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# Phase transition of $TiO_2$ thin films detected by the pulsed laser photoacoustic technique

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**Abstract** In this work, we present characterization of titanium oxide thin films by photoacoustic measurements to determine the ablation threshold and phase transitions from amorphous to crystalline states. The important advantages of this method are that it does not require amplification at the detection stage and that it is a non-destructive technique. The correlation analysis of the photoacoustic signals allows us to visualize the ablation threshold and the phase transitions with enhanced sensitivity. This correlation analysis clearly exhibits the changes in the thin-film morphology due to controlled variations of the fluence (energy/area) and the temperature of the surrounding medium. This is particularly important for those cases where the crystalline changes caused by temperature variations need to be monitored. The thin-film samples were prepared by the sputtering technique at room temperature in the amorphous state. The phase transformations were induced by controlled temperature scanning and then corroborated with Raman spectroscopy measurements.

## 1 Introduction

In recent years, particular interest has been shown in the study of metal oxide thin films. This has been due to the many possible technological applications of these thin films in information storage devices, solar cells, gas sensors, photocatalysis, coatings, and so on [1–3].

The structural transformation of various materials has been widely investigated by means of radiation–matter interaction, using pulsed or continuous lasers [4, 5]. Special attention has been devoted to amorphous–crystalline transformation or vice versa by means of laser radiation. This is because it has been the basis for optical storage devices and the advantages it has over the more conventional methods of hole burning, such as the requirement of low power radiation [6]. Therefore, it is very important that the material has a high absorption coefficient at the desired wavelength [3].

For storage devices, such as the CD-RW (compact disc rewritable), it was observed that system operation is based on mechanisms of phase transitions of a given material (from the amorphous to crystalline state or vice versa).

In the present work, we apply the photoacoustic (PA) technique to amorphous thin films to induce the transition to a crystalline state with pulsed laser irradiation as a function of the temperature.

Titanium oxide ($TiO_2$) is one of the most extensively studied transition–metal oxides; it has three different crystalline phases: brookita, anatase, and rutile. The transformation from amorphous to anatase and anatase to rutile in powder or bulk materials usually takes place at temperatures between 300–600°C and 700–1000°C, respectively [7]. These temperatures depend on the initial particle size, the impurity content, the initial phase atmospheric reactions, temperature and pressure, among other factors [8, 9]. In a thin-film, the temperatures at which the transitions occur are determined by the method of synthesis and by the conditions of deposition.

The PA technique has been used in the characterization of a wide variety of materials, regardless of their nature. Par-

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ticularly, this technique has proven to be a powerful tool for studying phase transitions in condensed matter (solid, liquid, gels, powders, etc.) [10–12]. Although this effect was first observed in 1880 by Alexander Graham Bell [13], it was not until the 1970s with the development and subsequent evolution of laser technology, that this field significantly expanded the range of application in the study of the interaction of matter with low energy laser radiation.

The PA phenomenon involves the generation of acoustic waves by absorption of pulsed or modulated light within a sample. In fact, through non-radiative relaxation processes that convert the absorbed energy into heat, this produces a local thermal expansion of the medium that travels within the sample as an acoustic-like wave. The pulse mode has advantages over continuous wave excitation. One can use higher power and a low duty cycle of the optical source to induce a PA wave [14].

The interaction between the laser beam and the lattice structure of the sample produces a PA signal, which is displayed with the help of an oscilloscope as a voltage versus time curve. One way of analyzing these signals is by performing normalized correlation. If there is no change between successive signals, the correlation between them will be equal to 1.0; if any change occurs then correlation values lower than 1.0 will be obtained [11, 15]. Thus the correlation analysis of the obtained signals show the PA changes obtained in the thin films due to controlled changes in fluence and as a function of the surrounding temperature. Additionally, from this analysis one can obtain useful phenomenological information related to the stability of the system.

## 2 Experimental

The thin films of titanium oxide were deposited at room temperature on (100) silicon (Si) substrates and grown by reactive DC magnetron sputtering. The target used was metallic titanium of 50 mm diameter and 5 mm thickness with 99.995% purity. The deposition conditions of the samples, namely, S1, S2 and S3 were varied in order to obtain different thicknesses. Film thickness was measure by means of a profilometer.

The characteristics of the deposition of each studied sample are shown in Table 1. In all cases the films were in amorphous state. In general it is known that oxide films appear as amorphous after sputtering preparation at room temperature and can be transformed to the most stable crystalline phase by thermal treatments [16].

