



VOC Resistant Niobium Thin Films with Modulated Refractive Index

R. Georgiev¹, L. Todorova², D. Christova², B. Georgieva¹, T. Babeva¹

¹*Institute of Optical Materials and Technologies "Acad. J. Malinowski", Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 109, 1113 Sofia, Bulgaria.*

²*Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl. 103-A, 1113 Sofia, Bulgaria.*

Abstract. In this study the formation of niobium oxide thin films with different refractive index and their resistance to most common VOCs (Volatile Organic Compounds) have been studied. The modulation of the refractive index is introduced by mixing niobium sol with organic matrix PEO-*b*-PDMAA poly[(ethylene oxide)-*b*-(N,N-dimethyl acrylamide)] followed by a proper annealing of the film. After the annealing the optical properties and the thickness of the films were determined. The resistance of the films was studied in terms of optical response prior to and after exposure to different VOCs-acetone, methanol, ethanol and chloroform. In order to study the type of generated porosity, the films underwent process of extraction during which the pores were cleaned from the organic matrix and their optical response were recorded when exposed to the same organic compounds and compared with the one before the extraction.

Keywords: Mesoporous materials, Nb₂O₅, VOCs, soft-template method, PEO-*b*-PDMAA copolymer.

1. INTRODUCTION

Nb₂O₅ emerges as a multifunctional material due to its properties such as photoelectric and photocatalytic activity (Ghandhi et al., 2008), excellent chemical stability, and corrosion resistance in both acidic and alkaline media (Mujawar et al., 2006). Another important asset of this material in areas such as photonics (Lee et al., 2002; Mizuuchi et al., 1997; Dhar et al., 2012) is that it is transparent and has high refractive index in the visible region that allows tuning its values for the needs of particular application. Engineering properties of metal oxide thin films is of utmost importance for having broader application and better functionality in the areas such as catalysis (Corma, 1997), sensing and energy conversion. A common approach for creation materials with tunable optical properties is to use a composite consisting of two materials with different refractive indices mixed in different volume fractions. Recently, we have developed composite material consisting of

Nb₂O₅ and Si-MFI zeolite that exhibits tunable refractive index in the range from 2.02 to 1.11 (Lazarova et al., 2017). Another possible approach for modulation and adjustment of refractive index values according to ones needs is to introduce porosity in the films and thus modulate the refractive index to lower values creating mesoporous Nb₂O₅ films. Mesoporous materials have pores with size in the range between 2 and 50 nm. However, in both cases the problem is that when films are exposed to VOCs (volatile organic compounds) they change their optical response due to condensation of VOC's in the pores resulting in improper operation. In order to produce stable films that do not change their properties when exposed to external stimuli a careful selection of materials and preparation conditions have to be done.

In the present paper for deposition of mesoporous films we used sol-gel method combined with the block copolymer based soft-template method because they represents

an easy, versatile and cheap approach towards structuring of mesoporous Nb_2O_5 of high quality and with fine reproducibility. The optical response of Nb_2O_5 mesoporous thin films when exposed to vapors of acetone, ethanol, methanol, and chloroform is studied. The particular choice of block copolymer and annealing regime that determine the VOC's resistance of the films are discussed.

2. MATERIALS AND METHODS

We prepared the niobium oxide thin films by using the spin coating technique. Niobium sol was synthesized 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 and then spun onto silicon wafer for 30 seconds at 3000 rpm to create non-porous films refer to as dense hereafter (Lazarova et al., 2014a). The porous films were synthesized by mixing the Nb sol with aqueous solution of PEO-*b*-PDMAA block polymer with concentrations of 0.5%, 1.5% and 5% and sol to polymer ratio of 5:1 and then spun at the same parameters as the dense film (Georgiev et al., 2015). Details about polymer synthesis can be found elsewhere (Todorova et al., 2016). The films were annealed in air environment at 320°C for 30 min with acceleration rate of 5°C/min.

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

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

The reaction towards VOCs was investigated by measuring reflection spectra of the films prior to and after exposure of vapors. The reaction of the films toward four common VOCs namely acetone, methanol, ethanol and chloroform was investigated. In order to understand the pore type of the

material (open or closed) we conducted additional experiment aiming at removing the pore-structuring polymer by extracting it and study the optical and sensing properties of the films.

