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SPECTROSCOPY OF CONDENSED MATTER

Electroluminescence of Ta_2O_5 Films Formed by Molecular Layer Deposition

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Abstract—The possibility of using electroluminescence to study Si–Ta_2O_5 and Si–SiO_2–Ta_2O_5 structures and obtain information on the electronic structure of the Ta_2O_5 layer and on the properties of the SiO_2–Ta_2O_5 interface is shows. A model of the electronic structure of the Ta_2O_5 layer formed by molecular layer deposition is proposed, which explains the spectral distribution of luminescence independently of the method of its excitation. It is shown that the formation of a Ta_2O_5 layer on the surface of thermally oxidized silicon is accompanied by transformation in the near-surface SiO_2 layer and by quenching of the luminescence band in the spectral region of 650 nm.

Keywords: electroluminescence, molecular layer deposition, spectral distribution, electronic structure
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INTRODUCTION

Double dielectric layers containing a Ta_2O_5 layer on a silicon surface are widely used in modern solid-state electronics as gate dielectrics, memory elements, interlayer insulators, etc. [1, 2]. At the same time, the structure and electronic properties of both the Ta_2O_5 layer itself and the dielectric–dielectric interface, in which the near-surface regions of dielectrics may be modified with formation of a second dielectric layer, remain almost unstudied. Luminescence methods, which can provide information on the properties and electronic structure of layered structures, proved effective in these studies [3–5].

The aim of the present work is to reveal the specific features of the electronic structure of the Ta_2O_5 layers and the SiO_2–Ta_2O_5 interphase that is formed in the process of the second dielectric layer deposition, using the electroluminescence (EL) method and applying our results obtained previously [6, 7] using the cathodoluminescence (CL) and photoluminescence (PL) methods.

EXPERIMENTAL TECHNIQUE

As the objects of investigation, we used Si–Ta_2O_5 and Si–SiO_2–Ta_2O_5 structures. The Ta_2O_5 layers were synthesized using a well-known molecular layer deposition method (a variant of the ALD method), which we used previously to synthesize dielectric layers in [8, 9]. The Ta_2O_5 films were grown either on single-crystalline silicon substrates (acceptor concentration of 3×10^{14} cm^{-3}) 100 mm in diameter or on wafers with a thermal SiO_2 layer (oxidation in dry oxygen at 1000°C, oxide thickness 50 nm) using two reagents, namely, tantalum chloride and water. To achieve a high growth rate, the Si–Ta_2O_5 and Si–SiO_2–Ta_2O_5 structures were synthesized on a rotating silicon substrate at a temperature in the range of 180–250°C with a tantalum chloride evaporator temperature of 45–90°C. The thicknesses of dielectric layers were directly measured at the cleavages of the structures using a Zeiss ORION scanning helium ion microscope and controlled by ellipsometry at a wavelength of 632.8 nm.

The EL spectra were recorded at a positive potential of the silicon substrate in the electrolyte–dielectric–semiconductor system in the range of 25–800 nm on an automated setup based on a wide-aperture monochromator based on the Czerny–Turner configuration with one 600-l/mm diffraction grating under conditions that did not allow breakdown and degradation of the oxide layer [4]. An aqueous solution of Na_2SO_4 was used as electrolyte. All measurements were performed at a temperature of 293 K.

EXPERIMENTAL RESULTS AND DISCUSSION

Electroluminescence of Si–Ta_2O_5 Structures

Figure 1 shows the EL spectrum of Si–Ta_2O_5 structures with a dielectric film thickness of 100 nm. As is seen, the spectrum contains the most efficient band peaking at about 564 nm (2.2 eV) and a broad short-

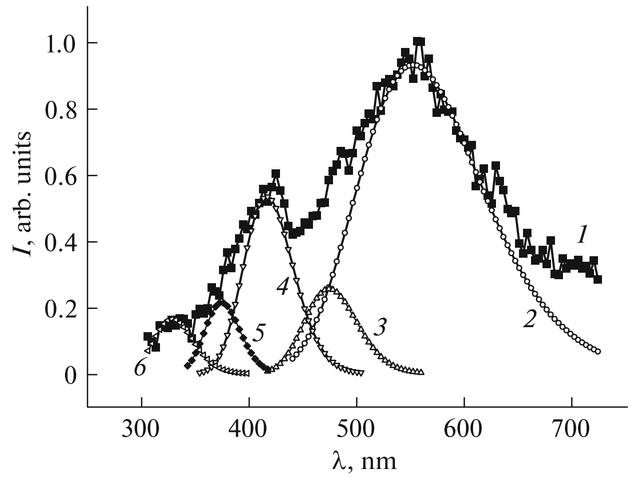

Fig. 1. (*1*) EL spectrum of Si–Ta_2O_5 (100 nm) structures and (*2*–*6*) its approximation by Gaussian distributions.

