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Optimization of optical and sensing properties of sol-gel oxides through zeolite doping

K. Lazarova[1]*, H. Awala[2], J. El Fallah[2], M. Vassileva[1], S. Mintova[2], T. Babeva[1]

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

[2]*Laboratoire Catalyse et Spectrochimie, Normandie Université, ENSICAEN, CNRS, 6 boulevard Maréchal Juin, 14050 Caen, France*

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The modification of the optical and sensing properties of Nb_2O_5 and SiO_2 oxides thin films through doping with nanosized zeolite crystals with MFI and EMT- types framework was studied. Thin films of pure oxides and oxo-zeolite composites consisting of oxide matrix embedded with zeolites were deposited by spin-coating method using pre-synthesized metal sols and colloidal stable zeolite suspension mixed at the desired ratios and subjected to post-deposition annealing. The surface morphology of the films and their optical properties were investigated by SEM and UV-VIS-NIR spectroscopy, respectively. The sensing behavior was studied by measuring the reflectance spectra before and after exposure to probe molecule (acetone vapors) and successive calculation of the changes in effective refractive index due to vapor condensation in the porous films. The potential of the developed materials for optical sensing applications is discussed.

Keywords: sol-gel materials; nanosized zeolites; films; optical properties; optical sensing.

INTRODUCTION

Enhanced performance, low manufacturing cost, simple processing and possibility for integration in different devices are essential preconditions for novel materials to be used in advanced technologies. In this context, the solution processed metal oxides have increasingly attracted scientific interest due to their potential applications for improving the performance of different devices such as Bragg gratings, optical filters, photonic crystals, sensors etc. [1-3].

Among these applications, the optical sensing is highly promising and it has also been intensively studied [4,5]. The idea behind the sensing is the change of refractive index of the oxide due to capillary condensation of vapors inside the pores. Therefore the generation of well-defined and interconnected pore system inside the oxide film is essential for its sensing application. Two general approaches have been reported in the open literature for porosity creation, each one with its pros and cons. In the first approach, porosity has been generated using sacrificing organic template which after its removal through an appropriate annealing or chemical treatment leaves interconnected or closed pores inside the films [6]. Alternatively, thin films with different porosity have been fabricated using suspensions of nanoparticles in different aggregation states [7].

In this paper, a different approach for porosity generation via using zeolites nanocrystals as dopants for dense metal oxide matrix is applied. The approach is similar to the one already used for preparing meso-structured silica films containing nanosized zeolite [8] and silica / zeolite composites [9]. Since zeolites are crystalline materials with well-defined ordered micropore structure on the molecular scale it is expected that their intrinsic microporosity will introduce additional porosity in the sol-gel oxide thus improving oxide-sensing properties. Besides, due to the low refractive index of zeolites [10] it is anticipated that the effective refractive index of oxo-zeolite composite can be tuned in wide range when matrix with high refractive index such as Nb_2O_5, V_2O_5 oxides is used [11, 12]. This will allow production of multilayered structures such as Bragg stacks where the same material with different doping level, i.e. different porosity can be used for achieving significant optical contrast instead of alternation of different materials thus overcoming the incompatibility issues.

Herein we report the optimization of optical sensing properties of Nb_2O_5 and SiO_2 oxides films through doping with EMT and MFI-type zeolite nanocrystals. Pre-synthesized metal sols and colloidal stable zeolite suspension were mixed together at the desired volume ratios and used for the preparations of thin films by spin-coating method. The optical and sensing properties are studied by measuring of reflectance spectra. The potential of the developed materials for optical

* To whom all correspondence should be sent:
E-mail: klazarova@iomt.bas.bg

sensing applications is demonstrated.

