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Investigation of Changes in the Topography of Ti_xO_y Thin Layers under Heat Process

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Abstract: Ti films of the same thickness and near normal deposition angle and the same deposition rate were deposited on glass substrates, at room temperature, under UHV conditions. Due to getting properties of Titanium atoms, they specially react with oxygen during evaporation and Ti_xO_y layers produced. Different annealing temperatures as 130 and 330 Celsius degree with uniform 9 $cm^3\ sec^{-1}$ oxygen flow, were used for producing titanium di oxide layers. Their nano structures were determined by AFM and XRD methods. Roughness of the films changed due to annealing process. The getting property of Ti and annealing temperature, can play an important role on the nano-structure of the films.

Key words: Titanium dioxide, thin films, AFM, XRD

INTRODUCTION

Titanium dioxide (TiO_2) is widely studied by researchers in the basic sciences as well as in engineering. It's phase transformation has been widely studied for optical and electronic applications. This material shows properties that are of special interest in wide range technological of applications such as: photo catalysis, solar cells, gas sensors, hard coating, self-cleaning windows (Karuppasamy and Subrahmanyam, 2007; Dakka *et al.*, 1999), optical wave guiding, optical coatings and microelectronics (Garapon *et al.*, 1996; Durand *et al.*, 1995; Kim *et al.*, 1994), antireflective coatings (Bange *et al.*, 1991), thin film capacitors (Prasad *et al.*, 1997), etc. Besides, these films are extensively used in optical thin film devices, because of their good transmittance in the visible region, high refractive index and chemical stability (Bach and Krause, 1997). As known, TiO_2 crystallizes in three different crystallographic structures: brookite (orthorhombic), rutile (tetragonal) and anatase (tetragonal). Brookite is formed only in extreme preparation conditions, while rutile is the most common TiO_2 crystal phase in nature. Anatase is metastable and thus it can be synthesized only in the restricted range of growth conditions. It is well known, however, that anatase exhibits the highest photocatalytic activity among the crystallographic phases of TiO_2, being more appropriate for related applications (DeLoach and Aita, 1998; Stromme *et al.*, 1996). Nano-crystalline TiO_2 thin films have been prepared up to now by a large variety of growth techniques, such as Metal-Organic Chemical Vapour Deposition (MOCVD) (Prasad *et al.*, 1997; Bach and Krause, 1997), reactive magnetron sputtering (DeLoach and Aita, 1998; Stromme *et al.*, 1996) filtered cathodic vacuum are (Zhao *et al.*, 2004) and Pulsed Laser Deposition (PLD) (Hsieh *et al.*, 2002; Matsui *et al.*, 2005; Nakamura *et al.*, 2005; Gyorgy *et al.*, 2005; Caiteanu *et al.*, 2006; Sharma *et al.*, 2003; Moret *et al.*, 2000; Tsai *et al.*, 2005; Yamamoto *et al.*, 2002), In this research we want to study the influence of annealing temperature and oxygen flow on the nano-structure and roughness of produced layers and also crystallographic directions and Reflectivity of layers and their dependence to mentioned parameters.

MATERIALS AND METHODS

Titanium films of 69 nm thickness were deposited on glass substrates at room temperature. The residual gas was composed mainly of H_2, H_2O, CO and CO_2 as detected by the quad ro pole mass spectrometer. The substrate normal was at 7 degree to the direction of the evaporated beam and the distance between the evaporation crucible and substrate was 43 cm.

Just before use all glass substrates were ultrasonically cleaned in heated acetone, then ethanol. Other deposition conditions were the same during coating. Vacuum pressure was about 4.5×10^{-5} tour and deposition rate was 0.9 A° sec^{-1}. Thickness of the layers were determined by quartz crystal technique. We used annealing oven and different annealing temperatures (130 and 330 Celsius degree) and uniform oxygen flow to change nano structure of layers and produce titanium dioxide layers. The nanostructure of these films was obtained using a Philips XRD X'pert MPD Diffractometer (CuK_α radiation) with a step size of 0.03 and count time of

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1 sec per step, while the surface physical morphology and roughness was obtained by means of AFM (Dual Scope™ DS 95-200/50) analysis.

RESULTS AND DISCUSSION

Figure 1a-c show the morphology of the produced layers in this study (AFM images). Figure 1a shows the AFM image of as deposited Ti film, at room temperature with 69 nm thickness. As it can be seen, the surface is full of small grains.

