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Influence of PEO, PDMAA and corresponding di- and triblock copolymers on the optical properties of niobia thin films

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The present study aims at investigation of the influence of poly(ethylene oxide) (PEO), poly(N,N-dimethylacrylamide) (PDMAA) and corresponding block copolymers (PEO-*b*-PDMAA and PDMAA-*b*-PEO-*b*-PDMAA) on the formation of porosity in thin Nb_2O_5 films using evaporation induced self-assembly (EISA) method. The addition of copolymer solution to Nb sol provoked phase separation and after appropriate annealing a system of pores was generated in the spin-on thin film. The annealing regimes providing complete removal of the polymer from the pores were optimized through Thermogravimetric Analysis (TGA). The morphology and structure of the films were studied by Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED). The optical parameters of the films, along with their thicknesses were determined from reflectance spectra and nonlinear curve fitting. The influence of copolymer structure and composition on the optical properties of thin Nb_2O_5 films was established and the tuning of refractive index in wide range was demonstrated.

Keywords: Nb_2O_5 films, spin-coating, sol-gel, optical properties, porosity.

INTRODUCTION

The creation of materials with tailored texture is regarded as a key step toward innovative technologies. Recently, advanced inorganic thin films and especially those with controlled porosity attract increasing attention because of the important roles they play in sorption, catalysis, photoconversion, sensors, and photonic and electronic microdevices. One of the approaches towards fine tunable mesoporous, crystalline inorganic materials relays on the use of block copolymer mesostructures as templates [1].

Amphiphilic copolymers which are composed of thermodynamically incompatible blocks (mostly including polystyrene, polybutadiene, or poly(propylene oxide) as hydrophobic blocks, and poly(ethylene oxide) or poly(vinyl pyridine) as hydrophilic blocks) provide possibilities for continuous tuning of the self-assembly characteristics by adjusting molecular weight, copolymer composition and architecture, or solvent composition [2]. This enables good control over the self-organized superstructures and the length scales and suppose introduction of specific functions as well. Block copolymer self-assembly has been proven as a powerful platform for structuring morphology and tuning size and porosity of various functional inorganic materials on the nanometer scale [3, 4]. Templating by using variety of amphiphilic diblock or triblock architectures has been widely applied in the synthesis of amorphous silica mesostructures, mesoporous metal oxides and crystalline films [1 - 8].

We have already demonstrated that using different amphiphilic tri-block copolymers (PE6100, PE6800, PE10100, Pluronic, BASF) and varying the molar ratio of polymer and $NbCl_5$ used for preparing the Nb sol it is possible to obtain thin Nb2O5 films with tailored pore structure and controlled optical and sensing properties [9, 10]. An improvement of sensing properties of mesoporous films is demonstrated as compared to the films prepared without template [9, 10].

In this work, we report for the first time the utilization of double hydrophilic block copolymers in the formation of porous Nb_2O_5 thin films when applying the evaporation induced self-assembly (EISA) method. Diblock and triblock copolymers comprising poly(N,N-dimethylacrylamide) (PDMAA) and poly(ethylene oxide) (PEO) blocks were synthesized and used as hydrophilic templates in the EISA. The influence of the composition and

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concentration of the organic templates on the optical properties of the films have been studied and the tuning of refractive index in a wide range has been demonstrated.

EXPERIMENTAL DETAILS

Niobium oxide thin films were prepared by the methods of evaporation induced self-assembly and spin coating (30 seconds at 3000 rpm) using a mixture of Nb sol and four organic templates (PDMAA, PEO, PEO-*b*-PDMAA and PDMAA-*b*-PEO-*b*-PDMAA) dissolved in water in different concentrations (0.5%, 1.5 % and 5%) thus obtaining ratios of polymers to $NbCl_5$ equal to 0, 0.07, 0.14, 0.23. Niobium sol was prepared by a sonocatalytic method using 0.400 g $NbCl_5$ (99%, Aldrich) as a precursor, 8.3 ml ethanol (98%, Sigma-Aldrich), and 0.17 ml distilled water [11]. The synthesis of used copolymers was carried out as follows [12]: double hydrophilic di- and triblock copolymers were synthesized by means of redox polymerization of DMAA (Sigma-Aldrich, Germany) in deionized water when using polyethylene glycol methyl ether (PEG-ME; 2000 g/mol; Fluka, Switzerland) or respectively polyethylene glycol (PEG; 2000 g/mol; Fluka, Switzerland)) as initiating moiety. PDMAA was synthesized by aqueous free radical polymerization of DMAA initiated by 4,4-azobis (4-cyanovaleric acid) (ABCVA). The obtained polymers were purified by dialysis against water and finally isolated by freeze-drying. The composition of the prepared copolymers was analyzed by Nuclear Magnetic Resonance (NMR): PEO_{45}-*b*-$PDMAA_{37}$, Mn = 5700 g/mol and $PDMAA_{28}$-*b*-PEO_{45}-*b*-$PDMAA_{28}$, Mn = 7500 g/mol, respectively.