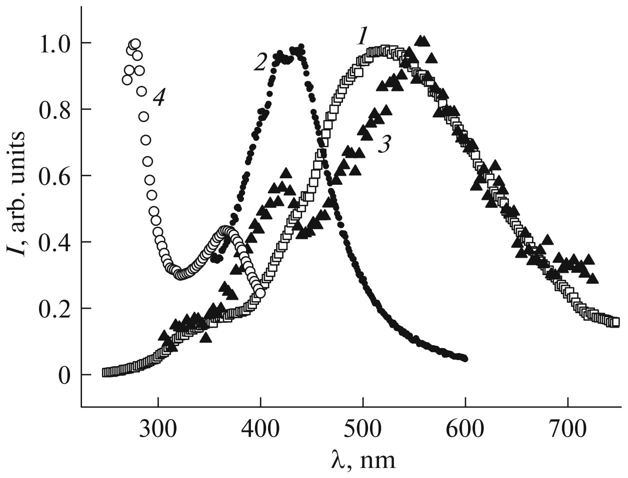

Fig. 2. (*1*) CL, (*2*) PL, (*3*) EL, and (*4*) PL excitation spectra of Si–Ta_2O_5 (100 nm) structures in the region of 450 nm.

wavelength wing, which suggests the presence of several overlapping bands. The EL spectrum of Si–Ta_2O_5 structures is approximated, as is shown in Fig. 1, by a set of Gaussian bands peaking at (*2*) 2.20 eV (564 nm), (*3*) 2.60 eV (477 nm), (*4*) 3.00 eV (413 nm), (*5*) 3.30 eV (376 nm), and (*6*) 3.80 eV (326 nm). The error of determination of the peak positions was 0.05 eV. It is necessary to note that the presence of the characteristic emission bands with maxima at 380, 430, 475, and 540 nm in the EL spectrum of Ta_2O_5 layers was reported in [10].

Figure 2 compares the EL spectra of Si–Ta_2O_5 structures with the CL, PL, and PL excitation spectra measured by us previously [6, 7]. The El spectrum of Ta_2O_5 layers on silicon contains the same set of characteristic emission bands as the CL spectrum of Ta_2O_5 layers on silicon that we described in [7]. However, the EL spectrum of the Si–Ta_2O_5 structures exhibits considerably lower relative intensity of the emission band with a maximum at an energy of 2.6 eV (477 nm). Analysis of the spectral distributions showed that, in a first approximation, all luminescence spectra of Si–Ta_2O_5 structures, independently of the excitation method, can be approximated by the same set of Gaussian distributions presented in Table 1.

Comparison of the EL, CL, and PL spectra sows that the CL and EL spectra contain identical sets of bands, while the PL spectrum contains a band at 2.8 eV, which is absent in the CL and EL spectra, while the bands at 2.2 and 3.8 eV are absent. It seems most reasonable to relate the observed discrepancies in the spectra with the different luminescence excitation methods. The main excitation mechanism in the case of CL is electron-impact excitation, i.e., transfer of a part of the incident-electron energy to electrons of the solid material. In this case, the quasi-momentum of the excited electron also changes. Direct electron-excited transitions need also phonon excitation to compensate the loss in the exciting electron momentum, because of which they seems less probable. In the case of EL in Ta_2O_5 layers, impact excitation of luminescence centers, which is one of the main EL excitation mechanisms in the case of SiO_2 layers [4, 11], can also be observed under the condition that an electron propagating in an applied electric field gains during a free path an energy sufficient for excitation. Apart from the impact excitation, EL can also be excited due to injection of electrons and holes into the dielectric layer and their successive recombination with participation of localized electronic states in the Ta_2O_5 band gap. However, the coincidence of the band sets in the EL spectra of tantalum pentoxide films on silicon and silicon dioxide sublayer contradicts this excitation mechanism, because the silicon dioxide layer prevents injection of holes into Ta_2O_5 layers. Thus, we can conclude that electron-impact excitation of luminescence centers occurs in the cases of both CL and EL of Ta_2O_5 layers.

