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Diagnosis of the technology of titanium and hafnium oxides by luminescence methods

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The article shows the role of oxygen vacancies in the formation of luminescence bands of titanium and hafnium oxides, and also demonstrates the relationship between the intensity of luminescence bands and the conditions for the synthesis of films of these materials. It is concluded that photoluminescence is a very sensitive method for diagnosing the composition of oxides. Luminescence bands at 2.45 eV in titanium oxide and 2.91 eV in hafnium oxide make it possible to analyze the change in the film composition under various technological conditions of their production.

Keywords: oxygen vacancies, titanium oxide, hafnium oxide, photoluminescence.

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1. Introduction

With the reduction of transistors to nanoscale sizes, there is growing interest in high-K dielectrics, including titanium and hafnium oxide, as well as their solid solutions, for use as gate dielectrics [1,2]. At the same time, high dielectric permittivity and high resistivity [3] come to the fore. Numerous studies show that the conductivity of oxides is carried out with the participation of intrinsic point defects and, first of all, oxygen vacancies [4–8]. In this regard, the diagnosis of the effect of oxygen vacancies on the electrical properties of oxides becomes an important task. The Auger method is widely used for analyzing the composition of a substance, but its accuracy is insufficient to determine the concentration of vacancies. A more complex but accurate method is X-ray photoelectron spectroscopy (XPS) [9]. The XPS allows to estimate the concentration of defects by the peak area, provided that side factors are taken into account in a calculated way. The sensitivity of the method is sufficient and is 0.1 at%. The disadvantage of this method is the complexity and high cost of installation for its implementation.

In this regard, a simpler and more rapid diagnostic method is needed to test the technology, especially since there is no need to determine the exact concentration of vacancies. It is important to trace the trends of their changes with variations in the parameters of technological processes. For this purpose, the photoluminescence method is useful, which allows you to identify the presence of vacancies and simply track the influence of technological factors on their content.

The luminescence of oxides has been studied quite well. Oxygen vacancies in titanium oxide create radiation bands with a band maximum energy of 2.4 eV [10,11]. Photoluminescence in TiO_2 nanostructures occurs due to the donor-acceptor mechanism [12]. The band with the maximum radiation in the region of 1.2 eV is caused by ions Ti^{3+} [13]. Its nature is associated with the recombination of free holes with electrons that are trapped in these traps. The luminescence band in the region of 1.4 eV is caused by the ions of interstitial titanium Ti^{+4} [14]. As shown in the paper [15], the wide peaks of infrared luminescence 1.87 and 1.47 eV arise due to the interstitial Ti_i^{4+}, and the band 1.21 eV is associated with Ti^{3+}-defect. The red band (2.05 eV) is the recombination of free holes with electrons on traps and can be caused by complexes of interstitial titanium and oxygen vacancy [15]. Photoluminescence of hafnium oxide is mainly associated with oxygen vacancy, and its emission bands are interpreted in the paper [16].

In this paper, a relationship is established between the parameters of technological processes and the intensity of luminescence bands in oxides.

2. Experimental results

2.1. Film synthesis

Titanium oxide films of the composition TiO_x were synthesized by magnetron sputtering of a titanium target in an atmosphere of argon and oxygen onto thermally oxidized plates of monocrystalline silicon *n*-type. The synthesis was carried out for 3 h, the thickness of the films was $1.7\,\mu$m. The operating pressure in the working chamber (p_{tot}) was maintained at $2 \cdot 10^{-4}$ mmHg. The supply of working gases to the chamber was carried out using two automatic gas flow regulators with the accuracy of setting and maintaining the composition of the gas mixture $\pm 0.8\%$. Argon flow was 20 cm^3/min, and oxygen X cm^3/ min, where X — varied

Table 1. The results of measuring the stoichiometric composition of titanium films by Auger method at a magnetron discharge power of 300 W and different partial pressures of oxygen in the reaction chamber

№	W, W	p_{O_2}, mTorr	O, at%	Ti, at%	Ti/O
1	300	0.33	52	22	0.92
2	300	0.43	62	7	0.61
3	300	0.45	64	4	0.56
4	300	0.48	65	3	0.54
5	300	0.51	66	1	0.51

