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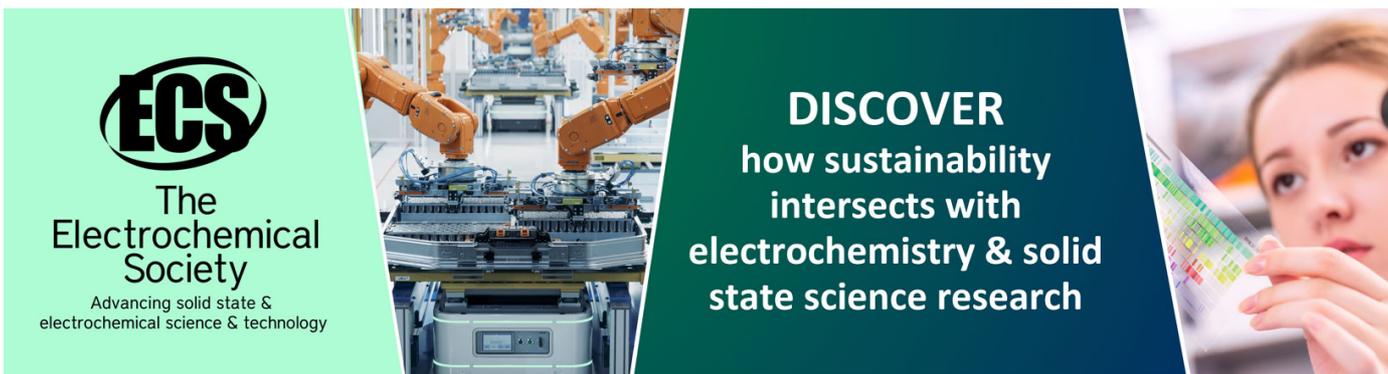
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Optical and sensing properties of sol-gel derived vanadium pentoxide thin films with porous and dense structures

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Abstract. The sol-gel and spin-coating methods were used for deposition of thin transparent V₂O₅ films on optical glass substrates and silicon wafers. Different synthesis and deposition conditions, including synthesis temperatures and post-deposition annealing, were used aiming at obtaining transparent films with high refractive index and good optical quality. The surface morphology and structure of the films were studied by SEM and XRD. The optical properties (refractive index, extinction coefficient and optical band gap) and thickness of the V₂O₅ films were determined from their transmittance and reflectance spectra. The potential application of the films as building blocks of optical sensors was demonstrated by preparation of multilayered structures comprising both V₂O₅ and BEA-type zeolite films and testing their response towards acetone vapors.

1. Introduction

High refractive index materials are needed in many areas, such as optics, photonics, photovoltaic etc., for improving the performance of optical devices. Among vanadium oxides, V₂O₅, being the most stable of them, has gained increasing interest due to its fascinating thermal, electric and photochromic properties. V₂O₅ thin films exhibit multicolor electrochromism and have high potential for use in electrochromic display devices, color filters, and smart windows [1-3]. Moreover, V₂O₅ has a wide optical energy gap, a layered structure, and good chemical and thermal stability that make it promising for use in microelectronic, electrochemical and optoelectronic devices [4, 5]. V₂O₅ has already been used as a resistance sensor for NO₂ [6] and ethanol [7], as a catalyst [8], as an infrared detector [9], and a high-performance cathode for lithium ion batteries [10]. Recently, we demonstrated the successful application of V₂O₅ thin films as building blocks of vapor-responsive Bragg stacks for selective optical detection of chloroform [11].

One of the simplest and flexible methods for deposition of V₂O₅ thin films is the sol-gel method, where the structural, morphological and optical properties of the films can be tailored by changing the deposition parameters, such as the precursor type and concentration, the choice of solvent, the duration and temperature of synthesis, the postdeposition annealing etc. In order to improve further the performance of Bragg stacks used for optical sensing [12], it is crucial to optimize the synthesis and

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deposition conditions so as to obtain materials, which, besides having a high refractive index and good optical quality, are permeable for molecules of the vapors to be detected.

In the present study, we applied the sol-gel and spin-coating methods for deposition of thin transparent V_2O_5 films using various synthesis temperatures and solvents, as well as duration and temperature of the post-deposition annealing. The relationship between the synthesis parameters and the deposition conditions on the one hand, and the structural, morphological and optical properties on the other was thus revealed. The potential application was demonstrated of the films as building blocks for optical sensors.

