DEPOSITION OF TiO_2 THIN FILMS USING ATMOSPHERIC DIELECTRIC BARRIER DISCHARGE

Y. Klenko, J. Píchal

Czech Technical University, Faculty of Electrical Engineering, Department of Physics, Technická 2, 166 27 Prague, Czech Republic

In this paper the influence of precursor (titanium tetraisopropoxide (TTIP)) temperature, precursor and gas flow rates on the surface properties of TiO_2 thin films deposited by atmospheric dielectric barrier discharge (ADBD) chemical vapour deposition (CVD) were investigated. Argon was used as working gas. Influence of O_2 used as oxidizer was evaluated for determination of hydrophilicity of the films. Surface morphology of the thin TiO_2 films deposited on glass substrates was studied by the atomic force microscopy (AFM) and water contact angle (CA) measurement. CA tests proved wettability improvement in experiments with oxygen addition.
PACS: 52.77.-j

1. INTRODUCTION

Titanium dioxide TiO_2 thin films are used in a variety of applications because of their outstanding physical and chemical properties and low cost. In particular, the high refractive index of the TiO_2 (2.75 at 550 nm) and its excellent transparency in the visible and near-IR spectral regions make it very appropriate as antireflection coating and waveguides. There is also growing interest in TiO_2 thin films due to their potential applications in electrochromic display devices [1, 2], gas sensors [3] and photovoltaics [4].

TiO_2 thin films can be prepared by different methods such as hydrothermal techniques [5], molecular beam epitaxy [6], sputtering [7], sol-gel [8], chemical vapour deposition [9, 10] and others. Among these, plasma enhanced chemical vapour deposition (PE-CVD) at the atmospheric pressure is a new sample of cheap way to prepare various thin films. This method offers important advantages such as: avoidance of wet and hazardous chemical processes, enhancement of chemical reactions, larger plasma volume, availability for in-line continuous deposition process without necessity of pumping. A new method of thin film deposition by low temperature plasma at atmospheric pressure might be ideally suited for deposition of inorganic and organo-inorganic thin films on different types of substrate, including thermal sensitive polymer substrates.

This paper presents results of study of TiO_2 thin films deposited on glass substrate by ADBD PE-CVD process (preliminary results were partially represented in [11]). We studied the influence of temperature of the precursor evaporation and gas flow rates on TiO_2 thin film formation and the quality of the TiO_2 film.

2. EXPERIMENTAL

The experiments were carried out in a plexiglass reactor (90x79x41) mm. ADBD CVD system consists of reactor, gas input and AC power supply as schematically shown in Fig. 1. Two parallel brass electrodes with discharge gap of 4 mm were placed into the plasma reactor. Films were deposited on the glass substrates. During deposition ADBD power was about 350 mW (ADBD supply voltage (12.5–14) kV/50 Hz). The dimensions of the HV and ground electrodes were (40x17x18) mm and (45x8x18) mm, respectively. HV electrode was covered by the glass plate ((70x46x1) mm). The deposition time (t) for all samples was 10 min.

Thin films deposition was performed at atmospheric pressure. Titanium tetraisopropoxide (TTIP) (97%) was used as metalorganic precursor and Ar as the carrier gas. Argon flow rate (Q_{Ar}) was 0.5 and 1 l/min, respectively. Experiments were carried out with oxidizer O_2 (flow rates (Q_{O2}) 3.0 and 5.0 l/min, respectively) and in the air without oxygen addition. Argon and oxygen were mixed in the ground electrode cavity and the mixture flew through the hole in the electrode (diameter 3 mm) into the discharge gap. The gas stream was monitored using mass flow meters. Experiments were performed with 20˚C, 30˚C and 40˚C temperature (T) of TTIP in the bubbler. Amount of TTIP in the mixture was governed by change of evaporator temperature and the Ar flow rate through the evaporator.