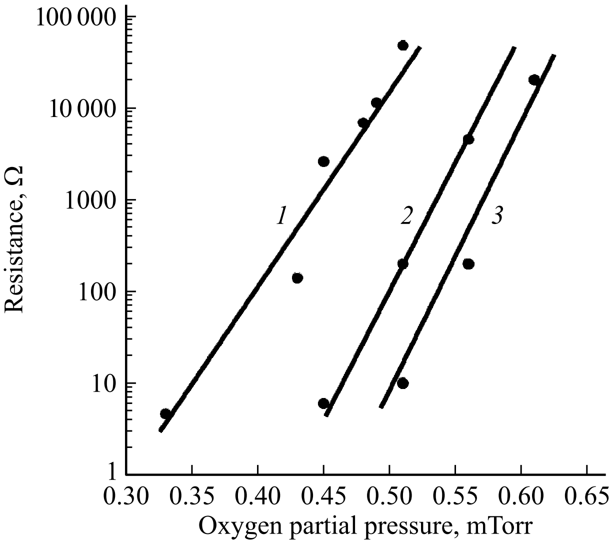

Figure 1. The effect of oxygen partial pressure during the synthesis of titanium oxide layers on their resistivity at different magnetron powers: *1* — 300, *2* — 330, *3* — 360 W.

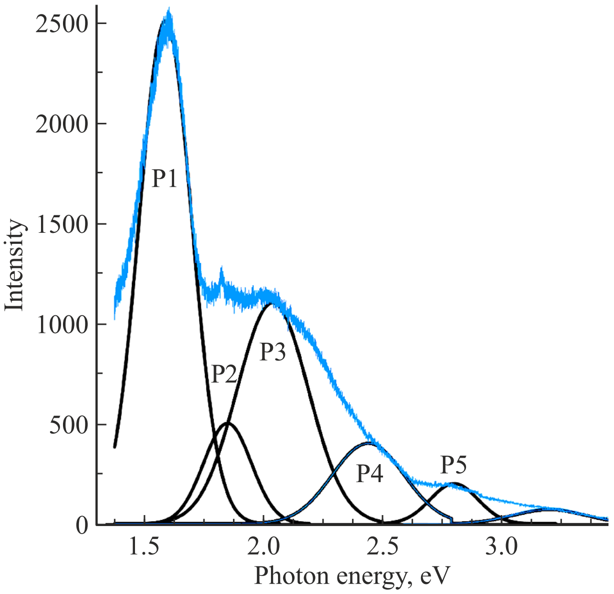

Figure 2. Photoluminescence spectra of titanium oxide thin films synthesized at oxygen partial pressure 0.33 mTorr.

from 3 to 6 cm^3/min. The gas flows in the reactor create a certain partial pressure, which was calculated (for example, the partial pressure of oxygen p_o^g) by formula:

$$p_o^g = \frac{J_o^g}{J_{\mathrm{Ti}}^g + J_{\mathrm{O}}^g + J_{\mathrm{Ar}}^g} p_{\mathrm{tot}},$$

where J_i^g — is the value of the flow of each of the components in the reactor.

Hafnium oxide films were deposited on a substrate of oxidized monocrystalline silicon (CEM mono-Si) by atomic layer deposition. At the same time, the substrate temperature varied in each of the experiments from 150 to 350°C. The synthesis was carried out by sequential feeding of the precursor $Hf(N(CH_3)_2)_4$ (TDMAH) for 0.4 s and H_2O for 0.01 s. The film thickness 10 nm was achieved by successive repetition of the precursor supply, argon washing and water supply.

2.2. Experimental results of titanium oxide synthesis

The stoichiometric composition of titanium oxide was evaluated by the Auger method, it is given in Table 1. Prior to the measurements, the surface was cleaned with argon ions.

The same measurements were carried out at different magnetron capacities. The change in the partial pressure of oxygen led to a significant change in the resistivity of the titanium oxide layers (Fig. 1), which was measured by the four-probe method.

It is obvious that a change in the partial pressure of oxygen in the reaction chamber of magnetron sputtering leads to a significant change in the resistance of titanium oxide films.

