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Fabrication and characterization of high refractive index optical coatings by sol-gel method for photonic applications

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The deposition and characterization of thin Ta_2O_5, TiO_2 and Nb_2O_5 film, obtained by the sol-gel methods using tantalum ethoxide, titanium isopropoxide and niobium chloride as precursors and specially developed water free sol-gel procedure are presented. Structure and morphology of the obtained layers are inspected through XRD and SEM measurements. Refractive index, extinction coefficient and thickness of the films are determined from reflectance spectra using non-linear curve fitting method. Refractive index values as high as 1.9, 2.28 and 2.39 are obtained for Ta_2O_5, TiO_2 and Nb_2O_5 film, respectively at wavelength of 500 nm. The possibility of controlled tuning of optical properties by appropriate annealing is demonstrated. The application of coatings as high refractive index building blocks of one dimensional photonic crystals is discussed.

Keywords: sol-gel materials; Ta_2O_5; TiO_2; Nb_2O_5; optical properties; spin-coating.

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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 a promising 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 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 is shown 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. The potential of using the films as high refractive index counterparts of one dimensional photonic crystals was discussed.

EXPERIMENTAL DETAILS

Thin films from TiO_2, Ta_2O_5 and Nb_2O_5 with thicknesses in the range 50-150 nm were prepared by using a sol–gel method. The Ti sol was prepared by method similar to that of Chrysicopoulou et. al.[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 humidity titanium tetra-isopropoxide

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$Ti(OC_3H_7)_4$ (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 (65 vol.%, Merck). Thus, the molar ratio between the constituents of solution was 1:63:0.01. The mixture was 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 $Ta(OC_2H_5)_5$ (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 was 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]: 0.400g $NbCl_5$ 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 60-650 ^oC 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 %.

RESULTS AND DISCUSSION

The surface morphology and the cross-section view of Ta_2O_5 film with thickness of 80 nm are presented in Fig. 1 (a) and 1 (b), respectively. It is seen that the film exhibits a uniform surface without any granular structure. 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 Fig. 1 and for sake of briefness are omitted from the results. The polycrystalline structure of the films annealed at 450 ^oC is confirmed by XRD measurements presented in Fig. 1 (c). The XRD spectra of films annealed at 320 ^oC (not shown here) indicate amorphous structure for Ta_2O_5 and weak initial crystallization for Nb_2O_5 films.

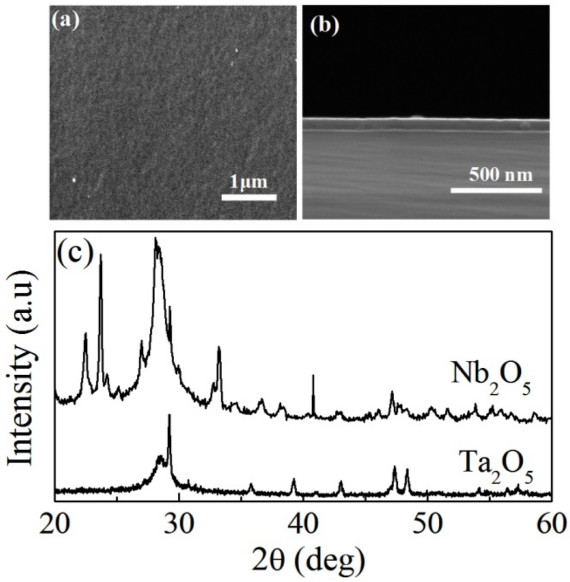

Fig. 1. Plane-view (a) and cross-section (b) SEM images of Ta_2O_5 film; XRD spectra of Ta_2O_5 and Nb_2O_5 annealed at 40 ^oC for 30 min (c).

Fig. 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. The refractive index, n, extinction coefficient, k and thickness, d of the films were determined simultaneously from measured reflectance spectra using non-linear curve fittin g 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. From Fig. 2 it is seen that in the temperature range from 60^{o}C to 650^{o}C the refractive index of the films at wavelength of 600 nm varies in the range n = 1.818

- 2.169 for Nb_2O_5, n = 1.576 - 1.848 for Ta_2O_5 and n = 1.880 - 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].

