

Photoacoustic and micro-Raman analysis of TiO₂ thin films obtained from IR laser beam

J.L. Jiménez-Pérez
CICATA-IPN

Legaria 694, Col. Irrigación, 11500 México D. F., México

A. Cruz-Orea, J.G. Mendoza-Álvarez.
Departamento de Física, Cinvestav-IPN
A.P. 14-740, 07000 México D. F., México

We have studied TiO₂ track thin films grown on Ti films previously deposited over glass substrates. The Ti films were heated in air by a moving laser beam, with different intensities of a pulsed Nd:YAG laser that sweeps the Ti surface at a 2 mm/s constant speed. We observed differences in the photoacoustic (PA) signal amplitude measured on the different TiO₂ tracks which are due to differences in the TiO₂ thickness for the growth thin films. This result showed that it is possible to follow the qualitative behavior of the oxide films with reasonable accuracy, using the present photoacoustic analysis. On the other hand, micro-Raman spectra measured for these TiO₂ samples showed two strong bands at 424 cm⁻¹ and 612 cm⁻¹ associated to the TiO₂ rutile structure. These results showed that both, the PA and Raman spectra give us useful information for the TiO₂ tracks characterization.

Keywords: Laser induced oxidation; Thin oxide films; Laser materials processing; Photoacoustic; micro-Raman

1. Introduction

Laser materials processing has been the subject of experimental and theoretical research since many years ago due to its inherent importance in a broad band of applications encompassing microelectronics and micro machinery industries. In most of these applications the materials processing is performed mainly by heating and photo-ablation of the materials by a laser source. The great advantage of using pulsed laser sources for materials processing is that it is possible to heat an extremely well localized region without affecting the properties of the surrounding environment. As an example of such versatility one may cite the thermo-chemical oxidation of a thin metallic surface of Ti on NbLiO₃ substrates for micro waveguide fabrication [1-3].

The thermochemical modification of Ti films is widely used for optical recording, deposition of masking layers and so on [4]. In previous papers we have considered the theoretical modeling and experimental study of the oxidation process, due to surface heating, under atmospheric environment of Ti films previously deposited over glass substrates, in short time, by a moving laser beam at constant speed, having a spot size larger than the film thickness [5,6]. In the above-mentioned applications it was very difficult to measure the thin film thicknesses, which are of considerable importance in semiconductor device processing. Direct measurement of the thickness of a thin film requires either microscopy examination of a cross-sectioned sample, a destructive procedure, or a profilometer measurement of a step height, a contact procedure. In this work we consider an indirect measurement of the thickness of a TiO₂ thin film by using the photoacoustic technique (PA) associated with a microprofilometer analysis of the sample. The PA nondestructive method utilizes low frequency thermal

waves, and can be used for multilayered samples, including optically transparent films. It is well known from photoacoustic theory [7-9] that one can, with thermal waves, obtain information of the thermal characteristics of a sample as a function of depth beneath its surface, by measuring the PA signal as a function of the frequency. Although there has been some experiments in thermal wave depth profiling, this capability has not been extensively explored, primarily because of the lack of adequate theoretical models.

Here we consider the theoretical and experimental results mentioned above [5,6] for TiO₂ track profiles for different laser intensities, and we compare them with our photoacoustic and micro-Raman analysis for TiO₂ grown over Ti films. With these results we show that it is possible to estimate the thickness and composition of an oxide film with a reasonable accuracy using a qualitative photoacoustic analysis and the micro-Raman spectra measured in each one of the TiO₂ tracks.

2. Experimental

The growth of the TiO₂ films was performed on Ti thin films (thickness of about 1000 Å) deposited on microscope glass slides by evaporation. The oxidation of the Ti film was performed using a Nd:YAG laser (Spectra Physics 3800 S) operating in the Q-switching mode-locked regime. In this regime a pulse train composes the laser output with an overall envelope of 290 ns and with individual pulses typically of 100 ps. The energy per laser pulse was changed between 5.47 a 7.21 mJ. A computer controlled X-Y translator realized the sample movement. The oxidation processes driven by the laser surface heating under the atmospheric environment produced TiO₂ tracks over the Ti films due its translation at a constant speed of 2mm/s, as it is shown in the schematic diagram of Fig. 1. The TiO₂

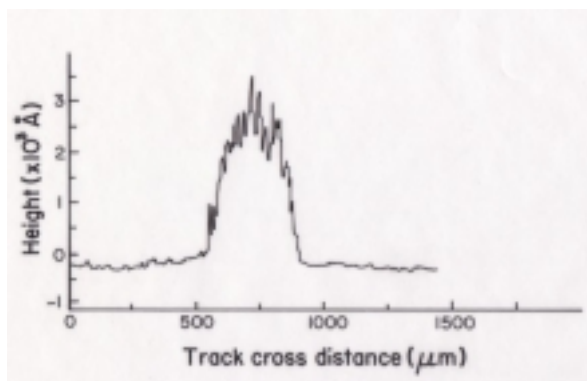


Figure 1. Schematic diagram of the experimental set-up used for the Ti oxidation by a moving laser source.