Experiments were performed in air (relative humidity of 35–40% and room temperature 20–22˚C). For contact angle measurements distilled water was used as the test liquid. Water drop size was kept constant (at ~0.5 µl). A drop of water was gently placed on the experimental surface, and a photograph of the side profile of the liquid drop was taken using a camera. The base of the liquid drop was held in the same horizontal plane as the camera lens. The images were taken in 60 s after release of the water drop.

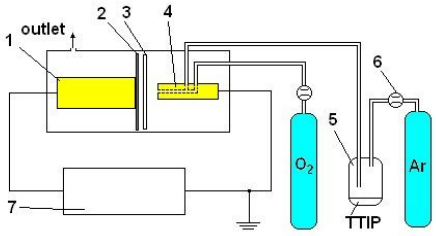

Fig.1. Scheme of the apparatus: 1 – HV electrode, 2 – dielectric barrier, 3 – substrate, 4 – ground electrode, 5 – evaporator, 6 – mass flow controller, 7 – HV supply

The values of the contact angles, shown in this paper, were obtained using Young curve fitting based on the imaged sessile water drop profile (average of measurements over an extended area of deposited samples).

3. RESULTS AND DISCUSSION

The morphology analysis of all samples was performed by atomic force microscopy (AFM) (for examples see Figs. 2). Fig. 2a shows the uniform and homogeneous surface with few sharp small tips; it indicates the needle growth of the films structure due to the non-homogeneous (streamers) discharge. Doping of oxygen during deposition process and relatively high precursor evaporation temperature led to the growth of some column-like protrusions (Fig. 2b) on the quite smooth surface. The surface roughness was measured in a (20×20) μm scan range. Reduction of the TTIP amount by means of decrease Ar flow rate through evaporator led to the lowering surface roughness to 10 nm (Fig. 2c). Increasing oxygen addition to 5.0 l/min resulted in the needle growth of the films with salient parts and increased surface roughness (up to 21 nm). Fig. 2d shows that these films are not fully homogeneous. Many elongated and pointed crystallites grew faster, the other led to existence of heterogeneities and to rougher surface. The inhomogeneous films growth has following explanation: the streamer's head hit locally on the substrate, where it caused higher temperature and activation of the surface in these areas. It gave rise to higher material growth rates than at other places on the substrate. The random distribution of the streamers resulted in irregularities of thin film growth.

Results of water contact angle measurements are shown in the Table. The wide range of CA values for samples with deposition parameters: Q_{Ar} 0.5 l/min; T_{TTIP} 20 ˚C can be explained by existence of deposited film surface-irregularities, small amount of oxygen bonds on the films surface and high concentration of carbon [11]. These assumptions were verified by the AFM results. Addition and oxygen mixing with Ar/TTIP in the electrode cavity led to the lowest CA values. CA value was heavily dependent on the oxygen flow rate and amount of TTIP.

