Tunable Bragg stacks from sol-gel derived $\text{Ta}_2\text{O}_5$ and MEL zeolite films

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Abstract. In this paper we investigated sol-gel derived $\text{Ta}_2\text{O}_5$ and nanosized MEL zeolite films obtained by spin coating of Tantalum sol and colloidal zeolite solution, respectively. Refractive index and thickness of the films were determined using non-linear curve fitting of measured reflectance spectra. The influence of the post deposition annealing on the optical properties and thickness of the films was studied. Besides tunable Bragg stacks were designed and prepared by layer-by-layer deposition of $\text{Ta}_2\text{O}_5$ and MEL suspensions with quarter-wave thicknesses. The influence of water, acetone and methanol on the optical behavior of Bragg stacks was discussed.

1. Introduction

Bragg stacks are multilayered systems comprising high and low refractive index materials with quarter-wave optical thicknesses: $nd = \lambda_c / 4$, $n$ refractive index, $d$-physical thickness, $\lambda_c$ - wavelength of incident light, arranged in periodic manner. When Bragg stack is illuminated with light, multiple reflected waves occur at each boundary that are in phase and interfere constructively, which is resulting in appearance of high reflectance band centered at $\lambda_c$. Because the position of the reflectance band is extremely sensitive to the changes in refractive index and thickness of the constituent layers it is possible the position of reflectance band to be controlled upon the influence of external stimuli. In this way tunable Bragg stacks, very attractive for sensing applications have been fabricated [1,2].

$\text{Ta}_2\text{O}_5$ is a typical high refractive index semiconductor with an advantage over $\text{TiO}_2$ of UV transparency. Among various deposition techniques used for production of thin films (layers) from $\text{Ta}_2\text{O}_5$, the sol-gel method attracts considerable scientific interest because of its versatility, low cost and low temperature processing. Besides, it allows control of the microstructure of the coating and produces durable and chemically stable films [3,4]. Additionally, thick films can be easy produced using sol-gel synthesis approach [5,6].

The most widely used starting material for sol-gel preparation of $\text{Ta}_2\text{O}_5$ is tantalum ethoxide ($\text{Ta}(\text{OC}_2\text{H}_5)_5$). Usually it is hydrolyzed in parent alcohol in the presence of catalyst, most often acid in order to form inorganic oxide network [7]. Because of the high sensitivity of $\text{Ta}(\text{OC}_2\text{H}_5)_5$ to moisture the process of obtaining clear sol is not trivial. It is well known that the rate of hydrolysis and condensation are very fast, causing complete gelation in few hours [8]. Therefore the sol stabilization is crucial for obtaining clear sols and good quality films. This was achieved by addition of a complex ligand - methacrylic acid, [9] or most often glacial acetic acid was used [3,10]. Both acids act as
chelating agents and decrease the reactivity of the employed metal alkoxide by formation of hybrid complexes in which the number of reactive alkoxide groups decrease [9].

In general, the porous structure of sol-gel films has smaller refractive index values - \( n \), in comparison to films obtained by other methods [11]. Besides, the heat treatment leads to an increase of the \( n \) value [3,10,12].

Nanosized zeolite films are appropriate for low refractive index counterpart of tunable Bragg stacks. Zeolites are a unique class of industrially significant materials with tunable physicochemical properties [13]. Their great utility in standard and advanced applications in diverse media is due to their large internal surface area, i.e., the presence of voids of controllable dimensions at the atomic, molecular, and nanometer scales [14]. The possibility to control their composition, pore shape and size, hydrophobicity, hydrophilicity and overall particle size and morphology are attractive advantages for using the zeolites in preparation of tunable Bragg stacks. Besides, the zeolites can be prepared with nanosized dimensions [15] and thus will act as optical transducers of physico-chemical processes that occur within the micropores and interparticle mesopores. The zeolite-analyte interactions such as sorption/desorption, ion exchange, diffusion etc. will cause changes of the refractive index and thickness of the zeolite films and subsequent shift of the reflectance band of Bragg stack is expected.