EXPERIMENTAL

Nb-sol was prepared by a sonocatalytic method using 0.40 g $NbCl_5$ (99%, Aldrich) as a precursor, 8.3 ml ethanol (98%, Sigma-Aldrich) and 0.17 ml distilled water [11, 13]. The solution was subjected to sonication for 30 min and aged for 24 h at ambient conditions prior to deposition. The Si-sol was prepared using 2.2 ml tetraethyl orthosilicate (TEOS) as a precursor dissolved in 4.6 ml H_2O and 11.8 ml ethanol and magnetically stirred for 4 h at 50 ºC. Pure silica MFI-type zeolite (Si-MFI) was synthesized according to the procedure described before; the synthesis was performed at 90 °C for 3 days. [14]. While the synthesis of nanosized EMT-type zeolite with particle size of 10-15 nm was performed according to the procedure published in [15]. The synthesis was performed at 35 °C for 36 h. Both zeolites were extracted *via* high-speed centrifugation (20 000 rpm, 60 min) followed by re-dispersion in double distilled water; this procedure was repeated several times until the final colloidal suspensions reached pH of 8.5.

The doping of metal oxides with zeolites was realized in liquid phase by adding different volumes of zeolites solutions to the already prepared metal sols thus achieving doping levels from 0% (pure metal oxide film) to 100 % (pure zeolite films) in the film. It should be noted here that in the case of Si-sol the highest doping levels were 60 % and 70 % for Si-MFI and EMT zeolites, respectively. Further doping deteriorated the film's optical quality and resulted in increased scattering. Prior to mixing, the zeolites and sols were sonicated for 30 minutes in order to redispersed the aggregated particles.

Oxo-zeolites thin films were prepared by pouring of 0.3 ml of sol / zeolite mixture on preliminary cleaned silicon substrates and spinning at a rate of 3000 rpm for 30 s. A post deposition annealing was applied to all films for 30 min at 320 ºC with temperature ramp of 10 ºC / min. Our additional experiments have shown that further annealing at 320 ºC did not modify the samples properties.

The aqueous cellulose solution (1.5 wt.%) is added to zeolite suspension in order to improve the adhesion of zeolite film on silicon substrate.

The surface morphology of the films and their structures were characterized by Philips 515 scaning electron microscope. The 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 [16]. The experimental errors for n, k and d were 0.005, 0.003 and 2 nm, respectively. The vapor sensing measurements on films were conducted by measuring reflectance spectra prior to and after vapor exposure using Cary 05E spectrophotometer equipped with a homemade bubbler system for generation of vapors from liquids with controlled concentrations [17].

RESULTS AND DISCUSSIONS

Thin films of Nb_2O_5 doped with Si-MFI type zeolites

Fig. 1 shows the surface morphology of the Nb_2O_5 films doped with Si-MFI zeolites with different volume ratio from 0 to 100 %. It is seen that the pure oxide film has a very smooth and featureless surface, while the pure zeolite film exhibits rough surface with grainy morphology. The surface morphology of the oxo-zeolite composites is dependent on the fraction volume between zeolites and oxides. The results show an increase of the surface roughness as the concentration of zeolite crystals increased (see Fig. 1c).

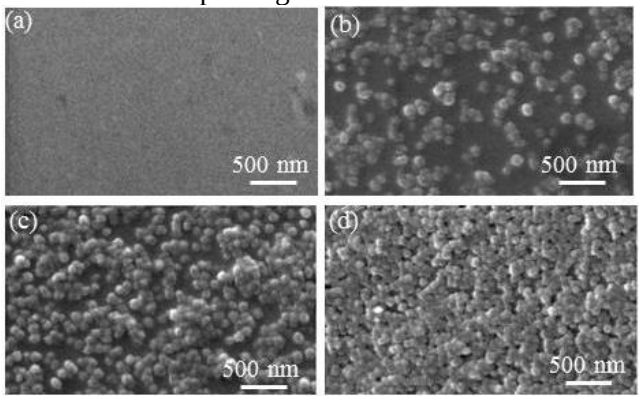

Fig. 1. SEM images of the surface of films (a) pure Nb_2O_5, (b) 50% Nb_2O_5:50% Si-MFI, (c) 25% Nb_2O_5:75% Si-MFI and (d) 100% Si-MFI.

