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Structural Analysis of RF Sputtered TiO_2 Thin Film on Cu Substrate for Various Annealing Temperatures

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***Abstract* — The structural parameters of RF sputtered TiO_2 thin film deposited on Cu substrates was tested using XRD spectra. Prepared TiO_2 thin film was polycrystalline nature with the mixture of cubic, orthorhombic and tetragonal phases. Orthorhombic phase was preferentially grown on Cu substrate. The crystallite size of the TiO_2 thin film was varied depends on the orientations and overall decreased crystallite size was noticed upto 300 °C. The observed residual stress was compressive nature as dominated at all temperature other than 400°C. Crystal defects such as dislocation density was high for cubic phase of TiO_2 at higher annealing temperature. Overall, the annealing temperatures influenced the structural parameters with respect to the observed orientations of TiO_2 thin film on Cu substrates.**

***Keywords*— TiO_2 thin film, XRD, Structural properties, residual stress.**

I. INTRODUCTION

Titanium dioxide (TiO_2) is an interesting material with many possible thin film applications. It has properties such as good chemical and abrasion resistance, high refractive index with excellent transmittance in the visible and near-infrared wavelength region [1–3]. Its semiconductor properties also make it as a suitable electrode material for the conversion of light energy into electrical energy. It is transparent to visible light, has high refractive index and excellent chemical stability over a wide pH range and in a large number of solvents [4]. There are three different crystalline phases of TiO_2, namely anatase, rutile, and brookite [5]. In addition, amorphous TiO_2 films are often observed when deposition temperature is low. Depending on the phase structure, the TiO_2 films can be tailored for different applications. So it is necessary to understand the phase structure of TiO_2 when it is deposited on different substrates. Normally, the TiO_2 thin film was deposited on Si substrates for semiconductor applications [6]. There have been many research works focused on metal substrate for TiO_2 thin film [7], [8] and [9]. Even though the TiO_2 thin film have been deposited on various metal substrates, stainless steel [10], Ni [11], most of the research papers on TiO_2 film are involved only in the study of the crystal structure, the catalytic reaction, etc. However, not many works have been undertaken to estimate the structural parameters such as stress, internal strain, dislocation density etc., with respect to their orientations. Thin film of titanium dioxide have been prepared by various methods such as rf magnetron sputtering, ion beam sputtering, e-beam evaporation, sol–gel, atomic layer epitaxy (ALE) and chemical vapour deposition (CVD).

From the published work, the preparation technique and processing conditions have a strong influence on the microstructure and physical properties of the material. Each of these methods has its own advantages and limitations [12]. Among the available TiO_2 thin film preparation techniques, Reactive rf sputtering is widely used to prepare Ti compound thin films such as TiO_2 and TiN [13]. In this work, TiO_2 thin film was prepared on various substrates by rf sputtering and studied their structural parameters by using XRD spectra.

II. EXPERIMENTAL METHOD

TiO_2 thin films were deposited on Cu substrates (23cm x 25 cm) using TiO_2 (99.99% purity) target (3 inch in diameter and 4 mm in thickness) using high pure Ar (99.999%) by RF sputtering (Edwards make, Model-Auto 500). Ultrasonically cleaned Cu substrates were used for coating. Initially, the sputtering system was pumped down to 2.6×10^{-6} mbar and loaded the sputtering target and substrates by venting the chamber. Before the TiO_2 thin film deposition, pre-sputtering was carried out for about 5 min at Ar pressure of 3.5×10^{-3} to remove the surface oxidation of the target and started the TiO_2 film coating. All thin film coating was prepared at 0.6 Å / sec deposition rate. 150W RF power was used to sputter the TiO_2 target and achieved 300 nm thickness which was monitored by digital thickness monitor during the TiO_2 film deposition. The substrate to target distance was fixed at 7 cm for all coating. After thin film preparation, the samples were annealed at various temperatures from 100 to 400 °C (100 °C step) for about 1 hr in CVD tube furnace at air atmosphere. For discussion, the as grown film is mentioned as the annealing temperature at 25°C throughout this manuscript.

The processed samples were tested for their structural parameters by X-ray Diffraction technique (XRD-Siemens diffractometer D5000) and the structural parameters such as micro-strain, dislocation density, crystallite size, internal stress and texture coefficient were evaluated and discussed here.

