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PE-CVD ADBD Created TiO_2 Thin Films

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Abstract

Plasma-enhanced chemical vapour deposition method (PE-CVD) applying dielectric barrier discharge (DBD) air/Ar/O_2 plasma was employed in deposition of TiO_2 thin films. For optimization of the film characteristics, study of relations between thin film parameters and deposition process conditions (e.g. gas flow rate, discharge power, TiO_2 films surface characteristics etc.) is of the outmost importance. Our research focused on interrelationship between concentration of the precursor titanium tetraisopropoxide transported by the Ar flow into the discharge region, concentration of the oxygen in the discharge atmosphere and surface properties of TiO_2 thin films deposited by PE-CVD DBD by means of the surface energy evaluation and atomic force microscopy (AFM) scans.

Introduction

Due to low operation expenses much attention has been paid to discharges, e.g. DBD, sustaining at atmospheric pressure. DBD at atmospheric pressure (ADBD) is mostly applied in a filamentary mode. In the past various tests of ADBD appliance for thin film deposition were reported, one of methods used was the plasma enhanced chemical vapour deposition method [1]. Development of the PE-CVD ADBD method is far from to be completed; it might provide thin films with characteristics to some extent adjustable by deposition process conditions [2], thus it still attracts experimental attention. Our contribution focused on the interrelationship between PE-CVD ADBD process and thin film characteristics.

Experimental

The films were prepared in ADBD plasma from the TTIP/Ar/O_2 gas mixture. Experiments were carried out in a Plexiglas discharge reactor with dimensions (90x79x41) mm.

The discharge sustained between two brass electrodes (45x8x18) mm and (40x17x18) mm respectively. The larger electrode was grounded and covered with the glass plate ((70x46x1) mm). Inter-electrode distance was fixed at 4 mm. ADBD input power was 250mW and 350mW respectively. ADBD sustained in the filamentary mode. Experiments were carried out in the air (relative humidity of 35÷45 %, pressure 741÷762 mm Hg and room temperature 20÷22˚C, current variations of the air temperature, pressure and humidity in the lab did not influence the experiments). The single molecular precursor, titanium tetraisopropoxide (TTIP, $Ti[OCH(CH_3)_2]_4$, 97% purity), was used as a source of titanium for TiO_x thin film deposition. It was heated, evaporated and mixed with argon and transported into the ADBD through cavity in the high voltage electrode. The cavity was connected to O_2 reservoir, too. The O_2, TTIP and Ar mixture was introduced into the discharge region of the reactor through hole in the electrode (diameter 3 mm). The temperature of the precursor evaporation was maintained at approx. 30˚C. Gas flow rate was adjusted by means of the mass flow controller. In all experiments films were deposited 10 minutes.

