Bulg. J. Phys. **40** (2013) 253–257

Temperature Tuning of Optical Properties of High Refractive Index Metal Oxide Films Obtained by the Sol-Gel Method*

T. Babeva, K. Lazarova, M. Vasileva, B. Gospodinov, J. Dikova

"Acad. J. Malinowski" Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl. 109, 1113 Sofia, Bulgaria

Abstract. The present study reports on the deposition and characterization of thin Ta_2O_5, TiO_2 and Nb_2O_5 film, obtained by the sol-gel method using tantalum ethoxide, titanium isopropoxide and niobium chloride as precursors and specially developed water free sol-gel procedure. Structure and morphology of the films were inspected trough XRD and SEM measurements. Refractive index, extinction coefficient and thickness of the films were determined from reflectance spectra using non-linear curve fitting method. Refractive index values as high as 1.85, 2.07 and 2.17 were obtained for Ta_2O_5, TiO_2 and Nb_2O_5 film, respectively at wavelength of 600 nm. The possibility of controlled tuning of optical properties by appropriate annealing was demonstrated and discussed.

PACS codes: 78.20.-e, 78.20.Ci, 78.40.-q, 81.20.Fw

1 Introduction

In recent years there is an increased scientific interest in high refractive index thin film materials due to their applications for improving optical performance of different devices such as Bragg gratings, optical filters, waveguide-based optical circuits, photonic crystals, sensors, *etc.* [1-3]. Because of its high dielectric constant Ta_2O_5 is promising storage dielectric material for high-density dynamic random access memory applications [4]. It was shown that thin sol-gel TiO_x film could dramatically increase the efficiency and lifetime of organic solar cells by using it as an optical spacer, hole-blocking layer, and oxygen-protecting layer [5,6]. Emerging applications of Nb_2O_5 films in the areas of electrochromic coatings, batteries, and nanocrystalline solar cells were also discussed [7]. Among various deposition techniques used for production of thin films from metal oxides, the sol-gel method attracts considerable scientific interest because of its versatility, low cost ant low temperature processing [8,9]. Besides, it allows

*Talk given at the Second Bulgarian National Congress in Physics, Sofia, September 2013.

control of the microstructure of the coating and produces durable and chemically stable films [9].

Reliable and non-destructive measurements of thin film characteristics such as the film thickness and refractive index (or dielectric constant) are beneficial for estimating the performance of films in the above mentioned applications. It has been confirmed that the post-deposition annealing of sol-gel films had a pronounced impact on their structure, thickness and optical properties. [5,10]. If the optical properties of sol-gel films can be controlled and optimized than the opportunity for variety of practical applications is opened up.

In this paper we study the optical properties of thin Ta_2O_5, TiO_2 and Nb_2O_5 films obtained by the sol-gel method and subjected to annealing in the temperature range 60 - 650 ^oC. The possibility of controlled tuning of refractive index and thickness of the films is demonstrated.

2 Experimental Details

Thin films from TiO_2, Ta_2O_5 and Nb_2O_5 with thicknesses in the range of 50–150 nm were prepared by using a sol–gel method. The Ti sol was prepared by a method similar to that of Chrysicopoulou [11]. It is based on the hydrolysis of metal alkoxide in alcoholic solution in the presence of acid stabilizer. The main difference in our procedure is the complete absence of water in the prepared sol. Besides, due to the greater stability toward the air conditions titanium tetra-isopropoxide $Ti(OC_3H_7)_4$ (97% Merck) was chosen as precursor instead of titanium tetra-ethoxide, used in the original recipe. The preparation procedure involved the dissolution of 6 ml of $Ti(OC_3H_7)_4$ in 94 ml of isopropyl alcohol (C_3H_7OH, 97% Merck), followed by the addition of 0.05 ml of nitric acid HNO_3 (65 vol.%, Merck). Thus, the molar ratio between the constituents of solution was 1:63:0.01. The mixture was sealed from atmospheric air and stirred at room temperature for 90 min to form slightly yellow transparent sol.

The tantalum sol was prepared according to the previously developed water free procedure [12]. Briefly, 35 ml of isopropyl alcohol were mixed with 1 ml of glacial acetic acid (CH_3COOH, Sigma-Aldrich) and then 1.5 ml Ta ethoxide $Ta(OC_2H_5)_5$ (99.98%, Sigma-Aldrich) was slowly added. Second solution was prepared by mixing 2 ml glacial acetic acid with 15 ml isopropyl alcohol. After 30 min stirring both solutions were mixed and then 1 ml diethanolamine ($HN(CH_2CH_2OH)_2$, 98%, Sigma-Aldrich) was added. The final mixture was transparent and colorless with pH of about 5. The obtained solution is subjected to slow stirring for 18 h. The solution was very stable and can be kept at ambient temperature for extended time.

