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Incidența minimă a suspiciunii / Minimum incidence of suspicion

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ANATASE – RUTIL TiO₂ THIN FILMS DEPOSITED IN A D.C. MAGNETRON SPUTTERING SYSTEM*

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Anatase TiO₂ thin films were deposited in a d.c. reactive magnetron sputtering system. It was found that there is a strong dependence between anatase-rutil structures of TiO₂ films and the technological conditions, the most relevant parameter being the oxygen percentage from the argon and oxygen mixture. Our measurements carried out for electrical properties of d.c. magnetron sputtering TiO₂ thin films revealed that it is possible to obtain TiO₂ films with controllable structure and properties.

Key words: TiO₂, d.c. magnetron, anatase, rutil, electrical properties.

1. INTRODUCTION

Titanium dioxide has been intensively studied over the last decades, because of its wide interesting technological applications [1–6]. Titanium dioxide occurs in three crystalline polymorphs: rutile (tetragonal) with D_{4h}^{14} -P4₂/mmm symmetry, anatase (tetragonal) with D_{2h}^{19} – I4₁/amd symmetry and brookite (orthorhombic) with D_{2h}^{15} -Pabc symmetry [1]. Rutile is known to be the most stable phase. Brookite and anatase are thermodynamically less stable than rutile. Heating the films at a temperature near 900°C converts them to rutile phase [7]. In contrast to the extensive studies on the rutile phase, very little is known about the other two less stable phases. The electrical properties of these less stable phases are often assumed to be similar to those of rutile. The recent interest in anatase revealed new significant differences in electrical properties related to rutile [8]. There have been found differences for dielectric constants, carrier effective mass, Hall mobility [8, 9]. The present work is motivated by the distinct properties of anatase versus rutile phase and as well as by the fact that thin films are often required for practical use. A better knowledge of these differences and the correlation with the technologically parameters should be beneficial to

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further exploitation of the electrical and optical properties of TiO₂ thin films, particularly in optoelectronic devices.

2. EXPERIMENTAL DETAILS

The films were deposited in a home built magnetron sputtering system [10]. The vacuum chamber was an 80 l volume stainless steel chamber; a circular magnetron with a 60 mm diameter erosion zone was used as the cathode. The discharge characteristics have been controlled using a variable d.c. power supply (3kV and 500 mA). Pure titanium (99.7) of 136 mm diameter and 3 mm thickness has been used as a sputtering target. Pure argon (4N) and oxygen were used as the sputtering and reactive gases respectively. The gases, argon and oxygen, were mixture prior the admission in the sputtering chamber at different volumetric proportion. The target substrate distance was 35 mm. Prior the deposition, the target was well cleaned in order to remove the surface oxides layers. The substrate temperature was varied by using a quartz halogen lamp whose power was controlled by varying the input voltage. Titanium oxide films were deposited on glass slides, polycrystalline silicium and KBr crystals. For investigation of the electrical properties sandwich-type and surface-type cells have been obtained on glass slides (50 × 25 × 1.5 mm) by vacuum deposition of the aluminum thin film (bottom electrode) than TiO₂ thin films that we have to investigate than the top electrode (aluminum thin films).

The sputtering time was chosen in order to obtain films of several thickness and the sputtering power was about 110 W (200 mA × 550 V), that is corresponding to a power density of 1.25 W/cm². The thickness of the films has been evaluated by using a multiple beam interferometry method to an accuracy of ± 10 nm. The structure M-O-M surface was about 10 mm².

The structure of the films was examined by using X-ray diffraction with Cu K_α radiation in a standard X-ray diffractometer (DRON). The conductivity of the films was recorded by four probe methods that is sensitive for resistivity up to 10¹¹ Ω·cm.

3. EXPERIMENTAL RESULTS

It was experimentally setup that the stable structures of films can be obtained if after preparation, the films are thermally treated in a vacuum better than 10⁻³ Torr, within a given temperature range between 300–350°C, for one hour. For the thermally treated samples, the temperature dependencies of the electrical conductivity become reversible.

