SPECTROSCOPIC STUDY OF THIN TITANIUM DIOXIDE FILMS GROWN BY ATOMIC LAYER DEPOSITION

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Abstract. We studied spectroscopically polycrystalline anatase films grown by atomic layer deposition at temperatures 300 and 425 °C. The thickness of films investigated ranges from 50 to 160 nm. Applying Raman spectroscopical study, we revealed the ratio of polycrystallinity and estimated the size of crystallites in different films. From transmittance spectra, corrected to the reflection and scattering, the absorption band gap parameter, E_g, was derived for different samples. Using a pulsed-laser excitation, photoluminescence spectra were measured, where time-resolved spectra indicate different trapping energies for excitons depending on the excitation wavelengths. We may conclude that surface states significantly affect the photoluminescence spectra in thin anatase films.

Key words: anatase, thin films, atomic layer deposition, spectroscopy.

1. INTRODUCTION

TiO_2 has many polymorphs, but in recent years rutile and anatase as promising technological materials have attracted the attention of scientists, see e.g. [1,2].

A detailed optical study of rutile crystals was presented in [3]. Data on anatase are less complete, yet, lately the fundamental absorption edge of anatase crystal has been carefully investigated. A comparison with rutile is given in [4].

Both polymorphs of TiO_2, rutile and anatase, are built of TiO_6 octahedra, but the coordination numbers of octahedra are different: in rutile each octahedron is surrounded with ten octahedra, in anatase only with eight octahedra. It has been suggested that the structural difference reduces the probability of intersite transfer of excitons and that self-trapping takes place in anatase, while in rutile excitons are free [4].

Thin TiO_2 films have been prepared by different methods (electrochemically, by sputtering or by atomic layer deposition – ALD) and some optical properties of these have been investigated, e.g. in [5,6]. Yet, among thin film deposition techniques ALD is the one allowing of the most comprehensive control of thin film thickness [7], particularly, when the deposition is carried out on a large area and/or on profiled substrates. However, to the best of our knowledge, there are no published data about the behaviour of ALD-grown TiO_2 films under optical excitation.

Therefore, our purpose is to give a versatile spectroscopic characterization of thin anatase films grown by ALD. Raman spectroscopy, spectrophotometry, and photoluminescence methods are applied in this study.

2. EXPERIMENTAL

The films investigated were grown in a flow-type low-pressure ALD reactor [7] by using $TiCl_4$ and H_2O as precursors. The films were grown at 300 and 425 °C on fused silica substrates.

For Raman studies Jarell–Ash monochromator and an Ar^+-ion laser with a 488 nm (2.54 eV) line were used. For excitation of luminescence we used a 308 nm (4.013 eV) XeCl excimer laser or an excimer-pumped dye laser operating with PBD dye at 365 nm (3.4 eV). A box-car integrator with time window was applied for the registration of time-resolved spectra.