The Nb sol was prepared by sonocatalytic method using $NbCl_5$ (99%, Aldrich) as a precursor according to the recipe in [13]: 0.400 g $NbCl_5$ was mixed with 8.3 ml ethanol (98%, Sigma-Aldrich) and 0.17 ml distilled water. The solution was subjected to sonification for 30 min and aged for 24 h at ambient conditions prior to spin coating.

Thin TiO_2, Ta_2O_5 and Nb_2O_5 films were deposited by dropping of 0.3 ml of the coating solution on pre-cleaned Si substrates and spin-on at a rate of 2500 rpm for 30 s. After deposition, the films were annealed in air at different temperatures in the range of 60–650°C for 30 min. The surface morphology of the films and their structures were inspected by Philips 515 electron microscope and Philips 1710 X-ray difractometer, respectively. The optical properties were investigated through measurements of reflectance spectra of the films with CARY 05E UV-VIS-NIR spectrophotometer with accuracy of 0.3%.

3 Results and Discussion

The surface morphology of Ta_2O_5 film with thickness of 100 nm was presented in Figure 1(a). The inset shows the cross-section view of the film. The film exhibits a uniform surface morphology without any granular structure. It is seen that the film is dense and smooth and covers the entire surface of the substrate. The top and side views of TiO_2 and Nb_2O_5 films are very similar to these of Ta_2O_5 shown in Figure 1(a) and for sake of briefness are omitted from the results. The polycrystalline structure of the films annealed at 450°C is confirmed by the conducted XRD measurements presented in Figure 1(b). The XRD spectra of films annealed at 320°C (not shown here) indicate amorphous structure for Ta_2O_5 and weak initial crystallization for Nb_2O_5 films.

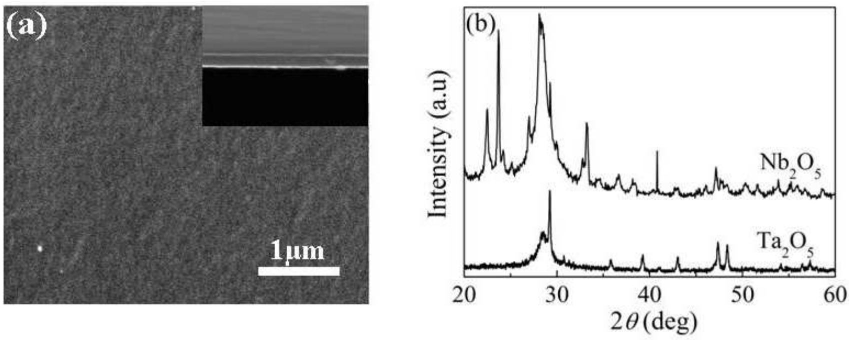

Figure 1: Surface and cross-sectional (inset) SEM images of Ta_2O_5 film (a); XRD spectra of Ta_2O_5 and Nb_2O_5 annealed at 450°C for 30 min (b).

Figure 2 presents refractive index and thickness of sol-gel derived Nb_2O_5, TiO_2 and Ta_2O_5 films as a function of the annealing temperature. The values are averaged over 3 samples and the error bars present the deviations from the average value. Refractive index, n, extinction coefficient, k and thickness, d of the films were determined simultaneously from measured reflectance spectra using non-linear curve fitting method described in details elsewhere [12]. The increase of n and decrease of d with annealing are clearly seen. The reasons are removing of residual solvent and organic additives along with polymerization into a metal oxide network that take place at high temperatures. The first also leads to densification of layers manifesting itself in decrease of thickness and increase of refractive index. The fastest decrease of d of Ta_2O_5 is due to the presence of bigger amount of organic additives in Ta sol (as acetic acid and diethanolamine) that are not used for preparation of Nb and Ti sols.

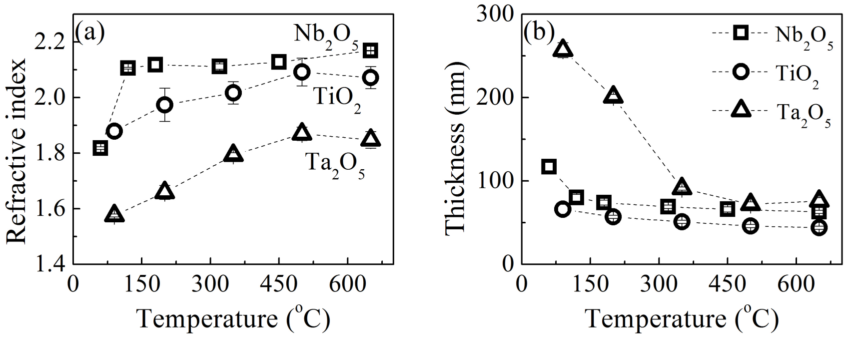

Figure 2: Refractive index at wavelength of 600 nm (a) and thickness (b) of Nb_2O_5 (square), TiO_2 (circle) and Ta_2O_5 (triangle) films as a function of annealing temperature.