X-ray diffraction analysis revealed that TiO₂ thin films are amorphous if the temperature substrate is lower than 250°C [10], and the sputtering pressure is higher than 10⁻² Torr. For TiO₂ thin films deposited for substrate temperature higher than 250°C and sputtering pressure lower than 5·10⁻³ Torr, we have found that the films are polycrystalline (Fig. 1), and for temperatures higher than 400°C, there are revealed the rutile diffraction peaks.

The temperature influence for electrical conductivity of TiO₂ thin films revealed that the electrical conductivity is thermally activated (Fig. 2) and we have found that the activation energies for anatase thermally treated films is varying from 1.55 eV and 0.76 eV.

For rutile thermally treated films it was found that the activation energy is varying between 21.3 and 16.4 eV.

We have studied the electrical conductivity, nonlinear I-U characteristics [11], in order to find the carrier effective mass and dielectric properties for d.c. magnetron TiO₂ thin films.

Fig. 1 – X-Ray diffraction of TiO₂ magnetron thin films.

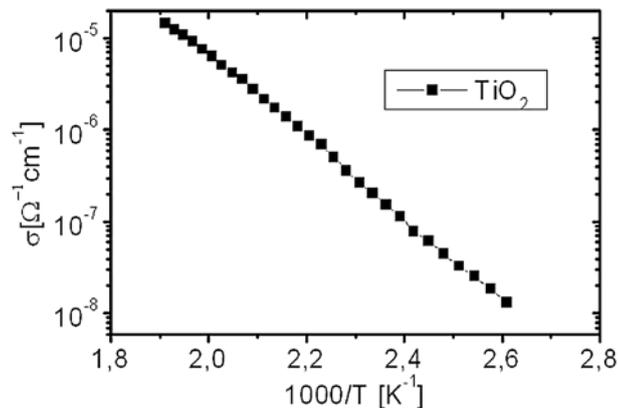
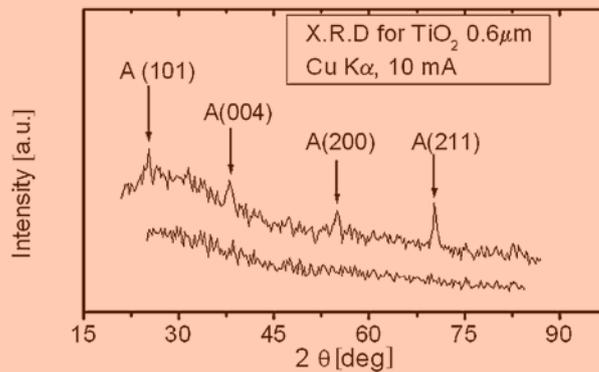


Fig. 2 – Thermally activated Conductivity.

From the nonlinear I-U characteristics (Fig. 3), we have found for the carrier effective mass values between 1.26 and $0.71 m_0$ for films with anatase structures.

In Table 1 are presented briefly the differences in electrical properties for anatase and rutile phases for TiO_2 thin films deposited by a d.c. magnetron sputtering system.