Table 1. Bands in the luminescence spectra of Si–Ta_2O_5 structures

Luminescence band, peak position, nm (eV)	Presence of bands in the luminescence spectrum		
	PL	CL	EL
564 (2.2)	–	+	+
477 (2.6)	+	+	+
443 (2.8)	+	–	–
413 (3.0)	+	+	+
376 (3.3)	+	+	+
326 (3.8)	–	+	+

The PL excitation implies photon energy transfer to electrons of the solid. In this case, a change in the quasi-momentum is low probable because this requires participation of the phonon subsystem. In addition, in the case of phonon excitation, it is necessary to take into account selection rules in the dipole approximation, which are absent in the case of electron excitation. This allows us to suggest that the bands at 2.2 and 3.8 eV are not excited in the case of PL either due to the selection rules or because their excitation requires indirect transitions. Concerning the appearance of the 2.8-eV band, we may suppose that its excitation requires a direct transition and, therefore, this band is not excited by electrons. The existence of the high-energy PL excitation band, whose energy corresponds to the Ta_2O_5 band gap width (4.4 eV) [1, 2], allows us to relate the observed PL bands to the set of electronic states with energies in the Ta_2O_5 band gap. The excitation of luminescence centers with energies lower than the Ta_2O_5 band gap width is related to the optically stimulated transition of electrons from the valence band of Ta_2O_5 to the corresponding energy level and subsequent radiative relaxation.

Thus, we can conclude that the presence of defects (luminescence centers) in the oxide layer leads to the formation of a set of energy levels in the tantalum pentoxide band gap, which manifest themselves in the luminescence spectra independently of the method of its excitation.

As concerns the nature of luminescence centers in Ta_2O_5 layers, note that we cannot relate the luminescence centers to the presence of defects caused by the oxygen deficit because annealing of the structures at 200°C in an oxygen atmosphere leads to an increase in the CL luminescence with the retained shape of the spectral distribution. This annealing should decrease the concentration of the above defects, and the annealing result indicates that luminescence centers have a different nature, determination of which requires additional investigations.

Electroluminescence of $Si–SiO_2–Ta_2O_5$ Structures

The EL spectra of $Si–SiO_2–Ta_2O_5$ structures under conditions without degradation of the Ta_2O_5 layer are presented in Fig. 3. The EL spectrum of the $Si–SiO_2–Ta_2O_5$ structure is a superposition of the EL spectra of the Ta_2O_5 and SiO_2 layers with the specific features caused by deposition of the additional Ta_2O_5 layer, namely, the considerable decrease in the intensity of the EL band in the region of 650 nm (1.9 eV) and the absorption of emitted radiation in the short-wavelength spectral region (Fig. 3b). It was also found that the intensity of the EL band in the region of 650 nm decreases with increasing thickness of the deposited Ta_2O_5 layer (Fig. 3a).

To consider the specific features of EL of the layered dielectric in more detail, we compared the normalized EL spectrum of the $Si–SiO_2–Ta_2O_5$ structures with the normalized spectrum obtained by summing the EL spectra of the $Si–Ta_2O_5$ and $Si–SiO_2$ structures (Fig. 4). As is seen from Fig. 4, the EL spectrum of the $Si–SiO_2–Ta_2O_5$ structures contains no additional bands with respect to the EL spectra of the $Si–SiO_2$ and $Si–Ta_2O_5$ structures.