The surface morphology and structure of the films were studied by Transmission Electron Microscopy (TEM) using HRTEM JEOL JEM 2100 (Japan) microscope.

Refractive index (*n*), extinction coefficient (*k*) and thickness (*d*) of the films were determined from reflectance spectra (*R*) of the films measured at normal incidence of light by UV-VIS-NIR spectrophotometer Cary 05E (Varian, Australia) using nonlinear curve fitting method [11]. The experimental errors for *R*, *n, k* and *d* are 0.3%, 0.005, 0.003 and 2 nm respectively.

Thermogravimetric analysis was performed using TGA-4000 Perkin Elmer analyzer supplied with PYRIS software. The samples were heated from r.t. to 600 °C at a heating rate of 10 °C/min in inert atmosphere (argon).

RESULTS AND DISCUSSIONS

Typical TEM images of Nb_2O_5 obtained using different organic templates and fixed ratio of 0.23:1 of polymer to $NbCl_5$ are shown in Fig. 1 along with an example of Selected Area Electron Diffraction pattern of the films as an inset. It is seen that the pores in the films are with similar sizes although these formed by addition of di-block copolymer are slightly bigger as compared to the others. The structure of all films at annealing temperature of 320 °C is amorphous.

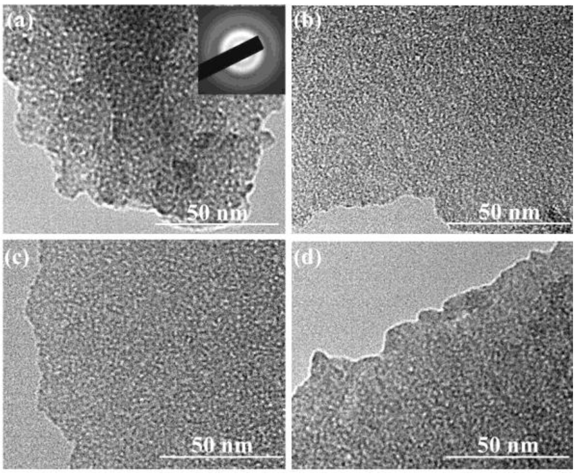

Fig. 1. TEM pictures of Nb_2O_5 thin films prepared using 5 wt % PDMAA-*b*-PEO (a), PDMAA-*b*-PEO-*b*-PDMAA (b), PDMAA (c) and PEO (d) as organic template (ratio polymer to $NbCl_5$ equals to 0.23) and annealed at 320 °C for 30 min. The inset shows Selected Area Electron Diffraction pattern.

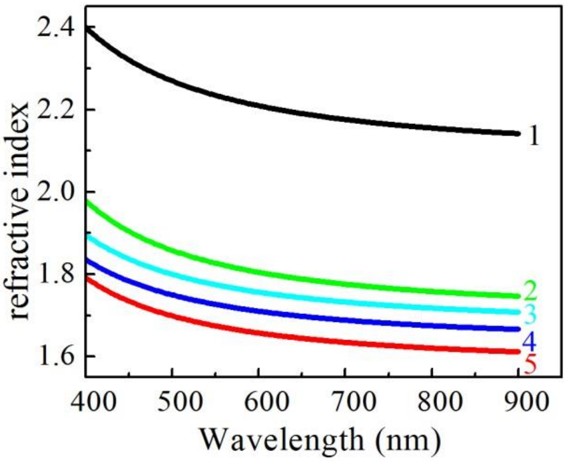

Fig. 2. Refractive index as a function of wavelength for Nb_2O_5 thin films deposited without organic template (curve 1) and with addition of PDMAA (curve 2), PDMAA-*b*-PEO-*b*-PDMAA (curve 3), PDMAA-*b*-PEO (curve 4) and PEO (curve 5) with ratio of template to $NbCl_5$ equals to 0.23. All films were annealed at 320 °C for 30 min.

