Physics of Complex Systems, 2021, vol. 2, no. 1
www.physcomsys.ru

Physics of Semiconductors.
Semiconductor Physics

UDC 537.311 https://www.doi.org/10.33910/2687-153X-2021-2-1-9-14

Luminescence of insulator layers on silicon excited by electrons

A. P. Baraban[1], V. A. Dmitriev✉[1]

[1] Saint-Petersburg State University, 7/9 Universitetskaya Emb., Saint-Petersburg 199034, Russia

Authors
Alexander P. Baraban, ORCID: 0000-0001-8745-7019
Valentin A. Dmitriev, ORCID: 0000-0003-3604-9490, e-mail: esssec@gmail.com

For citation: Baraban, A. P., Dmitriev, V. A. (2021) Luminescence of insulator layers on silicon excited by electrons. *Physics of Complex Systems*, 2 (1), 9–14. https://www.doi.org/10.33910/2687-153X-2021-2-1-9-14

Received 11 December 2020; reviewed 20 December 2020; accepted 21 December 2020.

Funding: This work was performed using the equipment of Saint Petersburg State University Research Park, in particular, the Interdisciplinary Resource Center for Nanotechnology and the Center for Innovative Technologies of Composite Nanomaterials.

Abstract. We present a comparative analysis of cathodoluminescence (CL) and electroluminescence (EL) spectra measured on Si–SiO_2 and Si–Ta_2O_5 structures with various thicknesses of insulator layers. Spectral distribution of luminescence depends on how the insulator layer was formed, its thickness and type of excitation. The analysis indicates that CL and EL spectra of Si–SiO_2 structures, grown by thermal oxidation of silicon in “dry” oxygen, are almost identical in spectral composition. Based on the dependence of intensity of the luminescence band with a maximum at energy of 2.2 eV, it was concluded that the corresponding luminescence centers are uniformly distributed over the oxide layer thickness in the range of 30–200 nm. It is assumed that these luminescence centers are oxygen vacancies formed during the thermal oxidation of silicon. In the case of Ta_2O_5 layers on silicon, the presence of defects (luminescence centers) in the oxide layer leads to the formation of a set of energy levels in the band gap of the Ta_2O_5 layers obtained by ALD. They appear in the luminescence spectra regardless of the excitation method.

Keywords: cathodoluminescence, electroluminescence, molecular layer deposition, spectral distribution, electronic structure, luminescence centers.

Introduction

Luminescence is widely used in fundamental studies of solids, including semiconductor-insulator structures (Baraban, Samarin et al. 2019; Coenen, Haegel 2017; Yacobi, Holt 1990; Zamoryanskaya, Sokolov 1998). Their luminescent properties of interest to researchers because of their potential applications in silicon-based optoelectronic devices. For this reason, our major focus on electroluminescence (EL) and cathodoluminescence (CL) in silicon-insulator structures.

The study compares the results obtained by two methods of luminescence excitation. Our aim was to secure additional information through comprehensive analysis of aggregate luminescence data.

Experimental procedure

The study focused on Si-SiO_2 and Si-Ta_2O_5 structures. Essentially, the SiO_2 film was grown on a single-crystal silicon wafer of *p*-type ($N_A = 8 \times 10^{14}$ cm^{-3}) by thermal oxidation in dry oxygen at a temperature of 1000°C. The Ta_2O_5 layers were synthesized using a well-known molecular layer deposition method (a variant of the ALD method), which we previously used to synthesize dielectric layers in (Baraban, Dmitriev et al. 2019; Baraban et al. 2020). The Ta_2O_5 films were grown on single-crystalline silicon substrates (acceptor concentration of 3×10^{14} cm^{-3}) of 100 mm in diameter using two reagents, namely, tantalum chloride and water. To achieve a high growth rate, the Si–Ta_2O_5 structures were synthesized on a rotating silicon substrateat a temperature in the range of 180–250°C with a tantalum chloride evaporator temperature of 45–90°C.

The obtained films were thoroughly investigated by SEM+EDX, TEM, XRD, CL and TDS methods in an attempt to understand their composition, inner structure and electronic properties. The thickness of the dielectric layers was determined on cleaved structures with the scanning helium ion microscope Zeiss ORION and monitored by ellipsometry at the wavelength of 632.8 nm.