From Figure 2 it is seen that in the temperature range from 60°C to 650°C the refractive index of the films at wavelength of 600 nm varies in the range $n = 1.818 \div 2.169$ for Nb_2O_5, $n = 1.576 \div 1.848$ for Ta_2O_5 and $n = 1.880 \div 2.07$ for TiO_2 films. Simultaneously the thickness changes from 117 nm to 63 nm for Nb_2O_5, from 257 nm to 76 nm for Ta_2O_5 and from 66 nm to 44 nm TiO_2 films. Annealing at temperature around 320°C is sufficient to produce stable films. Further annealing does not lead to significant changes in both n and d. It should be noted here that the values of n for Ta_2O_5 and TiO_2 films obtained in this study are lower as compared to those obtained in literature [10,14]. Different thicknesses and increased porosity in our case could be the possible reasons. The values of Nb_2O_5 films are in very good agreement with those obtained in [15].

4 Conclusions

A specially developed water free sol-gel procedure was applied for deposition of thin Ta_2O_5, TiO_2 and Nb_2O_5 films using tantalum ethoxide, titanium isopropoxide and niobium chloride as precursors. Reflectance spectra of the films deposited on Si-substrates by spin coating were used for calculations of refractive index (n) and thickness (d) of the films by means of non-linear curve fitting method. The smallest values of n were obtained for Ta_2O_5 (1.848 at 600 nm) films and the highest – for Nb_2O_5 (2.169). The values of n for TiO_2 are in the middle (2.072). An increase in n and decrease in *d* were observed with annealing. Two possible reasons are discussed: i) removing of residual solvent and organic additives and ii) polymerization into a metal oxide network. The possibility for controlled tuning of refractive index values of thin oxide films by appropriate annealing was demonstrated.

Acknowledgements

The authors are thankful to Prof. S. Mintova, Dr. J. El Fallah and H. Awala from LCS-Caen for XRD and SEM measurements of Ta_2O_5 films.

References

[1] A. Cusano, A. Iadicicco, D. Paladino, S. Campopiano, A. Cutolo, M. Giordano (2007) *Optical Fiber Technology* **13** 291.

[2] W.F. Ho, M.A. Uddin, H.P. Chan (2009) *Polymer Degradation and Stability* **94** 158.

[3] T. Kohoutek, J. Orava, T. Sawada, H. Fudouzi (2011) *Journal of Colloid and Interface Science* **353** 454.

[4] S. Ezhilvalavan, T.Y. Tseng (1999) *J. Mat. Science: Materials in Electronics* **10** 9.

[5] J. Li, A.M. Deberardinis, L. Pu, M.C. Gupta (2012) *Applied Optics* **51** 1131.

[6] S. Cho, K. Lee, J. Heeger (2009) *Adv. Mater.* **21** 1941.

[7] M.A. Aegerter (2001) *Sol. Energy Mater. Sol. Cells* **68** 422.

[8] A. Vioux (1997) *Chem. Mater*. **9** 2292.

[9] M.A. Aegerter, R. Almeida, A. Soutar, K. Tadanaga, H. Yang, T. Watanabe (2008) *J. Sol-Gel Science and Technology* **47** 203.

[10] F.E. Ghodsi, F.Z. Tepehan (1999) *Sol. Energy Mater. & Sol. Cells* **59** 367.

[11] P. Chrysicopoulou, D. Davazoglou, C. Trapalis, G. Kordas (1998) *Thin Solid Films* **323** 188.

[12] B. Gospodinov, J. Dikova, S. Mintova, T. Babeva (2012) *Journal of Physics: Conference Series* **398** 012026.

[13] N.J. Arfsten and J.F. Gavlas (2004) US patent 6811901 B1.

[14] R. Himmelhuber, P. Gangopadhyay, R. Norwood, D. Loy, N. Peyghambarian (2011) *Optical Materials Express* **1** 252.

[15] M.A. Aegerter (2001) *Sol. Energy Mater. & Sol. Cells* **68** 401.