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Optical Study of Ultrathin TiO_2 Films for Photovoltaic and Gas Sensing Applications

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TiO_2 ultrathin films of thickness below 20 nm were deposited by reactive RF magnetron sputtering. The optical properties of TiO_2 films were investigated by various optical techniques including UV-VIS-NIR spectroscopic ellipsometry. The Scanning Probe Microscopy (SPM) was used to determine thickness and surface roughness of the deposited films. The correlation between preparation conditions of ultrathin TiO_2 films and their physical properties has been studied.

The analysis of optical data revealed the parameters of deposited films and intrinsic properties of TiO_2 material before and after annealing. We found that deposited layers were predominantly amorphous with high porosity at the top sample, and absence of porosity at the bottom of TiO_2 layer. Annealing considerably improves structural order of the studied samples and the film transforms to the polycrystalline anatase phase. Also we evaluated the energy bandgap (about 3.1 eV – 3.2 eV) which increases after annealing (above 3.3 eV) and it is close to the bandgap of anatase.

Keywords: thin films, TiO_2, transition metal oxides, ellipsometry.

1. INTRODUCTION

Nowadays titanium dioxide (TiO_2) is extensively investigated due to its unique combination of optical, chemical and electronic properties [1]. Our main interest is in application of ultrathin TiO_2 films of anatase phase for photovoltaic [2] and gas sensing devices [3]. We expect to reduce thickness of the TiO_2 film in order to decrease response time for appropriate gases and to develop low temperature sensor. So we need to optimize deposition process and parameters for a given application and therefore we have to determine physical and other properties of TiO_2 layers.

We use magnetron sputtering because this technique has some advantages over other deposition methods. The properties and structure of TiO_2 films can be easily modified by changing deposition parameters [4]. The thickness of deposited TiO_2 films were up to 20 nm. During the measurements by conventional technique, for instance, by Fourier spectrometer, the optical response signal of TiO_2 film is very small and is obscured by the contribution of SiO_2 layer. Almost any measurement, which is routine for the thick TiO_2 layer, becomes "state of the art" in the case of ultrathin films.

Due to high accuracy in determination of relative phase changes in the reflected polarized light, the Spectroscopic Ellipsometry (SE) can be used for the characterization of ultrathin films of sub-nanometer thickness. To analyse SE data, the optical model of multilayer structure with a set of parameters characterizing each layer is constructed. The calculated results are fitted to the experimental data by varying the values of adjustable model parameters. So, the dispersion of optical constants, as well as thickness and inhomogeneity can be determined for each layer.

There are many SE studies of TiO_2 bulk samples and films in amorphous, in crystalline and in polycrystalline state (see, e. g., [5 – 8]). To our knowledge, the SE studies of amorphous TiO_2 samples have been carried out on films of thickness above 80 nm [9]. Here, we present SE investigations of ultrathin TiO_2 amorphous and polycrystalline anatase phase films.

2. EXPERIMENTAL DETAILS

The TiO_2 films where deposited on a thermally oxidized Si substrate by a DC reactive magnetron sputtering using pure titanium (99.995 %) as target in the $Ar:O_2$ (4 : 6) environment. Table 1 summarizes the parameters of deposition for two investigated samples. Both samples were annealed under the same conditions for 2 hours at 628 K in the O_2 environment. The thickness and surface morphology of substrate and TiO_2 films were measured by Scanning Probe Microscopy (Veeco SPM Dimension 3100/Nanoscope IV). The mean square roughness of the substrate was equal to 0.21 nm, while for the deposited TiO_2 films it was 0.79 nm and 0.97 nm for 0410 and 0412 samples, respectively. After annealing the roughness remained similar and was equal to 0.82 nm and 0.89 nm, respectivelly. Fig. 1 shows the surface morphology of 0410 sample before and after annealing. For the as-deposited samples the grains are more pronounced, while after annealing their borders look smeared, though analysed distribution of grain sizes does not change considerably. For the 0412 sample morphology before and after annealing is very similar with smaller grain sizes than for the 0410 sample. The thickness of the deposited layers was also estimated by SPM using the foil masked regions (3 mm × 3 mm) on the substrate. The SPM thickness values are shown in Table 1 and they are two times lower than those determined from SE studies.