To implement the CL method, we used the scanning electron microscope Zeiss SUPRA 40VP with the Gatan MonoCL3+ recording system. The CL spectra were recorded in the range of 250–800 nm while continuously scanning an electron beam over the sample surface. Each spectrum was recorded at a new location of the sample. The width of the scanning area was 30 microns, the acquisition time of one point of the spectrum was 1 s, the spectral resolution was 2 nm, incident electron energy was 5, 10, 15 keV, the beam current was 2–11 nA.

The EL spectra were recorded at a positive potential of the silicon substrate in the electrolyte-dielectric-semiconductor system in the range of 250–800 nm on an automated setup based on a wide-aperture monochromator (Czerny–Turner configuration) with one 600 l/mm diffraction grating under conditions that did not allow breakdown or degradation of the oxide layer (Baraban et al. 2009). An aqueous solution of Na_2SO_4 was used as an electrolyte.

All measurements were performed at a temperature of 293 K.

Results and discussion

Luminescence of SiO_2 layer excited by electrons (CL and EL)

In the cases of electroluminescence and cathodoluminescence of SiO_2 layers, low-energy electrons (energies below 10 eV) interact with defects (called Luminescence Centers (LC)) of the oxide layer that appear during oxide growth. In the case of CL, low energy electrons are produced by incident electrons in the volume of the oxide layer. The electron energy used in our experiments is enough to excite luminescence throughout the thickness of the whole oxide layer. In the case of EL, electrons are injected into the oxide layer from the field electrode (in this case, the spectrally transparent electrolyte). These electrons are subsequently accelerated (heated) in an electric field with a strength of more than 10 MV/cmin the 25 nm thick oxide layer energies (5–10 eV) sufficient to excite the luminescence centers (Baraban et al. 2009; Babaran et al. 1993). The excitation of EL, excited by hot electrons, occurs throughout the thickness of the oxide layer except a 25 nm layerand a tunnel-thin SiO_2 layer on the outer boundary of the structure (Baraban et al. 2009). The above consideration allows to use the same approach to analyze the results of CL and EL methods.

This is confirmed by the type of spectral distributions shown in Fig. 1 and Fig. 2A comprehensive analysis of the CL and EL spectra (for this method of oxide layer formation) allowed us to approximate them with a single set of Gaussian radiation bands, the maxima (and dispersions) of which corresponded to the energies in eV: 1.87 ± 0.04 (0.08 ± 0.01); 2.20 ± 0.05 (0.15 ± 0.04); 2.50 ± 0.08 (0.20 ± 0.06); 2.90 ± 0.08 (0.20 ± 0.06); 3.3 ± 0.1 (0.25 ± 0.8); 3.9 ± 0.1 (0.25 ± 0.06); 4.2 ± 0.1 (0.25 ± 0.08). Examples of such approximation are shown in Fig. 3. This result indicates the excitation of identical LC formed in the oxide layer during thermal oxidation.

It should be noted that when changing the method of oxide layer formation, the EL spectrum may be more informative (it allows to reliably select a larger number of characteristic radiation bands) than the CL spectrum, as shown in Fig. 4. In this case, the observed differences in the EL spectrum are due to the peculiarities of luminescence excitation by an electric field (Baraban et al. 2012).

The luminescence spectra of SiO_2 layers excited by electrons make it possible to distinguish the three most reliably recorded radiation bands, whose maxima are located at energies of 4.2 eV, 2.2 eV, and 1.9 eV. The results of normalizing the intensity of these radiation bands to the intensity of the luminescence band in the energy range of 1.9 eV are shown in Table. The choice of the 1.9 eV luminescence band intensity, as the normalizing coefficient is due to the similarity of the excitation mechanisms and the nature of the luminescence centers, as shown in (Baraban, Samarin et al. 2019).