Effective refractive indices (*n*) of Nb_2O_5 films prepared with organic templates (5 wt. %) are compared with the values for dense film (without template) in Fig. 2. Addition of polymers leads to a decrease in *n* depending on the type of the template: the strongest reduction is obtained for PEO, where *n* at wavelength of 600 nm changes from 2.21 for dense film to 1.65, and the smallest reduction is for PDMAA (*n*=1.81). The values for copolymers are in between: 1.71 and 1.76 for di and triblock copolymers, respectively.

Thermogravimetric Analysis (TGA) showed that the process of weight loss for PEO starts at a temperature around 200 ºC and the polymer has lost more than 95 % of its initial weight at temperature of 320 ºC [13]. However, for PDMAA the thermal decomposition starts at a temperature around 400 ºC and ends around 500 ºC where the polymer has lost its entire weight [14]. If we consider that all films have similar porosity (see Fig. 1) and comprise two phases (dense Nb_2O_5 and air or polymer) it can be expected the Nb_2O_5 films prepared using PEO as template to have the lowest effective refractive index because at 320 ºC PEO has been completely burnt and the films consist of air with *n*=1 as a second phase. However, the rest of the films contain polymer with higher refractive index (*n* = 1.43, 1.463 and 1.485 for PDMAA, di- and triblock copolymers, respectively [15]) as a second phase, because these templates have not been thermally decomposed at the temperature of 320 ºC. Using Brugemann effective medium approximation [16] and assuming that PEO has been fully decomposed we calculate that the free volume fraction in the films prepared with PEO as a template is 45 % (Table 1). The values are close to those previously obtained for mesoporous Nb_2O_5 films prepared using Pluronic template [9, 10].

Table 1. Calculated pore volume fractions in Nb2O5 films prepared using different organic templates and annealed for 30 min at 320 oC according to Brugemann EMA [16] and assuming pores filled with air or polymer.

Template type	Pore volume fraction (%)	
	Air	Polymer
PEO	45	n.a
PDMAA	32	50
diblock	39	65
triblock	36	61

The values calculated for the rest of the films, assuming two phases – dense Nb_2O_5 and polymer, are also presented in Table 1. In the case of using PDMAA as a template, the value of pore volume fraction (50 %) is similar to this for PEO template, but for both copolymers it is substantially greater (more than 60 %). Because TEM pictures do not show significant difference in porosity of the films we may speculate that the pores of Nb_2O_5 films prepared with copolymers as templates are filled with a mixed phase of polymer and air, due to the partially decomposed polymer. Thus their pore volume fractions vary between the values for pores filled with air and pores filled with polymer (Table 1).

To study further the decomposition of polymer inside the pores a mixture of Nb sol and PEO-*b*-PDMAA copolymer (5 wt.%) is prepared and thermogravimetric (TGA) curves are measured. The TGA curves along with derivative TGA curves of pure Nb sol and sol blended with PEO-*b*-PDMAA polymer are presented in Fig. 3. It is seen that the two samples degrade in two main stages. The temperatures of maximum degradation in the first stage are similar for the two samples, 122 ºC and 118 ºC for pure and blended Nb sol (Fig. 3(b)).