The optical absorption spectra of the samples were obtained using a UV–vis spectrophotometer (UV160U, Shimadzu), which covers the spectral range from 200 up to 1100 nm.

The PA experimental set-up employed consisted of: (a) a pulsed laser Nd:YAG, Continuum model Surelite I (355 nm, 10 Hz, 7 ns pulse width); (b) a piezoelectric (PZT), $PbZnTiO_3$, ceramic sensor, with a resonance frequency at 150 kHz; and (c) a commercial electric tubular furnace (Model 21100, Thermolyne). The energy variation of the laser was performed using a variable energy attenuator and was monitored with a pyroelectric detector connected to an energy display (RJP-7620, Laser Precision Corp). The averaged signals were recorded with a digital oscilloscope (TDS 5052B, Tektronix), having 300 averaged signals per measurement.

The amplitude of the signals was from $-1$ to 1 mV, without amplification. In the case when the thermal treatment was applied to the samples, the value of fluence remained constant and lower than 0.26 $J/cm^2$. This value was determined from a specific experimental analysis to identify this threshold value. For all experimental cases, the irradiated area was limited by a diaphragm. We used a cooling system placed on an optical guide, to ensure that there was no heat diffusion towards the microphone.

For each sample the heating rate was 10°C/min, starting from room temperature and up to 800°C. The acquisitions of the Raman spectra were performed with a micro-Raman spectrometer (Almega XR). An optical microscope and a 50× microscope objective were used to focus the laser on the sample with a spot size of ∼1 μm and to collect the scattered light in a configuration of 180°. Each Raman spectrum was obtained by taking signal averages during 15 s. The monochromator grating provided a resolution of 4 $cm^{-1}$.

The PA signals were registered with a piezoelectric transducer. This made it possible to use remote monitoring of the interaction of laser pulses with the given sample. Therefore this kind of experiment can assist us with the task of the remote monitoring of structural changes induced within a sample.

**Table 1** Deposition parameters of the titanium oxide thin films prepared at room temperature via sputtering

| Sample | $Pressure_{gas}$ (Pa) | Power (Watts) | Concentration of elements (a.u.) | Time for deposition (min) | Thickness (nm) | Deposition rate (nm/min) |
|---|---|---|---|---|---|---|
| S1 | 0.62 | 180 | Ar:24.4, $O_2$: 2.8 | 90 | 170 | 1.88 |
| S2 | 0.067 | 100 | Ar:22.2, $O_2$: 0.5 | 330 | 833 | 2.52 |
| S3 | 0.05 | 100 | Ar:22.2, $O_2$: 0.5 | 330 | 2300 | 6.96 |