The process of extraction was conducted at home-made equipment after preliminary film annealing at 120°C for 30 min with acceleration rate of 5°C. The films were treated with ethanol vapors at two stages- at the first stage the films were exposed to ethanol vapors for 8 hours and at the second - for 40 hours. Before the process of extraction and after each stage of extraction the refractive index and the thickness of the films were calculated and the reaction towards acetone was tested.

The refractive index (n), extinction coefficient (k) and the thickness (d) of the films were calculated from the reflection spectra (R) of the films at normal light incidence with UV-VIS-NIR spectrophotometer Cary 05E (Varian, Australia) using nonlinear curve fitting method (Lazarova et al., 2014a). The experimental errors for R , n and d are 0.3%, 0.005 and 2 nm, respectively.

3. RESULTS AND DISCUSSION

To investigate the thermal decomposition of PEO-*b*-PDMA, TGA of the block polymer was conducted and the results are given in Figure 1.

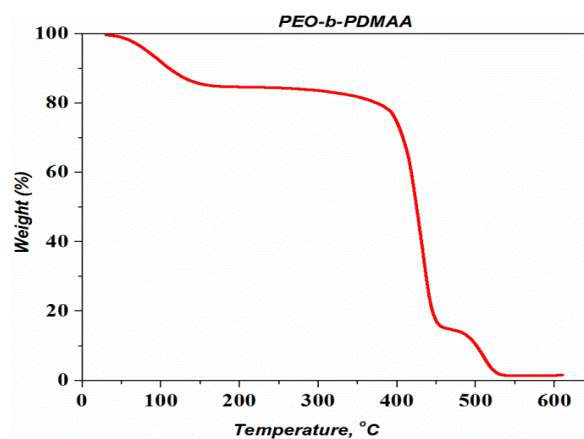


Fig 1. TGA curve of polymer PEO-*b*-PDMA in inert atmosphere.

The first mass loss around 100°C is associated with absorbed water from the ambient as both groups of the polymer are hydrophilic. The full decomposition of the polymer starts with sharp mass loss around 400°C degrees and continues to 550°C where the remaining mass of the polymer is less than 1%. It should be noted that this behaviour might be mainly due to the presence of PDMAA in the polymer structure as it burns at higher temperature. Therefore if the films are post-annealed at 320 °C it will be most likely the film pores to be filled with polymer.

TABLE 1. Film thickness change versus concentration of the introduced polymer PEO-*b*-PDMAA

| Polymer concentration (wt.%) | 0,5 % | 1,5% | 5% |
|------------------------------|-------|------|----|
| Thickness change (nm) | 0 | 8 | 63 |

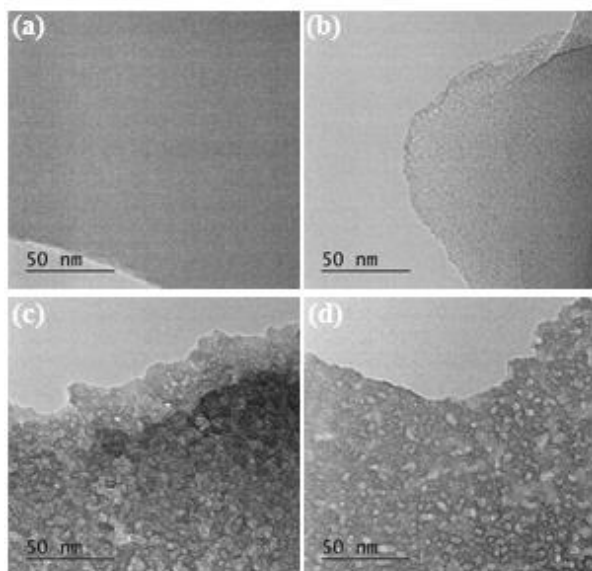


Fig. 2. TEM pictures of Nb₂O₅ films obtained using Nb sol and PEO-*b*-PDMAA polymers with concentration of 0 wt.% (a), 0.5 wt. % (b), 1.5 wt.% (c), and 5 wt.% (d) annealed at 320 °C for 30 min. The volume ratio of Nb sol and polymer is 5:1.

