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Sol-gel derived Nb_2O_5 thin films for photonic applications

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The fabrication and optical characterization of thin Nb_2O_5 films, obtained by spin coating of Nb sol on silicon substrate are presented. The Nb sol is prepared by sonocatalytic method using niobium chloride as a source for Nb and ethanol for solvent. The structure and morphology of the films are inspected through XRD and SEM measurements. Refractive index, extinction coefficient and thickness of the films are determined from measured reflectance spectra using non-linear curve fitting method. The impacts of ageing of the Nb sol, the duration of sonocatalytic treatment and post deposition annealing on the optical properties and thickness of the films are investigated. The possibility for fabrication of one dimensional photonic crystals using Nb_2O_5 and SiO_2 as high and low refractive index materials is discussed.

Keywords: sol-gel materials; Nb_2O_5 films; optical properties; optical characterization; spin-coating

INTRODUCTION

In recent years there is an increased scientific interest in Niobium pentoxide (Nb_2O_5) material because it is thermodynamically most stable as compared to other stoichiometries of niobium oxide and shows excellent chemical stability and corrosion resistance in both acidic and alkaline media [1]. Most often Nb_2O_5 was studied from the application in smart windows point of view and hereof the investigations of its properties are mainly devoted to optimization of its electrochromic behavior [2,3]. However, due to its interesting photoelectric and photocatalytic properties [4,5] Nb_2O_5 films may find application in different devices such as batteries and nanocrystalline solar cells [6,7], sensors [8], or transparent conductive electrodes [9].

A number of novel applications of Nb_2O_5 films rely on the ability to deposit high quality films with relatively simple and inexpensive techniques. Among various deposition techniques used for production of thin films from Nb oxides, the sol-gel method emerges as an attractive deposition method because of its versatility, low cost and low temperature processing [6]. Two types of precursors are currently used for formation of sol-gel Nb_2O_5 films: metal alkoxides (Nb ethoxide) [1] or metal salt-$NbCl_5$ [10]. The last one is preferred because of the lower price and weaker sensitivity to moisture as compared to the organic one.

For development of film application areas and implementation of Nb_2O_5 sol gel films in optical devices it is essential to characterize and optimize film properties (refractive index and extinction coefficient) and to be able precisely to control the film thickness. However, according to our knowledge there are only few studies on optical properties of sol-gel Nb_2O_5 films mainly concerning the determination of optical band gap and optical absorption [1,10,11].

The present paper studies the optical properties of thin sol-gel Nb_2O_5 films obtained by spin coating and their dependences on the duration of sonocatalytic treatment, time of sol ageing and post deposition annealing. The possibility of fabrication of one-dimensional photonic crystals is discussed.

EXPERIMENTAL DETAILS

The Nb sol was prepared by sonocatalytic method using $NbCl_5$ (99%, Aldrich) as a precursor according to the recipe in [12]. Briefly, 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. Transparent and stable sol was obtained easily and without additives.

Thin 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 the deposition, the films were annealed in

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air at different temperatures in the range 60-650 °C for 30 min and have thicknesses of 35-40 nm. In order to obtain thicker films the coating procedure is repeated several times. Prior to the next deposition, the films are dried at 60 °C with hot air to prevent the wash out of the underneath layer. 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 %. The refractive index *n*, extinction coefficient *k*, and thickness *d*, of the films were determined using non-linear curve fitting method described in details elsewhere [13].

RESULTS AND DISCUSSION

The structure and surface morphology of Nb_2O_5 film annealed at 320 and 450 °C are shown in Fig. 1. It is seen that films have similar surface morphology at different temperatures while their structures change from amorphous at 320°C to polycrystalline at 450 °C.