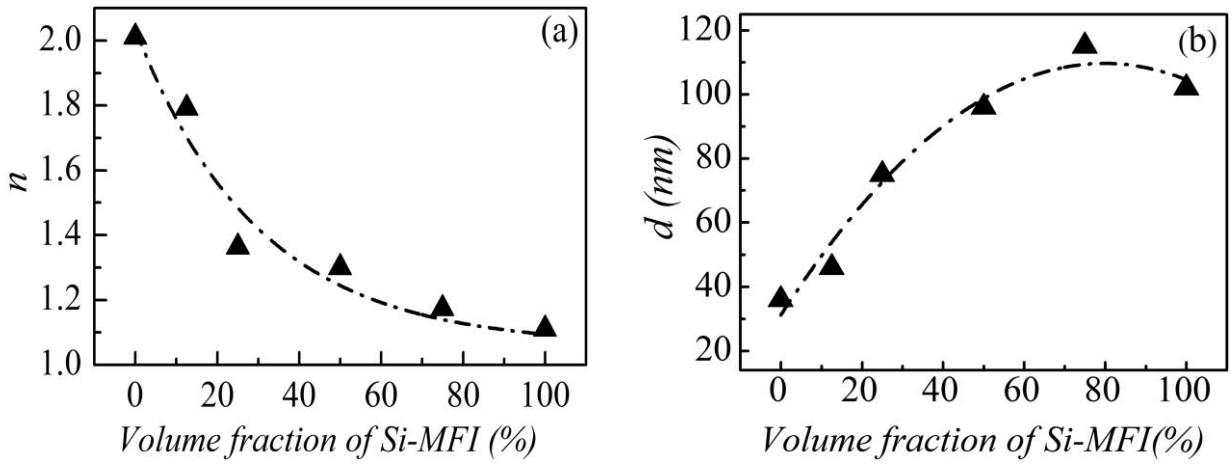

Fig. 2. (a) Refractive index and (b) thickness of the Nb_2O_5 films doped with Si-MFI zeolite.

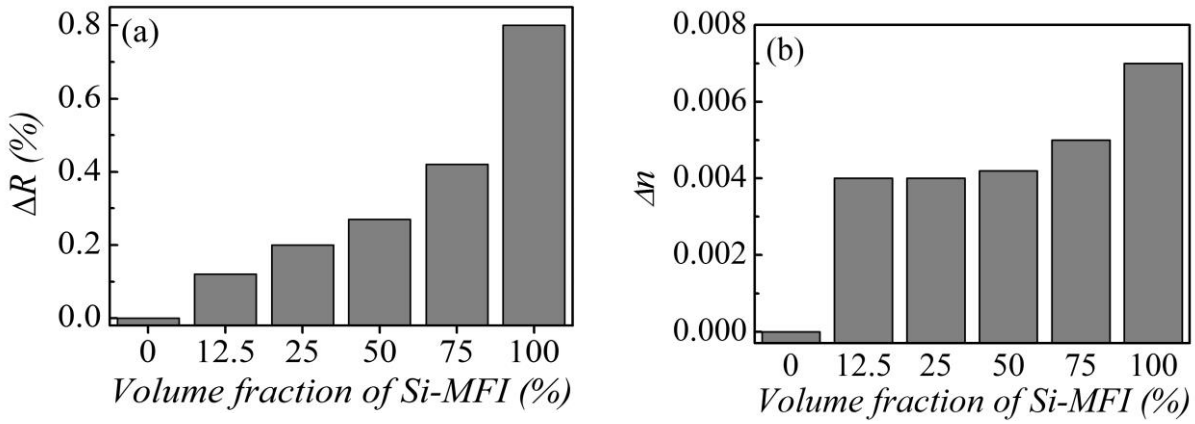

Fig. 3. Absolute change of (a) the reflectance and (b) effective refractive index of Nb_2O_5 films.