III. RESULT AND DISCUSSION

The XRD spectra of TiO_2 thin film deposited on Cu substrates are recorded as shown in fig.1. Table – 1 shows the observed peak positions and other structural properties for the TiO_2 thin film deposited on Cu substrate at various annealing temperature. The observed phases of TiO_2 are indexed by using JCPDS data as shown in fig. 1. Fig. 1 clearly indicates that the deposited TiO_2 on Cu substrates are polycrystalline nature and noticed the mixed phases from orthorhombic, tetragonal and cubic with respect to annealing temperatures. It is understood from the fig.1 that the annealing temperature also influences on changing the crystallite phases of TiO_2 when it is deposited on Cu substrates. At the diffraction angle at at ~2θ = 48.30°, the phase and orientation conversion from orthorhombic with (321) orientation to tetragonal with (200) orientation are noticed for the annealing temperature at 100°C.

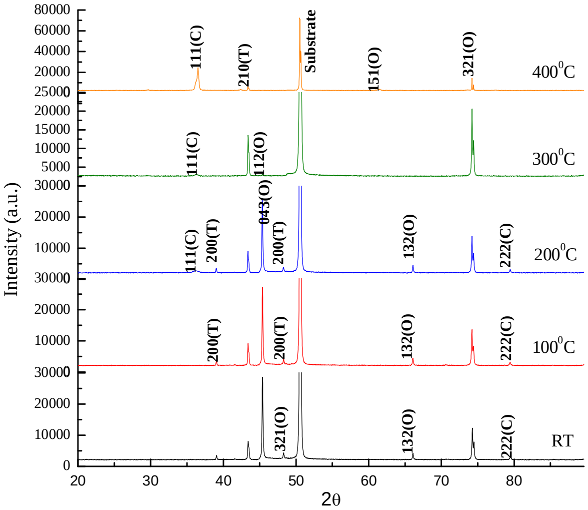

Fig.1. XRD spectra of annealed TiO_2 thin film deposited on Cu substrates at various temperatures.

In order to understand clearly the preferred growth, the texture coefficient was calculated using the formula in equation (1) [14].

$$P_i\ (TC) = N\,(I_i/I_o)/\sum(I_i/I_o) \qquad (1)$$

Where P_i is the Texture Coefficient of the plane I, I_i is the measured intensity, I_o is the intensity of the JCPDS powder diffraction pattern of the corresponding peak and N is the number of reflections considered for the analysis. When P_i is greater than unity, it is indicating that the peak is preferred orientation of the crystallites in that particular direction. The texture coefficient was calculated using the equation (1) and the results are summarized in Table – 1. As compared with standard JCPDS data, the TC value of the orthorhombic phase with (321) orientation is high and exhibited the preferred orientation with the other phases. The TC value is increasing for the annealing temperature increases from 100 to 400°C.

Since our process related to annealing temperature, it is expected to increases the crystallite size for TiO_2 thin film. Consequently, the crystallite size for all phases is calculated from the Debye - Sherrer's equation [15] and the observed values are given in table – 1.

$$D = 0.9\,\lambda/\beta\cos\theta \qquad (2)$$

Where λ is the wavelength of X-ray, β is the full-width at half-maximum of the peak (in radian), and the θ is the Bragg's angle of the X-ray diffraction peaks.

It is observed form the table – 1 that the crystallite sizes are varied with respect to the orientation of the growth. Especially, very low crystallite size cold be observed with cubical phase with (111) orientation but this phase is observed only the samples annealed at 200° C and above. Generally, the grain growth is expected during annealing process but decreased crystallite size is observed as the annealing temperature increases. Overall, the crystallite size decreases for most of the observed phases contrarily.

In addition to the changes in crystallite size, some other crystal defects may induce with respected to the annealing temperature. Consequently, crystal dislocation is the main defect related to crystallite size. It has to be addressed and hence the dislocation density available in the TiO_2 crystal is calculated from the formula [16];

$$\delta = 1 / D^2 \qquad (3)$$

where D is the crystallite size of TiO_2 thin film. The observed results are summarized in table – 1. It is evidenced the effect of crystallite size on the dislocation density of TiO_2 thin film. High value in dislocation density is observed with cubic phase for (111) orientation. Overall, the dislocation density increases with the annealing temperature increases. It may be due to the phase conversion from tetragonal to orthorhombic at high temperatures.

