Tailoring optical properties of pulsed laser deposited TiO_2 films

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Abstract. The paper is dedicated to the investigation into optical properties of TiO_2 thin films pulsed laser deposited at the temperature as low as 150 °C and subjected to the following heat treatment. Properties of obtained nanocrystalline films were compared to polycrystalline TiO_2 films grown at elevated temperatures. The highest transmission and the best morphology in polycrystalline films have been obtained at the growth temperature of 300 °C. The two methods of post-annealing of amorphous films were employed: annealing at thermodynamically equilibrium conditions and rapid thermal annealing (RTA). RTA at 500 °C enables achievement of the best optical performance: smooth surface and high films transparency.

1. Introduction

Nowadays TiO_2 is an extensively studied material. In view of high optical transmission and high refractive index, resistance to various chemical and physical impacts its films have long been known as promising materials for various applications, e.g. anti-reflection coatings [1], various optical components and waveguides [2], photonic crystals [3], high permittivity gate dielectric films in VLSI circuits [4]. These applications, however, imply some requirements for the films quality, viz. an adequate morphology, high transmission and high refractive index. As it is known, TiO_2 exists in three phases: brookite, anatase and rutile that possesses one of the highest refractive indices. So, it is favorable to obtain films in the rutile phase. On the other hand, occurrence of the crystalline phase leads to higher surface roughness which inevitably results in lower transmission and poor applicability for films to be integrated. Consequently, there is always a compromise between good enough morphology and optical performance.

Our research is aimed at tailoring optical properties of amorphous TiO_2 films by heat treatment to achieve high refractive index and transmission values, and simultaneously preserve good surface morphology. This is done having employed three strategies: i) depositing polycrystalline films at elevated temperatures (higher than 150 °C) and growing films at 150 °C with the subsequent ii) equilibrium post-annealing procedure and iii) RTA one.

2. Experiment and discussion

The films have been grown on the Corning glass 7059 substrates by excimer KrF laser Lambda Physik LPX 305iCC with the 248-nm wavelength, 25-ns pulse length and 300-mJ·cm^{-2} fluence.

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The vacuum chamber was firstly evacuated down to the pressure of 4.0×10^{-5} mbar and, afterwards, oxygen was introduced into it so as to set the constant pressure of 1.4×10^{-2} mbar. The substrate temperatures (T_s) were varied within the range of 150−500 °C.

Crystalline properties were controlled by X-ray diffraction (XRD) using Siemens D5000 powder diffractometer. Transmittance spectra have been recorded by FT-IR spectrometer Nicolet 5700 in the range of 400−2630 nm. Surface morphology has been investigated by atomic force microscope (AFM) NanoScope III. Films thicknesses were controlled by the Alpha Step 200 profilometer.

2.1. Films deposited at different substrate temperatures

Amorphous films were grown at $T_s = 150$ °C, as a starting point for all the following annealing procedures, at 300, 400 and 500 °C. Films deposited at elevated temperatures are denoted hereafter as T150, T300, T400 and T500.

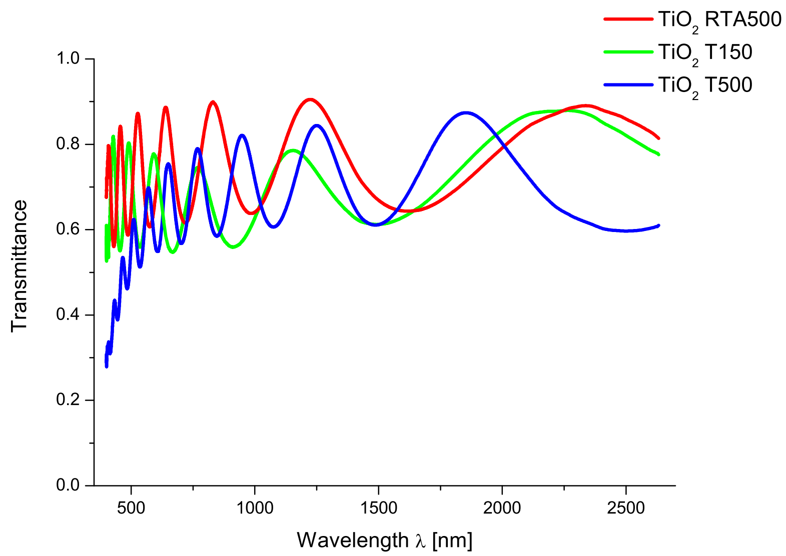

Figure 1. Transmittance spectra of the TiO_2 films: green line - as deposited at 150 °C; red - deposited at 150 °C and then subjected to rapid thermal annealing at 500 °C; blue - deposited at 500 °C.