The variation of the refractive index (*n)* and thickness (*d)* of Nb_2O_5/Si-MFI films as a function of the volume fraction of zeolites is shown in Fig. 2. For determination of the optical properties of the films, reflectance spectra of all samples were measured and their thicknesses and refractive indices were calculated according to [16]. It is seen from Fig. 2 that by increasing of the doping level of zeolite, the refractive index of the composite decreases exponentially from 2.02 for undoped film to 1.11 for 100 % doped film (pure Si-MFI film). The thickness for pure Nb_2O_5 and Si-MFI-zeolite films is 36 nm and 102 nm, respectively, while the thickness of the composites changes exponentially with increasing the doping level. Since the refractive index of zeolites is lower than oxides [10], the reduction of *n* can be expected due to the increase of zeolite volume fraction in the oxo-zeolite composites, which leads to a decrease of the effective refractive index of the films. Due to the small size of zeolite crystals (30 - 40 nm) there is no significant increase of optical losses due to scattering for doped samples as compared to the pure Nb_2O_5 films.

The results presented (Fig. 2) are very useful when materials with specific optical characteristics are required for certain applications. For example, this approach can be used for production of rugate filters that exhibit sine profile of the refractive index across the film thickness [18] because a wide range of refractive index values can be covered simply by doping of Nb_2O_5 films with zeolites.

We have already shown [10] that Si-MFI zeolite films change their effective refractive index when exposed to analytes due to adsorption and condensation of vapors in their micro- and meso-pores. To the contrary, no changes are observed for pure Nb_2O_5 films. However, when Nb_2O_5 film is doped with zeolites it may be expected the formation of mesoporosity in addition to the microporosity of the zeolites inside the films. In order to clarify the results, we studied the sensing properties of the films through measurements of reflectance spectra of the samples before (R_{air}) and after exposure to acetone vapors (R_{ac}), and the

change in effective refractive index (Δn) is calculated. The absolute changes in reflectance, ΔR (= $|R_{air} - R_{ac}|$) and refractive index, Δn, are displayed in Fig. 3. The calculation of Δn is performed using already measured values of ΔR and it is explained in details elsewhere [19].

As can be seen (Fig. 3a), with increasing of the volume fraction of zeolites, ΔR increases gradually from 0 % for undoped film to 0.27 % for 50 % doped one and reaches the value of 0.82 % for pure zeolite film. The total pore volume increases with doping of the films with zeolite, since the vapor penetrates more easily and condense in the pores due to the capillary condensation. As a result the effective refractive index increases with 0.004 - 0.005 for doped films to 0.007 for pure zeolite film (Fig. 3b). Thus doping of the Nb_2O_5 layers with Si-MFI zeolites improves their sensing properties and allows control of the optical characteristics.

Thin films of SiO_2 doped with Si-MFI and EMT-types zeolites

The same approach for preparing SiO_2-based oxo-zeolite composites was applied where thin films of SiO_2 was used as a matrix for incorporation of Si-MFI and EMT-type zeolites with different volume fractions (Fig. 4). The pure silica surface is not shown in Fig. 4 because it is very similar to the surface of pure Nb_2O_5 (Fig. 1a).