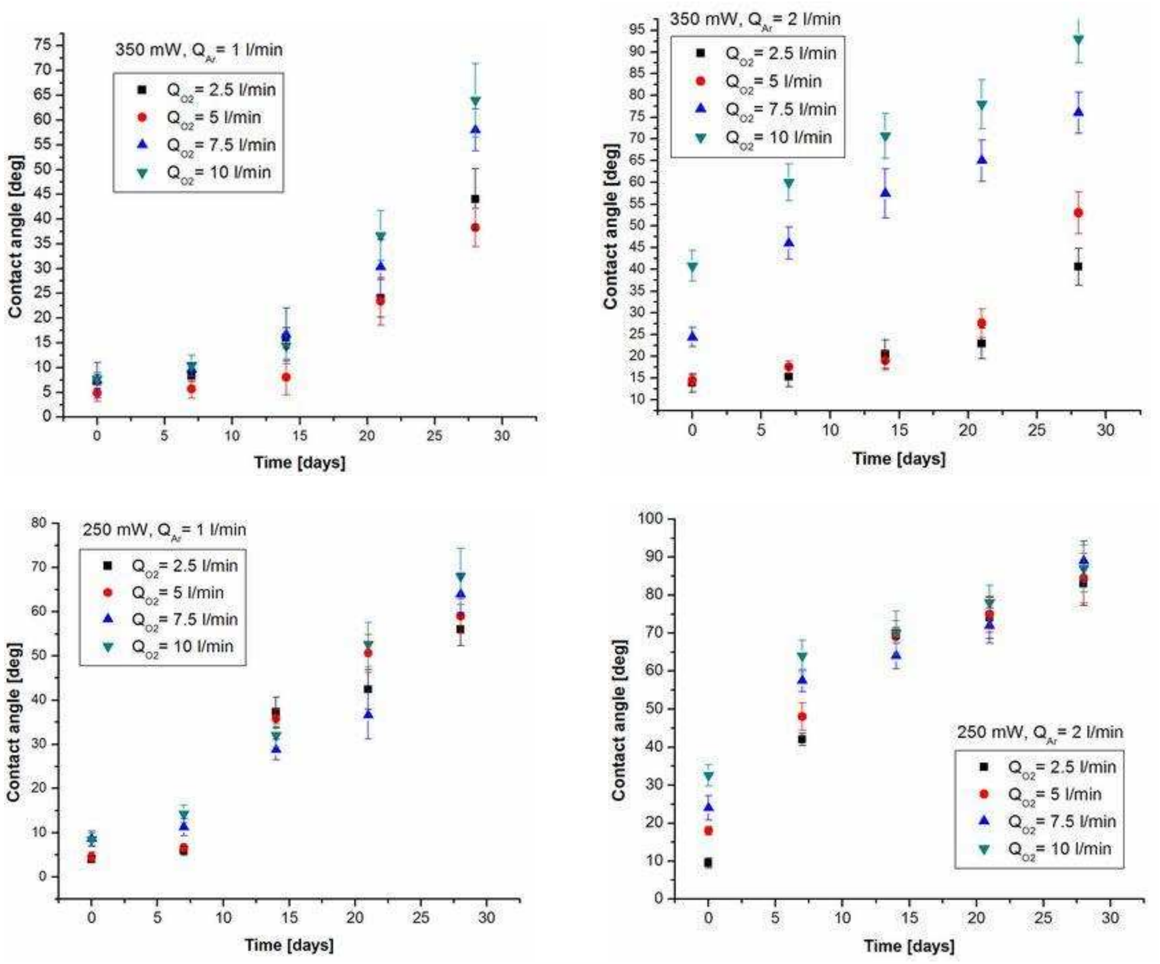

Figure 1. Dependence of the film hydrophilicity expressed by means of the contact angle on time (aging) for different O_2 flow rates and ADBD input powers.

Surface morphology of TiO_x layers deposited on glass substrates was studied by atomic force microscopy (AFM) and by water contact angle (CA) test (distilled water drop size was about 0.5 µl). Contact angle was measured by a sessile drop technique (room temperature 20-22°C, 30 sec). Contact angle values were determined from CCD snapshots of a solid-liquid meniscus. The film thickness was determined by a sulfometer (Planer Industrial, SF 200) via the scratch test.

Results and discussion

The thin films were deposited from TTIP at different monomer/Ar concentrations. Concentration was adjusted by Ar flow rate change. In dependence on PE-CVD ADBD process characteristics deposited film thickness was in range of (40÷200) nm. Dependence of TiO_x film hydrophilicity expressed by means of the contact angle on TTIP /Ar concentration and O_2 input flow rate is presented in figure 1. All samples were hydrophilic in the first day after deposition. Later on the hydrophilicity (and wettability of the film) diminished, after 28 days the contact angle value was about 90 degrees. Wettability changes are probably related with chemical reactions of the film surface and CH groups involved in atmosphere [3]. Tests of deposited films surface morphology were performed by AFM. Figure 2 shows typical topography of deposited TiO_x film for different TTIP/Ar mixtures. Scans display large differences of the film surface quality in dependence on Ar flow rate. Best result might be that for Ar flow rate 1l/min. O_2 high flow rates resulted in creation of powder on film surface.