3. RESULTS AND DISCUSSION

For every film grown by us unpolarized Raman spectra were measured. We can conclude from these measurements that all the films grown at 300 °C have an anatase structure with characteristic vibrations at 140, 395, 514, and 636 cm⁻¹, typical of anatase (cf. e.g. [8,9]). Also, the films grown at 425 °C are with an anatase structure when the thickness does not exceed 100 nm (see Fig. 1B, C). However, in a 150 nm thick film, the lines characteristic of a rutile phase (235, 447, and 612 cm⁻¹) appear, too (Fig. 1A). The existence of a small amount of high-pressure TiO_2-II phase in this film is questionable (characteristic lines should appear at 170 and 424 cm⁻¹ [9]).
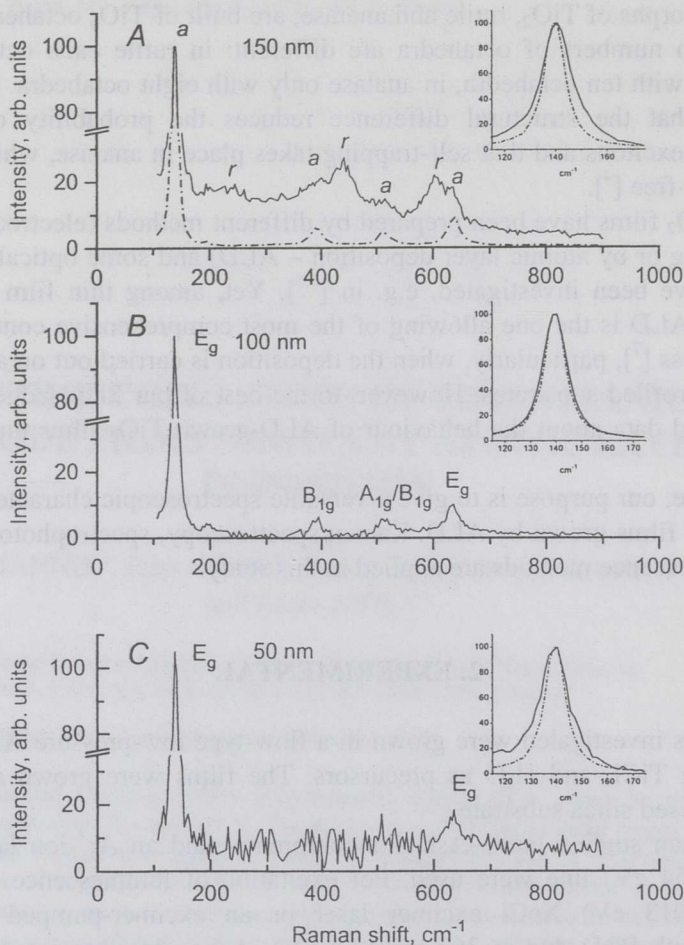
Fig. 1. Raman spectra of thin TiO_2 films grown by atomic layer deposition. *A*, Raman spectrum of a 150 nm film (solid line) and, for comparison, the spectrum of the ~870 nm anatase film (dashed-dotted line). *a* and *r* indicate the Raman line positions of anatase and rutile, respectively. *B* and *C*, Raman spectra of 100 and 50 nm films, with symmetry of vibrations indicated.
Inserts: 140 cm^{-1} Raman lines of thin films (solid lines) in comparison with the ~870 nm thick anatase film (dotted lines).

We can conclude that the 150 nm thick film grown at 425 °C is a mixture of anatase and rutile (Fig. 1*A*). To estimate the size of grains, the width of the most intensive, 140 cm^{-1} Raman line was carefully measured and compared with those in the 870 nm film (inserts in Fig. 1). In the inserts of Fig. 1 the widths of 140 cm^{-1} lines can be compared with this line in a 870 nm thick film. The results of films grown at different temperatures are given in the Table. To get real widths of Raman lines, experimentally measured values Γ_{exp} were corrected for the widths of the slits of the spectrometer, Γ_{corr} are given in the Table. The

870 nm thick anatase film, where the halfwidth of the line was ~ 8.7 cm^{-1} appeared to be of the highest quality. Using the relation between the linewidth Γ and the grain size L: $\Gamma = k(1/L^{1.55}) + \Gamma_0$ given in [10], we estimated linear dimensions of grains in our samples (see the Table). We explain the rather small shift of lines in our samples with a wide distribution of grain sizes which compensates the shift (cf. [11]).

Measured positions and widths of 140 cm^{-1} Raman lines in samples grown by atomic layer deposition in dependence on thickness and growth temperature. The mean grain size L estimated by using [12]

Thickness, nm	Growth temperature, °C	Position, cm^{-1}	Γ_{exp}, cm^{-1}	Γ_{corr}, cm^{-1}	L, nm
150	425	140.4	14.8	14.2	9.1
100	425	139.7	10.9	10.2	16.2
50	425	139.1	14.3	13.7	9.6
160	300	139.5	12.1	11.4	12.8
50	300	139.2	13.8	13.2	10.1
870	300	139.7	9.6	8.7	26.4

Measuring of the absorption coefficient α of thin films near the fundamental band gap is quite a complicated task due to the modulation of transmittance by interference and the strong dependence of reflection on the wavelength of light. To get the absorption coefficient from the transmittance near the edge of the band gap, it is necessary to make some corrections in the measured transmittance T. We used the equation $\alpha = 1/d \, [\ln T - \ln(1 - R_1) - \ln(1 - R_2)] - C\omega^4$, where the first addend takes the reflectance R from both surfaces of the anatase film into account (cf. [12]). The second addend takes account of the losses due to the Rayleigh scattering, where the value of C was estimated from direct measurements.

