Deposition and doping of TiO_2 films by laser ion source

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Abstract

In this work, we show the synthesis and doping of TiO_2 films by pulsed laser deposition (PLD) and low-energy ion implantation techniques, respectively. The peculiarity of this work consists that both the processes have been performed with the same apparatus. It consists of a laser ion source in which the plasma plume can expand in free mode or under accelerating DC voltages. We show preliminary results on the characterization of titania films deposited starting from a rutile target and then doped with Cu and Ni ions, accelerated at 20 kV. Such a low implantation energy was a suitable choice to have an implantation effect up to several nanometres in depth.

1. INTRODUCTION

The well-being and technological progress in human life are the major cause of the degradation of the environment, through air pollution, noise, poor quality water and the production of a wide range of waste. This results in the onset of new diseases and infections for the human health. Such a situation imposes on the scientific community the challenging task of finding efficient and eco-friendly technologies for the treatment of human diseases and for pollutants affecting the environment. Titanium dioxide has been long proposed as a possible solution for these problems, because of its potential applications in the decomposition of toxic organic compounds, degradation of environmental pollutants [1] from water or air and for its antibacterial properties [2, 3]. The degradation of environmental pollutants (absorbing the pollutant molecules onto the TiO_2 surface) and the antibacterial properties of the titanium dioxide are based on the mechanism of photocatalysis [4, 5]. It acts when the TiO_2 surface is excited by ultraviolet radiation of specific wavelength (e.g. $\lambda \leq 387$ nm in the case of the anatase). So, many electron and hole pairs are generated. These pairs could recombine or migrate to the oxide surface, producing highly reactive radicals that start redox reactions with surface-adsorbed molecules.

The wavelength dependence to the photoactivation represents a limit for this material. The most efficient strategy to enlarge the response of TiO_2 to visible light is the lattice doping [6, 7] with ions of metal and non-metal elements. Doping ions act as trapping sites and enhance the recombination of photogenerated electrons and holes, inducing a bathochromic shift [8] (decrease of the band-gap or introduction of intra-band gap states) which results in a more visible light absorption. Several papers present in literature show TiO_2

doping with alkaline earth ions (Ca, Sr and Ba) [9], rare earth ions (La, Ce, Er, Pr, Gd, Nd, Sm)[10] and Fe [11, 12], Cr [12], Co [13], Mo [14], Cu [15] and Ni [16] using different techniques.

In this work, we report preliminary results on the synthesis and doping of TiO_2 films by PLD and low-energy ion implantation techniques, respectively. The peculiarity of this work consists that both the processes have been performed with the same apparatus. It consists of a laser ion source (LIS) in which the plasma plume can expand in free mode or can be accelerated (applying DC high voltages). The titania films were deposited starting from a rutile target and then doped with Cu and Ni ions, accelerated at 20 kV. Such a low implantation energy was a suitable choice to have an implantation effect up to several nanometres in depth.

2. MATERIALS AND METHODS

2.1. Synthesis of the TiO_2 films by PLD

The TiO_2 films were deposited by Pulsed Laser Deposition (PLD) technique. The experimental apparatus is schematized in Fig. 1. A commercially sample of TiO_2 rutile (with purity of 99.9%) was used as target. It was fixed on a rotating target holder (T, 2 cm in diameter) which was mounted on an insulating flange. During this experiment, T and the PLD chamber were connected electrically, in order to have all the elements to ground. The chamber was evacuated by a turbo molecular pump supported by a rotary pump to a base pressure of about 10^{-5} mbar. A KrF excimer laser ($\lambda = 248$ nm, $\tau = 23$ ns) with a repetition rate of 4 Hz was used in the experiment. The laser beam was focused by a thin lens (L) onto the target surface. The laser spot resulted of 0.5 mm^2 obtaining a laser fluence of 4.8 J/cm^2. We applied 60000 laser pulses, for each deposition process. Single crystals of <111> oriented silicon substrates (size: 10 mm × 10 mm × 0.5 mm), cleaned in an ultrasonic bath with ethanol and acetone, were used as substrates (S). They were mounted on a plane metal electrode (ground electrode, GE), positioned at 5 cm far from the target.

