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Photoluminescence of Ta_2O_5 Films Formed by the Molecular Layer Deposition Method

A. P. Baraban*, V. A. Dmitriev, V. A. Prokof'ev, V. E. Drozd, and E. O. Filatova
St. Petersburg State University, St. Petersburg, 199034 Russia
**e-mail: bobapro@ya.ru*
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Abstract—Ta_2O_5 films of different thicknesses (20–100 nm) synthesized by the molecular layer deposition method on *p*-type silicon substrates and thermally oxidized silicon substrates have been studied by the methods of high-frequency capacitance–voltage characteristics and photoluminescence. A hole-conduction channel is found to form in the Si–Ta_2O_5–field electrode system. A model of the electronic structure of Ta_2O_5 films is proposed based on an analysis of the measured PL spectra and performed electrical investigations.

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One of the high-priority areas of modern solid-state electronics and optoelectronics is improvement of the technology of synthesizing insulators by low-temperature methods [1, 2] (in particular, the molecular layer deposition (MLD) method is most interesting). The MLD technique is based on the sequential use of self-terminating gas–solid chemical reactions. This method is a surface-controlled process, which makes it possible to grow layers of the material with a thickness down to one monolayer. The obtained films are uniform and have an identical thickness over the entire substrate area [3].

There is much interest in development of the process of synthesizing Ta_2O_5, which can be used in static and dynamic random access memory (RAM), new-generation solid-state capacitors characterized by the maximum capacitance-to-size ratio, and external blocking dielectric layers of elements of silicon-based memory and resistive memory [1, 2, 4]. Note that methods of luminescence investigation are intensively used along with electrical methods for diagnostics of semiconductor–insulator structures [5, 6].

The purpose of this study was to optimize the technology of synthesizing Ta_2O_5 layers with different thicknesses by the MLD method and analyze properties of the synthesized (Si–Ta_2O_5) structures by the photoluminescence method.

Ta_2O_5 films (20–100 nm) were grown by the MLD method on silicon substrates (*p*-type, dopant concentration 3×10^{14} cm^{-3}) 100 mm in diameter. We also synthesized layers on Si wafers with a previously formed SiO_2 layer. The silicon wafers were oxidized in oxygen with a minimum water content at 1000°C. The oxide was 50 nm thick. One cycle of the MLD synthesis of a Ta_2O_5 film included two reactions: tantalum chloride ($TaCl_5$) was used as a precursor in the first reaction, while water vapor was used in the second. Since tantalum chloride is crystalline material at room temperature, the main technological problem of successful implementation of the MLD method is optimization of the technology providing a well-controlled process of $TaCl_5$ evaporation. Based on the performed investigations, we chose the operating temperature ranges (180–250°C for the silicon substrate temperature and 45–90°C for the evaporator temperature), at which a further synthesis of the Si–Ta_2O_5 and Si–SiO_2–Ta_2O_5 structures was performed. The use of a rotating substrate provided a high film-growth rate.

The electronic structure of the formed Ta_2O_5 layers was identified by the methods of high-frequency capacitance–voltage (*C*–*V*) characteristics and photoluminescence (PL). *C*–*V* characteristics were recorded in the metal–insulator–semiconductor and electrolyte–insulator–semiconductor systems. The field electrodes were aluminum and the electrolyte was one-molar solution of sodium sulfate. The PL and PL excitation spectra were recorded by a Fluorolog-3 system (HORIBA Jobin Yvon) consisting of two independent monochromators based on the Czerny–Turner configuration with one diffraction grating of 1200 1/mm. PL excitation was performed by 450-W xenon lamp radiation. The spectra were recorded by the photon-counting method using an R928P photoelectron multiplier. The spectrum scan rate was 150 nm/s. The excitation radiation wavelength was varied in the spectral range of 275–400 nm. The spectral width of the PL excitation monochromator was