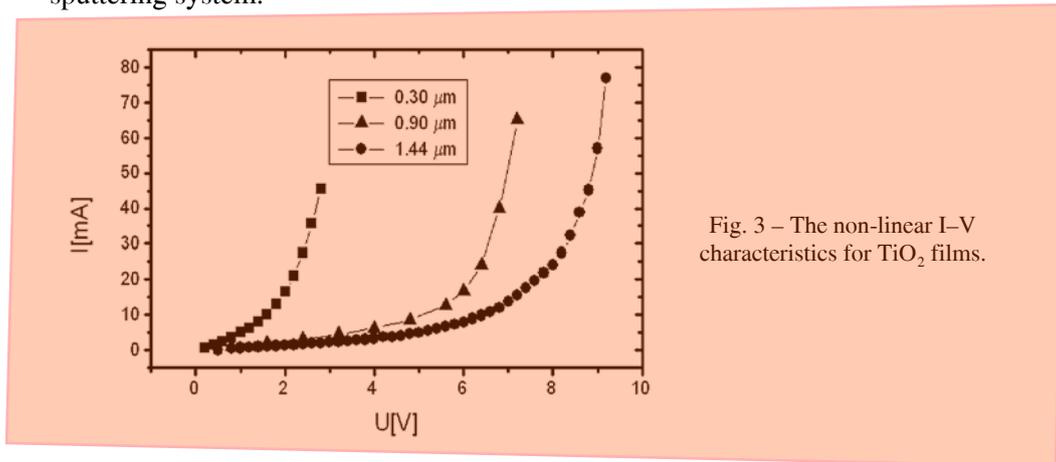


Fig. 3 – The non-linear I–V characteristics for TiO_2 films.

Table 1

Differences in electrical properties for anatase and rutile phases

Properties	Rutile	Anatase
Static dielectric constant	~ 100	~ 30
Thermally activation energy	~ 1,5 eV	~ 0,7 eV
Carrier effective mass	~ 20 m_0	~1 m_0

According to these results it is possible that from the electrical measurements to identify with a good accuracy the crystalline structure for TiO_2 thin films and to obtain TiO_2 films with controllable structure and properties. From the experimental results we may conclude that there are significant differences in electrical properties for the anatase and rutile phase of titania that could be used in order to design film with predictable properties.

CONCLUSION

In the paper we have studied the differences in structural and electrical properties of TiO_2 thin films prepared by a d.c. magnetron sputtering system. It was found that in dependence of the sputtering parameters and the thermally treatment after deposition it is possible to obtain films with controllable anatase or rutile structures.

REFERENCES

1. B. Karunagara, Kyunghae Kim, D. Mangalaraj, Junsin Yi, S. Velumani, *Structural, optical and Raman scattering studies on DC magnetron sputtered titanium dioxide thin films*, Solar Energy Materials & Cells, 88, 199–208, 2005.
2. B.-S. Jeong, D. P. Norton, J. D. Budai, *Conductivity in transparent anatase TiO₂ films epitaxially grown by reactive sputtering deposition*, Solid State Electronics, 47, 2275–2278, 2003.
3. P. Zeman, S. Takabayashi, *Effect of total and oxygen partial pressures on structure of photocatalytic TiO₂ films sputtered on unheated substrate*, Surface and Coating Technology, 153, 93–99, 2002.
4. K. Okimura, *Low temperature growth of rutile TiO₂ films in modified rf magnetron sputtering*, Surface and Coating Technology, 135, 286–290, 2001.
5. Diana Mardare, G. I. Rusu, *Structural and electrical properties of TiO₂ RF sputtered thin films*, Materials Science and Engineering B, 75, 68–71, 2000.
6. Yoshie Ishikawa, Yasumichi Matsumoto, *Electrodeposition of TiO₂ photocatalyst into nanopores of hard alumite*, Electrochimica Acta, 46, 2819 – 2824, 2001.
7. Cheol Ho Heo, Soon-Bo Lee, Jin-Hyo Boo, *Deposition of TiO₂ thin films using RF magnetron sputtering method and study of their surface characteristics*, Thin Solid Films, 475, 183–188, (2005).
8. O. Fan, B. McQuillin, A. K. Ray, M. L. Turner, A. B. Seddon, *High density, non-porous anatase titania thin films for device applications*, J. Phys. D, Appl. Phys. 33, 2683–2686, 2000.
9. B. H. Park, L. S. Li, B. J. Gibbons, J. Y. Huang, Q. X. Jia, *Photovoltaic response and dielectric properties of epitaxial anatase-TiO₂ films grown on conductive electrodes*, Appl. Phys. Letters, 79 (17) , 2797–2799, 2001.
10. M. Stamate, *Dielectric properties of TiO₂ thin films deposited by a dc magnetron sputtering system*, Thin Solid Films, 372, 246–249, 2000.
11. M. Stamate, *On the non-linear I–V characteristics of dc magnetron sputtered TiO₂ thin films*, Appl. Surf. Sci., 205, 353–357, 2003.