The addition of the polymer into niobium sol creates “polymer” volume in the films after deposition and that manifest itself in an increase of the film thickness. As it is seen

from Table 1 the higher the polymer concentration the bigger the thickness increase of the respective film with comparison to the dense film is. That is due to “polymer” volume introduced into the film. The films created with 0.5% polymer concentration was calculated to have the same thickness as the dense film that is probably due to the fact that the concentration was not high enough to create thickness change outside the experimental error of the methods being used in the current investigation. TEM images taken for each film, given on Fig. 2, confirm that the porosity is hardly noticeable for the lowest polymer concentration used. All films show unordered meso-sized pores.

The dispersion curves of the refractive index of the films are given on Fig. 3.

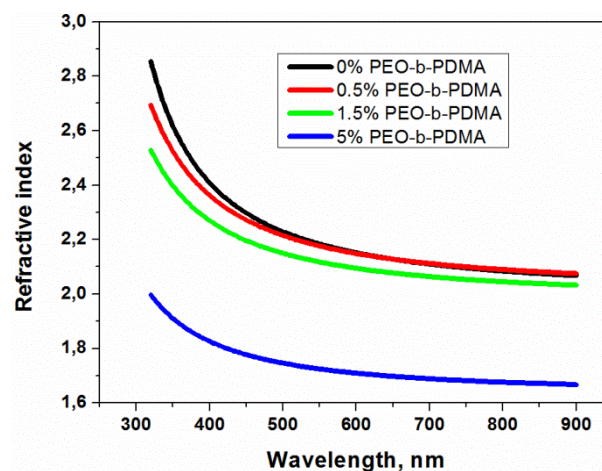


Fig. 3. Dispersion curves of refractive index of dense (0% polymer content) and mesoporous Nb₂O₅ thin film with corresponding polymer content.

It is well known that the refractive index is proportional to the density of the material and by introducing the porosity in the films the effective refractive index decreases from 2.15 for the dense Nb₂O₅ to 2.13 for the 0.5% concentration, to 2.09 for 1.5% concentration plummeting to 1.70 for the films with the highest polymer concentration for wavelength of 600 nm.

We expect that the type of pores (open or closed) is the same for all films prepared with

this polymer. Assumption is made that films which have highest degree of porosity will have largest area for vapors to condense onto and thus those should have the highest reaction towards vapors. Having those considerations in mind the reaction towards the organic compounds were tested only with films with 5% concentration of the polymer.

The vapors were generated by liquid in homemade bubbler system described elsewhere (Lazarova et al., 2014b). The organic compounds chosen for this test were acetone, chloroform, ethanol and methanol. The films were exposed for the same amount of time (300s) for all organic compounds. The reflection spectra of the films were taken prior to (at air ambient) and after vapors exposure and the spectra are given in Fig 4.

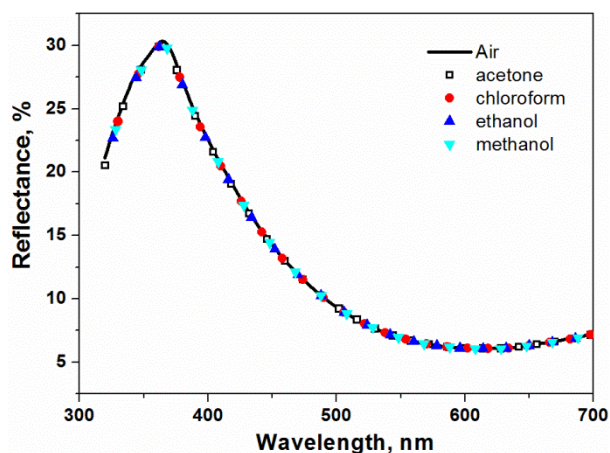


Fig 4. Measured spectra of the films before (air) and after exposure to different organic compounds-acetone, methanol, ethanol and chloroform. The exposure times was kept the same for all measurements.

All of the measurements overlap showing a minor reflection change that is summarized in Table 2. The maximum difference in the reflection spectra for all tested VOCs is less than 0.1% which is within the measurement error of the reflection method. The reason for those film not being able to react could be that either the polymer inside the pores have not being fully removed and thus blocking the access of the vapors to condense or the created pores are from closed

type and as such restrict the vapors from accessing the film volume.