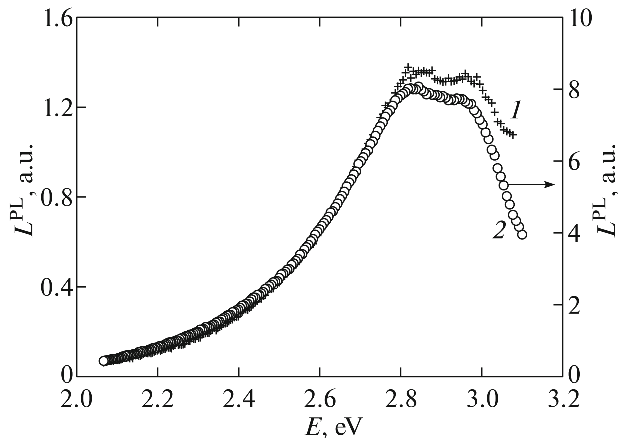

Fig. 1. PL spectra of the (*1*) Si–Ta_2O_5 (35 nm) and (*2*) Si–SiO_2 (55 nm)–Ta_2O_5 (100 nm) structures at an excitation energy of 3.35 eV (370 nm).

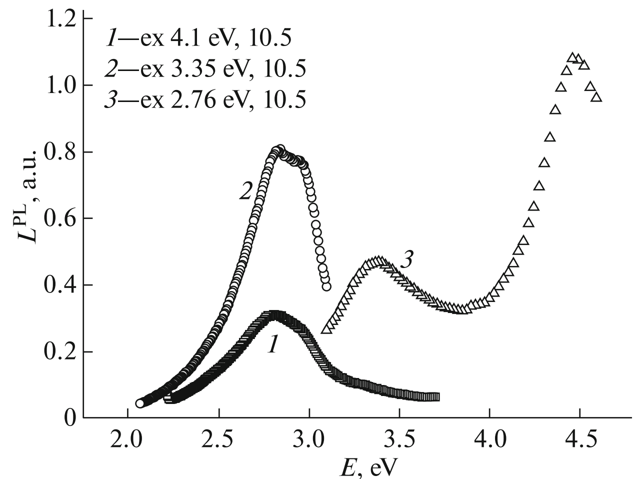

Fig. 2. (*1*, *2*) PL spectra at the excitation energy of (*1*) 4.1 and (*2*) 3.35 eV and (*3*) PL excitation spectra at the energy near 2.78 eV of the Si–SiO_2 (55 nm)–Ta_2O_5 (100 nm) structures.

10 nm, and the spectral width of the luminescence recording monochromator was 5 nm. The PL spectra were recorded in the range determined by the excitation wavelength λ_{exit} (from (λ_{exit} + 30 nm) to (2λ_{exit} – 30 nm)), which excluded the influence of the second-order diffraction on the recorded PL spectrum. The spectra were corrected for the equipment spectral sensitivity and normalized to the photodiode current proportional to the excitation-lamp intensity.

Photoinjection measurements showed that the Si–Ta_2O_5 structures (with the dielectric-layer thicknesses of 20–100 nm) are characterized by low potential barrier for electrons (~0.4 eV) at the Si/Ta_2O_5 interface, which is in agreement with the data in the literature [1]. The presence of a low potential barrier for electrons at the semiconductor–insulator interface and significant hole conductivity of the synthesized Ta_2O_5 layers hinder correct measurements of the *C–V* characteristics of the Si–Ta_2O_5 structures. Therefore, high-frequency *C–V* characteristics were measured for the Si–SiO_2–Ta_2O_5 structures, in which the SiO_2 layer makes electron and hole exchange between the silicon substrate and Ta_2O_5 layer impossible. As a result, the relative permittivity for Ta_2O_5 films with thicknesses in the range of 20–100 nm was found to be 13.5 ± 0.5. The Ta_2O_5 film thickness was determined using a Zeiss ORION scanning helium ion microscope from an image of the sample cross section.

Analysis of the PL spectra of the Si–Ta_2O_5 and Si–SiO_2–Ta_2O_5 structures and Si–SiO_2 check structures in the excitation energy range (4.51–3.1 eV) showed that the shape of the PL spectral distribution for the structures with a Ta_2O_5 layer is independent of the type (Si or SiO_2) of substrate used in the synthesis and the Ta_2O_5 layer thickness (in the range of thicknesses under study, 35–150 nm) and that the SiO_2 layer makes no PL contribution at Ta_2O_5 thicknesses exceeding 35 nm. Figure 1 shows the PL spectra of the Si–Ta_2O_5 (35 nm) and Si–SiO_2 (55 nm)–Ta_2O_5 (100 nm) structures measured at the excitation energy of 3.35 eV (370 nm). It can be seen that the luminescence intensity is approximately proportional to the tantalum pentoxide layer thickness. Based on the aforesaid, we can conclude that luminescence centers are formed in the volume of tantalum pentoxide directly during its synthesis. In this case, the PL spectra and PL excitation spectra presented in Fig. 2 are completely due to optical processes in the Ta_2O_5 layer.

