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Spectroscopic characterization of ZrO_2 thin films grown by atomic layer deposition

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Abstract. Zirconium dioxide films grown by atomic layer deposition from $ZrCl_4$ and H_2O at substrate temperatures of 500–870 K were characterized using spectroscopic methods. A significant influence of the phase composition on absorption and photoluminescence spectra was observed. The band-gap energies determined from absorption spectra of films with monoclinic structure grown at 670–870 K ranged from 5.25 to 5.28 eV. Low-temperature (10 K) photoexcitation of these films resulted in a non-elementary emission band with the maximum at 4.25–4.35 eV, tentatively assigned to the radiative decay of self-trapped excitons. The low-energy edges of the excitation spectra coincided with the edges of intrinsic absorption. A film that was grown at 500 K and contained tetragonal ZrO_2 with large amounts of impurities had an absorption edge at 5.26 eV and wide emission band at 3.0 eV, which could be excited at as low photon energy as 4.9 eV.

Key words: zirconium dioxide, atomic layer deposition, structure, absorption, photoluminescence.

1. INTRODUCTION

Zirconium dioxide (ZrO_2) is a material that has attracted attention because of its relatively high dielectric constant and wide band gap, which make this material a promising candidate to replace silicon dioxide as a dielectric in metal-oxide-semiconductor (MOS) field effect transistors [1–4]. In addition, ZrO_2 can be used as a high-refractive-index material in optical coatings for visible and ultraviolet spectral ranges [5]. Although the band gap is an important material parameter in these applications, the number of papers reporting band-gap energies for ZrO_2 thin films is still rather limited. Moreover, experimental and theoretical data that have been published [6–10] scatter significantly. For instance, the experimental band-gap energies vary from 5.16 [6] to 7.09 eV [7] for the

monoclinic ZrO_2 phase, from 5.78 to 6.62 eV [7] for the tetragonal phase, and from 6.1 to 7.08 eV [7] for the cubic phase. For amorphous ZrO_2 films, the band-gap energy of 5.5 eV has been determined [8]. For comparison, theoretical calculations have yielded band-gap energies of 3.12–5.42 eV for monoclinic [7,9,10], 4.10–6.40 eV for tetragonal [7,9], and 3.25–5.55 eV for cubic [7,9] ZrO_2.

Significant scattering of the experimental band-gap energies is evidently due to different ranges of absorption spectra and different approaches used to determine the band-gap energy. Furthermore, the samples studied have been of different origin and quality. For instance, in some cases the samples have contained considerable amounts of impurities (e.g. Y_2O_3 [7]) that have been used to stabilize the tetragonal and cubic phases. In addition, the crystallite sizes of polycrystalline samples might have varied and contributed to the scatter of the experimental band-gap energies. The impurities as well as material defects may also result in the formation of deep energy levels in the band gap that, in turn, influence the performance of the dielectric in MOS and optical devices. Recently, results of a theoretical study on defects in ZrO_2 have been published [10] but corresponding experimental data are still lacking. Therefore the present study was performed to obtain additional information about the band-gap energies as well as about possible defect levels. Absorption spectra were measured to characterize the band gap and its dependence on the phase composition while photoluminescence (PL) was studied to detect radiative relaxation of intrinsic excitations as well as a possible role of defect and impurity levels in the recombination of charge carriers.

Atomic layer deposition (ALD) was used to deposit the ZrO_2 thin films. The method was chosen because this is one of the most perspective techniques for growing gate dielectrics of MOS devices [4,11]. It also allows deposition of optical coatings with very uniform thickness, high optical density, and accurate thickness control [12]. In addition, using different substrate temperatures, it has been possible to grow ZrO_2 films with different crystalline structures by ALD [13,14]. This is important when investigating the effect of phase composition on the band-gap energy.