The SE was carried out by Woollam VASE RC-2 ellipsometer at (0.7 – 5.9) eV photon energy range at 55º,

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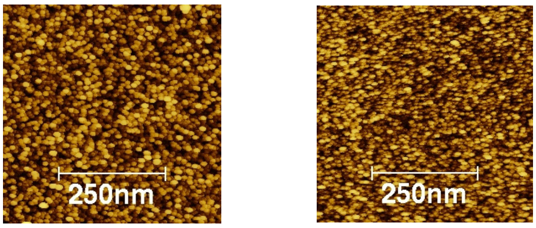
60º, 65º, 70º angles of light incidence. The data analysis was performed with commercial Woollam CompleateEase software.

Table 1. Sample deposition parameters (T is a substrate temperature, P is a pressure in the chamber, t is deposition time, d_{SPM} is a layer thickness determined by SPM)

Sample	T, K	P, Pa	t, min.	d_{SPM}, nm
0410	393	6.5	30	9.4
0412	528			8.3



a b

Fig. 1. The atomic force microscopy images of the 0410 sample before (a) and after (b) annealing

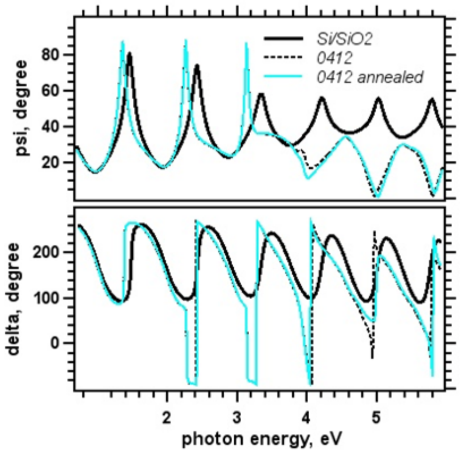


Fig. 2. Comparison of the experimental ellipsometric spectra for the substrate, for the ~15 nm thick TiO_2 film deposited on this substrate and the same film after annealing

The measured spectra of the substrate and TiO_2 were analyzed in the model system composed of several layers described below. The Si/SiO_2 substrate was described using standard approach with an interface layer between Si and thermal silicon oxide [10]. To describe physical properties of the deposited TiO_2, the layer was divided into three sub-layers of the same thickness. Inhomogeneity (porosity) was considered as mixture of dense TiO_2 with void and restricted only to step changes through sub-layer (linear approximation) and was evaluated using the Bruggeman effective medium approximation (BEMA). As the roughness of any surface is constructed as BEMA of 50 % material mixture with void, it was not separately analyzed and was a part of the top sub-layer of the TiO_2 layer. In the opposite case roughness analysis would introduce an additional independent TiO_2 top layer leading to strong correlation with the bottom sub-layers.

As the optical constants of thin films can be different compared to the bulk materials the parametrization by analytical function was applied. For data evaluation we used the Caushy formula for the transparent (0.7 eV – 3 eV) region and Tauc-Lorentz (TL) expression [11] to describe the full spectrum including absorption region. The Caushy model was used to evaluate the thickness, the refraction index and the inhomogeneity. The TL model was applied to find dispersion of optical constants and the bandgap.

The thickness non-uniformity of investigated layers was also taken into account as a variable parameter. Additionally, the depolarization spectra were utilized to improve modeling results.

3. RESULTS AND DISCUSSION

Fig. 2 demonstrates the sensitivity of SE technique. The experimental SE spectra for the substrate and the substrate with the ~15 nm thick TiO_2 film before and after annealing are shown. The deposited film considerably changes the optical response of the sample as compared to the spectra for substrate. Also, after sample annealing small changes in the spectra of ellipsometric parameters psi and delta are clearly observed below 3.5 eV.

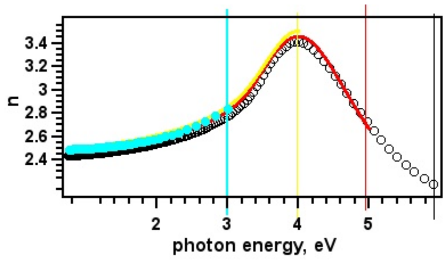


Fig. 3. The refractive index n spectra obtained by Tauc-Lorentz parametrization for different intervals of photon energy. The experimental ellipsometric data were fitted from 0.7 eV up to value shown by vertical lines (at 3, 4, 5 eV)

Fig. 3 shows the refractive index n spectra obtained in the Tauc-Lorentz approximation. All spectra were obtained by fitting experimental data for different photon energy intervals, including transparent region for TiO_2, as marked by the vertical lines. First, the good agreement of all spectra indicates that a correlation between refractive index and thickness is well controlled. Second, many experimental and theoretical studies have shown that TiO_2 is a material with indirect 3.35 eV and direct 4.2 eV bandgap (see [4] and references therein) and for correct description of SE spectra the two oscillator model should be considered. Thus, the interval (0.7 – 5) eV was chosen for parameters comparison. In the case of the full spectrum fitting, the discrepancy between the experimental and the model data is clearly observable by eye, which probably shows the contribution of additional direct optical transition. This transition is clearly observed for polycrystalline anatase film [5].