Photoluminescence of thin films of titanium oxide was excited by a laser with a wavelength of 325 nm. The background of the radiation was subtracted from the experimental results, and then the total luminescence spectrum was decomposed into separate bands using their approximation by the Gaussian function. Photoluminescence of hafnium oxide was treated in the same way. The results of measurements of titanium oxide films immediately after synthesis at various partial pressures of oxygen are shown in Fig. 2. The parameters of photoluminescence bands at different partial pressures of oxygen are shown in Table 2.

The results of the study of luminescence show that the change in the energy of the radiation band with variations in the partial pressure of oxygen is insignificant. It may be associated with a change in the band gap width of the material during synthesis. This fact allows us to assume the stability of the mechanisms that determine the emission of these bands. The bands nature was discussed in the

Table 2. Parameters of separation of titanium oxide photoluminescence spectra into components

The number of the radiation band (Fig. 2)	P1 Ti^{+4} [14]		P2 Ti^{+4} [15]		P3 V_OTi^{+4} [15]		P4 V_O [10,11]		P5 Free excitons	
Partial pressure of oxygen, mTorr	E_1, eV	σ, eV	E_2, eV	σ, eV	E_3, eV	σ, eV	E_4, eV	σ, eV	E_5, eV	σ, eV
0.33	1.59	0.11	1.85	0.10	2.05	0.12	2.49	0.12	2.82	0.10
0.45	1.60	0.10	1.84	0.09	2.04	0.13	2.48	0.13	2.82	0.10
0.48	1.59	0.10	1.82	0.10	2.02	0.14	2.45	0.14	2.81	0.10
0.51	1.60	0.10	1.82	0.10	2.05	0.15	2.43	0.15	2.80	0.10

Note. E_i — the maximum energy of the radiation band, σ — its dispersion.

Table 3. Change in the relative intensity of luminescence peaks at different oxygen pressures

Partial pressure of oxygen, mTorr	P1/P5	P2/P5	P3/P5	P4/P5
0.33	31	6	14	8
0.45	33	15	15	6
0.48	36	18	16	6
0.51	40	32	17	5

introduction. The band P5 has a significantly different nature compared to the bands P1–P4. It is caused by autolocalized excitons and is not associated with intrinsic defects of titanium oxide. The intensity of this band is determined only by the degree of ordering of the sample in general. The bands P1–P4 are associated with specific defects. Their intensity is also determined by the disordering of the sample, but also directly depends on the partial pressure of oxygen, which affects defect formation. Therefore, the intensities of the defect bands normalized to the intensity of the band P5–P*i*/P5 during synthesis at different partial pressures were further compared (Table 3).

An increase in the partial pressure of oxygen leads to a relative increase in the intensity of the luminescence bands in all samples. This may be due to the fact that the defects are concentrated in the surface layer of nanocrystals, which form a film immediately after synthesis. An increase in the partial pressure of oxygen increases the number of crystallization centers, as a result, nanocrystals become smaller, and their number increases, which is confirmed by the data of X-ray phase analysis [17]. Therefore, their combined surface becomes larger, and the concentration of defects as a whole increases. In accordance with the law of the acting masses [18] the pressure in the gas phase of the volatile component (in this case oxygen) affects both the content of interstitial titanium and the number of vacancies of the volatile component. The results of this work make it possible to write a quasi-chemical equation and the equation of the acting masses for the connection of the oxygen vacancy concentration with the partial pressure of this gas:

$$O_O \leftrightarrow V_O + \frac{1}{2}P_{O_2}\quad \frac{[V_O]}{[O_O]} = \frac{K_O}{P_{O_2}^{1/2}},$$

as well as concentrations of interstitial titanium and concentrations of oxygen vacancies:

$$Ti_{Ti}O_O \leftrightarrow Ti_i + V_O\quad \frac{[Ti_i][V_O]}{[Ti_{Ti}][O_O]} = K_i,$$

$$[Ti_i] = [Ti_{Ti}][O_O]\,\frac{K_i}{K_O}\,p_O^{1/2},$$

where $[O_O]$ — the concentration of oxygen that occupies places in the lattice sites of titanium oxide, $[V_O]$ — the concentration of oxygen vacancies, P_{O_2} — partial pressure of oxygen; K_i, K_O — equilibrium constants of quasi-chemical reactions, $[Ti_{Ti}]$ — titanium concentration in nodes, $[Ti_i]$ — titanium concentration in internodes.