In this paper we investigate sol-gel derived \( \text{Ta}_{2}\text{O}_5 \) and nano-sized MEL zeolite films obtained by spin coating of tantalum sol and colloidal zeolite suspension, respectively. The water free sol-gel route for obtaining clear and stable sol of \( \text{Ta}_{2}\text{O}_5 \) is developed. The influence of the post deposition annealing on the optical properties of the films is studied. Besides tunable Bragg stacks were designed by layer-by-layer deposition of \( \text{Ta}_{2}\text{O}_5 \) and MEL. The influence of water, acetone and methanol on the optical behavior of the Bragg stacks is discussed.

2. Experimental details

The coating solution (tantalum sol) was prepared using tantalum ethoxide Ta(OC\(_2\)H\(_5\))\(_5\) (99.98 %, Sigma-Aldrich) as a chemical precursor, isopropyl alcohol (Merck) as solvent, glacial acetic acid CH\(_3\)COOH (Sigma-Aldrich) as catalyst and chelating agent, and diethanolamine DEA (Merck) as a surfactant to prevent sediment impurities in the solution. Although the synthesis procedure for the Ta coating solution used in this paper is similar to that of Tepehan [10], three distinctive changes are made: (i) water free, (ii) isopropyl alcohol used instead of ethanol, and iii) small amount of DEA added.

The solution A was prepared by mixing of 35 ml of isopropyl alcohol with 1 ml of glacial acetic acid and then 1.5 ml Ta(OC\(_2\)H\(_5\))\(_5\) is slowly drop wise added. The solution B 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 DEA was added. The final mixture was transparent and colourless with pH of about 5. The obtained solution is subjected to slow stirring for 18 h. The solution was very stable and can be kept at ambient temperature for extended time without precipitates. There was no evidence of gelation after 30 days.

The \( \text{Ta}_{2}\text{O}_5 \) films were deposited by dropping of 0.2 ml of the coating solution on pre-cleaned Si wafer as substrates and then spin at a rate of 2000 rpm. The Si wafers were cleaned in a detergent solution, washed with isopropanol and then dried at room temperature. Prior to the deposition of the coating solution it was filtered with 0.2 \( \mu \)m pore-sized filter. After deposition, the films were annealed at different temperatures in the range 90-650 \( \degree \)C. The \( \text{Ta}_{2}\text{O}_5 \) film thickness after annealing at 500\( \degree \)C for 30 min was 40 nm. The coating procedure was repeated several times in order to obtain thicker films. The intermediate films were dried at 60\( \degree \)C to increase their mechanical stability.

Nanosized MEL zeolite crystals were synthesized from a colloidal precursor suspension with the following chemical composition: \( \text{SiO}_2 \) : 0.3TBAOH (tetrabutylammonium hydroxide) : 4.0EtOH (ethanol) : 18.0H\(_2\)O, at 90 \( \degree \)C for 68 h [16]. After purification the nanocrystals were redispersed in ethanol to obtain a suspension with a solid concentration of 5 wt. %. The zeolite ethanol suspensions were used for preparation of zeolite films by spin coating method: 0.3 ml of zeolite suspension with
desired concentrations was dropped onto the Si substrate. The speed and duration of spin-rotation were varied between 1000 to 2000 min\(^{-1}\) for 30-90 s. The zeolite films were annealed at 500 °C for 30 minutes with a heating rate of 10°C / min. The zeolite films under investigation had a thickness in the range 100 - 300 nm.

Bragg stacks with 5 layers were prepared by alternative deposition of Ta\(_2\)O\(_5\) and MEL zeolite films with target thicknesses of 72 and 110 nm, respectively on the Si substrate. The target thicknesses of both films were calculated aiming at their optical thicknesses - the product of physical thickness and refractive index, to be a quarter of the operating wavelength - 520 nm in our case. In order to achieve the correct thicknesses of the films, the concentration of the zeolite suspension was optimized by addition of appropriate amount of solvent - ethanol. The Ta-sol was used as prepared but two deposition steps were required with intermediate drying of layers with hot air. An annealing at 320°C for 15 min was applied after deposition of each film. Finally the stack was subjected to calcination at 500 °C for 45 min.