2. EXPERIMENTAL

The ZrO_2 thin films were grown in a flow-type low-pressure ALD reactor [15] using $ZrCl_4$ and H_2O as the precursors [13]. The films for absorption studies were grown on amorphous silica substrates, while the films for PL measurements were deposited on single crystal silicon substrates. In order to grow the films the substrates were alternately exposed to $ZrCl_4$ and H_2O vapours, which were transported to the substrates in the flow of nitrogen. The nitrogen gas was also used to purge the reaction zone after each precursor pulse. The precursor pulses and the purge times were 2 s, while the carrier gas pressure was set at 250 Pa in the reaction zone. Sufficient precursor doses were obtained at the $ZrCl_4$ source temperature of 430 K and at the H_2O pressure of about 5 Pa [13]. The growth temperature, T_G, was varied from 500 to 870 K.

The films studied in this work were 80–320 nm in thickness. The phase composition and crystallite sizes in the films were characterized using the X-ray diffraction (XRD) method. A diffractometer with symmetrical Bragg–Brentano geometry and CuKα radiation source were used for these measurements. The refractive index, thickness, and absorption coefficient values were determined from the transmission spectra of the films deposited on SiO_2 substrates [16]. All these measurements were performed at room temperature. Room-temperature and low-temperature PL experiments with synchrotron radiation excitation at photon energies of 3.7–7.5 eV were carried out at the SUPERLUMI station of HASYLAB at DESY [17].

3. RESULTS AND DISCUSSION

3.1. Composition and structure

The composition of the films has been studied in an earlier work [13]. According to those electron probe microanalysis data the films deposited at 500 and 570 K contained 2 and 0.6 at. % of residual chlorine, respectively. In the films grown at 670–870 K, the chlorine concentration was below 0.3 at. %.

All films studied in this work showed XRD reflections of the tetragonal and monoclinic phases. One can see in Fig. 1, however, that the relative amount of

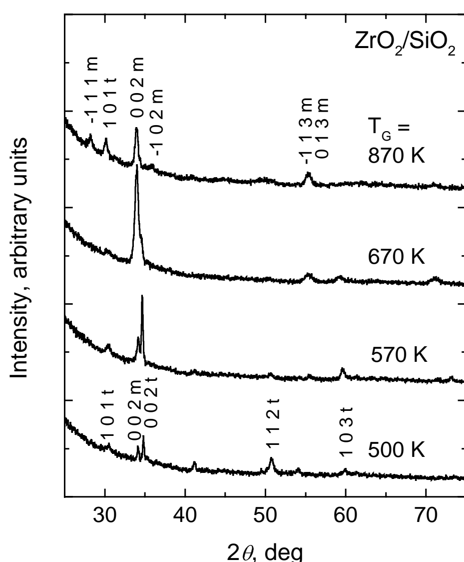

Fig. 1. Diffraction patterns of ZrO_2 films grown on amorphous silica substrates. Thickness of the films ranged from 200 to 230 nm. Here and in Fig. 2 Miller indices are shown for the most intense reflections of tetragonal (t) and monoclinic (m) ZrO_2.

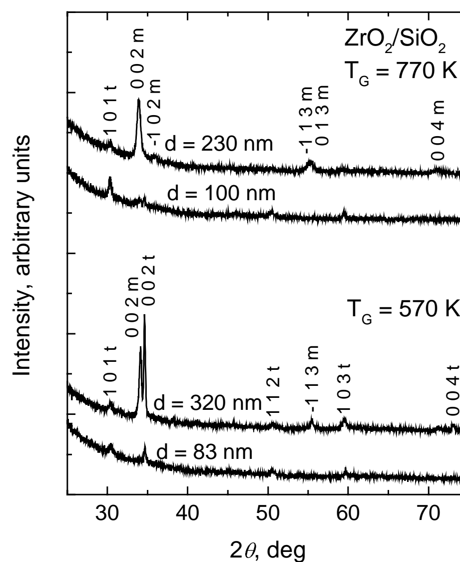

Fig. 2. Influence of thickness on diffraction patterns of ZrO_2 films grown on amorphous silica substrates at 570 and 770 K.