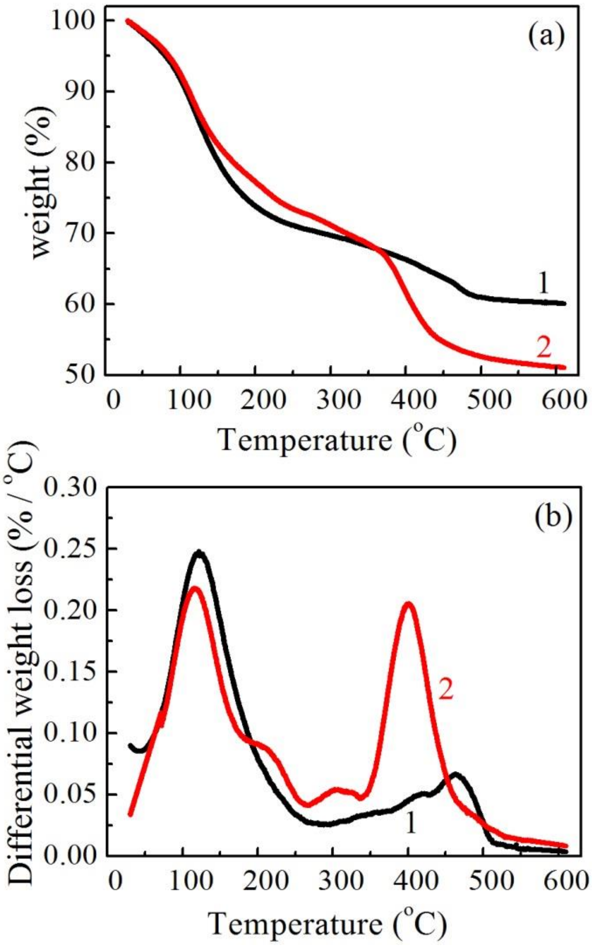

Fig. 3. Thermo gravimetric (TGA) (a) and differential TGA curves (b) for niobium sol (curve 1) and Nb sol blended with PEO-*b*-PDMAA polymer (curve 2) (5 wt%, volume ratio sol : polymer = 5:1).

The weight loss is apparently associated with evaporation of adsorbed water and solvents. However, there is a considerable difference between the samples behavior during the second stage. It is seen from Fig. 3 that the polymer degradation starts around 340 °C and the process ends after reaching 550 °C with temperature of the maximum degradation of 400 °C. For pure Nb sol there is a weak weight loss around 460 °C that may be due to the decomposition of some residual organic species. Knowing i) the mass ratio of polymer and $NbCl_5$ in the blended sample, ii) its initial weight and iii) the weight loss of pure sol it is possible to calculate the expected final weight of the blended sample in the assumption of complete mass loss of the polymer and to compare it with the measured one. The obtained difference is 3.10^{-5} g that is within the framework of measuring accuracy. Therefore we may assume that the high temperature annealing of the films would lead to complete thermal decomposition of polymer in the pores thus leading to decrease of refractive index of the films.

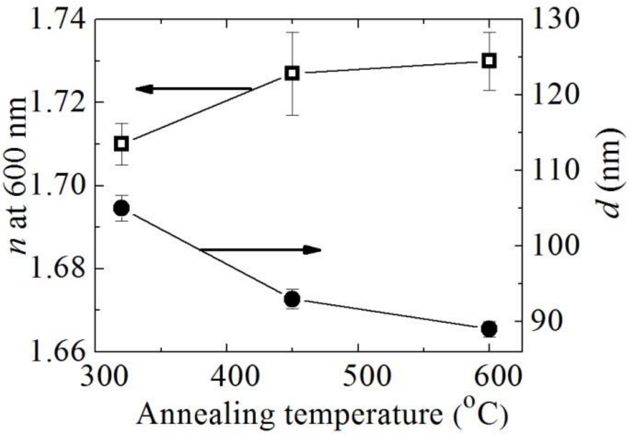

Fig. 4. Refractive index (*n*) at wavelength of 600 nm and thickness (*d*) of Nb_2O_5 films prepared with PEO-*b*-PDMAA template as a function of postdeposition annealing temperature

The temperature dependences of refractive index and thickness of Nb_2O_5 films prepared with PEO-*b*-PDMAA copolymer as a template are presented in Fig. 4. Refractive index slightly increases with temperature (the change is 1.1%), while the thickness decreases with 15 %. Almost the same reduction of *d* (10 %) is obtained for the triblock copolymer, while the increase in *n* is stronger – almost 10 % (Table 2). When PEO is used as a template there is no change of *n* and *d* of Nb_2O_5 films with annealing temperature, while for Nb_2O_5 films with PDMMA template a slight decrease in *n* accompanied with small reduction in *d* (5 %) are observed (Table 2).

Table 2. Refractive index and thickness of Nb_2O_5 films prepared using the denoted polymers as templates and annealed for 30 min at temperature of 320 °C and 600 °C.

Template	*n* at 600 nm		*d* (nm)	
type	320°C	600°C	320°C	600°C
PEO	1.64	1.64	87	89
PDMAA	1.77	1.75	94	89
diblock	1.71	1.73	105	89
triblock	1.76	1.93	97	84

With increasing the annealing temperature two competing processes take place and the overall film behavior is due to the balance between them. The first one is the densification of the pure Nb_2O_5 matrix that leads to an increase in *n* [11]. The typical changes in the temperature range 300 – 600 °C are 2-3 % in *n* and 7-8 % in *d* [11]. In the porous film this processes is further facilitated due to the thin pore walls and more free volume as compared to dense Nb_2O_5 films. The second process is the thermal decomposition of polymers in the films pores connected with the reduction of effective refractive index. The results presented in Table 2 and Fig. 4 show that when diblock and triblock copolymers are used as templates the first process is prevailing and net increase in *n* with temperature is observed mostly pronounced for the triblock copolymer where the thickness reduction is significant. On the contrary, in the case of PDMAA the second process is predominant and a decrease of *n* is detected although a slight decrease of film thickness occurs. For Nb_2O_5 films prepared with PEO as a template a balance between the two processes is achieved and the net change of *n* is almost zero.