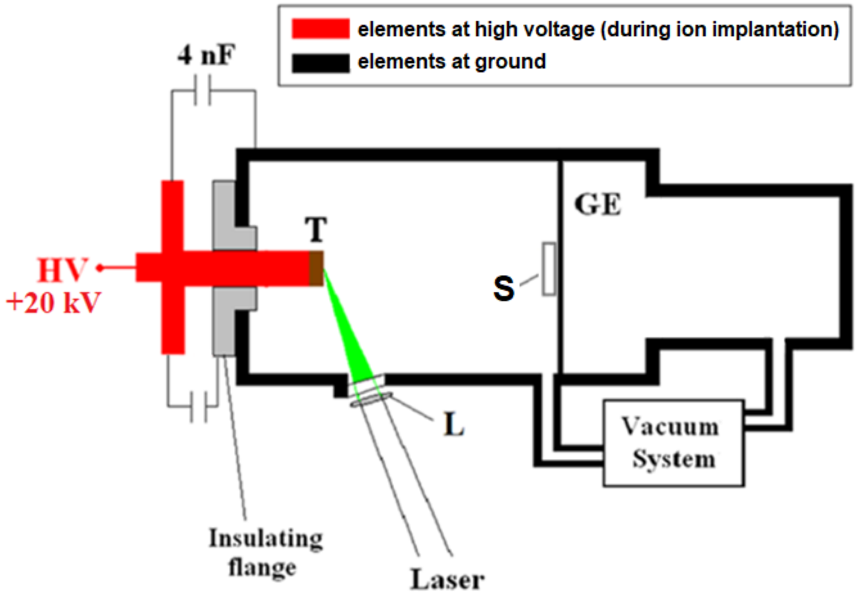

Figure 1: Sketch of the experimental apparatus: T: target holder, L: thin lens; S: substrate; GE: ground electrode.

2.2. *Doping by ion implantation*

We doped the titania films with Cu and Ni ions. The process was performed in the same PLD chamber using, as targets, samples (99.99 % of purity) of copper and nichel, developed by Goodfellow. They were mounted on the rotating target holder T. We maintained the same parameters (laser spot, fluence, T-S distance) used during the deposition. Conversely to the previous experiment, the target holder was maintained electrically separated from the chamber by the insulating flange. A high voltage of +20 kV was applied to T in order to accelerate the positive ions towards the titania films mounted on the GE. A high voltage capacitor of 4 nF, connected between T and the chamber, was used to stabilize the voltage during the ion implantation. This configuration was able to generate a longitudinal electric field. The process was performed at the repetition rate of 5 Hz for ten minutes (3000 laser pulses) and the vacuum chamber was evacuated up to 10^{-5} mbar. With such a low-energy value, we expect that most of the ions carried by the plasma plume have a +1 charge state in accordance with a previous work, in which an electrostatic spectrometer was utilized to study the ion charge states [17].

2.3. *Film characterization*

The characterization of the titania films was carried out by Raman and RBS (Rutherford Backscattering Spectrometry) spectroscopies. Raman spectra were recorded with a InVia spectrometer Renishaw PLC (Gloucestershire, UK), equipped with a Leica optical microscope. The excitation source was the 514.5 nm output of an Ar^+ ion laser working at a maximum output power of 25 mW. All spectra were recorded at room temperature using a resolution of 1.5 cm^{-1} over the spectral range 150–3000 cm^{-1}.

RBS analyses were carried out for determining the spatial uniformity and the layer thickness. The measurements were performed at CEDAD (CEnter of applied physics, DAting and Diagnostic) using a 3 MV tandem accelerator equipped with different beamlines including the RBS. The incident ion beam (2 MeV He^{++} ions) was directed along the normal to the sample surface. The beam spot on the target had a circular shape of 1 mm radius and the current in the range from 10-20 nA. A Camberra's PIPS detector (thickness of 300 μm, active area of 25 mm^2 resolution of 18 keV) was used to collect the particles backscattered from the sample at an angle of 170° with incident normal. SIMNRA software was used for spectra simulation and thickness estimation.

3. RESULTS AND DISCUSSION

Figure 2 shows the Raman spectrum of the pure TiO_2 film treated at 400 °C. The spectrum shows three characteristics of active modes. These fundamental phonons are observed at 144, 399 and 638 cm^{-1} and according to [18], they are attributed to the symmetries E_g, B_{1g} and E_g, respectively, of the anatase (A) phase. It is evident a very intense signal due to the 521 cm^{-1} long-wave optical phonon in silicon substrate, together with the signal at about 300 cm^{-1}, originating from two-phonon scattering phenomena (2TA) in silicon. The peak at 521 cm^{-1} probably covers the anatase peak at 515 cm^{-1} attributed to the A_{1g}/B_{1g} symmetry. The Raman spectrum aspect suggests a high amorphous content in the titania film. Another band centred around 970 cm^{-1} was also observed. This band is not associate to any fundamental mode, but it could be attributed to the Si-O stretching vibration of the substrate [19].