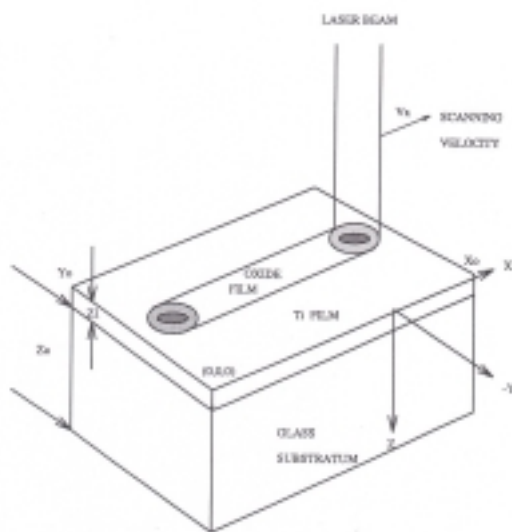


Figure 2. Oxide track surface's profile measured along a straight line perpendicular to the track axis, corresponding to the TiO₂ film grown at a laser intensity of 3.1 MW/cm².

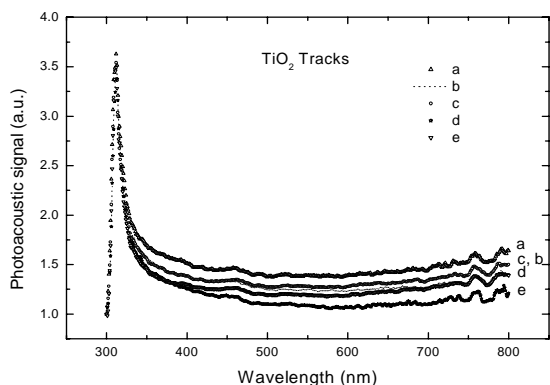


Figure 3. Photoacoustic absorption spectra of the TiO₂ track profiles for different laser intensities: (a) 3.17 MW/cm²; (b) 3 MW/cm²; (c) 2.78 MW/cm²; (d) 2.62 MW/cm²; (e) 2.40 MW/cm².

profiler Tencor Alpha Step –100TM with an accuracy of 10 Å. In Fig. 2 we show a typical oxide track surface's profile, which corresponds to a Ti film exposed to a laser density power of 3.1 MW/ cm². The spot size of the laser beam over the Ti film surface was 1mm in diameter. We observe in this figure that TiO₂ film has an inhomogeneous thickness, but it is possible to assign an average thickness for this films from the profilometer measurements.

For the PA spectra measurements we used a photoacoustic spectrometer which consists of a light source, obtained by passing a Xe lamp (1000 W) beam through a monochromator. The output beam was mechanically modulated with a chopper, at a frequency of 17 Hz, and focused on a sample placed inside a home-made photoacoustic cell. An electret microphone coupled to the cell was used to monitor the pressure fluctuations arising from the non-radiative recombination processes taking place in the sample following the absorption of light. The microphone signal was amplified with a lock-in amplifier. The photoacoustic signal was then acquired automatically by a PC. The chemical composition of the tracks was determined from the micro-Raman spectra measured in the samples by using the 514 nm line of an Ar ion laser (Coherent 90-5), operating in the power range from 300 to 400 mW, as the exciting source. Most of the Raman spectra were recorded with a spectral resolution of 3 cm⁻¹.

4. Theory

Applying the one-dimensional thermal diffusion model of Rosencwaig and Gersho [8] one gets for optically transparent and thermally thin solids, that the PA signal intensity is given by:

$$Q \approx \frac{(1-j)\beta\ell\mu_b}{2a_g\kappa_b} Y \tag{1}$$

where a_g , μ_b , k_b , ℓ and β are the thermal diffusion coefficient of air; the thermal diffusion length of the backing material (the sample support), the thermal conductivity of the backing material, the film thickness, and the optical absorption coefficient of the film for the wavelength λ , respectively; and Y as a constant factor. The acoustic signal is thus proportional to $\beta \ell$. For this thermally thin case in which $\mu_s \gg \ell$, the thermal properties of the backing material come play in the expression for Q . Here, by using eq. (1) and the experimental Q values of the PA spectra, at arbitrary λ -values, it is possible to obtain qualitative values for the TiO₂ film thickness by taking the ratio of the PA signal ($Q(\lambda)$) of each track by the corresponding $Q(\lambda)$ value of the sample irradiated at 3.2 MW/cm² (curve a in Fig. 3). In this way we obtained, according to eq. (1), the normalized TiO₂ film thickness for arbitrary λ values at: 384 and 470 nm. This procedures could be applied for different λ values, in the 350 to 800 nm range. We choose two λ values in order to take an average thickness value for each track.