It was established that all measured PL spectra can be represented in a unified way: as a sum of Gaussian distributions with a fixed energy position, relative intensity, and dispersion. It was found that, for all samples containing tantalum pentoxide, the PL spectrum is a set of emission bands peaking at energies of 2.6 ± 0.1, 2.8 ± 0.1, 3.0 ± 0.1, and 3.2 ± 0.1 eV. A set of the absorption bands peaking at energies of 3.3 ± 0.1, 3.9 ± 0.1, and 4.4 ± 0.1 eV was obtained for the PL excitation spectra. The dispersion was 0.20 ± 0.05 eV for all bands.

The PL spectra are determined only by radiative processes occurring in the Ta_2O_5 layers and, accordingly, contain information about their electronic structure. The results of expansion of the PL spectra and PL excitation spectra indicate rather complex electronic structure of the tantalum pentoxide layers. The presence of a high-energy band in the PL excitation spectrum with the energy corresponding to the Ta_2O_5 band gap (4.4 eV) [1, 4] allows one to relate the observed PL bands with the set of electronic states energetically located in the Ta_2O_5 band gap. The excitation of luminescence centers with an energy lower than the Ta_2O_5 band gap is related to the optically

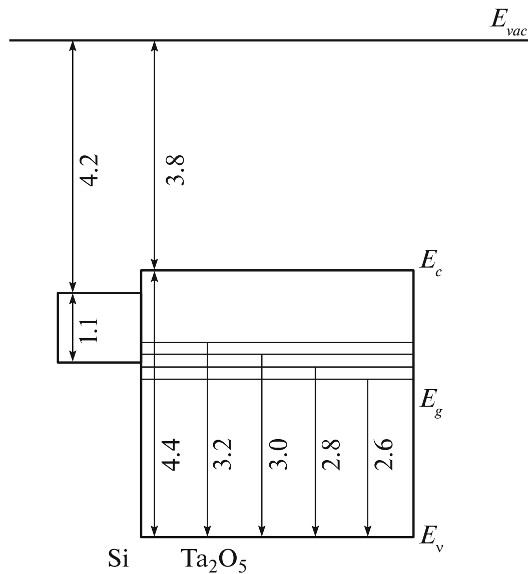

Fig. 3. Energy structure of the $Si-Ta_2O_5$ structure.

stimulated transition of electrons from the Ta_2O_5 valence band to the corresponding energy level with subsequent radiative relaxation. For example, the PL spectral distribution of Ta_2O_5 upon excitation with an energy near 3.3 eV (Fig. 2, curve *2*) consisted of three emission bands peaking at energies of 2.6, 2.8, and 3.0 eV.

Based on the performed analysis, we can propose a model of the electronic structure of tantalum pentoxide layers formed on the silicon (silicon dioxide) surface by the MLD method (Fig. 3).

A schematic shown in Fig. 3 makes it possible to explain the spectral composition of luminescence for any means of its excitation. It is noteworthy that the presence of the system of energy levels located above the top of the Ta_2O_5 valence band by 2.8–3.2 eV in the tantalum pentoxide band gap induces a hole-conduction channel in the $Si-Ta_2O_5$–field electrode system; the problems of measuring the high-frequency capacitance of the $Si-Ta_2O_5$ structures are due to specifically the presence of this channel. The SiO_2 layer in the $Si-SiO_2-Ta_2O_5$ system prevents the hole current, which makes it possible to measure the high-frequency capacitance in order to study the electrical characteristics of the formed structures.

Thus, Ta_2O_5 layers of different thickness (20–100 nm) were synthesized on a silicon substrate by the low-temperature MLD method. The main electrical characteristics of the formed structures were determined based on high-frequency capacitance and photoluminescence measurements, and a model of their electronic structure was proposed.

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