Films deposited at 150 °C had very smooth surfaces and were found to be X-ray amorphous. These as-grown films exhibited strong broad band absorption centered at about 900 nm (see the T150 sample in figure 1). Transmittance spectra of films with high optical performance contain Fabry-Perot oscillations with a flat enveloping curve. Instead, T150 samples show a clear drop in transmittance at $\lambda \simeq 900$ nm. With growth temperature increase the drop had already vanished at $T_s = 300$ °C and then transmittance spectrum remained almost unchanged for the film deposited at 400 °C. The rutile phase appeared in X-ray diffraction patterns only at $T_s = 500$ °C; however, the refractive index values exhibited hardly any changes for the cases of T300 and T500 films and moreover the transmittance values fell down with T_s increase (see T500 spectrum in figure 1). Fitting experimental transmittance spectra to the Swanepoel formula [5] we have obtained wavelength dependence of TiO_2 refractive index N:

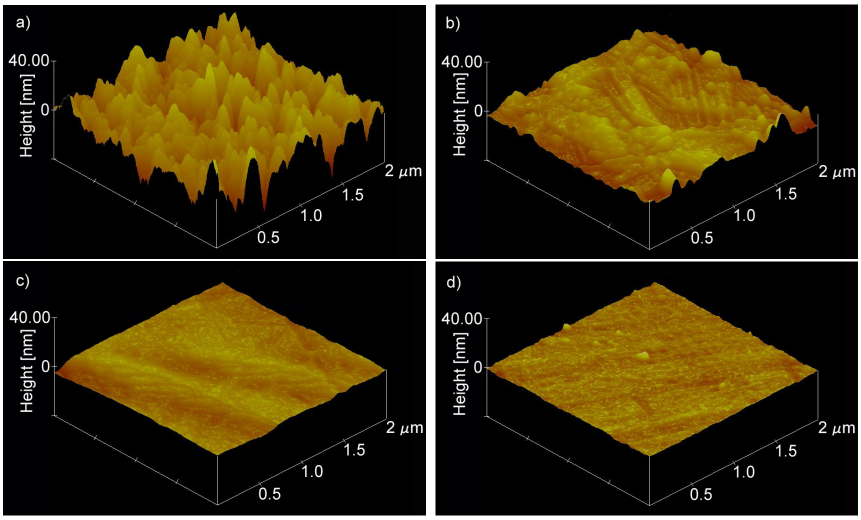

Figure 2. AFM images of the TiO_2 films: a) deposited at 500 °C, b) annealed at 800 °C, c) subjected to rapid thermal annealing (RTA) at 800 °C, d) subjected to RTA at 500 °C.

$$N^2 = 1 + \frac{4.35}{1 - (\frac{227nm}{\lambda})^2} \tag{1}$$

where λ is denoted as wavelength. The thicknesses of the films were measured to be 313 nm (T300) and 790 nm (T500).

The AFM examinations showed that the T500 film surface was rather rough (figure 2a) which led to a decrease of transmittance primarily at the short wavelength spectral range. As a consequence, the films deposited at 500 °C are not applicable. The best surface morphology among all of the films obtained at different substrate temperatures exhibited T300 film and it had rather high refractive index values and low optical insertion loss: $N = 2.33$ and $\alpha = 5953$ cm^{-1} at 1550 nm.

2.2. Post-annealing

The post-annealing of amorphous TiO_2 film has been carried out in the air sequentially: at first at temperature $T_{an} = 300$ °C and then at $T_{an} = 400$, 500, 600, 700 and 800 °C. In annealing process the temperature was raised with the rates T_{an}/hour except for the cases $T_{an} = 700$ and 800 °C when the rate was 600 °C/hour. Then the film was kept at the corresponding temperature T_{an} for 1 hour with the subsequent cooling down.

No rutile phase was detected even after the annealing at the temperature of 800 °C. As to the drop in transmittance at 900 nm, it had already disappeared at 300 °C and all the other transmittance spectra of this film annealed at $T_{an} > 300$ °C were nearly the same apart from the spectrum of the annealing stage at 800 °C that exhibited rather low transmittance values. The positions of extrema of Fabry-Perot oscillations did not change with annealing indicating the fact that the annealing does not affect the refractive index values.

The surface roughness increased gradually with the increase in annealing temperature reaching the highest values for the annealing stage at 800 °C (see figure 2b). As it turned out, the films annealed at temperatures higher than 300 °C are not potentially suitable for optical integrated circuits.

2.3. Rapid thermal annealing

RTA has been conducted by Heatpulse 410 instrument at different temperatures: $T_{RTA} = 500$, 600, 700 and 800 °C (with the sample designation as RTA500, etc. respectively). Films were heated with the rate of 200 °C/sec and kept at the aforementioned temperatures for 30 sec for $T_{RTA} = 500$ °C and 15 sec for all remaining temperatures T_{RTA}. After that the gradual cooling down took place. No rutile phase was detected by XRD while annealing the samples even up to $T_{RTA} = 800$ °C as well as there were no changes in refractive index.

Transmittance spectra of the films annealed at $T_{an} = 600-800$ °C showed similar high transmission values as the RTA500 sample but surface morphology was found to be appropriate only for the RTA500 film (cf. AFM scans of the RTA800 and RTA500 samples in figures 2c and 2d, respectively).

3. Conclusions

The optimal conditions for the heat treatment of TiO_2 films have been found in terms of the three strategies: deposition of polycrystalline films at different elevated substrate temperatures, deposition of the films in amorphous state at the temperature of 150 °C with the following annealing in equilibrium conditions and RTA process. With regard to the films deposited at elevated temperatures, the best surface morphology and optical properties exhibited the film obtained at 300 °C. In the case of annealing amorphous films the best results showed the first stage of annealing, namely 300 °C. In view of the fact that RTA at temperatures below 500 °C does not bring any changes in the initial film characteristics, the most adequate choice is RTA at 500 °C which enables simultaneous achievement of smooth film surface and high transmittance values. Among all the ways of TiO_2 film processing the best optical performance has shown the film subjected to RTA at 500 °C.

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