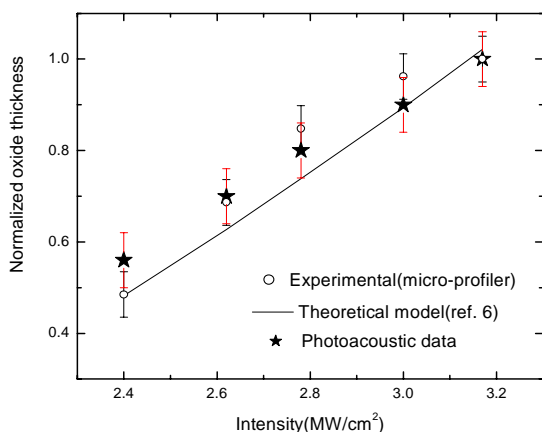


Figure 4. Experimental normalized data of average oxide thicknesses obtained by using a microprofilometer (○). Theoretical modeling curve (see references 5 and 6) (straight line); and normalized oxide thickness obtained from the Photoacoustic data (★). The value used to normalize the data obtained from the microprofilometer was 2700 Å corresponding to the oxide thickness grown by the highest (3.17 MW/cm²) laser intensity.

5. Results and discussions

Some of the most important applications of the photoacoustic technique arise from its capability of performing depth profile analysis, which can be accomplished just by changing the modulation frequency, f , of the incident excitation beam. For an optically transparent and thermally thick sample [7], the main contribution to the photoacoustic signal intensity comes from the light absorption taking place within a thermal diffusion length, $\mu = (\alpha / \square f)^{1/2}$, where α is the sample thermal diffusivity. Thus, the higher the modulation frequency, the smaller the thermal diffusion length. In our experimental set-up we have worked with a modulation frequency of 17 Hz. Considering a thermal diffusivity for TiO₂ of the order of 0.03cm²/s [8], a thermal diffusion length of 237 \square m can be estimated.

Typical photoacoustic absorption spectra of the TiO₂ tracks profiles for different laser intensities are shown in Fig. 3. These spectra correspond to the case when the incident beam is falling upon the surface of each TiO₂ track. In these spectra we can observe that there appear two characteristic main absorption bands, one centered around 455 nm, and the second one around 755 nm [10]. We can observe that these two absorption bands are present in all the TiO₂ tracks measured. In reference 10 optical absorption measurements in TiO₂ films deposited on SiO₂ showed a peak near to 22,000 cm⁻¹ (0.455 \square m) with a shoulder at around 12,000 cm⁻¹ (0.833 \square m) [10].

The theoretical [6], and experimental (obtained by using a microprofilometer) normalized results obtained for the dependence of the TiO₂ thickness on laser intensity are shown in Fig. 4. As can be observed, the oxide thickness increases monotonically as the laser peak intensity changes from 2.4 to 3.14 MW/cm² as it was expected [5]. The film

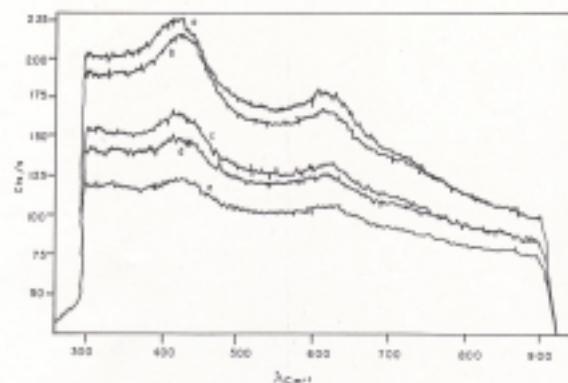


Figure 5. Micro-Raman spectra of the oxide tracks grown at different laser intensities: (a) 3.17 MW/cm²; (b) 3 MW/cm²; (c) 2.78 MW/cm²; (d) 2.62 MW/cm²; (e) 2.40 MW/cm². The bands centered at 424 and 612 cm⁻¹ correspond to the rutile phase of TiO₂.

thicknesses obtained from the microprofilometer measurements are really average thicknesses calculated from the irregular thickness shape as the one shown in Fig. 2; a weighting average was obtained by measuring a point-to-point thickness along the track. Also from, this thickness estimation from profilometer measurements we can obtain the error bars shown in the figure associated to the open circles. The solid line in Fig. 4 correspond to the calculation from the theoretical model which makes use of the heat equation coupled to the oxidation rate equation as was developed in reference 6.