We measured the transmittance of unpolarized light to get an estimation for the band gap absorption parameter E_g. In anatase for indirect interband transitions the equation $(\alpha E)^{1/2} = \sim(E - E_g)$ holds, where α is the absorption coefficient and E is the energy of the probing light [12,13]. For films, grown at 425 °C, the results are depicted in Fig. 2, where corrections of reflectivity and scattering have been made. We got the values of E_g for 50, 100, and 150 nm films 3.30, 3.28, and 3.00 eV, respectively (Fig. 2). These values agree with the ones reported in [12], where for 870 nm anatase and rutile films the values 3.2 and 3.0 eV for E_g were estimated. In our case for a 150 nm film we had to take into account that this film is a polycrystalline mixture of anatase and rutile, as follows from Raman measurements, and that this is the reason why the band gap is shifted to the red.
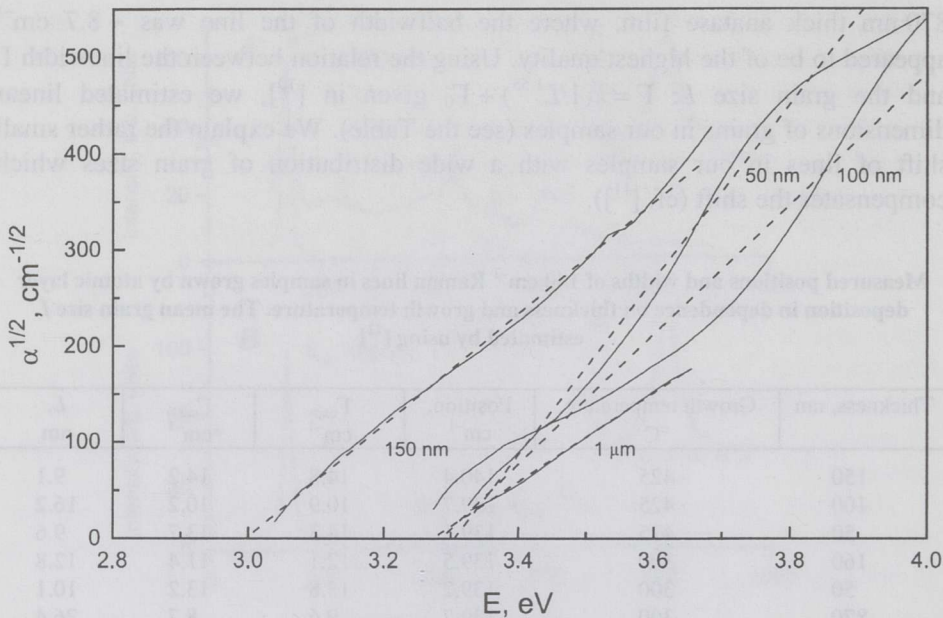
Fig. 2. Absorption spectra of thin TiO_2 films in dependence on thickness. Films grown at 425 °C. Results derived from transmittance measurements, plotted as $\alpha^{1/2}$ for the estimation of the band gap parameter E_g (fitting with dotted lines).

Time-resolved emission spectra of films grown at 425 °C were measured with a time window of 25 ns. The results are given in Fig. 3, where for clarity the optical density of each film is depicted on the right-hand side. Under 3.4 eV excitation (arrow 1) 50 and 100 nm films reveal a broad-band of luminescence, which peaks at ~2.8 eV and is asymmetric to the red. Under 4.0 eV excitation (arrow 2) the emission bands shift to the red (maximum at 2.6 eV). The luminescence band for a 150 nm film is, however, somewhat narrower. For this film at low temperature (6 K) also the time-integrated emission spectrum at 4.0 eV excitation was measured (curve 3, Fig. 3A). In this case deeper trapping energy (~0.25 eV) of excitons can be explained by the reduction of scattering caused by phonons.

