Preparation and characterization of mesoporous Nb$_2$O$_5$ films for sensing applications

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Abstract. The possibility of combining sol–gel synthesis with molecular self-assembly and phase separation is explored to produce Nb$_2$O$_5$ films with tailored pore structures at the nanometer scale. Thin Nb$_2$O$_5$ film are fabricated by spin coating of a Nb sol prepared by sonocatalytic method using NbCl$_5$ and ethanol mixed with structure directing agent Pluronic PE 6800 in different concentrations which acts as a supra molecular pore template. Post deposition treatment is applied for film consolidation and pore formation. Surface morphology and structure of the films are studied by Transmission Electron Microscopy and Selected Area Electron Diffraction. The optical properties (refractive index and extinction coefficient) along with the thickness of the films are determined from reflectance spectra of films deposited on silicon substrates. The overall porosity of the films and the amount of adsorbed acetone vapors are quantified by means of Bruggeman effective medium approximation using already determined optical constants. The sensing properties of the samples are studied by measuring reflectance spectra prior to and after exposure to acetone vapors with controlled concentrations. Furthermore, the potential of using the studied mesoporous Nb$_2$O$_5$ films for chemical sensing with optical read-out is demonstrated and discussed.

1. Introduction
Mesoporous materials have attracted the scientific interest due to their remarkable properties and potential applications in many advanced areas such as drug delivery systems, sensors, catalysis, photovoltaic cells, and fuel cells [1]. Among several advantages, mesoporous materials offer possibilities of functionalization and a high active surface area due to their controlled porosity in 2-50 nm range and narrow pore size distribution. Besides mesoporous oxide thin film is a promising matrix for embedding isolated or interacting metal nanoparticles modifying in this way its optical, electronic and catalytic properties [2].

One attractive application of mesoporous films is for building blocks of vapor responsive Bragg stacks [3-5]. The idea behind the detection is the change of refractive index and/or thickness of the layers in the Bragg stack due to condensation of vapors in the pores which results in a shift of the high reflectance band and consequent change of stacks color [6,7]. Because the high optical contrast (difference in refractive indices of the layers in the stack) is essential for proper operation of the device most commonly a combination of SiO$_2$ and TiO$_2$ mesoporous thin films is used in the stack [4,5,8]. It will be a real advantage if material with higher refractive index is used instead of TiO$_2$. Thus a higher optical contrast could be achieved enabling even an omnidirectional reflectance to be realized [9]. Recently we have shown that Nb$_2$O$_5$ thin films with tunable refractive index and good optical properties could be produced by simple sol-gel method [10]. Besides, Nb$_2$O$_5$ exhibits the highest
refractive index among the widely used TiO$_2$ and Ta$_2$O$_5$ sol-gel films [11]. Despite there are few reports for fabrication of mesoporous Nb$_2$O$_5$ films [12 and refs 27, 29, 56, 172-175, 238-240 cited herein] a lack of optical characterization exists.

In this paper we report studies of sol-gel derived mesoporous Nb$_2$O$_5$ thin films prepared by evaporation-induced self-assembly method using Pluronic PE6800 as a molecular pore template. Optical properties and thickness of the films are calculated from measured reflectance spectra. The refractive index curves are further used for determination of overall porosity of the films using Bruggeman effective medium approximation. The sensing properties of the films are studied by measuring reflectance spectra prior to and after exposure to acetone vapors. The potential application of films as sensitive elements of optical vapour sensors is explored.

2. Experimental details

Thin mesostructured Nb$_2$O$_5$ films were prepared through an evaporation-induced self-assembly method using spin-coating of Nb sol mixed with inorganic template Pluronic PE 6800 (BASF) in volume ratio of 5:1. The Nb sol was prepared by a sonocatalytic method using 0.400g NbCl$_5$ (99%, Aldrich) as a precursor, 8.3 ml ethanol (98%, Sigma-Aldrich) and 0.17 ml distilled water [10,13]. Instead of stirring, the solution was subjected to a sonication for 30 min and aged for 24 h at ambient conditions prior to deposition. For deposition of mesoporous Nb$_2$O$_5$ thin films mixtures of Nb sol and template in volume ratio 5:1 were prepared. Three different batch solutions of Pluronic in ethanol with weight concentration of 1.5, 3 and 5 wt.% were used in the mixtures. An amount of 0.3 ml was dropped on the pre-cleaned Si substrates and spun at a rate of 2500 rpm for 30 s. The template is eliminated by annealing at 320 °C for 30 min at 5 °C / min acceleration. Dense Nb$_2$O$_5$ thin films were also prepared for comparison. Purposely 0.3 ml of Nb sol was spun coated at 2500 rpm for 30 s on Si substrate. The annealing conditions were the same as for the mesoporous films.