Table 2. Summary of ellipsometric data analysis for TiO_2 films (d and E_g are a thickness and a bandgap energy; V_{top}, V_b is a porosity of the top and the bottom layers)

Sample	d, nm	V_{top}, %	V_b, %	E_g, eV
0410	19.83 ±0.03	47.7 ±0.4	0	3.25 ±0.01
0410a	18.82 ±0.04	45.3 ±0.5	0	3.40 ±0.01
0412	16.80 ±0.02	55.5 ±0.5	0	3.26 ±0.01
0412a	14.79 ±0.03	41.3 ±0.6	0	3.37 ±0.01

Fig. 4 presents the example of ellipsometric data analysis for the TiO_2 film before annealing (sample 0410). The data for a chosen optical model are in good agreement with experimental SE results. In Table 2 the parameters of ellipsometric data analysis for the studied TiO_2 films are summarized. Also Fig. 5 presents the derived spectra of optical constants for the studied samples and their comparison with literature data [5]. After annealing the film thickness d decreases, the bandgap E_g derived from Tauc-Lorentz approximation increases. The absorption of the sample increases as indicated by increased slope of the extinction coefficient. The refractive index n gets higher in the absorption region, too, and the peak half width decreases compared to the sample prior annealing. All these changes suggest that annealing considerably improves the structural order of the studied TiO_2 films.

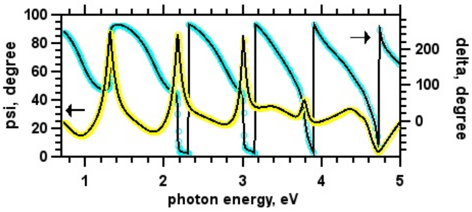


Fig. 4. Example of the ellipsometric data analysis for the TiO_2 film before annealing (sample 0410). Points are experimental values and solid line shows fitted data

The higher substrate temperature together with the annealing during the film deposition also leads to dramatic changes in the structure of TiO_2 film which is close to polycrystalline anatase as shown in Fig. 5 for the 0412 sample. The *n*, *k* spectra quantitatively are in a very good agreement with literature data for polycrystalline anatase [5]. Our assumption of polycrystalline structure confirms the Raman spectroscopy studies, which will be published elsewhere.

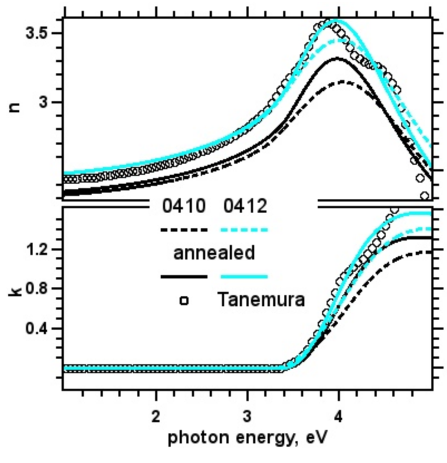


Fig. 5. Comparison of the refractive index *n* and the extinction coefficient *k* of the studied TiO_2 films with the literature data for the polycrystalline anatase film

As shown in Table 2 the porosity of the top sub-layer is rather high, probably because the surface roughness is included in the top layer. The value of the porosity decreases twice in the middle layer and there is no void closer to the substrate.

4. CONCLUSIONS

TiO_2 ultrathin films (< 20 nm) deposited by RF magnetron sputtering were studied by SPM and spectroscopic ellipsometry. The analysis of optical data revealed the parameters of deposited films and intrinsic properties of TiO_2 material before and after annealing. We found that deposited layers were predominantly amorphous with high porosity at the top sample, and absence of porosity at the bottom of TiO_2 layer. Higher substrate temperature during deposition and annealing considerably improves structural order of the studied samples and under some conditions the film transforms from amorphous to the polycrystalline anatase phase. Also, we evaluated the energy bandgap (about 3.1 eV – 3.2 eV) which increases after annealing (above 3.3 eV) and is close to the gap of anatase.

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