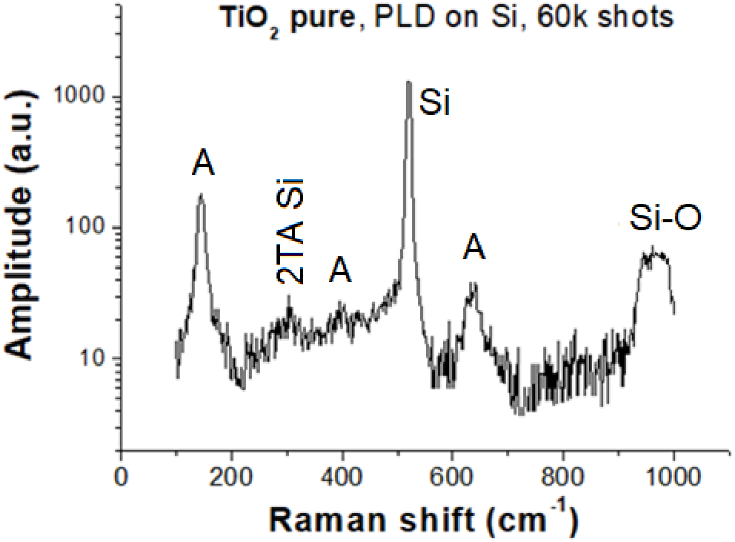

Figure 2: Raman spectrum of TiO_2 film deposited via PLD on Si substrate. The letter A indicates the anatase phase.

Fig. 3 shows the RBS spectrum (black line) and the simulation (red line) of a pure TiO_2 film deposited by PLD on silicon substrate after a thermal treatment of 400 °C for 3 hours. In the high energy side of the spectrum, the titanium peak is clearly visible. The Ti signal has well-defined margins, indicating a good quality film at the surface and at the film-substrate interface. In the low energy part of the spectrum the signals coming from silicon that constitutes the substrate and oxygen of titania are visible. The simulated thickness by SIMNRA software resulted of about 40 nm.

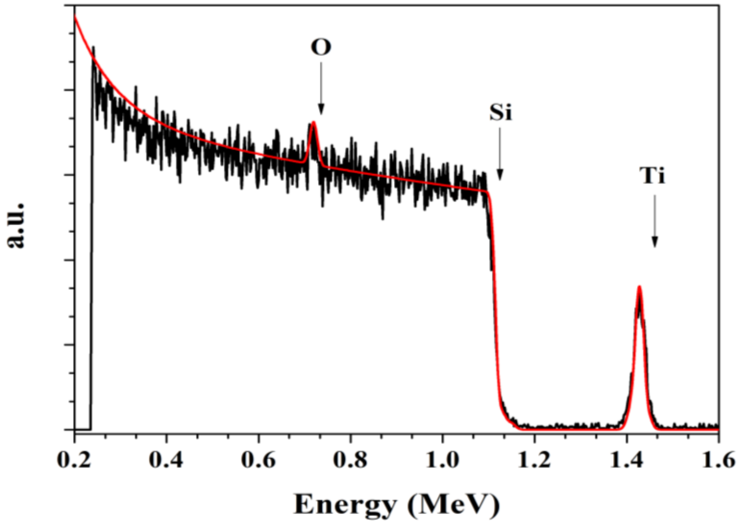

Figure 3: RBS spectrum of a PLD titania film thermally treated at 400 °C for 3 hour.

Expected implantation profile of Cu and Ni ions in TiO_2 layers was estimated using the well-known Monte Carlo simulation code, the stopping and range of ions in matter (SRIM) [20].