In presence of annealing temperature at 130°C and in presence of uniform oxygen flow (9 cm^3 sec^{-1}), oxygen will penetrate to the grain structure and brake them down to tinnier needle like grains (Fig. 1b). In Fig. 1c annealing temperature increases to 330°C and as it can be seen the grains are domed and clearly bigger. This is because of surface diffusion in this temperature so migration of grains will dominate to penetrating oxygen flow and grains are domed and bigger.

Figure 2 shows the diagram of roughness for layers produced in this work. In presence of annealing

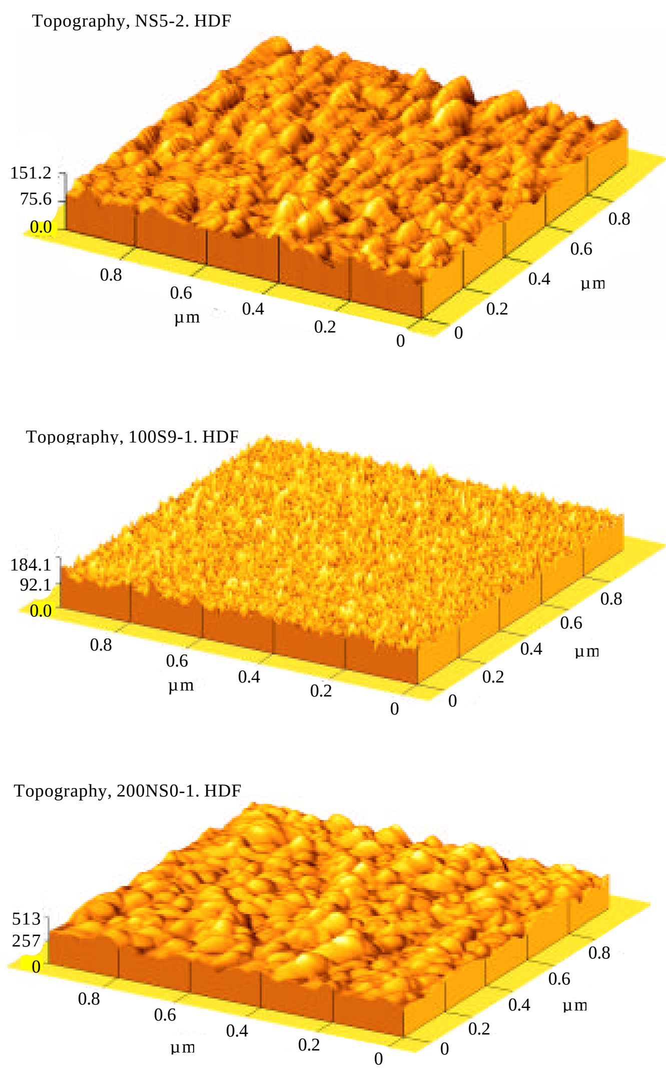

Fig. 1(a-c): AFM images of the as-deposited (a) Ti film and films annealed at (b) 130 K and (c) 330 K. The flow rate of oxygen during annealing was the same for all films, 9 cm^3 sec^{-1}

temperature, at first, roughness decreases, that is because of oxygen penetration to grain structure and break them down, that tends to uniform surface. But at 330°C annealing temperature and in presence of oxygen flow, because of surface diffusions and migration of grains, bigger domed grains appear, so roughness increases.

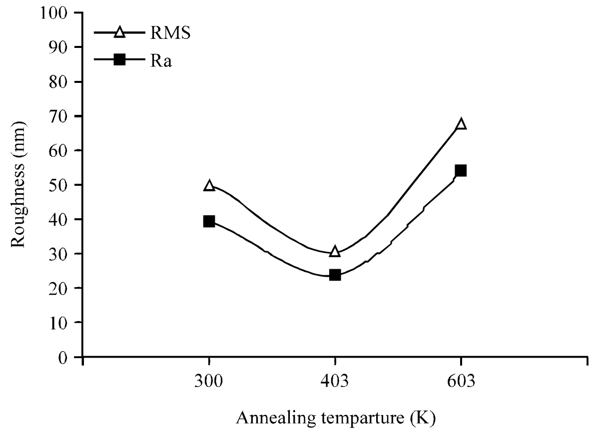

Fig. 2: The roughness diagram of the as-deposited.

As we know Ti is a getter metal and in presence of oxygen and heat will be Converted to Ti_xO_y combinations.

Figure 3a-c, shows XRD images for the layers produced in this work.