During the crystal growth on various surfaces, there may be possible for developing the stress as a result of growth temperature with respect to the substrate surface. In crystal, the residual stress is one which remains in material without application of an external load. Usually originates during synthesis and processing of materials due to heterogeneous plastic deformations, thermal contractions and phase transformations. Since our studies showed several phase transformation, it is necessary to study the residual stress of TiO_2 when it is deposited on Cu substrates. It is also evaluated using the following equation [17];

TABLE I: STRUCTURAL PARAMETERS OF RF SPUTTERED TIO_2 THIN FILM ON CU SUBSTRATES

2θ	FWHM	Crystallite size (nm)	*d* space	Texture coefficient	Residual stress (GPa)	Dislocation density (lines/m^2)	Phase	
Room Temperature (25°)								
39.08	0.0787	107	2.306	0.11	-0.0214	8.7215E+13	200	T
43.41	0.0984	87	2.084	0.60	-2.4325	1.32519E+14	210	T
45.39	0.1181	73	1.998	0.83	-2.1417	1.88219E+14	043	O
48.30	0.0787	111	1.884	0.04	0.7987	8.17637E+13	321	O
66.08	0.1200	79	1.413	0.09	-2.5020	1.60441E+14	132	O
74.27	0.1200	83	1.276	5.30	0.3321	1.45104E+14	321	O
79.48	0.1680	61	1.205	0.05	-0.0689	2.64596E+14	222	C
100°C								
39.04	0.0984	86	2.306	0.11	-0.0671	1.36E+14	200	T
43.42	0.1920	45	2.083	0.64	-2.2728	5.05E+14	210	T
45.39	0.1200	72	1.997	0.71	-1.9671	1.94E+14	043	O
48.28	0.0960	91	1.883	0.04	1.1318	1.22E+14	200	T
66.08	0.1440	66	1.413	0.09	-2.5193	2.31E+14	132	O
74.21	0.1200	83	1.277	5.37	0.1686	1.45E+14	321	O
79.44	0.0960	108	1.205	0.05	-0.1247	8.64E+13	222	C
200°C								
36.18	0.6298	13	2.476	0.58	0.2202	5.6825E+15	111	C
39.02	0.0984	86	2.308	0.11	-0.2060	1.36394E+14	200	T
43.40	0.0787	109	2.086	0.65	-2.5527	8.47751E+13	210	T
45.38	0.0984	87	1.999	0.72	-2.2407	1.30673E+14	043	O
48.32	0.1181	74	1.884	0.04	0.8520	1.84094E+14	200	T
66.08	0.1200	79	1.413	0.10	-2.4832	1.60441E+14	132	O
74.21	0.1200	83	1.277	5.79	0.1879	1.45218E+14	321	O
79.42	0.1440	72	1.205	0.05	-0.1787	1.94566E+14	222	C
300°C								
36.28	0.5510	15	2.477	0.001	0.0924	4.347E+15	111	C
43.42	0.1200	71	2.083	0.32	-2.2376	1.97071E+14	210	T
45.40	0.0960	90	1.996	---	-1.9181	1.24359E+14	112	O
74.21	0.1200	59	1.277	2.68	0.2055	2.90302E+14	321	O
400°C								
36.51	0.1968	42	2.461	0.11	1.5787	5.5381E+14	111	C
42.43	0.1968	43	2.131	---	-0.0463	5.33653E+14	221	O
43.40	0.0590	145	2.085	0.32	-2.5102	4.76459E+13	210	T
61.44	0.2160	43	1.507	---	1.2737	5.46688E+14	151	O
74.21	0.0720	68	1.277	2.7	0.1932	2.14017E+14	321	O

**C – Cubic, O – Orthorhombic and T – Tetragonal*

$$\sigma = -E\,(d_a - d_o) / (2d_o\,Y) \qquad (4)$$

where E and Y are the Young's modulus (157 GPa) and the Poisson's ratio(0.35) of TiO_2 respectively [18]. d_a and d_0 are the *d* spacing of bulk and TiO_2 thin film from JCPDS data. Residual stress is classified into two: a) tensile stress is the stress that can be applied to an object by pulling on it, or attempting to stretch it. Positive values of stress indicate tensile stress. b) Compressive stress is the stress applied to materials resulting to their compaction (decrease of volume). Negative values of stress indicate compressive stress.

