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Anomalous temperature dependence of photoluminescence in GeO_x films and GeO_x/SiO_2 nano-heterostructures

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The optical properties of GeO_x film and GeO_x/SiO_2 multilayer heterostructures (with thickness of GeO_x layers down to 1 nm) were studied with the use of Raman scattering and IR spectroscopy, ellipsometry and photoluminescence spectroscopy including temperature dependence of photoluminescence. The observed photoluminescence is related to defect (dangling bonds) in GeO_x and interface defects for the case of GeO_x/SiO_2 multilayer heterostructures. From analysis of temperature dependence of PL intensity, it was found that rate of nonradiative transitions in GeO_x film has Berthelot type, but anomalous deviations from Berthelot type temperature dependence were observed in temperature dependences of PL intensities for GeO_x/SiO_2 multilayer heterostructures.

Optical properties of silicon and germanium suboxide films with or without embedded semiconductor nanocrystals has been studied last time because of the potential applications in nanoelectronics and optoelectronics. Photoluminescence of Si suboxide films is quite well studied [1–4], but similar Ge suboxide films are poorly studied. Optical properties of Ge suboxide films containing Ge nanocrystals were studied experimentally [5–8]. It is known, that defects play important role in photoluminescence of dielectrics. Different groups have investigated point defects in germanium dioxide [9] and germanium suboxide [10]. Photoluminescence intensity of dielectric films is defined by the competition between a radiative process and nonradiative relaxation of photoexcitations [11]. Rate of both processes has it's own temperature dependence and studies of temperature dependence of photoluminescence intensity can give information about thermal activation energy of processes and so on. The purpose of this study is to elucidate the temperature dependence of rates of radiative and nonradiative processes in defect induced photoluminescence of GeO_x films and GeO_x/SiO_2 multilayer heterostructures.

GeO_x films and GeO_x/SiO_2 multilayer heterostructures were prepared by evaporation of GeO_2 powder or alternate evaporation of GeO_2 and SiO_2 powders in an ultrahigh-vacuum chamber from an electron beam gun onto (100) oriented silicon substrates maintained at 100 °C. The base pressure was 10^{-8} Torr. The pressure during the evaporation increases until $3 \cdot 10^{-6}$ Torr due to the partial decomposition of GeO_2. The deposition rate of 0.1 nm/s was controlled by a quartz microbalance. In fact, under electron bombardment of GeO_2, its partial decomposition onto Ge, O_2, and GeO takes place. The last two components are more volatile, but, unlike O_2, GeO is easily deposits onto cool substrate. So, the deposited germanium oxide is sub- stoichiometric, namely GeO_x, where x is close to 1 [7]. In the work [7] was shown, that silicon oxide layers have composition SiO_2. The set of samples was deposited. Relatively thick (100 nm) layer of GeO_x was covered by SiO_2 cap layer with thickness 100 nm. Two multilayer structures containing 10 periods of GeO_x(4 nm)/SiO_2(4 nm) and GeO_x(1 nm)/SiO_2(4 nm) were also covered by SiO_2 cap layer with thickness 100 nm. So, in the first case total thickness of GeO_x was 40 nm, in the second case it was 10 nm.

The obtained films were studied with the use of photoluminescence spectroscopy, Raman scattering spectroscopy, IR-spectroscopy techniques. The Raman spectra were registered in quasi back-scattering geometry, the 514.5 nm Ar^+ laser lines was used. Raman spectrometer T64000 (Horiba Jobin Yvon) with micro-Raman setup and the liquid nitrogen cooled CCD matrix detector were used. The spectral resolution was not worse than 1.5 cm^{-1}. All Raman spectra were measured at room temperature. To avoid heating of the films, the laser beam was slightly defocused; the spot diameter was about 4–6 μm; the laser power reaching the sample was within the 1–2 mW range. To study the stoichiometry of GeO_x films, the Fourier Transformed

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Infrared Spectroscopy (FTIR) was applied. The FTIR spectrometer FT-801 was used. The spectral range of the spectrometer is from 550 to 5500 cm^{-1}. The spectral resolution was 4 cm^{-1}. Ellipsometry was applied to detect the thickness and optical constant of the films. Laser (He–Ne, $\lambda = 632.8$ nm) scanning and spectral ellipsometers were used. The range of spectral ellipsometer was within 250 to 900 nm, xenon lamp was used as a light source, and the spectral resolution was 2 nm. The photoluminescence spectra were registered at room and low temperatures using a line of mercury lamp (312.6 nm) for pumping. All photoluminescence spectra were normalized taking into account the spectral characteristics of the spectrometer and detector (CCD matrix). For study of temperature dependence of photoluminescence standard Linkam thermo-cell was used.