As it can be seen from Fig. 3a and b, the layers are amorphous and there is no crystallographic direction. By increasing annealing temperature to 330°C and in presence of oxygen flow, Titanium Dioxide produced. Although, we use a thick 69 nm thickness Titanium layer, as it can be seen from Fig. 3c, two anatase A (004) and A (105) crystallographic directions, appear.

Figure 4 shows the Reflection of the layers produced in this work. As it can be seen, as deposited layer has

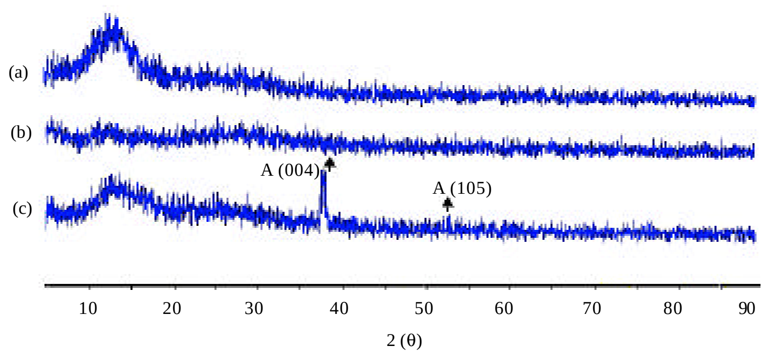

Fig. 3: The XRD patterns of the as-deposited (a) Ti film and films annealed at (b) 130 K and (c) 330 K. The flow rate of oxygen during annealing was the same for all films, 9 cm^3 sec^{-1}

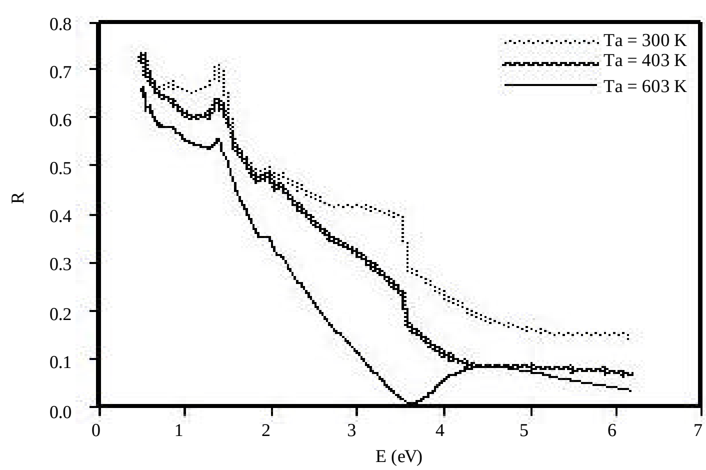

Fig. 4: The reflectance diagram of the films annealed at 130 K (a) and 330 K (b). The flow rate of oxygen during annealing was the same for all films, 9 cm^3 sec^{-1}

more Reflection than two other layers. By increasing annealing temperature in presence of uniform oxygen flow, because of surface diffusion and coalescence of grains more voids appear on layers and the Reflection has a decreasing trend.

CONCLUSION

The influence of annealing temperature and uniform oxygen flow on titanium layers of the same thickness were obtained. This was accomplished by studying the relationship between AFM and XRD results. The morphology of the layers changes by increasing heat and in presence of oxygen. By increasing annealing temperature and in presence of oxygen flow, at first, oxygen penetrates to grains structures and brake them down to needle like grains. By increasing heat, because of surface diffusion, grains get domed and bigger. Roughness decreases at first step and increases for the layer with 330°C annealing temperature, that is in agreement with AFM results. XRD patterns showed anatase structure in A (004) and A (105) crystallographic directions for the layer of 69 nm thickness in presence of 330°C annealing temperature. XRD patterns were amorphous for as deposited titanium layer in presence of 130°C annealing temperature. As it can be seen from XRD patterns, x is one and y is two and we have TiO_2 for this research at 330°C temperature and the other layers are amorphous. By increasing annealing temperature reflection has a decreasing trend because of migration of grains and formation of more voids on the layers.

REFERENCES

Bach, H. and D. Krause, 1997. Thin Films on Glass. Springer, Heidelberg, pp: 103.

Bange, K., C.R. Ottermann, O. Anderson, U. Jeschkowski, M. Laube and R. Feile, 1991. Investigations of TiO_2 films deposited by different techniques. Thin Solid Films, 197: 279-285.