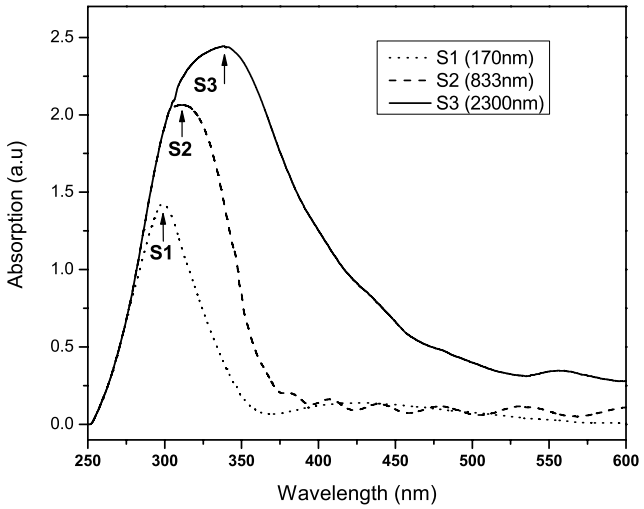



**Fig. 1** Absorption spectra of several titanium oxide thin films deposited by reactive DC sputtering

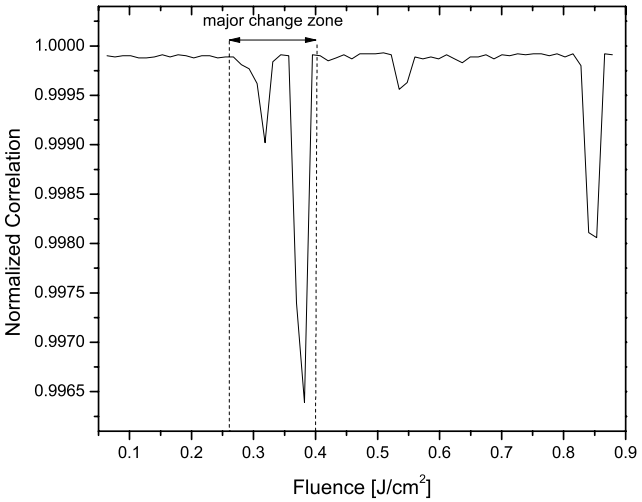



**Fig. 2** Correlation analysis of photoacoustic signals as function of fluence for a titanium oxide thin film

## 3 Results and discussion

It is known that the PA wave amplitude is proportional to the optical absorption [17], thus, in order to find the most suitable excitation wavelength to generate the PA signals in $TiO_2$, we obtained the absorption spectra of each sample (Fig. 1). From these measurements, we identified the interval of absorption bands in the ultraviolet region, ranging from 280 to 380 nm for each sample. This is consistent with other reports [16, 18, 19]. Notice that the absorption bands shift to longer wavelengths with an increase of the thin-film thickness. A likely explanation is that there are more defects in samples with larger thickness; this alone would induce optical dispersion processes that can explain this shift. According to the UV–vis spectra of $TiO_2$ thin films, the pulsed excitation laser wavelength was set to 355 nm.

### 3.1 Threshold ablation

When light interacts with matter, two types of mechanisms for generation of elastic waves may occur: those that modify the irradiated surface (ablation regime) and those that do not modify it (thermoelastic regime) [20]. In order to find the ablation threshold of the film under study, the sample was attached to one end of a quartz bar, which works as a waveguide, while the laser beam was focused on the sample with a positive lens. On the opposite end of this guide we firmly attached the PZT transducer. During the experiment the laser was kept at constant voltage; in this way the intensity of the incident energy also remained constant. Using an energy attenuator such as a variable neutral density filter, we changed the incident energy on the sample.

The PA signal was monitored in terms of fluence, starting in the thermoelastic regime until the regime of ablation from the film was reached.

Figure 2 shows the PA correlation analysis as a function of the fluence for one of the analyzed samples. The general features of this curve are quite similar to the other samples. Notice that the most substantial changes are between 0.26 and 0.4 $J/cm^2$ and at about 0.8 $J/cm^2$. These changes may be associated with structural phototransformations of the studied samples. After performing these PA-measurements as function of the fluence, the samples were observed through an optical microscope (OM). In this way we verified that these had already reached the ablation regime. The ablation threshold corresponds to a change in the interaction mechanism of the laser radiation with the material surface leading to the corresponding surface damage [21], which corresponds to the kind of patterns we observe with the OM. From these results we can assert that the structure of the $TiO_2$ thin films remain unchanged when they are illuminated with pulsed laser radiation at 355 nm at fluences below 0.26 $J/cm^2$.

Therefore, once we identified the ablation threshold, and in order to avoid ablation on the film samples, for the remaining analyses we performed measurements with fluences of the order of 0.09 $J/cm^2$.

### 3.2 Thermic treatment

Figure 3 shows the PA correlation analysis during the thermal treatment. The temperature rose from room temperature up to 800°C, at 10°C/min. In this case each of the $TiO_2$ thin-film samples was placed inside the furnace. The changes induced in the samples, as function of the temperature, were monitored in two stages: (I) from room temperature up to 215°C; the PA signal displays instabilities which start at 50°C and continue for higher temperatures. (II) Then above 200°C the analysis of the PA signals remain stable as temperature increases up to 568 ± 5°C. In order to determine