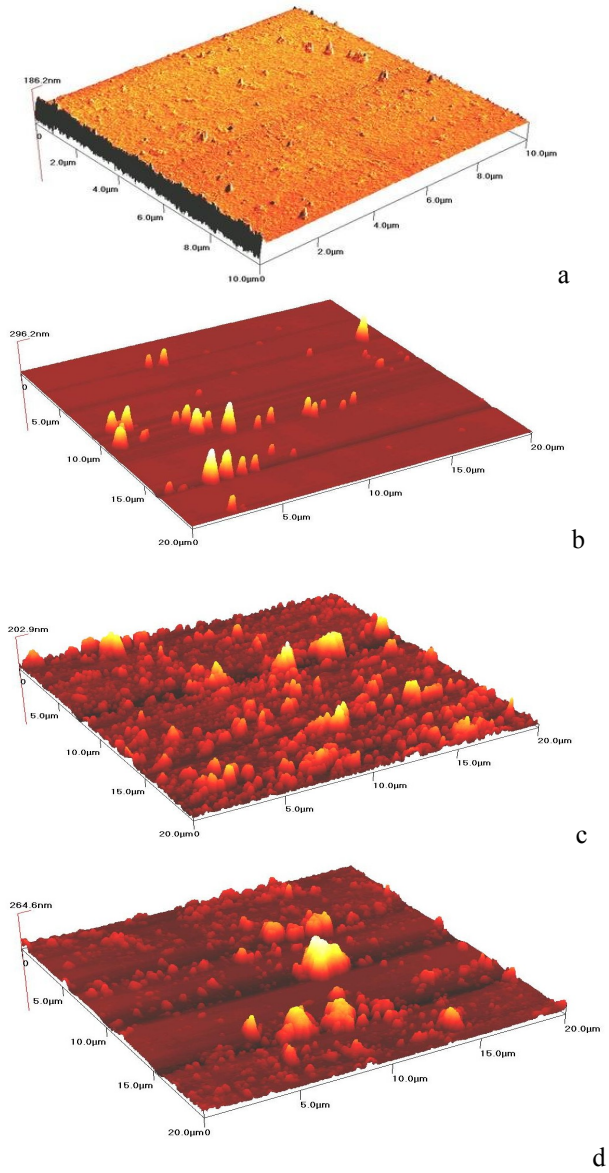

Fig.5. Topography of the TiO_2 thin films
a) deposited in air without oxygen addition; the scan size was (10×10) μm; t=1 min; Q_{Ar} 0.5 l/min; T_{TTIP} 20 ˚C;
b) t=10 min; Q_{Ar} 1 l/min; Q_{O2} 3.0 l/min; T_{TTIP} 40 ˚C; the scan size was (20×20) μm;
c) t=10 min, Q_{Ar} 0.5 l/min; Q_{O2} 3.0 l/min; T_{TTIP} 40 ˚C; the scan size was (20×20) μm;
d) t=10 min; Q_{Ar} 1 l/min; Q_{O2} 5.0 l/min; T_{TTIP} 30 ˚C; the scan size was (20×20) μm

Contact angle values: t – deposition time, Q – gas flow rate, T_{TTIP} – precursor evaporator temperature

Deposition parameters	Angle [degree]
t=10 min; Q_{Ar} 0.5 l/min; T_{TTIP} 20 ˚C	48.5˚ - 98.2
t=10 min; Q_{Ar} 1 l/min; Q_{O2} 3.0 l/min; T_{TTIP} 40 ˚C	29.5
t=10 min; Q_{Ar} 0.5 l/min; Q_{O2} 3.0 l/min; T_{TTIP} 40 ˚C	32.5
t=10 min; Q_{Ar} 0.5 l/min; Q_{O2} 5.0 l/min; T_{TTIP} 30 ˚C	36.3

CONCLUSIONS

Titanium dioxide (TiO_2) thin films were prepared on the glass substrate by ADBD CVD deposition method. Samples were deposited for different ratios of argon and oxygen flows and various precursor (TTIP) evaporation temperature (20˚C, 30˚C and 40˚C). For deposition in air without oxygen addition contact angle values were observed in the wide range (48.5˚ - 98.2˚), probably due to low content of oxidiser (O_2) in plasma chemical reactions. Oxygen in plasma has dual role: dissociation of TTIP molecules and carbon removal from the reactor (this was confirmed with XPS measurements, see [11]. Mixing of Ar/TTIP with oxygen led to more hydrophilic film deposition with CA ~30˚.

ACKNOWLEDGMENTS

This research was supported by the Czech Technical University in Prague Research Project CTU 0806213.

