

## Structure of sol-gel derived Nb<sub>2</sub>O<sub>5</sub> films for active coating devices

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**Abstract**— This work presents the results of structure investigations of sol-gel derived Nb<sub>2</sub>O<sub>5</sub> thin films. Traditional thermal annealing of as-prepared films leading to Nb<sub>2</sub>O<sub>5</sub> crystalline structure formation [1] was substituted by microwave irradiation. The proposed method allows for covering substrates with a different size and shape. The structure of the films was studied using X-ray diffraction (XRD), atomic force microscopy (AFM) and VIS optical absorption measurements. The films exhibit a quantum size effect. The diameter of nanocrystals depends on microwave radiation power and irradiation time.

Transparent conducting oxide (TCO) and transparent oxide semiconductors (TOS) are important materials for numerous applications in photonics. Such materials should be well transparent in the visible range of light spectrum and should be characterized itself by good conductivity or semiconducting properties at room temperature for TCO and TOS, respectively [2]. One of the most popular TOS materials, niobium pentoxide, reveals many interesting properties, like electrochromic, photoelectric and photocatalytic activity [3-5]. Moreover, Nb<sub>2</sub>O<sub>5</sub> coatings have good chemical stability and corrosion resistance to acidic and alkaline conditions [3]. Consequently, Nb<sub>2</sub>O<sub>5</sub> is used in various devices, especially in a field of smart windows [6-7]. Smart windows can reversibly change their optical properties like transmittance, as an effect of applied voltage, incident of light or other factors. The fabrication of smart windows requires a low cost depositing method for covering large area substrates with metal oxides. Uniform coatings with high quality films can be obtained by the sol-gel method. Additionally, the substitution of traditional thermal annealing of as-prepared films (carried out at a temperature over 1000°C) by microwave irradiation makes the fabrication process faster and deposition possible in low temperature on window glass [8].

In the present work, structure investigations of sol-gel derived Nb<sub>2</sub>O<sub>5</sub> thin films are presented. The starting solution was prepared by mixing niobium (V) chloride (99.9%), from Aldrich, with ethanol and acetylacetone as a complexing agent. The films were deposited on a silica glass substrate by a spin coating technique at a rate of 100rps, then aged for 24 hours at room temperature and heated at 250°C for 1 hour.

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Repeating the above procedure three times resulted in approximately 450-nm-thick films. The samples were subsequently exposed to microwave irradiation. To examine the influence of power radiation and the deposition time on the films structure, three series of samples were prepared: irradiated at 600W, 720W and 900W by 1, 5 and 15 minutes.

The structure of the films was studied using XRD, AFM and optical transmittance measurements. XRD patterns were taken at room temperature with a Philips X'Pert diffractometer system using CuK $\alpha$  radiation. Nanotopography of the samples was carried out with a Solver P47-SPM-MDT. Absorption spectra were recorded with Shimadzu UV1240 spectrophotometer at room temperature

After microwave irradiation, regularly shaped grains appeared in all films. There are no great differences between the samples irradiated for 1 and 15 minutes at the same radiation power. Typical AFM topographical images of the films irradiated at 720W for 1 and 15 minutes are presented in Figs. 1(a)-(b). The average diameter of grains increased a little with irradiation time, from about 0.3 $\mu$ m for the sample irradiated for 1 minute to about 0.5 $\mu$ m for the sample irradiated for 15 minutes. As may be seen from Figs.1(a) and (c), (presenting a topographical image of the films irradiated at 720W and 600W for 1 minute), also the power of microwave radiation influences a little the size of the grains. Lower irradiation power seems to lead to the formation of larger grains.