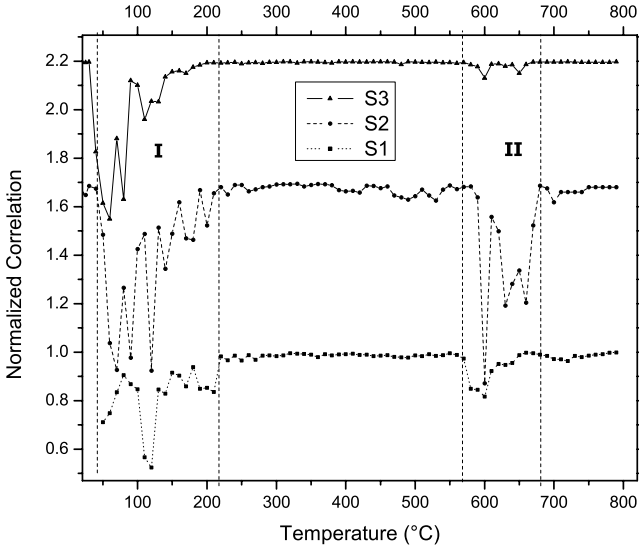
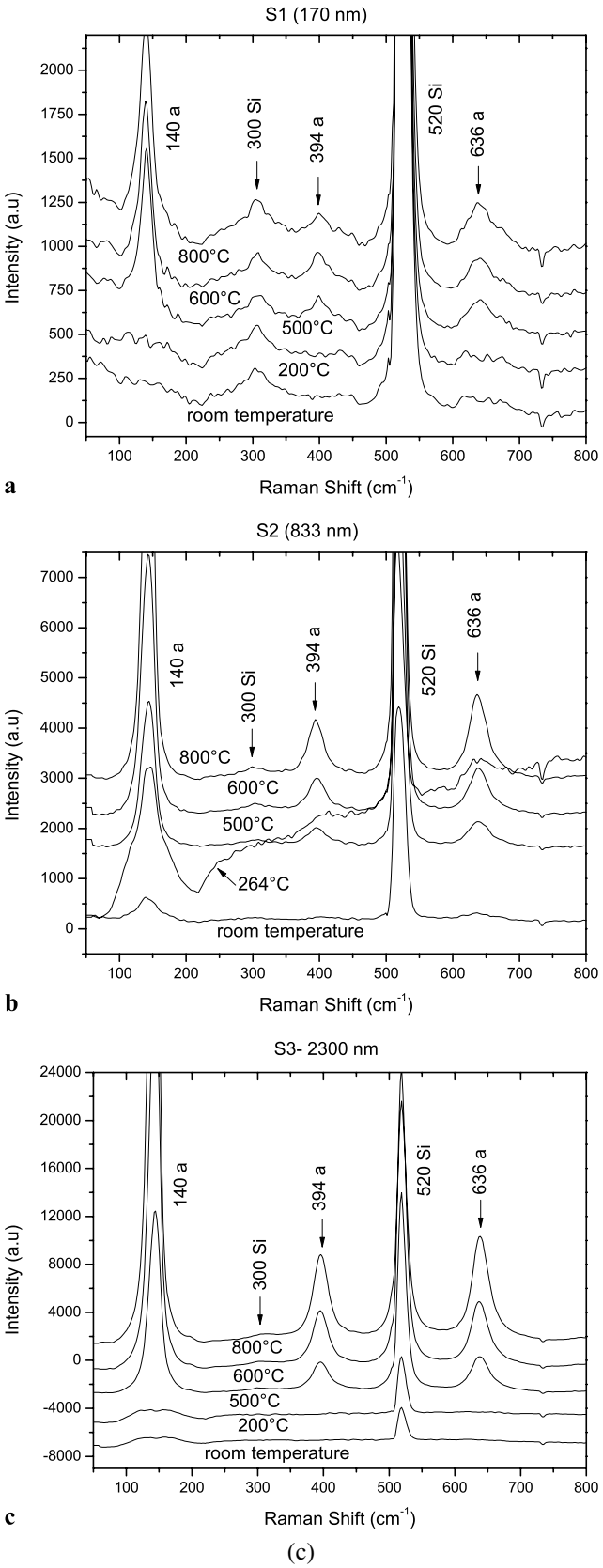



**Fig. 3** Correlation analysis of photoacoustic signals as function of temperature for the samples S1, S2 and S3. Zones of major changes: (I) at the beginning and up to 215°C and (II) before of to 568°C

whether the observed changes in the PA signal are due to phase transitions or not, we performed Raman spectroscopy measurements before and after the heat treatment. Notice that we also heated the samples at intermediate temperatures and we obtained the corresponding Raman spectra, as a way to validate our observations. These measurements are shown in Fig. 4.

Figure 4 shows the Raman spectra obtained at different temperatures for each of the analyzed films; the spectra of the samples are shown at temperatures of 200, 500, 600 and 800°C. The measurements corresponding to the first two temperatures (room temperature and 200°C) confirm the amorphous state of the samples; from 500°C the onset of a defined crystalline phase takes place and is maintained up to 800°C. It can be noticed that the Raman band intensities increase with increasing temperature. Measurements were also performed at 400°C, however, although it presents the most intense $TiO_2$ band at 140 $cm^{-1}$ (in some cases at 636 $cm^{-1}$), a definitive anatase $TiO_2$ phase is not achieved. This may explain the slight changes occurring in the stability correlation analysis in the range of 200–500°C; these changes are more noticeable for the sample labeled as S2. As shown in each of the Raman measurements, all the samples without thermal treatments have an amorphous phase state. This phase remains up to temperatures above 500°C. With temperatures above 500°C bands located around 140, 394 and 636 $cm^{-1}$ appear, corresponding to a well-defined titanium oxide anatase phase [22].