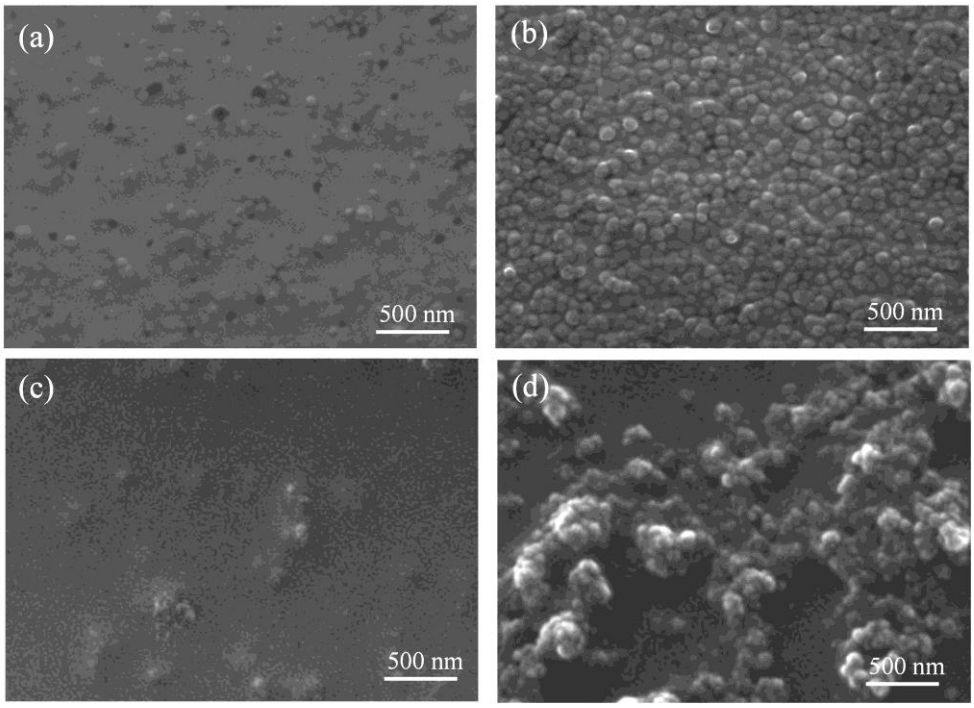

Fig. 4. SEM images of the surface of SiO_2 films doped with Si-MFI (a, b) and EMT (c, d) type zeolites with a volume fraction of 17 % (a, c) and 60 % (b, d).

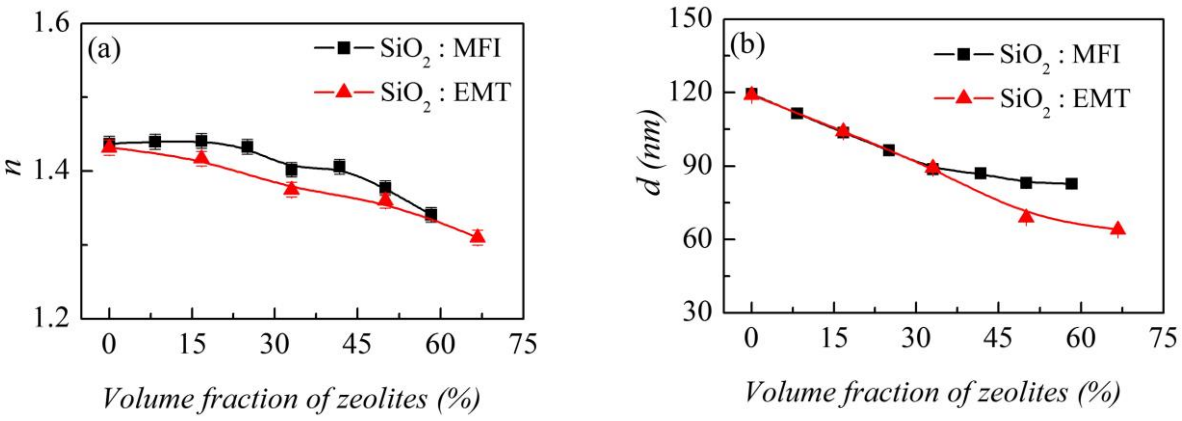

Fig. 5. Dependence of (a) the effective refractive index (n) and (b) thickness (d) of SiO_2 based oxo-zeolites films on the volume fractions of zeolite crystals.

With increasing the doping level, the smooth oxide surface changes to a granular one where the Si-MFI zeolites are distributed almost homogeneously on the surface in comparison with

the EMT-type zeolite crystals. It should be noted that the addition of zeolites in the volume fraction greater than 60% and 70 % in the cases of Si-MFI and EMT, respectively, leads to films with strong scattering and it is practically impossible to be realized.