However, crystalline structure is not seen in XRD measurements. The XRD patterns of the films irradiated at 600 and 900W for 1 and 15 minutes are shown in Fig.2. A broad bump between the 2 $\theta$  angle 15° and 40° arises from the silica glass support. The character of the patterns may suggest that the grains seen in AFM pictures are formed by Nb<sub>2</sub>O<sub>5</sub> nanocrystals. This suggestion could be confirmed in visible light absorption investigations. Particles of nanometric dimensions should exhibit a quantum size effect [9]. This behavior was observed, for instance, in sol-gel derived TiO<sub>2</sub> films [10]. According to this theory, the nanocrystal radius R dependence of the band gap shift  $\Delta E_g$  in a quantum size semiconductor is:

$$\Delta E_g \approx \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4\pi\epsilon_0\epsilon R}, \quad (1)$$

where  $h$  is the Planck constant,  $\mu$  is the reduced effective mass of the electron and the hole in the semiconductor,  $e$  is the electron charge,  $\epsilon_0$  is the electric constant and  $\epsilon$  is the dielectric constant of solid [11].

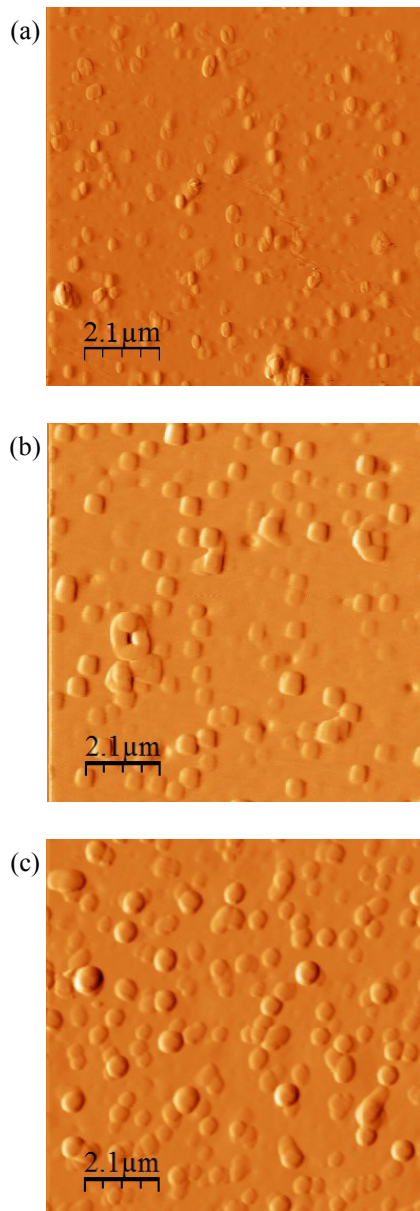


Fig. 1. AFM images of  $\text{Nb}_2\text{O}_5$  thin films prepared at: 720W for 1 minute (a), 720W for 15 minutes (b), 600W for 1 minute (c).

The first term in Eq. (1) is the shift to a higher energy gap (between valence and conduction bands) due to quantum localization, while the second term is the shift to a lower energy gap due to the electrostatic interaction between the

electron and the hole. The shift of the energy gap is calculated from the difference in the absorption edge of the small particle and the bulk material. Absorption spectra presenting the influence of the radiation power and irradiation time on the structure of sol-gel derived  $\text{Nb}_2\text{O}_5$  films are shown in Fig. 3. A blue-shift in the absorption edge is seen as the power of radiation decreases (the time of irradiation is the same) and as the time of irradiation decreases (the radiation power is the same). The radii of nanocrystals calculated from Eq. (1) are given in Table 1. It may be noticed that nanocrystals diameter is larger when the radiation power and/or irradiation time increase.

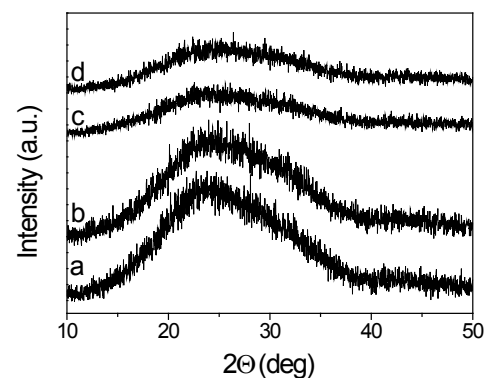


Fig. 2. XRD patterns of  $\text{Nb}_2\text{O}_5$  samples prepared at: 600W for 1 minute (a), 600W for 15 minutes (b), 900W for 1 minute (c), 900W for 15 minutes (d).