The surface morphology and structure of the films were studied by Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) using HRTEM JEOL JEM 2100 (Japan) microscope. The optical properties (refractive index ($n$) and extinction coefficient ($k$)) along with the thickness ($d$) of the films were determined from reflectance spectra of the films measured at normal light incidence by UV-VIS-NIR spectrophotometer Cary 05E (Varian, Australia) using non-linear curve fitting method [10]. The experimental errors for $n$, $k$ and $d$ are 0.005, 0.003 and 2 nm, respectively. The vapor sensing measurements on films were implemented in a Cary 05E spectrophotometer equipped with a homemade bubbler system for generation of vapors from liquids with controlled concentrations [14].

3. Results and discussions

3.1. Morphology study of Nb$_2$O$_5$ thin films

Figure 1 shows typical TEM images of the samples with different concentrations of Pluronic from 1.5 to 3 to 5 wt.% (figure 1(b), 1(c) and 1(d), respectively) which are compared to dense Nb$_2$O$_5$ thin films shown in figure 1(a). It is seen that the addition of template leads to formation of pores arranged non-periodically. The size of the pores gradually increases with concentration of Pluronic. The SAED diffraction (not shown here) had proven that all samples were amorphous.

3.2. Optical properties and porosity of Nb$_2$O$_5$ thin films

The measured reflectance spectra ($R$) of both dense and mesoporous Nb$_2$O$_5$ films deposited using different concentrations of Pluronic are presented in figure 2 (a). The reflectance spectrum of uncoated silicon substrate is also shown. Comparison of $R$ spectra of films and bare substrate shows that reflectance of the films decreases with increasing of template concentration. Besides, the reflectance minimum shifts towards longer wavelengths. This means that the growth of pore size manifest itself in increase in optical thickness (the product of refractive index and physical thickness) of the films.
Figure 1. TEM images of dense Nb$_2$O$_5$ film (a) and porous Nb$_2$O$_5$ films consisting of Nb sol and Pluronic in the same volume ratio (5:1) but with different concentrations of Pluronic: 1.5 wt.% (b), 3 wt.% (c) and 5 wt.% (d).

In order to clarify the optical thickness dependence of $R$ the measured spectra are used further for calculation of $n$, $k$ and $d$ of the films. The calculation procedure is explained in details elsewhere [10]. Briefly, a Wemple-diDomenico single oscillator model [15] and an exponential decay function are used for the description of wavelength dependences of $n$ and $k$, respectively. The models parameters along with the thickness of the films are determined through a non-linear minimization of the discrepancies between the measured and calculated $R$ spectra. The refractive index curves of the films with different Pluronic concentration (i.e different pore sizes) along with dispersion curve of dense Nb$_2$O$_5$ film are presented in figure 2(b). All curves show normal dispersion (decrease in $n$ with wavelength) that is typical for transparent or slightly absorbing materials. With increasing the pore size a significant decrease of refractive index is observed. The values of $n$ at wavelength of 600 nm decrease from 2.14 for the dense film to 1.88, 1.77 and 1.53 for porous films with Pluronic concentration of 1.5, 3 and 5 wt.%, respectively (table 1). Simultaneously there is no change in the extinction coefficient (table 1). Interestingly an increase in thickness is observed: $d$ changes from 37 nm for the dense film to 47, 57 and 85 nm for porous films with different concentrations of Pluronic (table 1). We may conclude that the annealing conditions are appropriately chosen so that no contraction of pores to take place.

In order to quantify the degree of porosity of the studied films we used Bruggeman effective medium approximation (BEMA) [16]. The idea is to regard the mesoporous film as an effective medium consisting of dense Nb$_2$O$_5$ and voids filled with air. The effective dielectric constant $\varepsilon_e$ depends on the dielectric constants of the phases presented and their volume fractions:

$$f_d \frac{\varepsilon_d - \varepsilon_e}{\varepsilon_d + 2\varepsilon_e} + f_{air} \frac{\varepsilon_{air} - \varepsilon_e}{\varepsilon_{air} + 2\varepsilon_e} = 0, \quad f_d + f_{air} = 1,$$

(1)
\( \varepsilon_d \) and \( \varepsilon_{air} \) are the dielectric constants of dense \( \text{Nb}_2\text{O}_5 \) and air, respectively, and \( f_d = \frac{V_d}{V_{tot}} \) and \( f_{air} = \frac{V_{air}}{V_{tot}} \) are their volume fractions (\( V_d \) and \( V_{air} \) being the volumes occupied by dense \( \text{Nb}_2\text{O}_5 \) and air, respectively, \( V_{tot} = V_d + V_{air} \) is the total volume of the film).