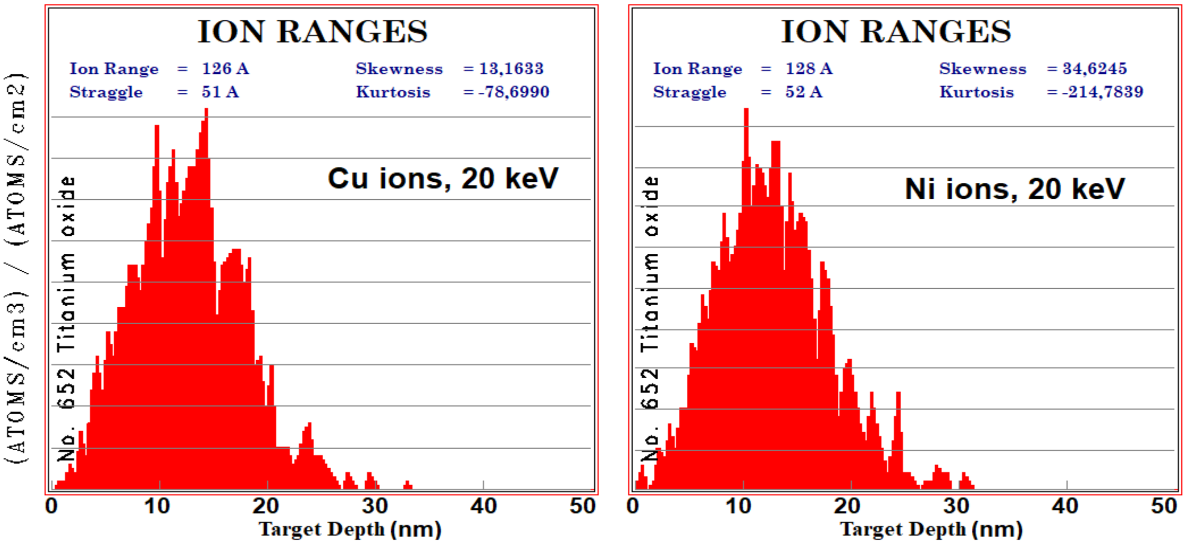

Figure 4: SRIM simulations of the implanted profile of Cu and Ni ions on TiO_2 film.

Figs. 4a and 4b show SRIM simulation results for Cu and Ni accelerated ions +1, respectively, implanted at 20 kV into TiO_2 layer. At this value of accelerating voltage, the profile of the implanted dose for Cu and Ni ions resulted in the range of few tens of nm below the titania film surfaces.

In order to estimate the implanted ion dose, we carried out measurement of collected charge. As ion detector, we used a Faraday cup (FC) mounted in the same position of the substrate. It was polarised by a negative voltage (to collect the positive ion charge) and connected to a digital oscilloscope by a RC fast circuit [21]. Fig. 5 shows, as example, FC time of flight signals for Ni ions at 0 and 20 kV accelerating voltage. The area of the curves represents the total ions per laser pulse. It is noteworthy to observe that for accelerated ions, the current peak shifts towards shorter times due to the fast extraction of the ion from the plasma. The estimated dose was of the order of 10^{12} ions/pulse which multiplied by the total number of laser pulses (3000), provided us the total implanted dose of $3x10^{16}$ ions/pulse. Considering a FC diameter of 8 cm, we obtained a total ion dose of about 10^{15} ions/cm^2.

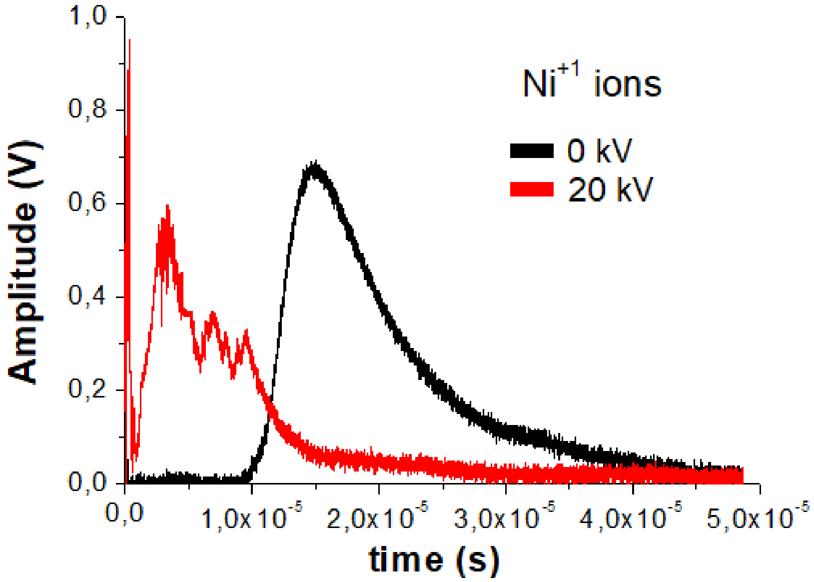

Figure 5: Faraday cup signals of the nickel ions at 0 and 20 kV accelerating voltages.

Further measurements are in progress to measure the incorporated dose of the doping ions, the electronic band-gap, the photocatalyst activity through the degradation of methylene blue, the bacteria adhesion and so on.

4. CONCLUSIONS

In this work we show preliminary results on the synthesis and doping of TiO_2 films by PLD and low-energy ion implantation techniques, respectively. The peculiarity of this work consists that both the processes have been performed with the same apparatus. It consists in a laser ion source (LIS) in which the plasma plume can expand in free mode or can be accelerated (applying DC high voltages). The characterization of the titania films has shown that anatase is the favoured TiO_2 phase. The doping with Cu and Ni ions at low energy (20 kV of accelerating voltage) represents a suitable choice to have an implantation effect up to several nanometres in depth, sufficient value since the photocatalyst activity of the titania films works on the surface.

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