The equations show that the higher the partial pressure of oxygen in the reactor, the lower the concentration of oxygen vacancies in titanium oxide films and the greater the concentration of interstitial titanium. Therefore, the relative intensity of the bands P1–P3, which are associated with interstitial titanium, increases, and the intensity of the band P4, which is due to oxygen vacancy, decreases.

2.3. Results of hafnium oxide synthesis

The photoluminescence spectra of hafnium oxide were excited by laser radiation with a wavelength of 325 nm and a power of 200 mW. The photon energy excited by laser radiation with a wavelength of 325 nm was less than the band gap width and did not excite electron-hole pairs. However, it was sufficient to excite radiation with the participation of defects (Fig. 3).

The approximation of the radiation bands made it possible to accurately determine the maximum of the radiation band and find the variance of this distribution. These parameters for the bands P1–P4 are given in Table. 4.

Fig. 4, *a* shows the dependence of the intensity of the peak of P4 photoluminescence on the substrate temperature

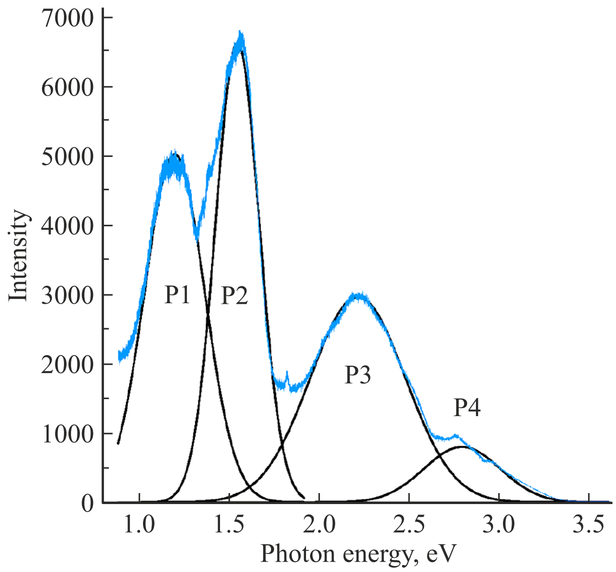

Figure 3. Photoluminescence spectrum of hafnium oxide at $T = 173\,\mathrm{K}$. Thin lines are the division of the spectrum into separate bands using Gaussian functions.

Table 4. Parameters of radiation bands of synthesized hafnium oxide samples measured at $T = 173\,\mathrm{K}$

№	$h\nu_i$, eV	σ^2, eV^2	Transition
P1	1.21	0.028	Intra-center transition between local states V^{-2} [16]
P2	1.56	0.015	Intra-center transition between local states V^{-1} [16]
P3	2.23	0.070	Transition from the local state V^{+2} to the valence band [16]
P4	2.91	0.040	Transition from the local state V^{+1} to the valence band [16]

during the synthesis of hafnium oxide film. Fig. 4, *b* shows the increasing part of the peak intensity is plotted in Arrhenius coordinates.

The results presented in Fig. 4, *a*, show that synthesis at different substrate temperatures leads to a change in the concentration of oxygen vacancies. At low temperatures, a repulsive barrier for attaching water to the substrate prevents oxygen from entering the growing film. At high temperatures, water evaporates faster. Both processes deplete the film in oxygen. Therefore, the intensity of the luminescence band increases, which is associated with oxygen vacancy. The dependence of the luminescence intensity at high temperatures makes it possible to estimate the adsorption energy of water with the silicon surface. In order to estimate this energy, the experimental data on the radiation of the P4 band were rearranged depending on the inverse temperature expressed in energy units. The line on Fig. 4, *b*, which approximates the experimental results, was constructed by regression analysis. The adsorption energy was of the order of 0.8 eV and was calculated by the formula