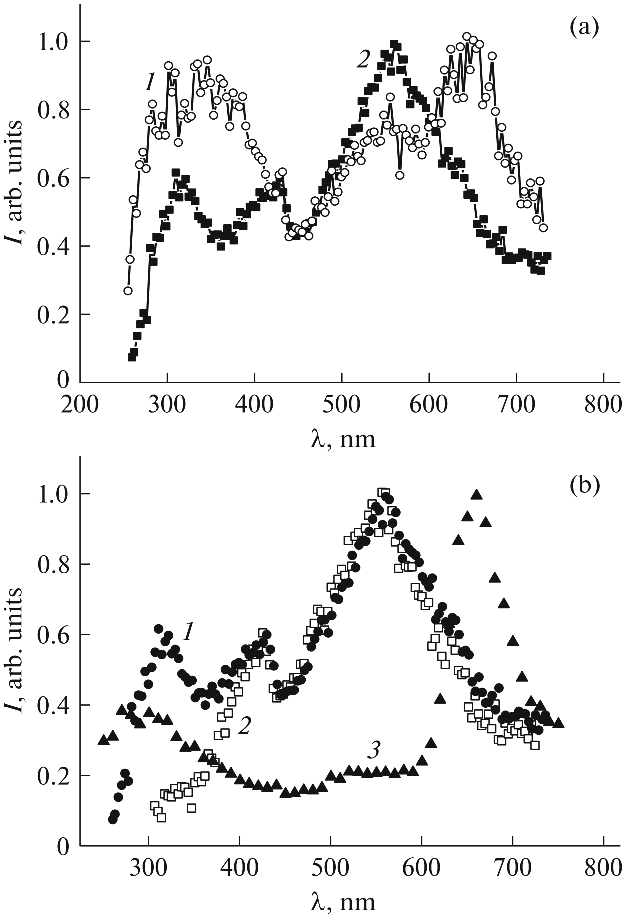

Fig. 3. (a) EL spectra of $Si–SiO_2–Ta_2O_5$ structures with Ta_2O_5 layer thicknesses of (*1*) 35 and (*2*) 100 nm obtained in a galvanostatic regime. (b) EL spectra of (*1*) $Si–SiO_2–Ta_2O_5$ (100 nm), (*2*) $Si–Ta_2O_5$ (100 nm), and (*3*) $Si–SiO_2$ (50 nm) structures obtained under weak excitation (average field strength in the SiO_2 layer was 8 MV/cm).

Considering the obtained experimental results, we can conclude that the EL spectra reflect the processes occurring upon formation of double-layer dielectrics, first of all, upon formation of the dielectric–dielectric interface. In all the cases considered, one can first of all note changes in the concentration and/or properties of 1.9-eV luminescence centers. Previously, we revealed a relation between these luminescence centers and the presence of silanol groups in the external SiO_2 layer [4, 11, 12]. The absence of this luminescence band in the spectra of $Si–SiO_2–Ta_2O_5$ struc-

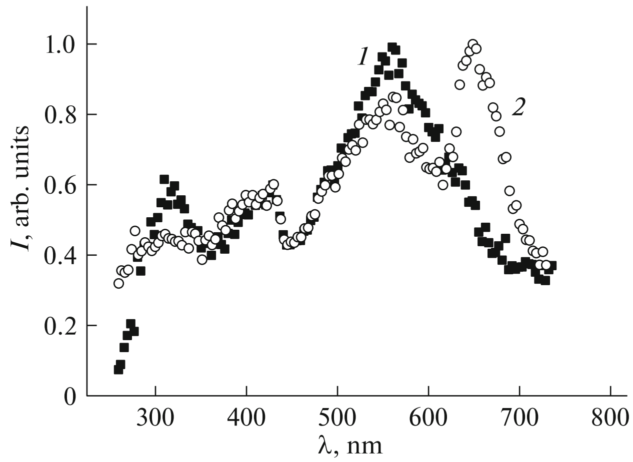

Fig. 4. (*1*) EL spectrum of the $Si–SiO_2–Ta_2O_5$ (100 nm) structure and (*2*) simulated spectrum.

tures (Figs. 3, 4) testifies to a considerable transformation of the external SiO_2 layer related to the almost complete dissociation of silanol groups. Tantalum is a hydride-forming metal, and it is natural to suggest that hydrogen formed in the process of dissociation is spent on the formation of tantalum hydrate (or hydroxide) in the dielectric–dielectric interface and/or in the Ta_2O_5 layer adjacent to SiO_2 surface.

CONCLUSIONS

(1) The use of luminescence methods allowed us to obtain information on the existence of localized electronic states in the Ta_2O_5 band gap, which was used to reliably interpret the results of luminescent and electrophysical measurements.

(2) Formation of double-layer dielectrics is accompanied by the formation of a dielectric–dielectric interface with some specific features. An essential process of the formation of this interface is the dissociation of silanol groups in the near-surface SiO_2 layer. As a result, a transition layer, which has its own characteristic properties that differ from the properties of the layers of the dielectric structure and, in some cases, may influence the electrophysical properties of the semiconductor–layered dielectric structures, is formed on the interface between the dielectrics.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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