A revealing fact is that some of the samples contain crystalline elements in particular areas that were defined as the temperature increased, so that at the end of the thermal ramp, the crystalline phase was already formed. On the other hand,




(c)

**Fig. 4** Temperature dependent Raman measurements for **a** S1, **b** S2 and **c** S3 samples. The *Si* and *a* symbols indicate the Raman modes of silicon and anatase phase of $TiO_2$, respectively

it was not possible to obtain the most stable thermodynamic phase of $TiO_2$, i.e. the rutile phase. There is evidence that crystallinity preferentially occurs at temperatures which are higher for thin films than for bulk materials [23, 24]. The influence on the transformation temperature of the type of material microstructure (porosity, thickness, columnar growth, etc.) or other factors, such as crystal size, is not yet fully understood.

The correlation analysis of photoacoustic signals of each sample with increasing thickness shows instabilities in the same temperature regions. From these results it is not possible to clearly identify the relationship between thickness and phase transition; such information is obtained directly from the photoacoustic signals (voltage vs. time), where the arrival time is sooner for the thinner sample and later for the thicker. The arrival time gives the speed of sound; this is a useful quantity, since both the density and the elastic constants can be calculated from it [10].

With the correlation analysis of the PA signals, the temperature at which the amorphous–crystalline transition is initiated can be identified with high precision. The differences observed in the Raman and the PA measurements reveal a higher PA accuracy when measuring the amorphous–crystalline transformation. Raman spectroscopy presents this transformation before the PA analysis. This may be due to some crystallized grains within the thin-film structure and the occurrence of the transition in just one of these grains and therefore micro-Raman signals can be detected. Our interpretation is that the titanium oxide phase transitions in the thin-film samples are produced at temperatures above 500°C. However, at temperatures below 200°C the observed PA changes are not associated with any phase transition. These findings beg the question: what is the nature of these changes?

According to Wang's research, there is evidence that UV illumination of the $TiO_2$ could produce highly hydrophilic surfaces [25]. Thus, the transition between the hydrophobic and hydrophilic properties of the $TiO_2$ can be attributed to the formation and extinction of existing surface hydroxyl groups. UV irradiation promotes reduction of Ti ions from $Ti^{4+}$ to $Ti^{3+}$ and production of oxygen vacancies on $TiO_2$ surfaces [26–28]. When the titanium dioxide is photoexcited, an electron–hole pair is generated. The electrons tend to reduce +4 charged titanium cations to the 3+ state, producing oxygen vacancies [29]. Water molecules can heal these oxygen vacancies, contributing to the formation of surface OH groups [30]. Therefore, these investigations allow us to attribute changes in the films during thermal treatments at temperatures below 200°C, to evaporation of water molecules on the surface because of UV irradiation effects as well as to the resulting realignment of the corresponding surface $TiO_2$ molecules after evaporation. It was also reported that the surface does become relatively hydrophilic and oleophobic when exposed to UV light for a longer time [30, 31].

## 4 Conclusions

In this study, we have demonstrated that the PA technique is a useful tool for obtaining phenomenological information in terms of the thermal stability of a system. The correlation analyses of PA wave signals show high sensitivity to structural material changes. This was particularly the case for thin films of titanium oxide affected by fluence and temperature effects. In this regard, we find that pulsed laser fluences below 0.25 $J/cm^2$ do not produce any structural changes within these thin films. However, at temperatures above 500°C, the titanium oxide anatase phase can be formed.

The Raman spectra obtained at different temperatures for each sample showed that the crystalline structure of the $TiO_2$ anatase phase appeared in every case close to 500°C. At 800°C, however, the anatase phase is completely defined. These differences observed in the Raman and PA measurements reveal that the accuracy in the PA analysis is comparatively larger than in the Raman results, particularly when the amorphous-crystalline transformation takes place. It is known that the transition temperature from one phase to another depends on various factors such as impurities, reaction atmosphere and synthesis conditions. Consistent with the conclusions of previous studies, we also assume that the PA changes observed during thermal treatments within the first 200°C are due to evaporation of water molecules on the surface and are the result of UV irradiation and the $TiO_2$ molecular rearrangement occurring after evaporation.

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