2. Experimental part

The V_2O_5 films were deposited using both the sol-gel and spin-coating methods. Vanadium sols were synthesized by dissolving 1.5 ml vanadium(V) oxytriisopropoxide (Sigma Aldrich) in 35 ml of 0.2% v/v Pluronic PE 6100 (BASF) solution in isopropanol and stirring for 60 min at temperatures of 25 °C or 55 °C. Alternatively, in some experiments half of the above solvent was replaced with acetone. Thin V_2O_5 films with thickness of 55 nm were deposited on optical glass BK-7 and silicon wafers by spin-coating of 0.3 ml of vanadium sol for 30 s at a rotation speed of 3000 rpm. A post-deposition annealing for 30 min at 320 °C and 450 °C was applied at an acceleration rate of 10 °C/min. The films' surface morphology and structure were studied by scanning electron microscopy (SEM) using a JEOL JSM6700F SEM (accelerating voltage of 30.0 kV, JEOL, Tokyo, Japan) and a PANalytical X'Pert Pro diffractometer with Cu $K\alpha$ monochromatic radiation ($\lambda = 1.5418 \text{ \AA}$), respectively. The transmittance (T) and reflectance spectra (R) of the films were measured at normal light incidence by a Cary 05E UV-VIS-NIR spectrophotometer (Varian, Australia). The optical properties (refractive index (n) and extinction coefficient (k)), along with the thickness (d) of the V_2O_5 films were determined simultaneously from the T and R measurements of films deposited on both types of substrates with an accuracy of 0.01, 0.005 and 1 nm in n , k and d , respectively, using a previously developed calculating procedure [13, 14]. The optical band gap was determined using already calculated values of the absorption coefficient α ($= 4\pi k/\lambda$, where λ is the wavelength) and Tauc's plots [15].

A stable coating suspension of discrete nanosized BEA-type zeolite synthesized from a colloidal precursor suspension under hydrothermal condition was prepared according to the procedure described elsewhere [16]. The sensing properties of multilayered structures comprising thin films of BEA zeolites and V_2O_5 were studied under their exposure to acetone vapors. An infrared (IR) reactor-cell was used connected to a saturator gas-system with different vapors (concentrations from 5 to 35000 ppm). The IR spectra under adsorption and desorption of analytes were collected in a continuous mode by a Tensor 27 spectrometer (Bruker) equipped with a DTGS detector.

3. Results and discussion

The influence of the temperature of the synthesis of vanadium sol on the optical properties of the deposited thin V_2O_5 films is demonstrated in figure 1(a), where the optical constants (refractive index, n , and extinction coefficient, k) are presented as functions of the wavelength. The plot of $(\alpha E)^2$ versus the energy, E , (the so-called Tauc's plot), where α ($= 4\pi k/\lambda$, λ being the wavelength) is the absorption coefficient, is presented in figure 1(b). The optical band gap values, E_g , for direct transitions are determined by extrapolating the linear part of Tauc's plot to $\alpha = 0$.

As seen in figure 1, the increase of the synthesis temperature from 25 °C to 55 °C results in a decrease of k for wavelengths higher than 500 nm, thus improving the transparency of the films in the visible and near infrared regions. For example, at the wavelength of 1000 nm, k has values of 0.275 and 0.014 at 25 °C and 55 °C, respectively. To the contrary, for smaller wavelengths ($\lambda < 500$ nm) the higher synthesis temperature leads to a stronger absorption associated with the slightly smaller values of E_g in this case (2.66 eV), as compared to the values at 25 °C (2.69 eV). Both films have similar refractive indices values (at 600 nm, n is 2.00 and 1.93 for the films synthesized at 25 °C and 55 °C, respectively); except for the region of shorter wavelengths, where the films synthesized at 25 °C

exhibit higher n -values (2.34 at 400 nm) compared to $n = 2.04$ in the case of the film prepared at the higher temperature. Our additional studies (not presented here) have shown that the surface morphologies of the films and their structures are very similar, regardless of the synthesis temperature. The slightly different compositions due to the presence of non-stoichiometric oxides, evidenced by the gradually increasing absorption in the near IR region in the case of 25 °C, could be the possible reason for the different optical behavior of films deposited from vanadium sols synthesized at different temperatures [17].