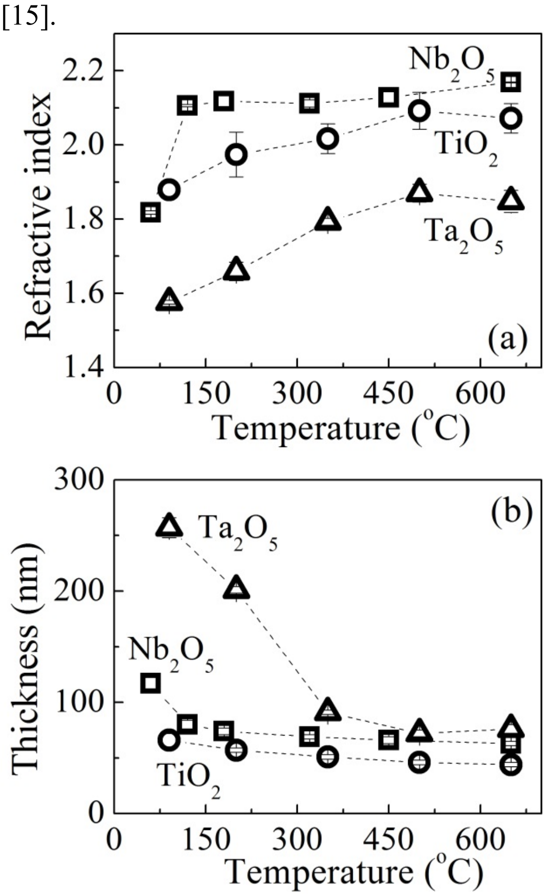

Fig. 2. Refractive index at wavelength of 600 nm (a) and thickness (b) of Nb_2O_5 (square), TiO_2 (circle) and Ta_2O_5 (triangle) films as a function of annealing temperature

One possible application of the studied oxides is in omnidirectional reflectors (ODR) that comprise alternating materials with high and low refractive index. Because ODR have high reflectance for all angles of incidence and types of light polarization they also are referred to as one-dimensional photonic crystals. Additional experiments on sol-gel derived SiO_2 films show that they are suitable low-n materials for ODR (n = 1.435 – 1.391 for λ =

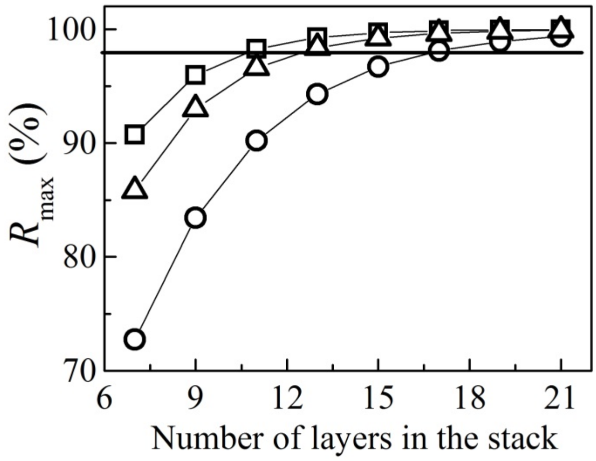

Fig. 3. Maximum reflectance calculated as a function of number of the layers in the stacks consisting of alternating SiO_2 and Nb_2O_5 (squares), SiO_2 and TiO_2 (triangles) and SiO_2 and Ta_2O_5 (circles). The horizontal line indicates level of R = 98%