The normalized film thickness values obtained from the PA spectra, with the method discussed above, are shown also in Fig. 4 as the stars, the error bars come from the thicknesses calculated using the three wavelengths already mentioned for the PA spectra. Also, it can be observed that their behavior is in fairly good agreement with the experimental data measured with the profilometer, giving higher values for thinner oxides and lower values for thicker oxides. As the thickness estimation from the comparison of the PA spectra can be look at as a way of averaging the contribution of the whole TiO₂ film to the PA signal, we believe that these values for the film thickness are in some way more precise than those estimated from the profilometer graphs.

In the Fig.5 we show the micro-Raman spectra of the oxide tracks grown at different laser intensities. It can be observed that these spectra present two bands centered at 424 cm⁻¹ and 621 cm⁻¹ associated to the TiO₂ rutile crystalline structure [8]. These results indicate that the experimental parameters used to grow the oxide tracks were compatible with favorable conditions to grow a particular TiO₂ stoichiometry.

6. Conclusions

We have shown that the optical absorption spectra in the 280-800 nm region of each one of the TiO₂ tracks profiles is formed by two main absorption bands, one of these, in 384 nm, and the other, in the 470 nm region. On the other hand, we have observed differences in the amplitude of the photoacoustic signal related to the different thicknesses of each one of the TiO₂ films. We showed that it is possible to use these PA intensity spectra to estimate the film thickness using different wavelengths which corresponds to absorption peaks. By comparing to the thickness estimations obtained from profilometer graphs we obtained good agreement between both types of thickness estimations, showing that the PA spectra can be used for this purpose with good accuracy, and that this thickness measuring approach is comparable to the profilometer results for highly rugged film surfaces as is the case for these pulsed laser-processed TiO₂ tracks. The chemical composition of the tracks was determined from micro-Raman spectra which show two strong bands at 424 cm⁻¹ and 621 cm⁻¹ associated to TiO₂ rutile structure. These results showed that both PA and Raman spectra are complementary convenient techniques for TiO₂ tracks characterization.

Acknowledgements

We gratefully acknowledge the technical support of M.C. C. Ponce- Parra, One of the authors (J. L. Jiménez Pérez) wants yo thank the partial financial support of Conacyt-Mexico, Cegepi-IPN, and COFAA-IPN-Mexico

References

- [1] M. Harana, Y. Murata and H. Nishihara, *Jpn. J. Appl. Phys.* **31**, 1593 (1992).
- [2] B. Haba, B.W. Hussey and A. Gupta, *J. Appl. Phys.* **69**, 2871 (1991).
- [3] A. Ferrari, L. Schirone, G. Maiello, C. de Cesare, F. Carassitti M. Bertolotti, M.A. Caparonero, A. Luches, M. Martino, M. Dimescu, N. Chitica, I.N. Mihailescu and I. Ursu, *J. Mod. Opt.* **40**, 1043 (1993).
- [4] M. Wautelet, *Appl. Phys. A* **50**, 131 (1990).
- [5] J.L. Jiménez Pérez, P.H. Sakanaka, M.A. Algatti, J.G. Mendoza-Alvarez and A. Cruz Orea, *Appl. Surf. Sci.*, **175**, 709 (2001).
- [6] J.L. Jiménez Pérez, P.H. Sakanaka, M.A. Algatti, J.G. Mendoza-Alvarez and A. Cruz Orea, *Appl. Surf. Sci.*, **175**, 703 (2001).
- [7] A. Rosencwaig and A. Gersho, *J. Appl. Phys.* **42**, 166 (1983).
- [8] A. Rosencwaig. *Photoacoustic and Photoacoustic Spectroscopy* (Wiley Interscience, New York, 1980).
- [9] A. Beadle, K. Kirkbright, *Analyst*, **101**, 553(1976).
- [10] M. Tomozawa and R.H. Doremus, *Treatise on Materials Science and Technology* (Academic Press, New York, 1977), Vol. 12.
- [11] G.V. Sansonov, *The oxide Handbook*, New York: IFI/Plenum 1973.