3. Results and discussions

Refractive index \(n\), extinction coefficient \(k\), and thickness \(d\), of the films were determined from reflectance measurement at normal incidence in the spectral range 400 – 1000 nm using Wemple-DiDomenico dispersion equations for \(n\) [17] and exponential decay function for \(k\) according to the following:

\[
 n(E) = \sqrt{1 + \frac{E_0 E_d}{E_0^2 - E^2}}, \quad k(E) = a_0 \exp\left(\frac{E}{A}\right), \tag{1}
\]

where \(E\) is the light energy in the measured spectral range. The coefficients \(E_0, E_d, a_0\) and \(A\) in eq. 1 along with \(d\) were determined through minimization of a goal function \(G\) (eq. 2) consisting of the discrepancies between measured \(R_{\text{meas}}\) and calculated \(R_{\text{calc}}\) reflectance spectra. A non-linear subspace trust region method combining the interior-reflective Newton method with a preconditioned conjugate gradients method [18] was used for minimization:

\[
 G(E_d, E_0, a_0, A, d) = \sum_i (R_{\text{meas}} - R_{\text{calc}})^2, \tag{2}
\]

where \(i\) is the number of the points in the used spectral range. For accurate and unambiguous minimization, proper initial values for the unknown parameters are required. Because such information is not available we used the approach explained in details elsewhere [19]. Briefly, the minimization procedure was run using a wide grid of initial values for the unknown parameters and the error function \(Err\) of the minimization was calculated as the residual value of the goal function at each solution:

\[
 Err = \sqrt{\sum_i G(E_d, E_0, a_0, A, d)^2}. \tag{3}
\]

The values of \(E_0, E_d, a_0, A\) and \(d\) in the global minimum of \(Err\) were used as initial values in the next minimization step and the calculation algorithm is continuously repeated until the value of \(Err\) at the minimum did not change any longer. The \(n, k\) and \(d\) of film were obtained by substitution of the final values of \(E_0, E_d, a_0, A\) and \(d\) in eq.1.
Figure 1 presents refractive index and thickness of films from MEL zeolites and sol-gel derived Ta$_2$O$_5$ as a function of temperature annealing. The values are averaged over 5 samples and the error bars present the deviations from the average values. The increase of $n$ for Ta$_2$O$_5$ and decrease for MEL films with annealing are clearly seen. The removing of residual solvent and organic additives as acetic acid and DEA leads to densification of the Ta$_2$O$_5$ films and formation of inorganic oxide network manifesting itself in fast decrease of thickness and increase of the refractive index. Annealing at 500 °C for 30 min is sufficient to produce stable films. Further annealing at 650°C does not lead to significant changes of $n$ and $d$. The values of $n$ in our case are lower as compared to those obtained in [12,20], which can be explained with different thickness and increased porosity of the films. In the case of MEL film the pores empty during calcination and thus the refractive index decreases. Simultaneously a small collapse of the film volume is observed as well.

![Figure 1. Dependence of refractive index (a) and thickness (b) of the films as a function of annealing temperatures.](image)

The good optical contrast i.e the difference of refractive indices between the films - about 0.7, is sufficient for obtaining high reflectance Bragg stacks using comparatively low number of films. Simultaneously very good linear dependence of MEL thicknesses on the concentration is observed (not shown in the paper) that enable us to choose precisely the appropriate suspensions concentration to obtain the correct quarter wave thickness of the MEL films for the stack.