TABLE 2. Maximum reflection change (ΔR) for different VOC's - Acetone (A), Methanol (M), Ethanol (E) and Chloroform (C).

| Organic compound | A | M | E | C |
|-------------------|------|------|------|------|
| max ΔR ,% | 0.09 | 0.09 | 0.05 | 0.10 |

In order to understand the type of porosity created by the polymer, open or closed, we deposited Nb_2O_5 films under the same conditions but instead of annealing the films at 320°C we tried to remove the polymer at lower temperature. As we have previously reported in (Lazarova et al., 2014a), the formation of the Nb_2O_5 has already being completed at around 120°C . Films have been prepared from niobium sol with 5% water concentration of PEO-*b*-PDMAA. They were annealed to 120°C , and treated with ethanol vapors consecutively for 8 and 40 hours. Before the extraction and after each stage of it, the refractive index and the thickness of the films were calculated (shown on Fig. 5) and the optical reflection change from the film was measured after acetone exposure.

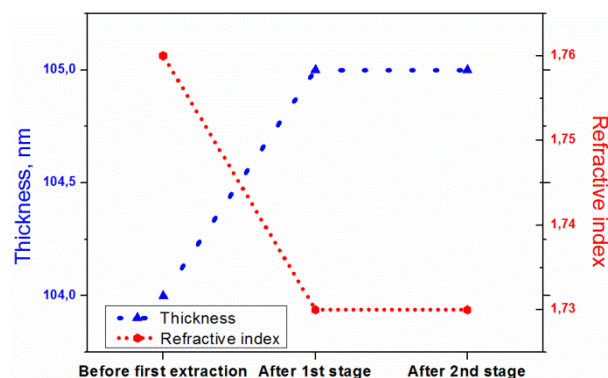


Fig 5. Refractive index (blue) and thickness (red) of the film during the extraction measurements.

As it is seen from Fig. 5 after the first stage of extraction the refractive index drops slightly and stays the same after the second stage of extraction. This could be explained with polymer removal from the pores of the films as this will decrease the refractive index

of the medium. As PEO-*b*-PDMAA could be dissolved in ethanol, at this temperature the polymer has not been decomposed yet and it is being rinsed from the pores and thus allowing vapor condensing in film's volume. This is also confirmed by the acetone exposure testing as after the first extraction there is considerable change in the reflection coefficient of the film prior to and after exposure of vapors –from 0.05% to 0.4%. The results from the acetone reflectance change are given after each stage in Table 3.

TABLE 3. Reflection change (ΔR_{Ac}) before the extraction and after each stage of the extraction

| Measurement stage | Before 1 st extraction | After 1 st extraction | After 2 nd extraction |
|-------------------------|-----------------------------------|----------------------------------|----------------------------------|
| max ΔR_{Ac} , % | 0.05 | 0.40 | 0.40 |

4. CONCLUSIONS

In the current study we demonstrate the successful deposition of VOC's resistant Nb₂O₅ thin films with refractive index modulated in the range from 2.15 to 1.70. The films are prepared by using sol-gel and soft-template methods with incorporation of PEO-*b*-PDMAA polymer and post deposition annealing at moderate temperatures where there is no full decomposition of polymer. Using reflectance measurements prior to and after exposure to analytes it is proven that the films could be regarded as non-reacting medium for four common volatile organic compounds - acetone, methanol, chloroform, and ethanol. The change in reflectance is in the framework of experimental error. The access of vapours to the film volume is restricted due to the fact that PEO-*b*-PDMAA copolymer is not fully removed from the pores thus blocking the condensation of vapours inside them. By the method of extraction it is demonstrated that the porosity created by PEO-*b*-PDMAA copolymer in the Nb₂O₅ film is of open type which could make those films also applicable for optical detection.

ACKNOWLEDGMENTS

The financial support of project DFNP-17-97/28.07.2017 of the Program for career development of young scientists and Bulgarian National Science Fund (BNSF) under the project DN08/15 (14.12.2016) is highly appreciated.

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