![Figure 2](image)

**Figure 2.** Reflectance spectra (a) and refractive index (b) of \( \text{Nb}_2\text{O}_5 \) films deposited on Si-substrate using Pluronic with different concentrations indicated by the numbers in the figures and the same volume ratio of Nb sol and Pluronic equal to 5:1.

For clarity, it is important to note that the two parameters \( \varepsilon \) and \( n \) are related as follows: \( \varepsilon = n^2 \). Thus using the already determined values of refractive index \( n_d \) and \( n_e \) (\( \varepsilon_d \) and \( \varepsilon_e \), respectively) (figure 2 (b)) and considering that \( \varepsilon_{air} = 1 \), the voids volume fractions \( f_{air} \) are calculated from eq. 1 and presented in table 1. As can be expected the increase of the pore size leads to significant increase of the free volume fraction that reaches value of 51 % for the film with the highest concentration of Pluronic (table 1).

**Table 1.** Refractive index \( n \), extinction coefficient \( k \), thickness \( d \), volume fractions of air \( f_{air} \) and acetone \( f_{ac} \) in % calculated from eq. 1 and 2 respectively, relative reflectance change \( \Delta R_{ac}/R_{Ar} \) and refractive index change \( \Delta n_{ac} \) after exposure to acetone vapors as a function of Pluronic concentration.

| Pluronic, wt. % | \( n \) (600 nm) | \( k \) (600 nm) | \( d \), nm | \( f_{air} \), % | \( \Delta R_{ac}/R_{Ar} \), % | \( \Delta n_{ac} \) = \( n_{ac} - n_{Ar} \) | \( f_{ac} \), % |
|----------------|----------------|----------------|-------|----------------|----------------|----------------|-------|
| 0              | 2.14           | 0.020          | 37    | 0              | 0              | 0              | 0     |
| 1.5            | 1.88           | 0.018          | 47    | 22             | 1.2            | 0.0034         | 0.9   |
| 3              | 1.77           | 0.018          | 57    | 31             | 2.3            | 0.011          | 2.8   |
| 5              | 1.53           | 0.021          | 85    | 51             | 2.7            | 0.007          | 1.4   |

3.3. Vapor sensing experiment

Reflectance spectra of the samples are measured prior to and after exposure of the films to acetone vapors at relative pressure \( p/p_0 = 1 \) (\( p_0 \) is the pressure of saturated vapors at zero degrees). The generation of acetone vapors from liquid and the control of their concentrations are realized by homemade bubbler system explained in details in [14]. Before running the spectra all films are exposed to dry Ar flow with rate of 500 sccm for 10 min in order to empty the pores. The values of relative reflectance changes \( \Delta R_{ac}/R_{Ar} \) (where \( \Delta R_{ac} = R_{ac} - R_{Ar} \), \( R_{ac} \) and \( R_{Ar} \) are reflectance spectra after acetone and argon exposure, respectively) as a function of Pluronic concentration are presented in...
figure 3 (a) and in table 1. No change of $R$ is observed for dense Nb$_2$O$_5$. For porous films a gradual increase of $\Delta R_{ac}/R_{ac}$ with Pluronic concentration is obtained. Considering that $R_{ac}$ is a function of $n$, $k$ and $d$ of the films we can write $\Delta R_{ac}$ as follows:

$$\Delta R_{ac} = \frac{\partial R_{ac}}{\partial n} \Delta n_{ac} + \frac{\partial R_{ac}}{\partial k} \Delta k_{ac} + \frac{\partial R_{ac}}{\partial d} \Delta d_{ac},$$

(2)

where $\frac{\partial R_{ac}}{\partial n}$, $\frac{\partial R_{ac}}{\partial k}$, $\frac{\partial R_{ac}}{\partial d}$ are the partial derivatives of $R_{ac}$ with respect to $n$, $k$ and $d$ and $\Delta n_{ac}$, $\Delta k_{ac}$ and $\Delta d_{ac}$ are the absolute changes in $n$, $k$ and $d$ of the films due to exposure to acetone vapors, respectively.