The most significant difference in relative intensity was observed for the band with a maximum energy of 2.2 eV. Note that this EL band is characterized by the maximum excitation energy in the EL

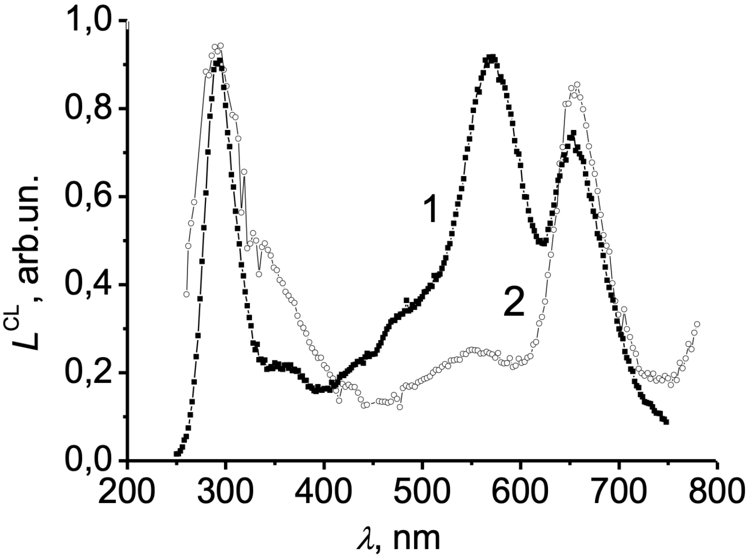

Fig. 1. Luminescence Spectra of a SiO_2 (184 nm) on silicon obtained by CL (1) and EL (2) methods

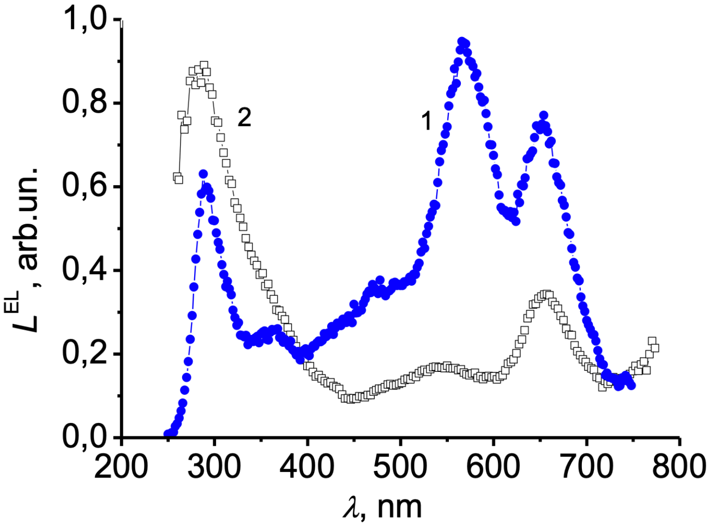

Fig. 2. Luminescence Spectra of a SiO_2 (70 nm) on silicon obtained by CL (1) and EL (2) methods

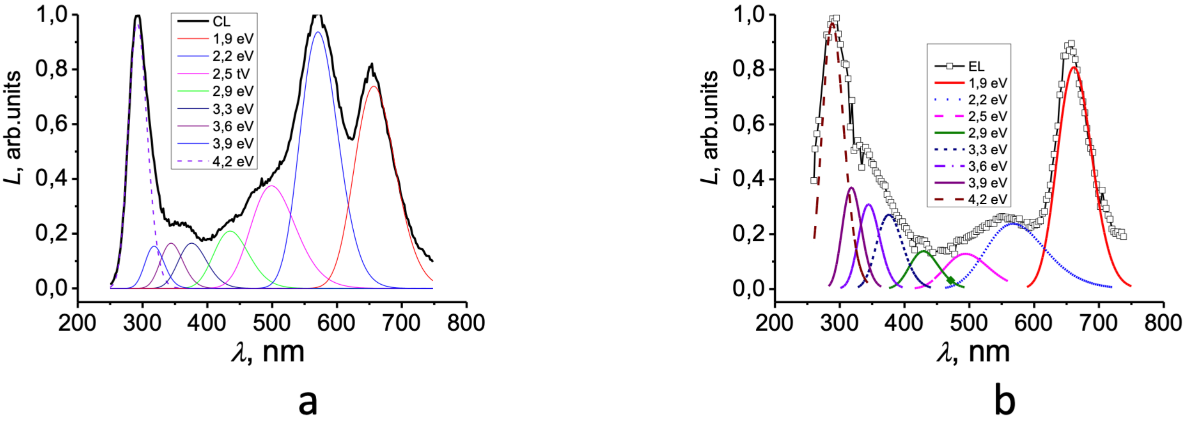

Fig. 3. An example approximation of the CL (a) and EL (b) spectra of Si–SiO_2 structures with an oxide layer thickness of 184 nm by a set of Gaussian distributions