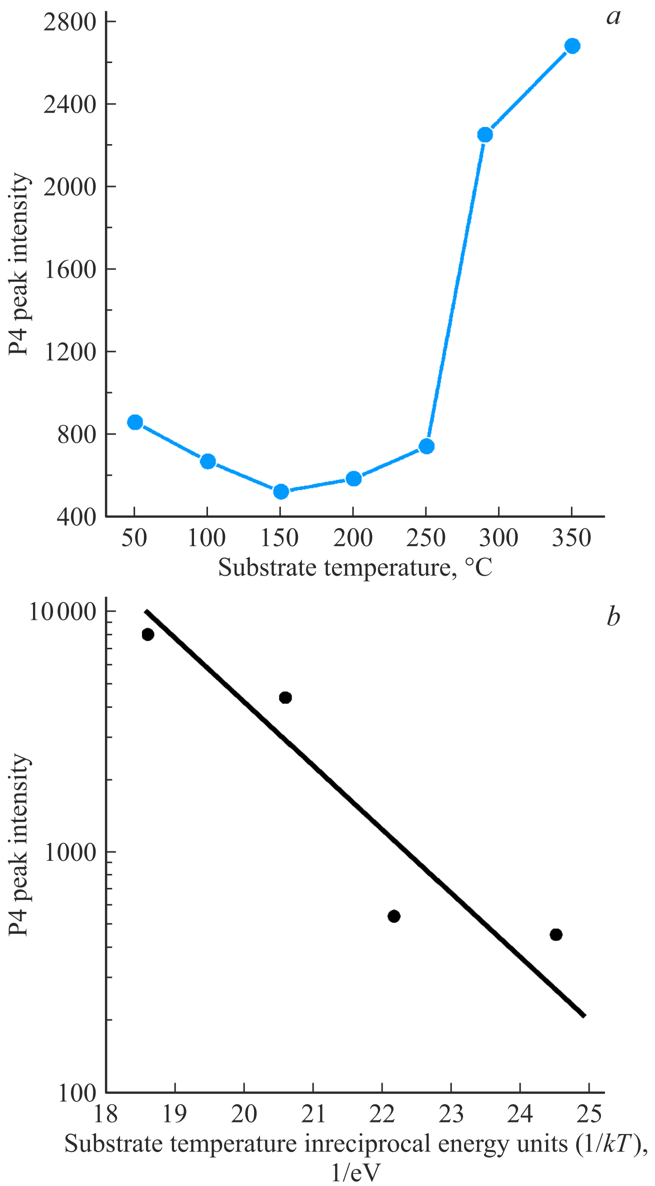

Figure 4. Dependence of peak intensity P4 on substrate temperature.

$$E = \ln\left(\frac{I_1}{I_2}\right) \Big/ \left(\frac{1}{kT_2} - \frac{1}{kT_1}\right), \qquad (1)$$

where I_i — is the luminescence intensity at temperature T_i, k — Boltzmann constant. To estimate the energy, two points were selected on a straight line approximating the experiment, the radiation intensities and inverse temperatures in energy units corresponding to these points were determined, and the calculation was carried out using the formula (1).

3. Conclusion

The experiment on the synthesis of titanium oxide showed that with a decrease in the concentration of oxygen vacancies, the conductivity of the film decreases, along with this, the concentration of interstitial titanium atoms increases. These processes change the relative luminescence intensity of titanium oxide. In particular, the bands associated with interstitial titanium flare up. The luminescence of the oxygen vacancy in hafnium oxide is closely related to the substrate temperature, which is maintained during the synthesis of the film by atomic layer deposition. At low temperatures, the decomposition of the precursor with the addition of hafnium to the growing layer is difficult, so there are more vacancies, and their concentration decreases with increasing substrate temperature. At high temperatures, water evaporates from the substrate, and there are more oxygen vacancies in the film. It can be concluded that the study of the change in the intensity of the band 2.9 eV of hafnium oxide makes it possible to optimize the conditions for the synthesis of the film.

Thus, luminescence is a very sensitive method of diagnosing the composition of oxides and allows analyzing the change in composition under various technological conditions.

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Conflict of interest

The authors declare that they have no conflict of interest.

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