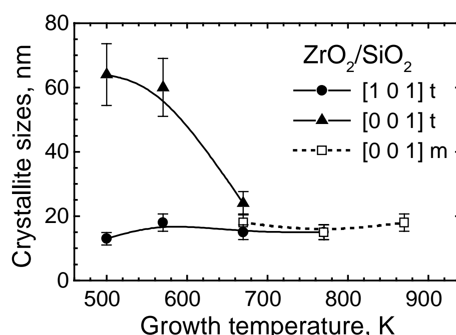

Fig. 3. Crystallite sizes determined for [1 0 1] and [0 0 1] directions of tetragonal (t) ZrO_2 and for [0 0 1] direction of monoclinic (m) ZrO_2. The films were 200–230 nm in thickness and had been grown on amorphous silica substrates.

the monoclinic phase increased considerably at the expense of the tetragonal phase when the growth temperature was raised from 570 to 670 K. A similar effect and approximately the same phase composition were observed in the case of films grown on single crystal silicon substrates. With the increase in film thickness, d, the amount of the monoclinic phase increased faster than that of the tetragonal phase (Fig. 2). An interesting result was that at 770 K and higher growth temperatures, the tetragonal phase formed in the initial stage of the film growth was evidently transformed into the monoclinic phase when the thickness increased. Crystallite sizes did not change considerably when the film thickness was varied from 200 to 320 nm. Neither did they depend on the substrates used in this work. At the same time a significant effect of growth temperature on the crystallite sizes was observed (Fig. 3).

3.2. Refractive index and absorption coefficient

Transmission spectra (Fig. 4) showed that the films were transparent at the wavelengths, λ, exceeding 240 nm. The refractive indices determined for the transparency region ranged from 2.12 to 2.21 at $\lambda = 580$ nm and from 2.50 to 2.60 at $\lambda = 250$ nm and, thus, relatively weakly depended on T_G.

The growth temperature most significantly influenced the transmission spectra in the range of strong absorption. As can be seen, a kink appeared at the wavelengths of 225–230 nm in the transmission spectra of the films grown at 670 K and higher temperatures. The effect was evidently not due to interference that contributed to spectral modulation in the transparency range, because the spectral position of the kink was independent of the film thickness. Thus, one can conclude that a local maximum of the absorption coefficient probably caused the transmission minimum that appeared at the wavelengths of 225–230 nm.

The absorption coefficient, α, as a function of photon energy, $h\nu$, most significantly varied with the increase in T_G from 500 to 670 K (Fig. 5). The effect of film thickness on absorption spectra was studied for films grown at $T_G = 570$

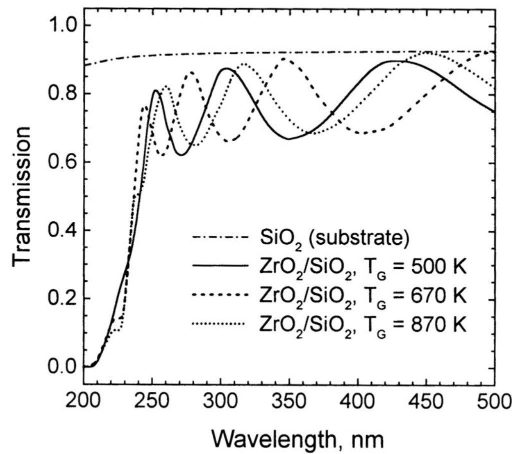

Fig. 4. Transmission spectra of ZrO_2 films grown on silica substrates at 500, 670, and 870 K.

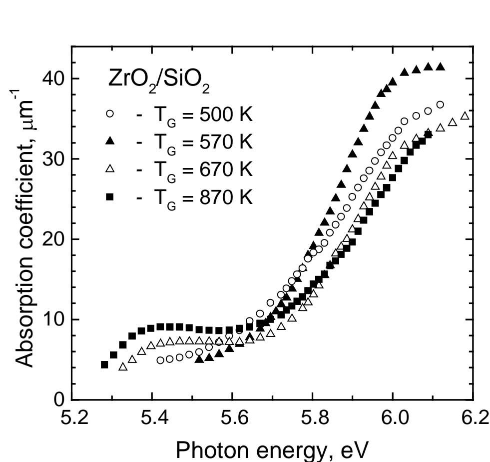

Fig. 5. Absorption spectra of ZrO_2 films grown on silica substrates at 500, 570, 670, and 870 K.