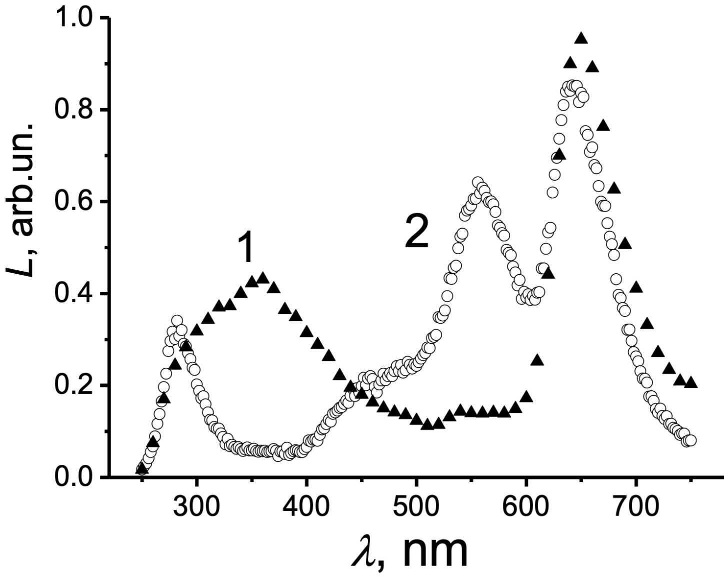

Fig. 4. EL (1) and CL (2) Spectra of SiO_2 layers (100 nm) obtained by thermal oxidation of silicon in a mixture of oxygen and chlorine (Baraban et al. 2012)

Table. Parameters of characteristic CL and EL bands for SiO_2 layers (184 nm). The intensity of spectral bands is indicated in units of the luminescence band intensity of 1.9 eV.

Excitation method	**CL**	**EL**
Spectral band, eV	Relative intensity	Relative intensity
1.87 ± 0.04	1	1
2.20 ± 0.05	1.4 ± 0.2	0.2 ± 0.2
4.20 ± 0.1	1.4 ± 0.2	1.1 ± 0.2

spectrum, which is recorded at an electric field strength that does not cause the development of the impact ionization process in the oxide layer (Baraban et al. 2009).The significantly lower intensity of this band in the EL spectra is due to the peculiarities of the excitation a significantly smaller number of hot electrons providing its excitation in comparison with the CL spectrum and even with the EL band with a maximum at 4.2 eV (peculiarities of EL excitation) and, as noted above, a smaller regionexcitation of luminescence centers in comparison with CL (Baraban et al. 2009). There is practically no information in the literature on the mechanisms of excitation, emission, and the nature of this luminescence centers. Therefore, obtaining additional information on the properties of this LC is, undoubtedly, of interest.

To obtain additional information on the properties of LC in the oxide layer, a set of EL and CL spectra was obtained for Si–SiO_2 structures with different oxide layer thicknesses (30–200 nm) and their approximation was carried out using the obtained set of Gaussian distributions. As a result, the dependences of the intensity of the luminescence bands on the thickness of the oxide layer were obtained. It was found that the intensity of the 2.2 eV EL band is proportional to the length of the region of its excitation (d_{ox}-d_0, where $d_0 \approx 30$ nm is the outer part of the oxide layer with no hot electrons). In the case of CL the intensity of the 2.2 eV band is proportional to the energy losses of the electron beam at this thickness of the oxide layer, calculated using the program "Casino" (Drouin et al. 2006). This made it possible to conclude that there is a uniform distribution of LC responsible for the luminescence band with a maximum at an energy of 2.2 eV over the entire thickness of the oxide layer in the thickness range of 30–200 nm. In this case, it is logical to assume that the formation of these LC is a consequence of the thermal oxidation of silicon and is associated with the formation of an equilibrium concentration of oxygen vacancies over the entire thickness of the oxide layer.