The optical properties of the oxo-zeolite composites were studied, i.e., the refractive index and extinction coefficient were calculated from the reflectance spectra. Fig. 5 shows the refractive index (n) and thickness (d) of SiO_2 doped with Si-MFI and EMT-types zeolites. It is seen that the influence of zeolites on the effective refractive index of the film is similar in both cases: n decreases from 1.43 to 1.34 for Si-MFI-type zeolite and to 1.31 for EMT-type zeolite, when the volume fractions vary from 0 to 60% and from 0 to 70 %, respectively. The smaller values of n could be due to the existence of bigger empty spaces between the EMT-type zeolites in comparison with Si-MFI-type zeolite as dopants (Fig. 4 (b) and 4 (d)). According to the thickness dependences, the difference in thickness values of oxo-zeolite composites prepared using different zeolite types is stronger for volume fractions higher than 30 % while for small amount of zeolites added to the matrix, the d-values are very similar in both cases (Fig. 5b). The similar film morphologies for small doping levels and significantly different surface status for higher doping (Fig. 4) may explain the observed dependences.

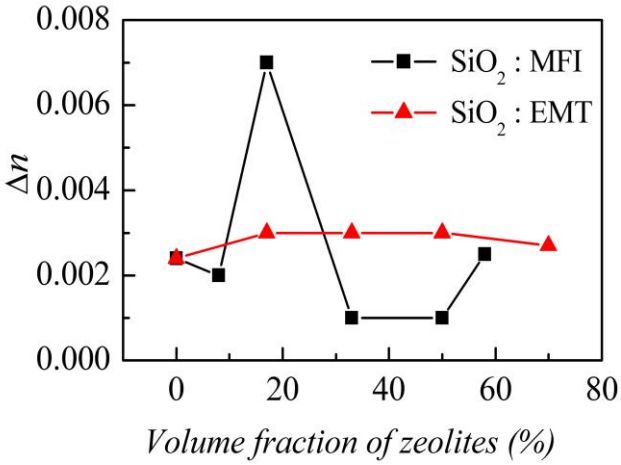

Fig. 6. Refractive index change of SiO_2 films doped with different volume fraction of Si-MFI and EMT-zeolites exposed to acetone vapors at partial pressure p/p_0=0.15 (p_0 is the saturated vapors pressure at 0°C)

To check whether there is an improvement of sensing properties of oxo-zeolite composites in comparison with pure silica matrix, the reflectance spectra of the films are measured prior to and after exposure to acetone vapors with partial pressure p/p_0=0.15 (p_0 is the saturated vapors pressure at 0 °C). The changes in reflectance are used further for calculation of the refractive index (Δn) shown in Fig. 6. For EMT composites there is a weak enhancement of sensitivity that is independent of the volume fraction of added zeolites. The refractive index of EMT/SiO_2 composites changes with 0.003 after exposure to acetone vapors, while for pure silica the change is 0.002. In addition EMT-type zeolite is highly hydrophilic, which decreases its selectivity and adsorption toward acetone vapors. However, when hydrophobic Si-MFI type zeolite is used as dopant, there is a significant improvement of the sensing properties of the composite with zeolite volume fraction around 20 % where the increase in sensitivity is more than 3 times. The achieved change in n is comparable with Δn for pure zeolite film (Fig. 3b).

The supplementary advantage of the SiO_2/MFI film is the smoother surface and higher refractive index, both are very important if the films are used as building blocks of vapor responsive Bragg stacks. The first one will guarantee smooth interfaces between the layers in the stack thus leading to the stronger reflectance band. The higher value of n for the composite (1.43) as compared to 1.11 for zeolite film will allow an omnidirectional reflectance to be achieved because the condition of refractive index higher than 1.2-1.30 for one of the stack's constituents will be fulfilled [20].