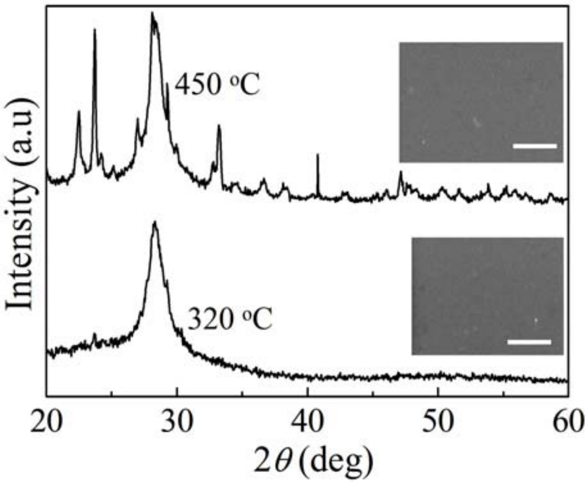

Fig. 1. XRD spectra of Nb_2O_5 films on Si-substrates annealed at 320 and 450 °C; Insets: SEM images of the films surface; the scale bar is 1μm.

In order to study the effect of the sol ageing on the optical properties and thickness of the films we prepared films at the same conditions but at different sol ageing time.

Fig. 2 presents reflectance spectra, refractive index and thickness of the prepared films. It is seen that during the first 10 days the films have very similar thicknesses (about 25-27 nm) while the refractive index decreases after period of 3 days. The most probable reason for the thickness increase of the films prepared from sol aged more than 10 days is the evaporation of the solvent and consequent increase of the sol concentration. Besides, we can speculate that the higher concentration of the sol prevents to some extent the reaction of polycondensation to take place, thus decreasing the refractive index. Another possible reason is particle aggregation that increases interparticles gaps thus decreasing the density and *n* values.

Our investigations on the influence of sonocatalytic treatment of the Nb sol prior the spin coating shows that higher refractive index are obtained for duration of 20 min. For shorter and longer time of sonification the values of *n* decrease. There is no influence on the thickness of the films.

In order to enable controllable tuning of the refractive index and thickness of the films we have studied the temperature dependence of optical properties of thin Nb_2O_5 films. Fig. 3 (a) presents the dispersion curves of *n* at different temperatures in the range 60 - 650 °C and the changes of *d* and *n* at wavelength of 600 nm with annealing (Fig 3(b)). Two different regimes of annealing are presented: i) consecutive annealing at 60, 120, 180, 320, 450 and

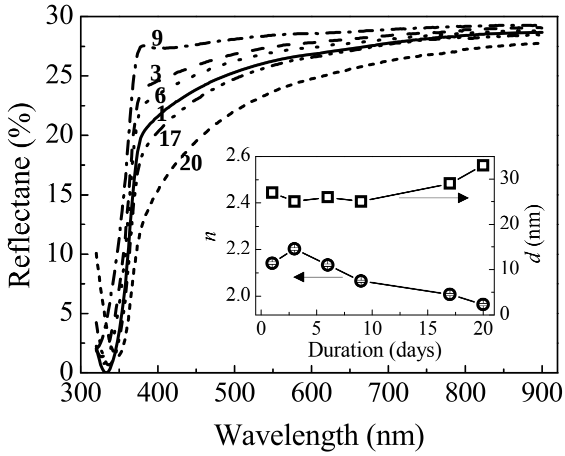

Fig. 2. Reflectance spectra of Nb_2O_5 films obtained from Nb sol aged for the denoted time; Inset: refractive index (circles) and thickness (squares) of Nb_2O_5 films as a function of the ageing time

650 °C and ii) separate annealing at the specific temperature, i.e no cumulative annealing history. It is seen that the two regimes yield almost the same values of *n* and *d*. Besides, Nb_2O_5 films have similar values of *n* in the temperature range 120 - 650 °C (2.11-2.17). The most pronounced changes of *n* are for temperatures from 60 to 120 °C where *n* changes from 1.82 to 2.11, respectively. Similarly, a fast decrease of *d* is observed for temperatures in the range 60 - 180 °C followed by weak variation for *T* up to 650 °C.