To get the shape of emission bands, we had to make some corrections, taking account of interference. The luminescence bands measured in our samples were shifted to the blue (~0.5 eV) compared to the results of [6], where a steady excitation by the 360 nm line of a mercury lamp was used and the emission from self-trapped excitons was concluded. We used a short (~15 ns) laser pulse excitation and the detection was carried out through a 25 ns time window after excitation. Yet, according to our estimation of the lifetime of excitonic luminescence ($\tau < 10$ ns), the time window used is still too large to see the dynamics of exciton trapping. By a shorter wavelength excitation appeared to be

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trapped at deeper levels and luminescence shifted to the red. This could be caused by an additional contribution of the surface states to the process of the trapping of excitons in thin films. Indeed, using the measured values of the absorption coefficient (Fig. 2), we can estimate the deepness of excitation under different excitation wavelengths. In the case of 3.4 eV excitation 10% of excitation light is absorbed in a 10 nm layer, while in the case of 4.0 eV excitation 25% of light is absorbed in that layer.
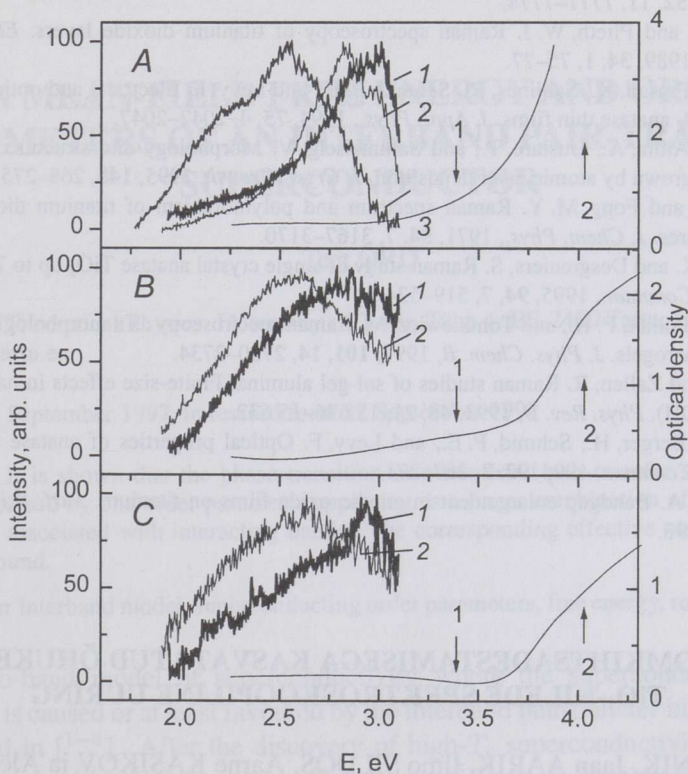

Fig. 3. Time-resolved emission spectra of thin TiO_2 films grown by atomic layer deposition. *A*, *B*, and *C*, time-resolved emission spectra of 150, 100, and 50 nm thick films, respectively, measured at room temperature. Curves *1* and *2* were measured by using excitations at 3.4 and 4.0 eV (arrows 1 and 2), respectively. Curve *3* in part *A* represents the time-integrated spectrum of the 150 nm film measured at 6 K. On the right-hand side optical density of each film is depicted.

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AATOMKIHTSADESTAMISEGA KASVATATUD ÕHUKESTE TiO₂-KILEDE SPEKTROSKOOPILINE UURING

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Spektroskoopiliselt on uuritud 300 ja 425 °C juures aatomkihtsadestamisega kasvatatud polükristallilisi õhukesi (50–160 nm) anataaskilesid. Ramanspektroskoopilised mõõtmised võimaldasid määrata erineval režiimil kasvatatud kilede polükristallilisuse astet ja kristalliitide suurust. Läbilaskvusspektritest, mis olid korrigeeritud hajumise ja peegeldumise osa arvestades, määrati neeldumisriba serva iseloomustav parameeter E_g. Kasutades impulsslaseriga ergastamist, mõõdeti aeglahutusega luminestsentsspektrid, millest ilmneb eksitonide lõksustamisenergia erinevus ergastusenergiast. On järeldatud, et pinnaseisund mõjutab oluliselt fotoluminestsentsi karakteristikuid õhukestes anataaskiledes.