Interestingly, for the rest of composites there is no improvement of Δn, even weaker changes are obtained as compared to SiO_2 matrix. Previously, we have shown that the surface hydrophobicity and tension mainly influence the adsorption strength [21]. We can speculate that there is an optimal value of MFI volume fraction where the interplay between these two parameters intensifies their positive impact on adsorption thus leading to the highest optical response.

For further increase of the sensitivity, the SiO_2/Si-MFI composite can be used as a building block of Bragg stack along with an appropriately chosen material with high refractive index (doped Nb_2O_5 for example). Our additional calculations have shown that the reflectance changes of 0.14% for single film can be increased to 0.7%, 1.6 % and 2.6 % using 3, 5 and 7 layered stacks, respectively.

CONCLUSIONS

The fabrication of oxo-zeolite composites comprising SiO_2/Nb_2O_5 matrix doped with Si-MFI and EMT-type zeolites was demonstrated. It was shown that in the case of Nb_2O_5 matrix the refractive index of the resulting composite can be tune in a wide range from 2.02 to 1.11, while for

SiO_2 the refractive index varies from 1.43 to 1.34 and 1.31 for MFI and EMT zeolites, respectively. Besides, the highest possible volume fraction of zeolites inserted in SiO_2 matrix depends on zeolite type, and it is 60 % and 70 % for zeolites with MFI and EMT-types frameworks, respectively. Further increase of the doping level leads to deterioration of the optical quality of the films and increased scattering.

A significant improvement of sensing properties was observed for the Nb_2O_5 composites where there is no change for pure oxide: the effective refractive index of composites increases with 0.004 - 0.005 after exposure to the probe molecules (acetone vapors) that is very close to the change obtained for pure zeolite films (0.007). The reason is the porosity induced in the oxide matrix through doping with zeolites. The increase in sensitivity more than 3 times was achieved for SiO_2 film doped with Si-MFI zeolites with volume fraction around 20%.

Although the obtained changes in refractive index are comparable with these for pure Si-MFI films the composites have the supplementary advantages of smoother surface and higher refractive index, both opening the pathway of using them in vapor responsive Bragg stacks.

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ОПТИМИЗИРАНЕ НА ОПТИЧНИТЕ И СЕНЗОРНИ СВОЙСТВА НА ОКСИДИ, ПОЛУЧЕНИ ПО ЗОЛ-ГЕЛ МЕТОДА, ЧРЕЗ ДОТИРАНЕ СЪС ЗЕОЛИТИ

К. Лазарова[1]*, Х. Авала[2], Дж. Ел Фаллах[2], М. Василева[1], С. Минтова[2], Цв. Бабева[1]

[1]*Институт по оптически материали и технологии ''Акад. Й. Малиновски'', Българска Академия на Науките, ул. Акад. Г. Бончев бл.109, 1113 София, България.*
[2]*Лаборатория по катализ и спектрохимия, Нормандски университет, ENSICAEN, CNRS, бул. Маршал Жуен 6, 14050 Каен, Франция*

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(Резюме)

В настоящото изследване е изучено модифицирането на оптичните и сензорни свойства на тънки слоеве от Nb_2O_5 и SiO_2 чрез дотиране с наноразмерни зеолити MFI и EMT - тип. Тънките филми от чисти оксиди и оксо-зеолитни композити, съдържащи оксидна матрица с вградени зеолити, са получени чрез центрофужно нанасяне и последващо загряване, използвайки предварително синтезиран зол и стабилизирани колоидни разтвори на зеолити, смесени в различно съотношение. Повърхностната морфология на филмите и техните оптични свойства са изследвани съответно чрез SEM и UV-VIS-NIR спектроскопия. Сензорните свойства са изучени чрез измерване на спектъра на отражение преди и след излагането на филмите на тестваните молекули (ацетонови пари) и пресмятане на промените на ефективния показател на пречупване, вследствие на кондензацията на парите в порите на филма. Дискутиран е потенциалът на разработените материали за оптични сензорни приложения.