In the case of a luminescence band with a maximum at anenergy of 4.2 eV, the relative intensity of which is comparable to the EL and CL spectra of Si-SiO_2structures, the dependences of the intensity on the thickness of the oxide layer differ significantly. In the case of EL, the intensity of this band is proportional to the region of its excitation, and in the case of CL, the intensity of the band increases with an increase in the thickness of the oxide layer much more than is assumed for a uniform CL distribution. The final conclusion about the spatial distribution of LC data requires additional studies and detailed analysis.

Luminescence of Ta_2O_5 layer excited by electrons (CL and EL)

Fig. 5 shows the EL and the CL 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 560 nm and a broad short-wavelength wing, which suggests the presence of several overlapping bands. Aggregate analysis of the obtained spectra allowed us to approximate them 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 peak positions was 0.05 eV.

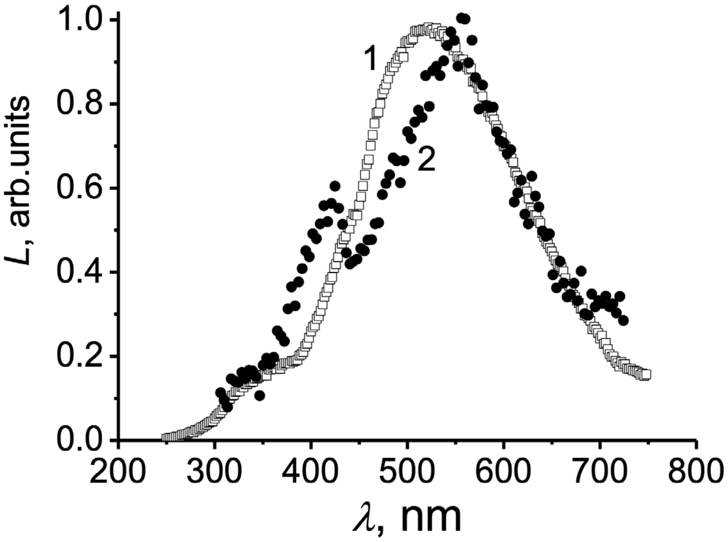

Fig. 5. CL (1) and EL (2) spectrum of Si–Ta2O5 (100 nm) structures

The analysis of approximation results showed a significant decrease in the intensity of the luminescence band with a maximum at an energy of 2.6 eV in the EL spectra in comparison with the CL spectra. It was noted that a decrease in the thickness of Ta_2O_5 layers led to a decrease in the intensity of this EL band up to its complete quenching at a layer thickness of 35 nm. Relative intensities of the remaining emission bands are comparable in a wide range of Ta_2O_5 layer thicknesses. This circumstance, taking into account the specific features of CL and EL excitation of Ta_2O_5 layers, may be used to obtain additional information both on the mechanism of the observed luminescence and the electronic structure of the luminescence center.

To explain this feature, it is necessary to recall that earlier PL studies of Ta_2O_5 layers on silicon (Baraban et al. 2016) showed the presence of localized energy levels in the Ta_2O_5 band gap, which are inherent in luminescence centers. The PL was excited due to the band-band generation of electron-hole pairs and/or the transfer of an electron from the valence band of Ta_2O_5 to the LC energy level in the forbidden band. The minimum EL band intensity of 2.6 eV is due to the fact that the position of this level in the Ta_2O_5 band gap is the most convenient one for the implementation of the hopping conduction of holes from the valence band of silicon to the electrolytic field of the electrode used for recording EL spectra. In this case, the nonradiative channel of electron energy dissipation turns out to be dominant, which manifests itself in the quenching of this luminescence band. In the case of recording CL spectra, the process of charge carrier transfer over localized electronic states in the Ta_2O_5 band gap is absent, which manifests itself in the generation of radiation in the corresponding band. This fact confirms the validity of the previously proposed model and indicates the possibility of its use for electron-excited luminescence in Ta_2O_5 layers.

In addition, the complete resemblance of the form of the CL and EL spectra of Si–Ta_2O_5 structures in the rest of the spectral range indicates the possibility of using the EL method to study the recombination mechanism of luminescence.