The sensing experiments were performed by soaking the samples into specific liquids - water, methanol and acetone, for 180 s and the reflectance spectra of the films prior and after soaking were measured. Figure 2 presents the reflectance spectra $R$ of single Ta$_2$O$_5$ and MEL films and Bragg stack consisting of 5 alternating films of Ta$_2$O$_5$ - $d = 72$ nm and MEL - $d = 102$ nm, before and after exposure to acetone, methanol and water liquid. The highest changes of $R$ obtained for the films are shown in figure 3. It is seen that for all liquids the changes of $R$ for single films are smaller as compared to the changes of $R$ for the Bragg stack. The change of reflectance is associated with increase of the effective optical thickness - $nd$, which could be mainly due to the increase of the effective refractive index. The liquid penetrates into the pores of the films and substitutes the air that occupies the pores. Considering that the liquids have refractive index higher than the air the increase of effective refractive index could be expected.

The measured reflectance spectra presented on figure 2 were used to calculate the optical thickness of the films. An increase of 1.25%, 2.4% and 3.06% was observed for Ta$_2$O$_5$ and 3.4%, 0.9% and 0.1% for MEL exposed to acetone, methanol and water respectively. The films of Ta$_2$O$_5$ are more sensitive to water and less sensitive to acetone while the opposite trend is observed for the MEL zeolite film.

Recently, we have shown that the strength of the optical response of MEL zeolites depends on the interplay between hydrophobicity, polarity, surface tension, refractive indices and molecular size of the liquids under investigation [21]. Thus, due to the high hydrophobicity the optical response of MEL
zeolite in the case of water exposure is very weak, while the hydrophilic nature of Ta$_2$O$_5$ is the most probable reason for the increased optical response toward water. The smaller polarity of methanol and especially acetone leads to weaker response of the Ta$_2$O$_5$ film. Considering that acetone has the highest refractive index among the studied liquids, the strongest response of the MEL film towards acetone may be expected [21].

**Figure 2.** Reflectance of Ta$_2$O$_5$ and MEL single films and Bragg stack consisting of 5 alternating Ta$_2$O$_5$ and MEL films before (solid line) and after (dashed line) soaking in denoted liquid analytes for 180 s.

In the case of the Bragg stack, the acetone exposure leads to shift of the reflectance band with 30 nm towards longer wavelengths, while methanol and water result in considerably smaller shift of 6 and 8 nm, respectively. Due to the band shift a decrease of the stack reflectance with 20 % is observed in the case of acetone and 5 % and 8 % for methanol and water, respectively.

**Figure 3.** The changes of reflectance of Bragg stack and single films under exposure to acetone, methanol and water liquids.

The selective change in $R$ of the Bragg stack when exposed to acetone is clearly seen in figure 3.
The contribution of Ta$_2$O$_5$ to the overall methanol and water response is stronger as compared to the pure MEL zeolite film. As already mentioned due to the more hydrophilic nature of Ta$_2$O$_5$ as compared to the MEL zeolite, methanol and especially water penetrates more easily through and thus changes the effective optical thickness which is resulting in the reflectance change.

4. Conclusions

In this paper we investigated sol-gel derived Ta$_2$O$_5$ and nanozeolite MEL films obtained by spin coating of sol solution and zeolite suspension, respectively. It is demonstrated that clear and stable Ta sol can be obtained by water free sol-gel synthesis approach with addition of diethanolamine as stabilizer and acetic acid as chelating agent. Optical characterization has shown that the annealing at 500 °C is sufficient to obtain stable and high refractive index Ta$_2$O$_5$ films.

Tunable Bragg stacks consisting of five sol-gel derived Ta$_2$O$_5$ films and nanosized MEL zeolite films are fabricated by alternative spin coating deposition with quarter-wave thickness at 520 nm. A selective shift of reflectance band with 30 nm towards longer wavelength is observed when the Bragg stack is exposed to liquid acetone. In the case of methanol and water the shifts are 6 and 8 nm, respectively. Due to acetone exposure a substantial change of reflectance of the Bragg stack with almost 20 % is observed that is important prerequisite for application of the Ta$_2$O$_5$ / MEL stacks as sensors with optical encoding.

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