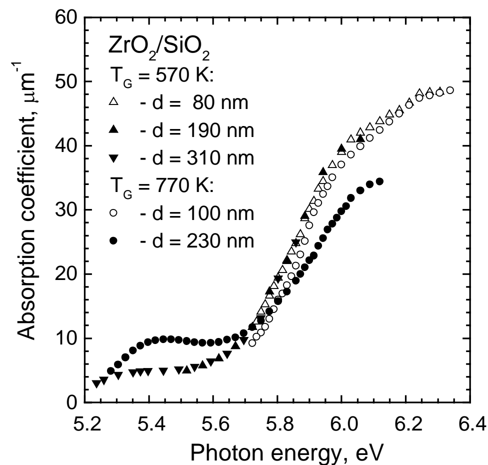

Fig. 6. Influence of thickness on the absorption spectra of films grown on silica substrates at 570 and 770 K.

and 770 K. The effect was insignificant at 570 K (Fig. 6). At T_G = 770 K, by contrast, a strong influence of the film thickness on the absorption spectra was observed (Fig. 6). The spectrum of a 100 nm thick film was very similar to the spectra of the films grown at 570 K, while the spectrum of a 230 nm thick film resembled the spectra of the films with a similar thickness grown at 670 and 870 K (Fig. 5). The XRD patterns depicted in Figs. 1 and 2 indicate that tetragonal ZrO_2 dominated in the films grown at 570 K as well as in the 100 nm thick film grown at 770 K. In the 200–300 nm thick films grown at 670–870 K, in turn, monoclinic ZrO_2 was the dominating phase. Thus, one can conclude that

the shapes of absorption spectra were in correlation with the phase composition rather than with some other film parameters, such as the mean crystallite size and concentration of residual chlorine in the films.

The band-gap energies, E_g, were estimated extrapolating the linear parts of the $(\alpha h\nu)^2$ versus $h\nu$ plots (Fig. 7) to $\alpha = 0$. This approach, frequently employed to determine widths of direct energy gaps [6,7,18,19], gave us band-gap energies of 5.25–5.28 and 5.82 eV for monoclinic ZrO_2 when the α ranges of 5–10 and 10–40 μm^{-1}, respectively, were used. Balog et al. [6] obtained $E_g = 5.16$ eV from a similar extrapolation performed for the absorption coefficient of monoclinic ZrO_2 films at α values of 3–16 μm^{-1}. French et al. [7] studied twinned single crystals of monoclinic ZrO_2 and determined $E_g = 5.83$ eV from the α range of 25–70 μm^{-1} and $E_g = 7.09$ eV from the α range of 70–150 μm^{-1}. As can be seen, the former value of French et al. [7] coincides with our result obtained for monoclinic ZrO_2 from a comparable range of absorption coefficients.

From the $(\alpha h\nu)^2$ versus $h\nu$ plots (Fig. 7) of films with dominating tetragonal structure grown at 500–570 K, we obtained band-gap energies of 5.75–5.78 eV when the α range of 20–35 μm^{-1} was used. These band-gap values are also consistent with the results of French et al. [7] who have found $E_g = 5.78$ eV from the α range of 25–70 μm^{-1} in the case of polycrystalline ZrO_2 samples with tetragonal structure stabilized with Y_2O_3.

No linear parts on the $(\alpha h\nu)^2$ versus $h\nu$ plots of the films grown at 500–570 K could be found at $\alpha < 20$ μm^{-1}. For this reason we also tried to find a linear fit to the $(\alpha h\nu)^{1/2}$ versus $h\nu$ curve to determine possible indirect gaps [19,20]. In the case of films grown at 500 K, a good fit was obtained for the absorption coefficient range of 8–35 μm^{-1}. The corresponding band-gap energy equalled 5.26 eV. Unfortunately, this E_g value cannot be treated as a parameter describing phase-pure tetragonal ZrO_2 because, in addition to the dominating tetragonal phase, the films contained a considerable amount of the monoclinic phase, which significantly contributed to absorption in the range used in this extrapolation.