Based on absorbance characteristics (Fig. 3), optical transmission ( $T_\lambda$ ), absorption edge ( $\lambda_{\text{cutoff}}$ ) and Urbach energy ( $E_U$ ) were calculated.

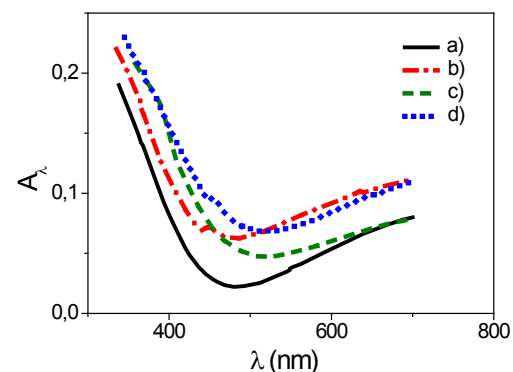


Fig. 3. Optical absorption  $A_\lambda$  spectra of  $\text{Nb}_2\text{O}_5$  thin films irradiated at: 600W for 1 minute (a), 720W for 1 minute (b), 720W for 5 minutes (c), 720 W for 15 minutes (d).

The optical parameters of  $\text{Nb}_2\text{O}_5$  films are collected in Table 1. It can be seen that all manufactured films have high transparency and fulfill the requirements for transparent materials [12]. For the sample irradiated at

600W for 1 minute the transmission coefficient is 92% (at 550nm) while for the sample prepared at 720W for 1 minute it decreases to 83% (at 550nm). The dependence of  $\lambda_{\text{cutoff}}$  and  $E_u$  versus irradiation time and power is presented in Fig 4. The value of Urbach energy is often interpreted as the width of the tail of localized states and is also used to quantify the degree of structural disorder [12-13]. Larger values of  $E_u$  for samples prepared at higher energy can be attributed to increased structural disorder [14-15].

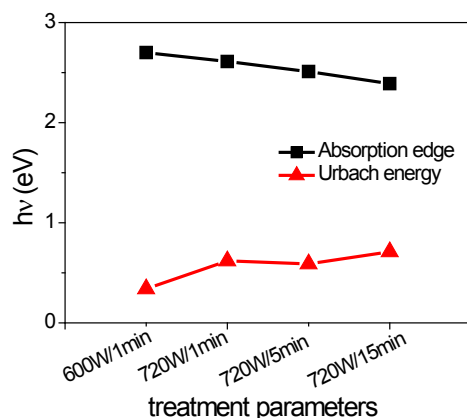


Fig. 4. Absorption edge and Urbach energy vs. irradiation time and radiation power.

Table 1. Optical properties of the prepared  $\text{Nb}_2\text{O}_5$  thin films.

| Sample     | $T_\lambda$<br>(at 550nm)<br>[%] | $\lambda_{\text{cutoff}}$<br>[nm] | $E_U$<br>[eV] | R<br>[nm] |
|------------|----------------------------------|-----------------------------------|---------------|-----------|
| 600W/1min  | 92                               | 459                               | 0.34          | 1.5       |
| 720W/1min  | 83                               | 475                               | 0.62          | 1.7       |
| 720W/5min  | 89                               | 494                               | 0.59          | 1.8       |
| 720W/15min | 85                               | 519                               | 0.71          | 2.2       |

In conclusion, microwave irradiation of sol-gel derived  $\text{Nb}_2\text{O}_5$  films leads to nanocrystalline structure formation, with nanocrystals diameter dependent on microwave radiation power and irradiation time. The optical properties of the films allow for their application in photonics.

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