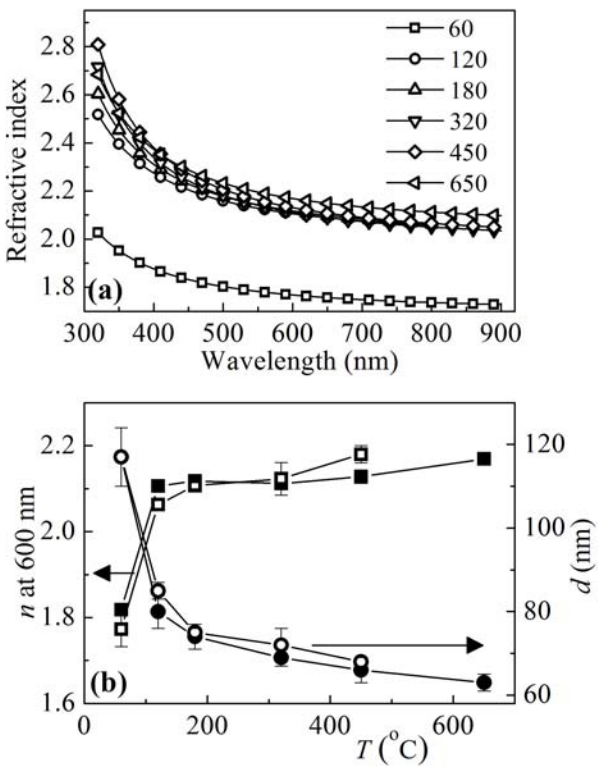

Fig. 3(a) Dispersion curves for refractive index of Nb_2O_5 annealed at different temperatures; (b) temperature dependence of refractive index (squares) and thickness (circles) of the films; the symbol interior shows different sequence of annealing - see the text.

The increase of *n* and decrease of *d* with annealing is due to removing of residual solvent and organic additives along with polymerization into a metal oxide network that takes place at high temperatures. The first also leads to densification of layers manifesting itself in the initial sharp decrease of thickness. It should be noted here that even at temperatures below 120 °C Nb_2O_5 films with high refractive index could be deposit. This can be regarded as an advantage because allows deposition of high refractive index materials onto heat-sensitive substrates.

For many applications the precise control of the film thickness is essential for right performance of the device. For example the implementation of Nb_2O_5 as a high refractive index building block of interference filters requires films with specific thickness to be deposited [14]. One way of tuning the film thickness is using sol with different concentrations. Our experiments show that very good linear dependence of film thickness as a function of sol concentration was obtained. Thus, by changing the concentration from 2.35 to 4.7 wt.% and repeating the coating procedure twice,

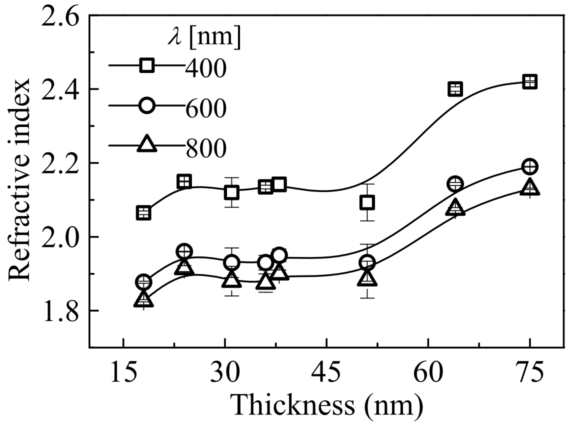

Fig. 4. Thickness dependence of refractive index of Nb_2O_5 films at three different wavelengths.