Caiteanu, D., E. Gyorgy, S. Grigorescu, I.N. Mihailescu, G. Prodan and V. Ciupina, 2006. Growth of oxide thin films for optical gas sensor applications. Applied Surf. Sci., 252: 4582-4586.

Dakka, A., J. Lafait, M. Abd-Lefdil and C. Sella, 1999. Optical study of titanium dioxide thin films prepared by R.F. sputtering. Moroc. J. Cond. Matter, 2: 153-156.

DeLoach, J.D. and C.R. Aita, 1998. Thickness-dependent crystallinity of sputter-deposited titania. Vac. Sci. Technol. A. Vol. 16, 10.1116/1.581204.

Durand, H.A., J.H. Brimaud, O. Hellman, H. Shibata and S. Sakuragi *et al*., 1995. Excimer laser sputtering deposition of TiO_2 optical coating for solar cells. Applied Surf. Sci., 86: 122-127.

Garapon, C., C. Champeaux, J. Mugnier, G. Panczer, P. Marchet, A. Catherinot and B. Jacquier, 1996. Preparation of TiO_2 thin films by pulsed laser deposition for waveguiding applications. Applied Surf. Sci., 96-98: 836-841.

Gyorgy, E., G. Socol, E. Axente, I.N. Mihailescu, C. Ducu and S. Ciuca, 2005. Anatase phase TiO_2 thin films obtained by pulsed laser deposition for gas sensing applications. Applied Surf. Sci., 247: 429-433.

Hsieh, C.C., K.H. Wu, J.Y. Juang, T.M. Uen, J.Y. Lin and Y.S. Gou, 2002. Monophasic TiO_2 films deposited on $SrTiO_3$(100) by pulsed laser ablation. J. Applied Phys., Vol. 92, 10.1063/1.1499522

Karuppasamy, A. and A. Subrahmanyam, 2007. Studies on the room temperature growth of nanoanatase phase TiO2 thin films by pulsed dc magnetron with oxygen as sputter gas. J. Applied Phys., Vol. 101, 10.1063/1.2714770

Kim, T.W., M. Jung, H.J. Kim, T.H. Park and Y.S. Yoon *et al*., 1994. Optical and electrical properties of titanium dioxide films with a high magnitude dielectric constant grown on p-Si by metalorganic chemical vapor deposition at low temperature. Applied Phys. Lett., Vol. 64, 10.1063/1.111898.

Matsui, H., H. Tabata, N. Hasuike, H. Harima and B. Mizobuchi, 2005. Epitaxial growth and characteristics of N-doped anatase TiO_2 films grown using a free-radical nitrogen oxide source. J. Applied Phys., Vol. 97, 10.1063/1.1929889

Moret, M.P., R. Zallen, D.P. Vijay and S.B. Desu, 2000. Brookite-rich titania films made by pulsed laser deposition. Thin Solid Films, 366: 8-10.

Nakamura, T., T. Ichitsubo, E. Matsubara, A. Muramatsu, N. Sato and H. Takahashi, 2005. Preferential formation of anatase in laser-ablated titanium dioxide films. Acta Mater., 53: 323-329.

Prasad, K., A.R. Bally, P.E. Schmid, F. Levy, J. Benoit, C. Barthou and P. Benalloul, 1997. Ce-doped TiO_2 insulators in thin film electroluminescent devices. Jpn. J. Applied Phys., 36: 5696-5702.

Sharma, A.K., R.K. Thareja, U. Wilier and W. Schade, 2003. Phase transformation in room temperature pulsed laser deposited TiO2 thin films. Applied Surf. Sci., 206: 137-148.

Stromme, M., A. Gutarra, G.A. Niklasson and C.G. Granqvist, 1996. Impedance spectroscopy on lithiated Ti oxide and Ti oxyfluoride thin films. J. Appl. Phys., 79: 3749-3757.

Tsai, M.H., S.Y. Chen and P. Shen, 2005. Laser ablation condensation of TiO_2 particles: Effects of laser energy, oxygen flow rate and phase transformation. J. Aerosol Sci., 36: 13-25.

Yamamoto, S., T. Sumita, T. Yamaki, A. Miyashita and H. Naramoto, 2002. Characterization of epitaxial TiO_2 films prepared by pulsed laser deposition. J. Cryst. Growth, 237: 569-573.

Zhao, Z.W., B.K. Tay, S.P. Lau and G.Q. Yu, 2004. Optical properties of titanium films prepared by off-plane filtered cathodic vacuum arc. J. Crystal Growth, 268: 543-546.