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 band gap of Ta_2O_5 layers obtained by ALD, which appear in the luminescence spectra regardless of the excitation method. Note that it is not possible to associate the luminescence centers with the presence of defects caused by oxygen deficiency in Ta_2O_5 layers, since annealing of the structures at 200 °C in an oxygen atmosphere led to an increase in the intensity of the EL and CL spectra, retaining the shape of the spectral distribution.

Conclusion

Based on the approximation of the EL and CL spectra of SiO_2 layers on silicon with a single set of Gaussian emission bands, the dependences of the band intensity on the SiO_2 layer thickness were obtained. On this basis, for the emission band with a maximum at an energy of 2.2 eV, it was concluded that the corresponding luminescence centers are uniformly distributed in SiO_2 layers. It is assumed that the formation of these CL is a consequence of thermal oxidation of silicon and is associated with the formation of the equilibrium concentration of oxygen vacancies. In the case of Ta_2O_5 layers on silicon, a similar approach revealed a significant decrease in the intensity of the emission band with a maximum of 2.6 eV in the case of the EL method, which confirms the participation of luminescence centers in charge transfer processes in Si–Ta_2O_5 structures.

References

Babaran, A. P., Bulavinov, V. V., Troshikhin, A. G. (1993) Changes in the state of Si-SiO_2 structures studied by the method of field cycling in a system with electrolytic contacts. *Technical Physics Letters*, 19 (9), 577–578. (In English)

Baraban, **A.** P., Denisov, E. A., Dmitriev, V. A. et al. (2020) Features of SiO_2 layers synthesized on silicon by molecular layer deposition. *Semiconductors*, 54 (4), 506–510. https://www.doi.org/10.1134/S106378262004003X (In English)

Baraban, A. P., Dmitriev, V. A., Petrov, Yu. V. (2009) *Elektrolyuminestsentsiya tverdotel'nykh sloistykh struktur na osnove kremniya [Electroluminescence in silicon-based solid-state layered structures].* Saint Petersburg: Saint Petersburg State University Press, 195 p. (In Russian)

Baraban, A. P., Dmitriev, V. A., Petrov, Yu. V., Timofeeva, K. A. (2012) Electron-excited luminescence of SiO_2 layers on silicon. *Physics of the Solid State*, 54 (6), 1149–1152. https://www.doi.org/10.1134/S1063783412060066 (In English)

Baraban, A. P., Dmitriev, V. A., Prokof'ev, V. A. et al. (2016) Photoluminescence of Ta_2O_5 films formed by the molecular layer deposition method. *Technical Physics Letters*, 42 (4), 341–343. https://www.doi.org/10.1134/S1063785016040040 (In English)

Baraban, A. P., Selivanov, A. A., Dmitriev, V. A. et al. (2019) Cathodoluminescence of TiO_2 films formed by molecular layer deposition. *Technical Physics Letters*, 45 (3), 256–258. https://www.doi.org/10.1134/S1063785019030210 (In English)

Baraban, A. P., Samarin, S. N., Prokofiev, V. A. et al. (2019) Luminescence of SiO_2 layers on silicon at various types of excitation. *Journal of Luminescence*, 205, 102–108. https://www.doi.org/10.1016/j.jlumin.2018.09.009 (In English)

Coenen, T., Haegel, N. M. (2017) Cathodoluminescence for the 21st century: Learning more from light. *Applied Physics Reviews*, 4 (3), article 031103. https://www.doi.org/10.1063/1.4985767 (In English)

Drouin, D. (2006) CASINO a powerful simulation tool for cathodoluminescence applications, *Microscopy and Microanalysis*, 12 (S02), 1512–1513. https://www.doi.org/10.1017/S1431927606069686 (In English)

Yacobi, B. G., Holt, D. B. (1990) Cathodoluminescence. In: *Cathodoluminescencemicroscopy of inorganic solids*. Boston: Springer Publ., pp. 55–88. https://www.doi.org/10.1007/978-1-4757-9595-0_4 (In English)

Zamoryanskaya, M. V., Sokolov, V. I. (1998) Structural study of thermal-oxide films on silicon by cathodoluminescence. *Physics of the Solid State*, 40 (11), 1797–1801. https://www.doi.org/10.1134/1.1130659 (In English)