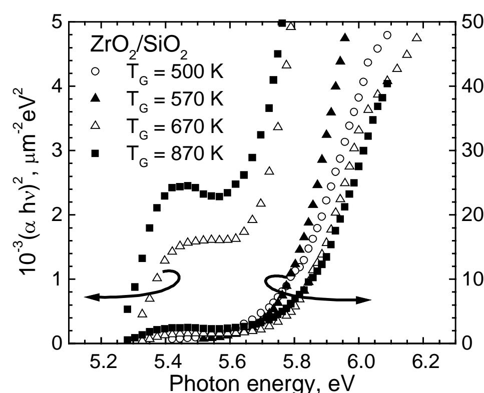

Fig. 7. $(\alpha h\nu)^2$ versus photon energy ($h\nu$) plots for the films grown on silica substrates at 500, 570, 670, and 870 K.

3.3. Photoluminescence spectra

Low-temperature PL of a film grown at 500 K revealed a wide peak with the maximum at 3.0 eV (Fig. 8a). The corresponding excitation spectrum had a steep edge at 5.25 eV and maxima at 5.50 and 5.75 eV. In addition, a low-energy tail in the energy range of 4.9–5.2 eV was observed. The emission bands of the film grown at 670 K (Fig. 8b), and especially that of the film grown at 870 K (Fig. 8c), were relatively narrow, peaking at 4.25 and 4.35 eV, respectively. Both emission spectra were non-elementary, containing weaker bands in the low-energy side. The films grown at 670 (Fig. 8b) and 870 K (Fig. 8c) showed similar excitation spectra with maxima at 5.4 and 6.3 eV, but none of these spectra had the low-energy tail. At room temperature, the main emission bands were practically quenched, but some weak low-energy emission probably arising from the impurity or defect centres was still detected.

The interpretation of PL results is complicated because our samples are not phase-pure, and according to theoretical calculations [7,9], zirconia is expected to have several valence band maxima and conduction band minima that can simultaneously participate in electron transitions. Comparing the PL excitation spectra with absorption spectra and assuming the direct gap, the following interpretations are possible. Provided that the band-gap energy of monoclinic

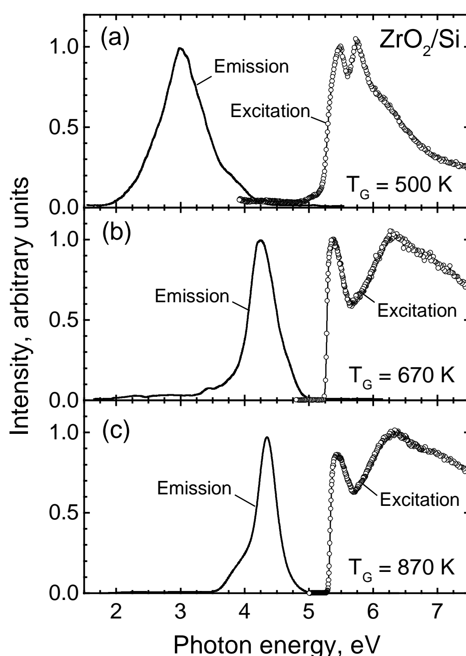

Fig. 8. Photoluminescence spectra measured at 10 K for ZrO_2 films grown on single crystal silicon substrates at (a) 500, (b) 670, and (c) 870 K. Emission spectra were recorded at excitation energies of (a) 5.60, (b) 5.88, and (c) 6.34 eV. Excitation spectra were measured at the emission energies of (a) 2.95 and (b, c) 4.42 eV.

ZrO_2 films grown at 670 and 870 K is 5.82 eV, the first excitation peak at 5.4 eV can be assigned to excitonic states, whereas band-to-band transitions occur at $h\nu > 5.82$ eV. Assuming that $E_g = 5.25$ eV, the first excitation peak can be attributed to band-to-band transitions creating electron–hole pairs. In any case the excitation leads to the efficient PL at 10 K, while the emission is practically quenched at room temperature. The Stokes shift of the low-temperature emission peaking at 4.3 eV is about 1 eV, being comparable with the Stokes shift observed for self-trapped excitons (STE) in other wide-gap oxides [21]. Therefore, the strongest low-temperature emission peak of our films grown at 670–870 K could also originate from radiative decay of STE. Alternatively, the recombination of electrons and holes created at the direct or indirect transitions starting above 5.25 eV can form STE as well. Recombination at defects and impurities evidently contributes to the emission at lower energies as observed for low-temperature PL in the films grown at 500 K and for room temperature emission of the films grown at higher temperatures. Contribution of impurity and/or defect levels agrees with the observation that in the film grown at 500 K, PL was excited at $h\nu < 5.26$ eV, i.e. at lower energies than the band-gap energy determined for this film from the absorption spectrum. Considerable concentration of residual chlorine in the films grown at 500 K is a possible explanation for the formation of the impurity levels and band tails.