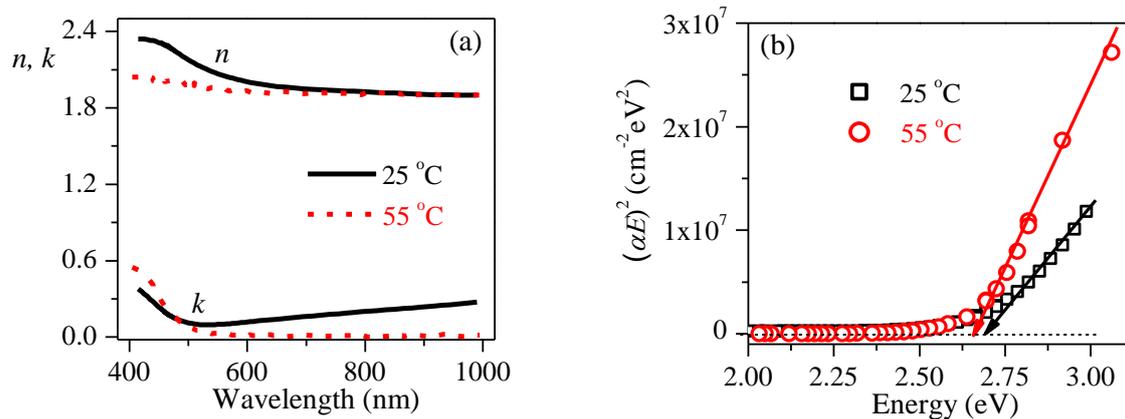


Figure 1. Dispersion curves of the refractive index (n) and absorption coefficient (k) (a) and Tauc's plots (b) for V_2O_5 thin films synthesized at 25 °C and 55 °C.

The SEM images representing the surface morphology and the XRD patterns of V_2O_5 films annealed at 320 °C and 450 °C for 30 min are shown in figure 2. It is seen that increasing the annealing temperature leads to the formation of grains with a bigger size and improves the crystallinity of the films, as indicated by the sharper XRD peaks in the case the film obtained at 450 °C (figure 2c); these results are consistent with the data reported previously [18]. Unfortunately, the optical quality of the films deteriorates at higher temperatures, and the scattering losses rise due to the rough surface. It is important to mention that for optical sensing applications, where the temporal variation of the specular transmittance or reflectance signals are monitored, the optical quality of thin films is essential for proper operation of the particular device. Thus, the post-deposition annealing of V_2O_5 thin films at temperatures higher than 320 °C were not considered further in our study. Our additional experiments have shown that an annealing duration increase from 30 min to 60 min does not influence the thickness and optical properties of the films. This means that isothermal annealing for 30 min at 320 °C is sufficient for stabilization of the films and there is no need for further annealing.

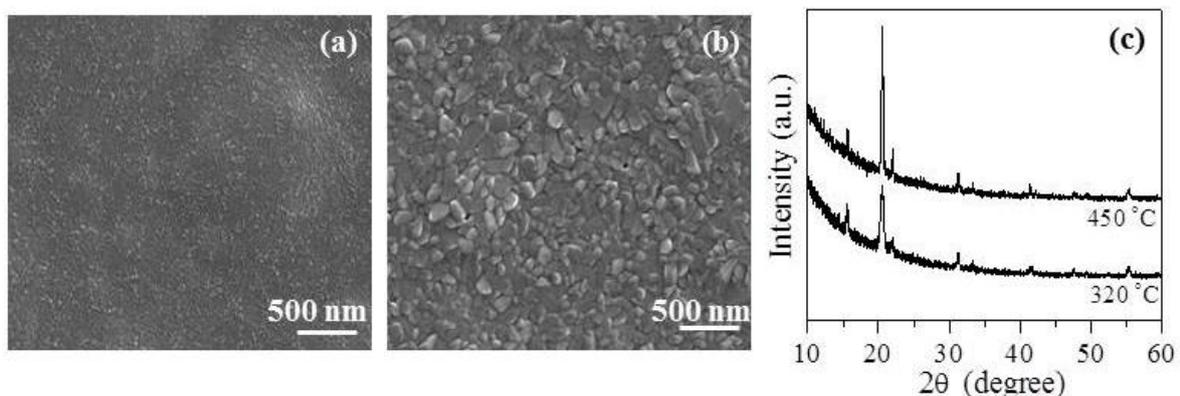


Figure 2. SEM images presenting the surface of V_2O_5 films with a thickness of 55 nm annealed at temperature of 320 °C (a) and 450 °C (b), and their XRD patterns (c).

Figure 3 presents the dispersion curves of n and k for V_2O_5 films (thickness of 55 nm) obtained by vanadium sol prepared with addition of acetone. This particular synthesis included 1.5 ml of Vanadium(V) oxytriisopropoxide dissolved in a mixture of 17.5 ml acetone and 17.5 ml isopropanol.