REFERENCES

1. Z. Wang, X. Hu. Electrochromic properties of TiO_2-doped WO_3 films spin-coated from Ti-stabilized peroxotungstic acid // *Electrochimica Acta*. 2001, v. 46, № 13-14, p. 1951-1956.
2. P. Bonhote, E. Gogniat, M. Gratzel, P.V. Ashrit. Novel electrochromic devices based on complementary nanocrystalline TiO_2 and WO_3 thin films // *Thin Solid Films*. 1999, v. 350, № 1, 2, p. 269-275.
3. O.K. Tan, W. Cao, Y. Hu, W. Zhu. Nano-structured oxide semiconductor materials for gas-sensing applications // *Ceramics International*. 2004, v. 30, № 7, p. 1127-1133.
4.
5. E.M.J. Johansson, A. Sandell, H. Siegbahn, et. al. Interfacial properties of photovoltaic TiO_2/dye / PEDOT–PSS heterojunctions // *Synthetic Metals.* 2005, v. 149, № 2-3, p. 157-167.
6. H. Yin, Y. Wada, T. Kitamura, et al. Hydrothermal synthesis of nanosized anatase and rutile TiO_2 using amorphous phase TiO_2. // *Journal of material chemistry*, 2001, v. 11, № 6, p. 1694-1703.
7. Y. Gao, S.A. Chambers. MBE growth and characterization of epitaxial TiO_2 and Nb-doped TiO_2 films // *Materials Letters*. 1996, v. 26, № 4-5, p. 217-221.
8. Q. Ye, P.Y. Liu, Z.F. Tang, L. Zhai. Hydrophilic properties of nano-TiO_2 thin films deposited by RF magnetron sputtering // *Vacuum*. 2007, v. 81, № 5, p. 627-631.
9. L.M. Nikolić, L. Radonjić, V.V. Srdić. Effect of substrate type on nanostructured titania sol–gel coatings for sensors applications // *Ceramics International.* 2005, v. 31, № 2, p. 261-266.
10. D. Byun, Y. Jin et. al. Photocatalytic TiO_2 deposition by chemical vapor deposition // *Journal of Hazardous Materials*, vol. 73, № 2, 2000, p. 199-206.
11. C. Jimenez, D.De Barros, A. Darraz et. al. Deposition of TiO_2 thin films by atmospheric plasma post-discharge assisted injection MOCVD // *Surface & Coating Technology*. 2007, v. 201, p. 8971 - 8975.
12. Y. Klenko. Atmospheric DBD Plasma Application for Thin TiO_x Film Deposition // *Proc. of POSTER 2008*, *Prague, May 15, 2008.* CD-ROM.

Article received 22.09.08.

НАНЕСЕНИЕ ТОНКИХ ПЛЕНОК TiO_2 С ИСПОЛЬЗОВАНИЕМ АТМОСФЕРНОГО ДИЭЛЕКТРИЧЕСКОГО БАРЬЕРНОГО РАЗРЯДА

Ю. Кленько, Я. Пихал

Было исследовано влияние температуры прекурсора тетраизопропоксида титана, скорости потока прекурсора и газа на поверхностные свойства пленок диоксида титана, нанесенных в атмосферном диэлектрическом барьерном разряде методом химического осаждения из газовой фазы. Аргон был использован как рабочий газ. Также исследовалось влияние кислорода как окислителя на гидрофильность пленок. Морфология поверхности тонких пленок TiO_2, нанесенных на стеклянные подложки, была исследована атомно-силовой микроскопией и измерением контактного угла. Тестирование методом измерения контактного угла доказало улучшение гидрофильности пленок в экспериментах, проведенных с дополнительной подачей кислорода.

НАНЕСЕННЯ ТОНКИХ ПЛІВОК TiO_2 З ВИКОРИСТАННЯМ АТМОСФЕРНОГО ДІЕЛЕКТРИЧНОГО БАР'ЄРНОГО РОЗРЯДУ

Ю. Кленько, Я. Пихал

Було досліджено вплив температури прекурсору тетраізопропоксиду титану, швидкості потоку прекурсора і газу на поверхневі властивості плівок діоксиду титану, нанесених в атмосферному діелектричному бар'єрному розряді методом хімічного осадження з газової фази. Аргон був використаний як робочий газ. Також досліджувався вплив кисню як окислювача на гідрофільність плівок. Морфологія поверхні тонких плівок, нанесених на скляні підкладки, була досліджена атомно-силовою мікроскопією і виміром контактного кута. Тестування методом виміру контактного кута довело поліпшення гідрофільності плівок в експериментах, проведених з додаванням кисню.