The stress developed during the synthesis and also annealing process of TiO_2 thin film on Cu substrates are evaluated using the relation (4) and the observed values are summarized in table -1. It is clear that the residual stress is related to the crystal growth orientations and it varies also with respect to annealing temperature. Table - 1 shows that the as grown TiO_2 on Cu is having more compressive stress than annealed samples. It is also noticed that the tensile stress is created during the annealing of TiO_2 at 400°C. Overall, at all temperature, compressive stress is dominated with respect to the annealing temperature. High value and low value in residual stress (compressive) could be observed for the tetragonal phase with (210) orientation (at 200°C) and (200) orientation (at room temperature) respectively. Similarly, high and low value in tensile stress developed in the TiO_2 thin film was identified for cubic phase with (111) orientation at 400 and 300 °C respectively.

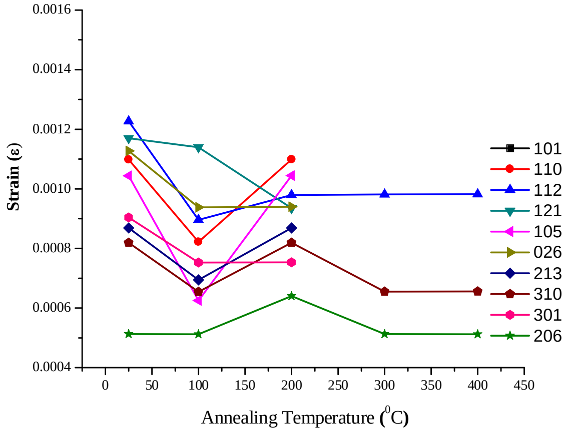

Fig.2. Variation in micro strain observed in TiO_2 for different orientations

If the stress is identified, the strain occurs consequently. In order to study in detail, the strain created during the synthesis as well as annealing process was calculated using the related between full width half maximum of the peak and the diffraction angle observed from the XRD spectra as given below;

$$\varepsilon = \beta \cos\theta / 4 \qquad (5)$$

Where β is FWHM and θ is half diffraction angle. The strain developed in the prepared TiO_2 thin film on Cu substrates for various temperatures are plotted in fig.2 and shows the change in strain with respect to different orientations present in the prepared thin film. Fig. 2 reveals that the strains observed for TiO_2 thin film lies in between 0.0003 to 0.0023. A noticeable change in strain could be observed for tetragonal phase with (210) orientation when the sample annealed at 100 °C. A small change in strain is also observed for some other orientations (132), (200) and (222) at the same annealing temperature of 100°C.

IV. CONCLUSIONS

TiO_2 thin film was synthesized on Cu substrates by RF sputtering followed by annealing at various temperatures. The structural parameters were evaluated for various temperatures and noticed the influence on TiO_2 structural properties with respect to the phase as well as their orientations. Polycrystalline phase was observed with orthorhombic phases as dominated and preferentially grown along with cubic and tetragonal phase. Non-linear change in crystallite size was observed and low value was observed with 300°C. Compressive stress was dominated at all temperatures other than 400°C.

REFERENCES

[1] A. Islam, S.P. Singh, and L. Han, "Thiocyanate-Free Panchromatic Ruthenium (II) Terpyridine sensitizer having a Tridentate Diethylenetriamine Ligand for near-IR sensitization of the nanocrystaline TiO_2," *Functional Materials Letters*, Vol. 4, pp. 21–24, 2011.

[2] J.G. Yu, and X.J. Zhao, "Effect of substrate on the photocatalytic activity of nanometer TiO_2 thin films," *Material Research Bulletin*, Vol.35, pp. 1293-1301, 2000.

[3] S.C. Sun, and T.F. Chen, "Effects of electrode materials and annealing ambients on the electrical properties of $\bf TiO_{2}$ thin films by metalorganic chemical vapor deposition," *Japanese Journal of Applied Physics*, Vol.36, pp. 1346-1350, 1997.

[4] B. Guo, Z. Liu, L. Hong, H. Jiang, and J. Yang-Lee, "Photocatalytic effect of the sol-gel derived nanoporous TiO_2 transparent thin film," *Thin Solid Films*, Vol.479, pp.310-315, 2005.

