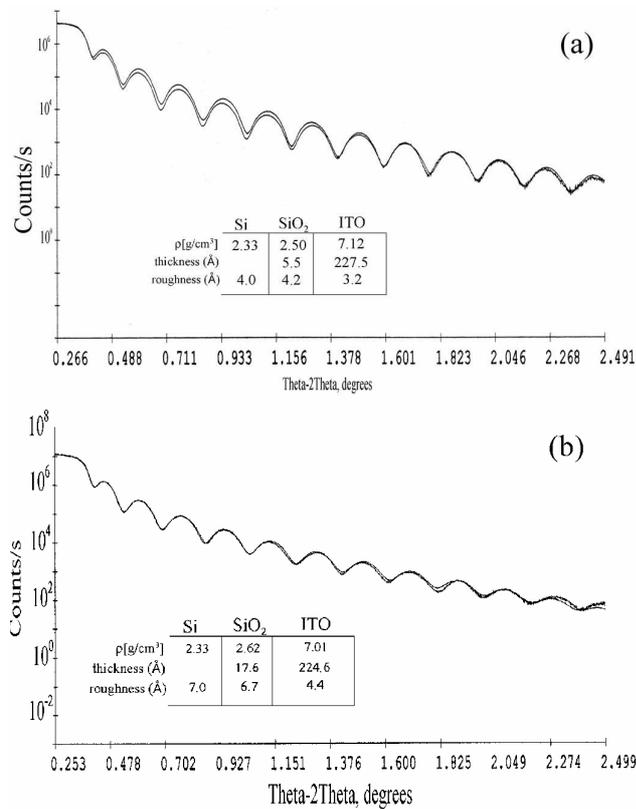

Fig. 3. XRR spectra and simulations (shown also as inserts) of ITO films grown at 150 ^{o}C by (a) UVPLD and (b) PLD.

It is interesting to note that when repeating the fitting of the acquired VASE data including an interfacial layer whose starting thickness was that obtained from the XRR fitting process, a small improvement of the values of refractive index and extinction coefficient was noted as one can see in Fig. 4. Moreover, there was generally good agreement between the thickness of the interfacial and ITO layers determined from XRR simulations and those determined from these new VASE simulations.
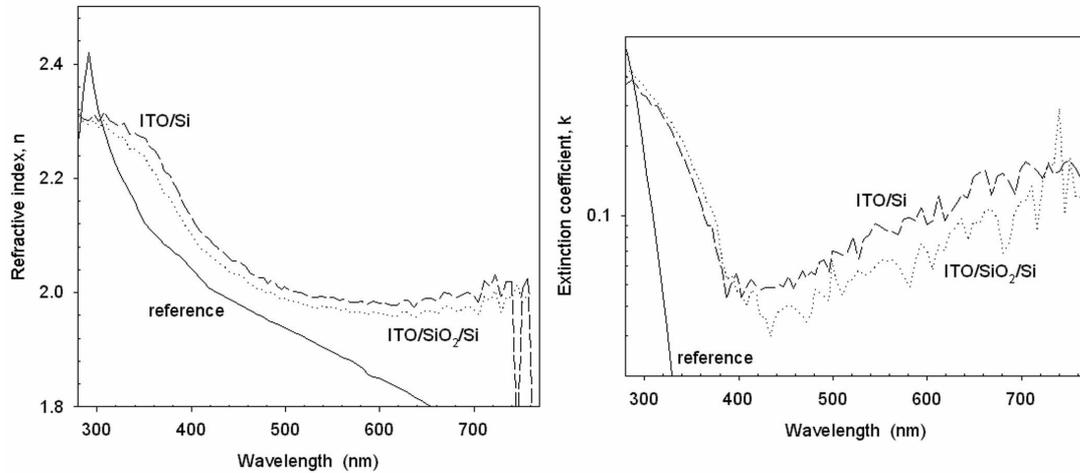
Fig. 4. Comparison of refractive index and extinction coefficient values of an ITO film grown at 150 $^{\circ}$C by UVPLD obtained by modeling the structure with and without the presence of a thin SiO$_2$ interfacial layer.