The films from this synthesis are referred to here as “dense” to distinguish them from the “porous” films deposited from vanadium sol synthesized using 17.5 ml acetone in addition to 17.5 ml of 0.6 % v/v Pluronic PE 6100 (BASF) in isopropanol. After post-deposition annealing, the added polymer evaporates leaving pores in the film, which increases the volume fraction of empty space inside the film. It is expected that the effective refractive index of the film (porous) will decrease in comparison to the film without Pluronic (dense). At the same time, it is very likely that the permeability of the porous films to analyte molecules will be improved due to generation of additional porosity. As seen in figure 3, the addition of acetone results in a higher refractive index at the wavelength of 600 nm; the refractive index of the dense film is 2.24, while n for the porous film is 2.01; i.e., almost equal to that of the film without acetone (figure 1a). However, considering that the concentration of Pluronic is 0.6 % v/v in the former case, we can assume that the porosity of this film is significantly higher as compared to the film without acetone, which will be beneficial if sensing application is contemplated. Besides, the films deposited from sol with acetone are more transparent as compared to those without acetone and have an optical band gap of 2.75 eV.

In addition to high refractive index and transparency, the films should be permeable to the analyte vapors to be suitable for sensing applications. To check the V_2O_5 films' permeability, we deposited two types of double-layered systems on silicon consisting of a V_2O_5 film on top of a porous BEA zeolite film and vice versa, and followed their sensing response to acetone vapors using IR spectroscopy. As the concentration of acetone increases, the intensity of the IR band at $2825\text{--}2938\text{ cm}^{-1}$ increases (figure 4) reaching saturation at a concentration of 20 000 ppm. It is seen that in the case of the sample with a top layer of V_2O_5 , the adsorption is slightly weaker compared to the structure having a top layer of BEA zeolite; this could be explained by a reduced meso-porosity due to the penetration of the V_2O_5 film into the gap between the zeolite crystals. Nevertheless, the significant response in the case of V_2O_5 on top could be regarded as evidence for the good permeability of the V_2O_5 thin films.

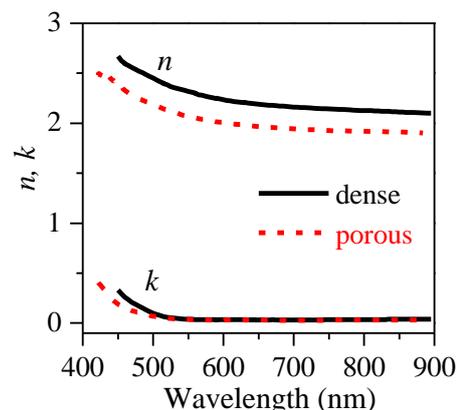


Figure 3. Dispersion curves of the refractive index (n) and absorption coefficient (k) for V_2O_5 thin films synthesized with addition of acetone, without Pluronic (dense) and with Pluronic (porous).

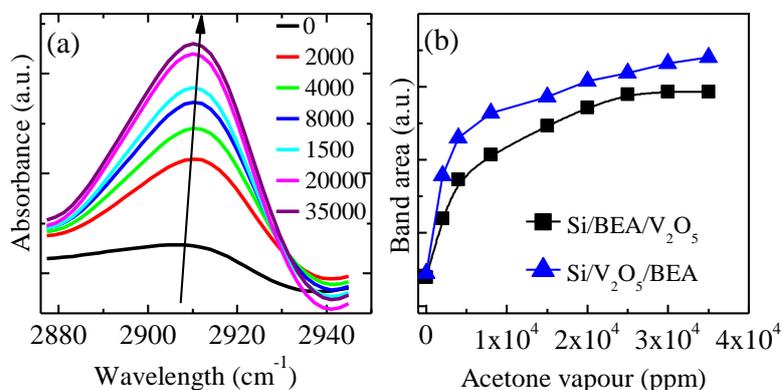


Figure 4. IR absorption spectra of BEA/ V_2O_5 double-layered systems at different concentrations of acetone vapors (a); the arrow indicates the concentration increase from 0 ppm to 35 000 ppm; and adsorption isotherms of acetone of the Si/BEA/ V_2O_5 (black squares) and Si/ V_2O_5 /BEA (blue triangles) double-layered systems (b).

4. Conclusions

Vanadium pentoxide films (V_2O_5) with high refractive index and good optical quality were successfully deposited onto optical glass and silicon substrates using both sol-gel and spin-coating methods. The highest refractive index (2.24 at a wavelength of 600 nm) and optical band gap (2.7 eV) were obtained for films synthesized with addition of acetone into the vanadium sol, while the change of synthesis temperature from 25 °C to 55 °C did not lead to a substantial modification of the films' properties. However, the increase of the post-deposition annealing temperature from 320 °C to 450 °C led to deterioration of films' optical quality, i.e., the films became milky due to increased scattering. The suitability of the films studied to optical sensing applications was demonstrated by in-situ IR adsorption measurements of a probe molecule (acetone). The similarity of the adsorption isotherms obtained for two double-layer systems comprising a V_2O_5 film on top of a BEA zeolite film or a BEA zeolite film deposited on top of a V_2O_5 film confirmed the V_2O_5 films' good permeability and their possible further applications in optical sensing.

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