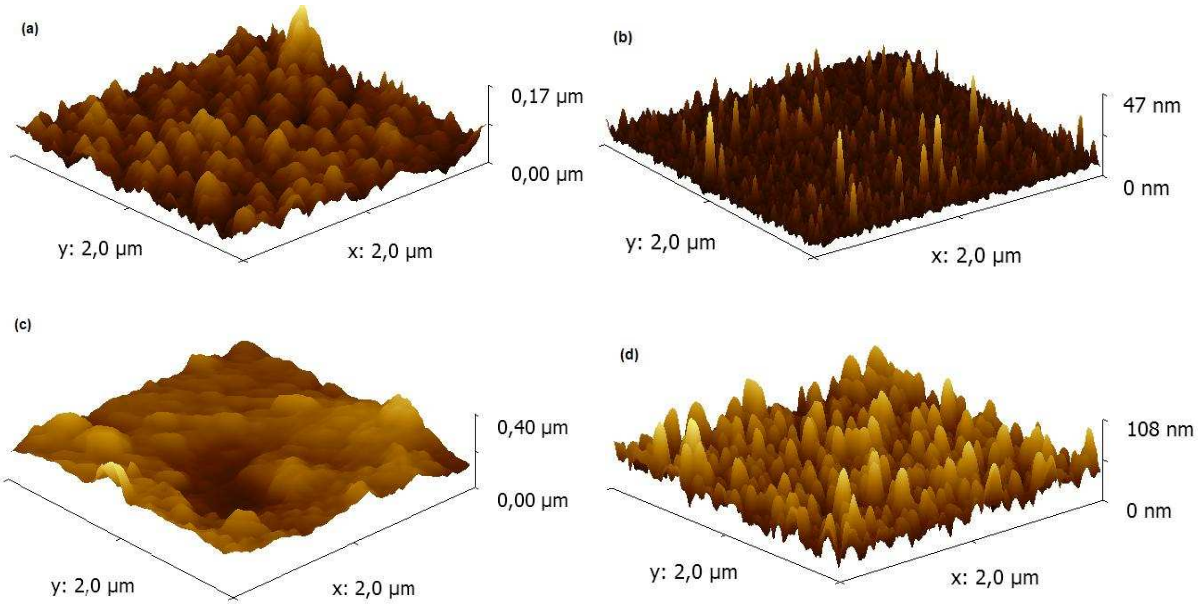

Figure 2. Topography of TiO_x film deposited, input power 350 mW, Q_{O2}=10 l/min, a) Q_{Ar}=1 l/min b) Q_{Ar}=2 l/min; Q_{O2}=5 l/min, c) Q_{Ar}=1 l/min d) Q_{Ar}=2 l/min.

Deposited film roughness (figure 3) was estimated from AFM scans (scan area 2x2 μm, resolution 256 dpi). It seems, there is no distinct relationship between hydrophilicity and roughness of deposited films. Chemical composition affects more the film wettability than surface morphology [4]. Unfortunately, at the moment we have no results of deposited films XPS scans for our disposal.

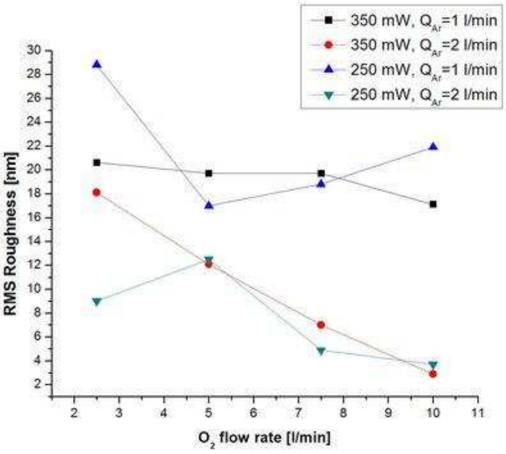

Figure 3. Dependence of RMS surface roughness on oxygen and argon flow rates and discharge input power.

Conclusion

- Thin films were prepared in ADBD plasma with PE-CVD technology in TTIP/Ar/O_2 gas mixture.
- After deposition films were hydrophilic, later on hydrophilicity diminished.
- AFM scans displayed large differences of the film surface quality in dependence on Ar flow rate.
- There is probably no distinct relationship between hydrophilicity and roughness of deposited films.

Acknowledgments

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