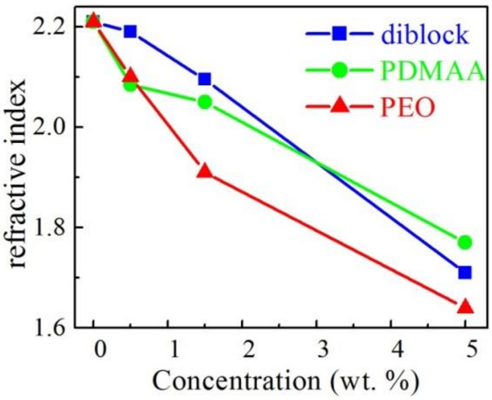

Fig. 5. Template concentration dependence of refractive index of porous Nb_2O_5 films prepared with denoted polymers as templates and annealed at 320 °C for 30 min.

By measuring the reflectance change prior to and after vapors exposure we may conclude that the refractive index of all films does not change under the influence of vapors of various organic solvents (acetone, ethanol, methanol, etc.) and humidity as well. This means that the porosity is predominantly of closed type, i.e. there is no a connectivity between the pores.

The dependence of refractive index of porous Nb_2O_5 films prepared with studied polymers as a function of their concentration is presented in Fig. 5. As the polymer concentration increases, the effective refractive index decreases mostly pronounced when using PEO as a template. At annealing temperature of 320 ºC PEO decomposes leaving empty pores in the film, while for PDMAA and PEO-*b*-PDMAA the temperature is not sufficiently high in order complete thermal decomposition to take place.

CONCLUSIONS

The successful fabrication of Nb_2O_5 thin films with tunable refractive index using simple methods of sol-gel and evaporation induced self-assembly is demonstrated. Double hydrophilic block copolymers (PEO-*b*-PDMAA and PDMAA-*b*-PEO-*b*-PDMAA) and hydrophilic homopolymers (PEO and PDMAA) used as organic templates induce closed porosity proven by reflectance measurements of films prior to and after exposure to different probe molecules. Fine tuning of refractive index can be accomplished through post deposition annealing at various temperatures. Depending on the organic template used an increase or decrease of *n* can be achieved. By varying the concentration of organic template a variation of refractive index in a wide range can be obtained. In the case of using PEO-*b*-PDMAA copolymer as a template almost linear decrease of *n* from 2.21 to 1.71 is observed. The stability of the films when exposed to external stimuli is assigned to the formation of closed porosity. Tunable refractive index attained by the simple methods of post deposition annealing or variation of template concentration opens new opportunities for applications of Nb_2O_5 thin films in optics and photonics.

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ВЛИЯНИЕ НА PEO, PDMAA И СЪОТВЕТНИТЕ ДИ- И ТРИБЛОКОВИ СЪПОЛИМЕРИ ВЪРХУ ОПТИЧНИТЕ СВОЙСТВА НА ТЪНКИ СЛОЕВЕ ОТ Nb_2O_5

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(Резюме)

Целта на представеното изследване е изучаване на влиянието на полиетиленоксид (ПЕО), поли(N.N-диметилакриламид) (ПДМАА) и съответните блокови съполимери (ПЕО-*б*-ПДМАА и ПДМАА-*б*-ПЕО-*б*-ПДМАА) върху формирането на пори в тънки слоеве от Nb_2O_5. Добавянето на полимерния разтвор към Nb зол провокира фазово разделяне и след подходяща термична обработка на слоевете се създава система от пори. Използваните режими на нагряване, осигуряващи пълно изгаряне на полимера в порите, са оптимизирани чрез термогравиметричен анализ. Морфологията и структурата на филмите е изучена чрез ТЕМ и електронна дифракция от избрана област. Оптичните параметри на слоевете и техните дебелини са определени от измервания на спектрите на отражение и нелинейно минимизиране на разликите между измерените и изчислените стойности. Установено е влиянието на структурата и състава на използваните съполимери върху оптичните свойства на тънки Nb_2O_5 и е демонстрирана възможността за вариране на показателя на пречупване в широки граници.