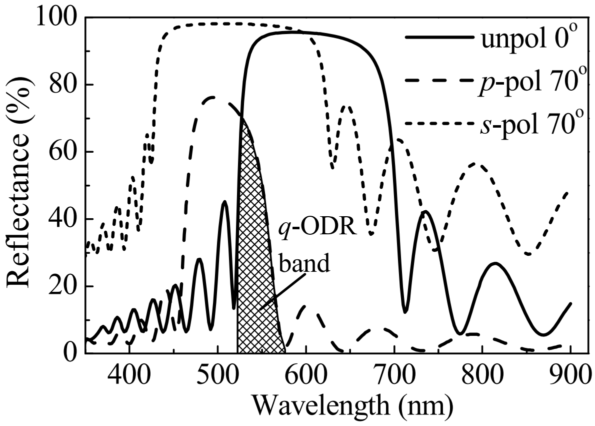

Fig. 5. Calculated reflectance spectra for 11 layered quarter-wavelength stack of Nb_2O_5 and SiO_2 films.

films with thicknesses from 19 to 75 nm are obtained. The ratio of film thicknesses from the first and second coating steps is equal to 2 and remains constant over the whole studied concentration range. Another possible way for obtaining thicker films is decreasing of deposition rate. However, our experiments show deterioration of the quality of the films at low rotation speeds.

For application of sol-gel derived Nb_2O_5 films in photonics it is very important the thickness dependence of refractive index to be studied. Fig. 4 presents the refractive index of Nb_2O_5 films as a function of thickness for 3 different wavelengths.

It is well seen from Fig. 4 that refractive index has similar values for film thicknesses in the range 20-60 nm while a decrease for thinner films and an increase for thicker is observed. Because refractive index can be directly connected to density of the films the obtained results indicate that the packing density increases with thickness manifesting itself in an increase of refractive index.

The final step of our investigation concerns the application of Nb_2O_5 films as high refractive index material in omnidirectional reflectors consisting SiO_2 as low refractive index material. Fig. 5 presents calculated reflectance spectra of 11 layered stack from alternating Nb_2O_5 and SiO_2 films with quarter-wave thicknesses.

It is seen that with increasing of angle of incidence from 0 to 70 degrees the reflectance band shifts towards shorter wavelengths, widening for s-polarization and narrowing for p-polarization. Quazi omnidirectional band opens up centered at 530 nm with width of 35 nm and maximum reflectance values of 71%. This means that the quarter-wave reflector of alternating Nb_2O_5 and SiO_2 layers exhibits R > 71 % for incident angle range 0 - 70^o and all types of polarizations.

CONCLUSIONS

Thin films from Nb_2O_5 were fabricated by sonocatalytic sol-gel method using inorganic precursor ($NbCl_5$) dissolved in ethanol. The investigations of the sol ageing processes have shown that during the first week the films have identical thicknesses and similar values of refractive indices varying in the range 2.14-2.20 with the highest value reached after 3 days of ageing. A decrease in n and increase of d were observed afterwards. Two possible reasons were discussed: particles aggregation and increase of sol concentration. Further it was demonstrated that a precise control of film thickness could be achieved simply by controlling the sol concentration. The tuning of n in the range 1.82 to 2.20 could be achieved by post deposition annealing in the temperature range 60-650^{o}C. Possible application of Nb_2O_5 films in quazi-omnidirectional reflectors was demonstrated.

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ТЪНКИ СЛОЕВЕ ОТ NB_2O_5, ПОЛУЧЕНИ ЧРЕЗ ЗОЛ-ГЕЛ МЕТОД С ПРИЛОЖЕНИЕ ВЪВ ФОТОНИКАТА

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(Резюме)

Настоящото изследване е фокусирано върху получаването и оптичното характеризиране на тънки слоеве от Nb_2O_5, получени чрез нанасяне от разтвор на Nb зол върху силициева подложка. Nb зол се получава чрез ултразвуково третиране на $NbCl_5$ и етанол. Структурата и морфологията на слоевете е изследвана чрез XRD и SEM. Показателите на пречупване и поглъщане, както и дебелината се определят от измерените спектри на отражение чрез нелинейно фитване. Изследвано е влиянието на стареенето на зола, времетраенето на ултразвуковото третиране и температурата на нагряване върху оптичните параметри и дебелината на слоевете. Дискутирана е възможността за изработване на едноразмерен фотонен кристал от Nb_2O_5 и SiO_2 като материали с висок и нисък показател на пречупване, съответно.