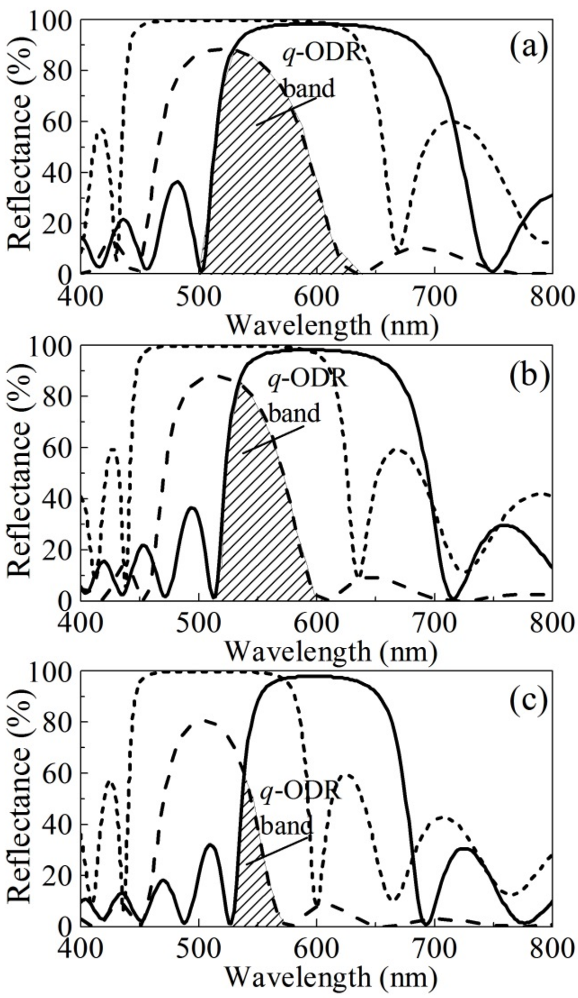

Fig 4. Calculated reflectance spectra for quarter-wavelength stacks consisting of (a) 11 layers of Nb_2O_5 and SiO_2; (b) 13 layers of TiO_2 and SiO_2 and (c) 19 layers of Ta_2O_5 and SiO_2 films

400 – 800 nm). Fig. 3 presents the calculated values of maximum reflectance (R_{max}) for stacks consisting of different number of layers of Nb_2O_5, Ta_2O_5 and TiO_2 as high-*n* and SiO_2 as low-*n* materials.

It is well seen that R_{max} increases with the number of the layers in the stacks mostly pronounced for the stacks with the highest refractive index contrast. Thus to obtain R = 98% a different number of layers in the stack are needed: 11 layers of Nb_2O_5 and SiO_2, 13 layers of TiO_2 and SiO_2 and 19 layers of Ta_2O_5 and SiO_2. Fig. 4 presents the calculated reflectance spectra for angles of incidence of 0 and 60^o for 11, 13 and 19 layered stacks of Nb_2O_5, TiO_2 and Ta_2O_5, respectively combined with SiO_2. With increasing of angle of incidence the reflectance band shifts towards shorter wavelengths, widening for s-polarization and narrowing for p-polarization. The overlap of reflectance bands is referred to as quazi-omnidirectional band (*q*-ODR). It consists of spectral range with high reflectance for all polarization types of light incident at angles from 0 to 60^o. It is seen that for all three types of stacks a *q*-ODR band opens. However the reflectance value, the central wavelength and the width depends on the optical contrast. The widest band is for Nb_2O_5 / SiO_2 stack (90 nm) that have the highest optical contrast. It is centered at wavelength of 550 nm and has reflectance value of 80 %. In order to obtain ODR band higher contrast is needed.

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. 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 potential of using the films as building blocks of quazi-omnidirectional reflectors was demonstrated theoretically.

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ОТЛАГАНЕ И ХАРАКТЕРИЗИРАНЕ НА ЗОЛ-ГЕЛ ОПТИЧНИ ПОКРИТИЯ С ВИСОК ПОКАЗАТЕЛ НА ПРЕЧУПВАНЕ ЗА ПРИЛОЖЕНИЕ ВЪВ ФОТОНИКАТА

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(Резюме)

Тънките слоеве от Ta_2O_5, TiO_2 и Nb_2O_5 са получени по метода зол-гел посредством разработена процедура без използване на вода. Структурата и морфологията на слоевете е изследвана чрез рентгенова дифракция и електронна микроскопия, а оптичните им свойства - чрез нелинейно минимизиране на разликата между измерените и изчислените спектри на отражение. Демонстрирана е възможността за контролирано вариране на оптичните параметри и дебелината на слоевете чрез подходящо загряване. Дискутиран е потенциала на изучаваните филми за приложение като градивни блокове на едномерни фотонни кристали.