Although not very evident from the XRR spectra shown in Fig. 3, the critical angle values were marginally but consistently higher for UVPLD films than for PLD films. This indicates a higher density of the ITO layer, which was estimated to be 6.92 g/cm^3 for films grown at 50 $^{\circ}$C and reached 7.12 g/cm^3 for films grown by UVPLD at 150 $^{\circ}$C, very close to the tabulated value [19] of In$_2$O$_3$. As one can also see in Fig. 3, the amplitude of oscillations in the recorded XRR spectra is higher for the UVPLD grown films. This indicates that the roughness values are smaller and that the difference between the density of the interfacial layer and that of the grown ITO is larger for the UVPLD grown structures than for conventional PLD grown films. Routinely all grown films, both by PLD and UVPLD exhibited roughness values always below 0.5 nm. These are very good values, confirming previously reported results [5-7, 10, 11]. Moreover, even for much thicker films the roughness values did not increase. As one can see in Fig. 5, the simulation of the acquired spectra of an ITO film 250 nm thick returned a value of only 0.4 nm for the surface roughness.
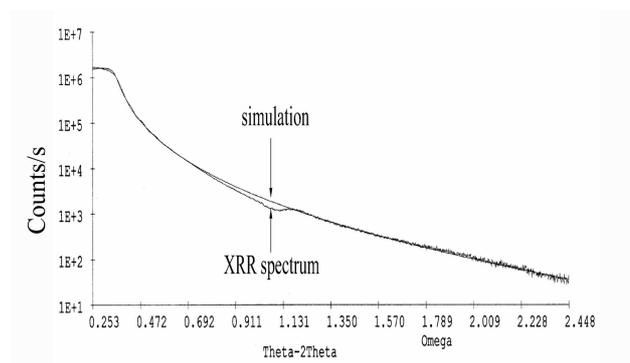

Fig. 5. XRR spectrum and simulation of a thick ITO film grown at 50 $^{\circ}$C by UVPLD.

4. Conclusions

Good quality ITO films have been grown held at temperatures from 50 $^{\circ}$C up to 150 $^{\circ}$C on Si substrates using an *in situ* ultraviolet-assisted pulsed laser deposition technique. Dense films, exhibiting good optical properties and surface roughness values below 0.5 nm were routinely grown. Both x-ray reflectivity and spectroscopic ellipsometry investigations techniques indicated the

presence of an interfacial layer between the Si substrate and the deposited ITO layer. The density of this layer was closer to that of stoichiometric SiO_2 while its roughness is significantly lower for structures deposited using the UVPLD technique than for those deposited using the conventional PLD technique.

References

[1] H. Wulff, M. Quaas, H. Steffen, Thin Solid Films **355-356**, 395 (1999).

[2] J. L. Huang, Y. T. Jah, B. S. Yau, C. Y. Chen, H. H. Lu, Thin Solid Films **370**, 33 (2000).

[3] Z. W. Yang, S. H. Han, T. L. Yang, L. Ye, D. H. Zhang, H. L. Ma, C. F. Cheng, Thin Solid Films **366**, 4 (2000).

[4] J. H. Shin, S. H. Shin, J. I. Park, H. H. Kim, J. Appl. Phys. **89**, 5199 (2001).

[5] H. Kim, A. Pique, J. S. Horwitz, H. Mattoussi, H. Murata, Z. H. Kafafi, D. B. Chrisey, Appl. Phys. Lett. **74**, 3444 (1999).

[6] H. Kim, C. M. Gilmore, A. Pique, J. S. Horwitz, H. Mattoussi, H. Murata, Z. H. Kafafi, D. B. Chrisey, J. Appl. Phys. **86**, 6451 (1999).

[7] H. Kim, J. S. Horwitz, G. P. Kushto, Z. H. Kafafi, D. B. Chrisey, Appl. Phys. Lett. **79**, 284 (1999).

[8] J. H. Ma, G. M. Wu, J. Shen, J. Wang, J. Inorg. Mat. **16**, 1174 (2001).

[9] K. Nishizawa, K. Suzuki, T. Miki, K. Kato, Key Engr. Mat. **7**, 145 (2002).

[10] H. Wengenmair, J. W. Gerlach, U. Preckwinkel, B. Stritzker, B. Rauschenbach, Appl. Surf. Sci. **99**, 313 (1996).

[11] V. Craciun, E. S. Lambers, N. D. Bassim, R.K. Singh, D. Craciun, J. Mater. Res. **15**, 488 (2000).

[12] V. Craciun, D. Craciun, Z. Chen, J. Hwang, R. K. Singh, Appl. Surf Sci. **168**, 118 (2000).

[13] V. Craciun, D. Craciun, Z. Chen, J. Hwang, R. K. Singh, MRS Proc. Vol. **617**, J12.3 (2000).

[14] F. O. Adurodija, H. Izumi, T. Ishihara, H. Yoshioka, M. Motoyama, K. Murai, Appl. Surf Sci. **177**, 114 (2001).

[15] J. Bartella, J. Schroeder, K. Witting, Appl. Surf Sci. **179**, 181 (2001).

[16] CRC Handbook of Chemistry and Physics, 78th Edition, CRC Press, Boca Raton, New York, p. 4-83, 1997.

[17] V. Craciun, I. W. Boyd, B. Hutton, E. J. Nichols, J. Perriere, J. Mater. Research **14**, 3525 (1999).

[18] V. Craciun, I. W. Boyd, B. Hutton, D. Williams, Appl. Phys. Lett. **75**, 1261 (1999).

[19] CRC Handbook of Chemistry and Physics, 78th Edition, CRC Press, Boca Raton, New York, p. 4-62, 1997.