Comparison of our PL data with theoretical results of Foster et al. [10] indicates that vacancies and interstitial oxygen ions unlikely have a decisive role in low-temperature PL of our films grown at 670–870 K. However, these defects can be important for the films grown at 500 K. The transitions at the photon energies of 3.33, 3.54, and 3.73 eV, which are related to a positively charged vacancy, doubly positively charged vacancy, and neutral interstitial oxygen, respectively [10], might contribute to the PL emission that has considerable intensity at these energies (Fig. 8a).

4. CONCLUSIONS

Our results show that variations in the phase composition caused significant changes in absorption and luminescence spectra. Moreover, even in a phase-pure ZrO_2 sample, several mechanisms evidently contributed to the absorption and therefore different band-gap energies were obtained from absorption spectra using different absorption coefficient ranges. For the films with monoclinic structure, which were grown at 670–870 K, the band-gap energies of 5.25–5.28 eV were determined from the absorption coefficient range of 5–10 μm^{-1}. Preferential formation of the tetragonal phase at lower growth temperatures and in thinner films resulted in a marked decrease in absorption in the energy range of 5.3–5.7 eV and increase in that at higher photon energies. From the absorption spectrum of the film grown at 500 K, the band-gap energy of 5.26 eV was determined assuming an indirect gap.

Low-energy edges of PL excitation spectra for films grown at 670–870 K coincided with the band-gap energies determined from absorption spectra. The dominant emission with a maximum at 4.25–4.35 eV observed at 10 K was tentatively assigned to the radiative decay of self-trapped excitons. Recombination at deep levels and impurity centres evidently contributed to the emission at $h\nu < 4.0$ eV. In the case of a film grown at 500 K, the PL excitation spectra extended to the lower energies than the band-gap determined from absorption data. Furthermore, the less intense maximum of the much broader emission band was at notably lower energy (3.0 eV) than the emission maxima of the films grown at 670–870 K. These results indicate that impurities (probably chlorine) and/or defects much more strongly influenced PL of the films grown at 500 K.

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Aatomkihtsadestamise meetodil kasvatatud õhukeste ZrO_2 kilede spektroskoopiline uurimine

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Spektroskoopiliste meetoditega uuriti tsirkooniumdioksiidist kilesid, mis olid kasvatatud temperatuuril 500–870 K, kasutades aatomkihtsadestamisel lähteainetena tsirkooniumtetrakloriidi ($ZrCl_4$) ja veeauru. Näidati, et kilede faasikoostis avaldab olulist mõju neeldumis- ja fotoluminestsentsi spektritele. Temperatuuril 670–870 K kasvatatud monokliinse struktuuriga ZrO_2 keelutsooni laius oli 5,25–5,28 eV. Nende kilede fotoergastus madalal temperatuuril (10 K) andis mitte-elementaarse kiirgusriba maksimumiga 4,25–4,35 eV, mis esialgsete andmete põhjal omistati autolokaliseeritud eksitoni kiirguslikule rekombinatsioonile. Seejuures langesid ergastusspektrite väiksemate energiate poolsed servad kokku neeldumisspektritest määratud neeldumisservadega. Temperatuuril 500 K kasvatatud kilel, mis sisaldas tetragonaalset faasi ning olulisel määral lisandeid, oli neeldumisserv 5,26 eV juures. Lisaks oli sellel kilel lai kiirgusspekter, mille maksimum oli 3,0 eV juures ning mida sai ergastada 4,9 eV ületaval footoni energial.