The exposure of the porous films to acetone results in vapor condensation in the pores and replacement of the air inside with acetone with higher refractive index. As a result the effective refractive index of the films increases, i.e $\Delta n_{ac} > 0$. We assume no changes in $k$ and $d$, i.e $\Delta k_{ac}=0$ and $\Delta d_{ac}=0$. The values of $\Delta n_{ac}$ are calculated through equation 2 using the measured values of $\Delta R_{ac}$ (table 1) and numerically derived partial derivatives. Figure 3 (b) and table 1 show $\Delta n_{ac}$ as a function of Pluronic concentration. It is seen that the change of $n$ is the strongest at Pluronic concentration of 3 wt.%. After acetone adsorption the exposed films consist of three phases: dense Nb$_2$O$_5$, acetone and air with respective dielectric functions $\varepsilon_d$, $\varepsilon_{ac}$ and $\varepsilon_{air}$ and volume fractions $f_d$, $f_{ac}$ and $f_{air}$. Then BEMA can be written in the form:

$$f_d \frac{\varepsilon_d-\varepsilon_e}{\varepsilon_d+2\varepsilon_e} + f_{air} \frac{\varepsilon_{air}-\varepsilon_e}{\varepsilon_{air}+2\varepsilon_e} + f_{ac} \frac{\varepsilon_{ac}-\varepsilon_e}{\varepsilon_{ac}+2\varepsilon_e} = 0,$$

$$f_d + f_{air} + f_{ac} = 1$$

(3)

The values of the volume fraction of acetone vapors in the film are calculated using equation 3 and are presented in table 1. Surprisingly, the highest value of $f_{ac}$ is obtained for porous film with Pluronic concentration of 3 wt.%. For higher and lower concentration of Pluronic the amount of adsorbed acetone vapors is smaller.

![Figure 3](image-url)  
**Figure 3.** Relative reflectance change $\Delta R_{ac}/R_{ac}$ (a) and refractive index change $\Delta n_{ac}$ (b) after exposure to acetone vapors as a function of Pluronic concentration.

Previously we have shown that the strength of the optical response is determined by the interplay between surface hydrophobicity and tension, refractive index and molecular size of the analyte [17]. Considering that the refractive index and molecular size are the same for all studied samples we can assume that the surface hydrophobicity and tension mainly influence the adsorption strength. It may happen these two parameters to vary with the pore size maximizing its positive impact on adsorption...
at particular pore size. Another possible reason for the peak in adsorption is the interconnectivity of the pores that could be the highest for the sample with 3wt.% Pluronic. We suppose that the periodical arrangement of the pores will improve further the optical response.

As we note in the introduction part a possible application of the studied mesoporous films is in responsive Bragg stacks [18,19]. Bragg stacks are multilayered systems comprising high and low refractive index materials with quarter-wave optical thicknesses \((nd = \lambda/4)\) arranged in a periodic manner. Due to the interference phenomena, Bragg stacks exhibit a band of high reflectance that is centered at \(\lambda_c\), and it is highly sensitive to changes in optical thickness of the constituent films. If vapor sensitive materials are used as building blocks, then the position of the reflectance band can be used as an indication of the concentration of the detected analyte [18,19].

For achieving high sensitivity of vapor responsive Bragg stacks all layers across the stack should be accessible to the detected analyte. Our previous studies have shown that for Bragg stack comprising alternatively deposited MEL-type zeolites films and dense \(\text{Nb}_2\text{O}_5\) films only five layers are accessible to the analyte (acetone in the current case) [14]. We expect that the implementation of mesoporous \(\text{Nb}_2\text{O}_5\) films in Bragg stack instead of dense ones will improve the effective penetration of the analyte through the layers resulting in increased sensitivity and simultaneously preserving the high optical contrast. These experiments are ongoing in our group.

### 4. Conclusions

It is shown that the combination of sol–gel synthesis with phase separation is successful approach for deposition of mesoporous \(\text{Nb}_2\text{O}_5\) films with enhanced porosity. The fabrication of thin \(\text{Nb}_2\text{O}_5\) films with tailored pore structure at the nanometer scale through evaporation-induced self-assembly method is demonstrated. Purposely a mixture of Nb sol and Pluronic PE 6800 in different concentrations is spun coated on silicon substrate and subjected to post deposition annealing at 320 \(^\circ\)C for 30 min at 5 \(^\circ\)C/min acceleration of the temperature for pore formation and film consolidation. An increase in film thickness from 37 to 85 nm is observed when Pluronic concentration changes from 0 to 5 wt.\% thus confirming the appropriateness of the choice of the annealing conditions ensuring no pore contraction to take place. Simultaneously a decrease of refractive index from 2.14 to 1.53 is obtained due to the higher free volume fraction originating from the increased pore size.

An improvement of sensing properties of mesoporous films is demonstrated as compared to the dense films. The strongest response of \(\text{Nb}_2\text{O}_5\) films towards acetone vapors is achieved for films with Pluronic concentration of 3 wt.%. For higher and lower concentrations of Pluronic the amount of adsorbed acetone vapors is smaller. Two possible reasons are discussed: i) the interconnectivity of the pores that maximizes at certain pore size and ii) a specific interplay between surface hydrophobicity and tension that favours acetone adsorption at a particular Pluronic concentration / pore size.

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