[5] P. Zeman, S. Takabayashi, "Nano-scaled photocatalytic TiO_2 thin films prepared by magnetron sputtering," *Thin Solid Films*, Vol.433, pp.57-62, 2003.

[6] W. Zhou, X. Zhong, X. Wu, L. Yuan, Q. Shu and Y. Xia, "Structural and Optical Properties of Titanium Oxide Thin Films Deposited on Unheated Substrate at Different Total Pressures by Reactive dc Magnetron Sputtering with a Substrate Bias" *Journal of the Korean Physical Society*, Vol. 49, No. 5, pp. 2168-2175, 2006

[7] P.R. Mishra, P.K. Shukla, and O.N. Srivastava, "Study of modular PEC solar cells for photoelectrochemical splitting of water employing nanostructured TiO_2 photoelectrodes," *International Journal of Hydrogen Energy*, Vol.32**,** pp. 1680-1685, 2007.

[8] M.G. Kang, N.G. Park, K.S. Ryu, S.H. Chang, and K.J. Kim, "A 4.2% efficient flexible dye-sensitized TiO_2 solar cell using stainless steel substrate," *Solar Energy Material Solar Cells*, Vol.90, pp. 574-581, 2006.

[9] A. Maloney, and E.L. Schoonman, "Gas-Phase synthesis of nanostructured anatase TiO_2," *Journal of Chemical Vapor Deposition*, Vol.4, pp.109-114, 1998.

[10] J. Krzak-Roś, J.Filipiak, C. Pezowicz, A. Baszczuk, M. Miller, M. Kowalski, and R. Będzińsk, "The effect of substrate roughness on the surface structure of TiO2, SiO2, and doped thin films prepared by the sol gel method," *Acta of Bioengineering and Biomechanics*, Vol.11, pp.21-29, 2009.

[11] P. Sun, H. Liu, H. Yang, W. Fu, S. Liu, M. Li, Y. Sui, Y. Zhang, and Y. Li, "Synthesis and characterization of TiO_2 thin films coated on metal substrate," *Applied Surface Science*, Vol.256, pp.3170-3173, 2010.

[12] A. H. Mayabadi , V. S. Waman , M. M. Kamble, S. S. Ghosh , B. B. Gabhale , S. R. Rondiya , A.V.Rokade , S. S. Khadtare , V. G. Sathe , H. M. Pathan , S. W. Gosavi , and S. R. Jadkar, "Evolution of structural and optical properties of rutile TiO_2 thin films synthesized at room temperature by chemical bath deposition method," *Journal of Physics and Chemical of Solids*, Vol.75**,** pp.182-187, 2014.

[13] H. Kikuchi, M. Kitano, M. Takeuchi, M. Matsuoka, M. Anpo, P. V. Kamat, "Extending the Photoresponse of TiO_2 to the Visible Light Region: Photoelectrochemical Behavior of TiO_2 Thin Films Prepared by the Radio Frequency Magnetron Sputtering Deposition Method" *Journal of Physical Chemistry B*, Vol. 110, pp. 5537 - 5541 (2006).

[14] H. Hadouda, J. Pouzet, J. C. Bernede, and A. Barreau, "MoS_2 thin film synthesis by soft sulfurization of a molybdenum layer," *Material Chemistry and Physics*, pp.42, pp.291-297, 1995.

[15] B.D. Cullity, In: *Elements of X-Ray Diffraction*. 2nd edition. Cohen M, editor. Reading, Mass, USA: Addison-Wesley; 1978.

[16] C. Mehta, J. Abass ,G. Saini, S. Tripathi, "Effect of deposition parameters on the optical and electrical properties of nanocrystalline CdSe", *Chalcogenide Letter.*, Vol. 11, pp. 133 - 138 2007.

[17] A.J. Perry, "The state of residual stress in TiN films made by physical vapor deposition methods; the state of the art", *Journal of Vacuum Science Technology A.*, Vol. 8, pp. 1351 – 1358, 1990.

[18] L. Borgese, M. Gelfi, E. Bontempi, P. Goudeau, G. Geandier, D. Thiaudière, and L.E. Depero, "Young modulus and Poisson ratio measurements of TiO_2 thin films deposited with atomic layer deposition," *Surface and Coating Technology*, Vol.206, pp.2459-2463, 2012.