It is known that Raman signal from amorphous Ge is a broad peak with maximum at 270–280 cm^{-1}. The Raman signal from crystalline Ge is narrower peak with position depending on nanocrystal sizes. The confinement effect shifts the position of Raman peak to low frequencies from bulk-Ge Raman peak position (about 301 cm^{-1}). The nanocrystal sizes can be estimated from position of Raman peaks [5]. The Raman spectra of the films and mono-crystalline Si substrate are shown in Fig. 1. One can see no Raman peak due to scattering by vibration of Ge-Ge bonds. All peculiarities that one can see in Raman spectra are due to two-acoustic phonon scattering in Si substrate. Peak at 305 cm^{-1} is due to 2-TA scattering, peak at 420–430 cm^{-1} is due to TA-LA scattering [12]. In two-phonon scattering process quasi-impulse of phonons can be change in broad range, so, due to acoustic phonon dispersion, there is broad peculiarity from two-phonon Raman scattering from Si substrate (from 225 to 450 cm^{-1}). From Raman spectra one can conclude, that GeO$_x$ films are not de-composited and do not contain Ge clusters at least in quantity that can be detected by Raman spectroscopy technique.

Fig. 2 presents the IR absorption spectrum of GeO$_x$ film in range from 700 to 1250 cm^{-1}. The observed peak at 815 cm^{-1} is assigned to Ge-O-Ge stretching vibration mode. It is known, that in GeO$_x$ films this peaks approximately linearly shift depending on stoichiometry parameter x [7, 13]. In article of Jishiashvili and Kutelia [14] there is formulae connecting vibration frequency ω (in reversed centimeters) and the stoichiometry parameter x:

$$\omega = 72.4x + 743. \qquad (1)$$

In our case, the experimental peak position is about 815 cm^{-1}, so, one can assume, that deposited at low temperature GeO$_x$ films are close to germanium monoxide. According to position of peak due to absorption by Si-O-Si stretching vibration mode (1072 cm^{-1}), the stoichiometry of silicon oxide film is close to silicon dioxide [15].

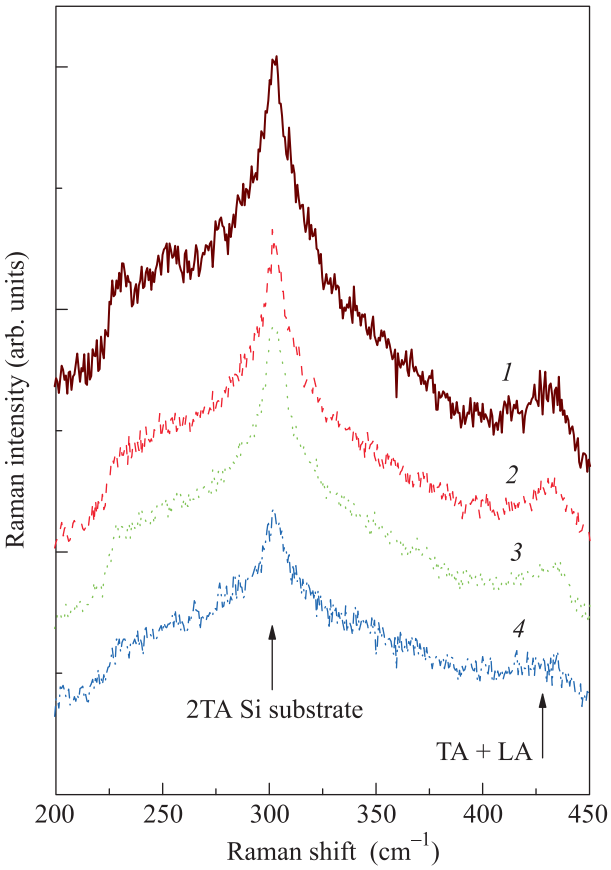

Fig. 1. Raman spectra of the films: *1* – 100 nm GeO$_x$ film; *2* – multilayer film GeO$_x$(4 nm)/SiO$_2$(4 nm); *3* – multilayer film GeO$_x$(1 nm)/SiO$_2$(4 nm); *4* – Si substrate

Ellipsometry was applied to detect the thickness and optical constants of the GeO$_x$ layer. For this case, the multi-angle measurements were carried out for the different angles of incidence (45, 50, 55, 60, 65, and 70°), the sets of experimental ellipsometic parameters (Ψ and Δ angles) were obtained. Then, a special computer approximation was carried out. The ellipsometic parameters for the model of many-layers (native SiO$_2$ oxide/GeO$_x$/SiO$_2$) on the mono-crystalline Si substrate were approximated using the experimental ellipsometic data. The optical constants for mono-crystalline Si were taken from the work of Aspens and Studna [16], spectral dependence of refractive index for SiO$_2$ was taken from work [17]. The spectral dependences of refractive and absorption indexes for GeO$_x$ film are shown in Fig. 3. According to ellipsometry data, the thickness of GeO$_x$ film is 115 nm, what is in good agreements with data es-

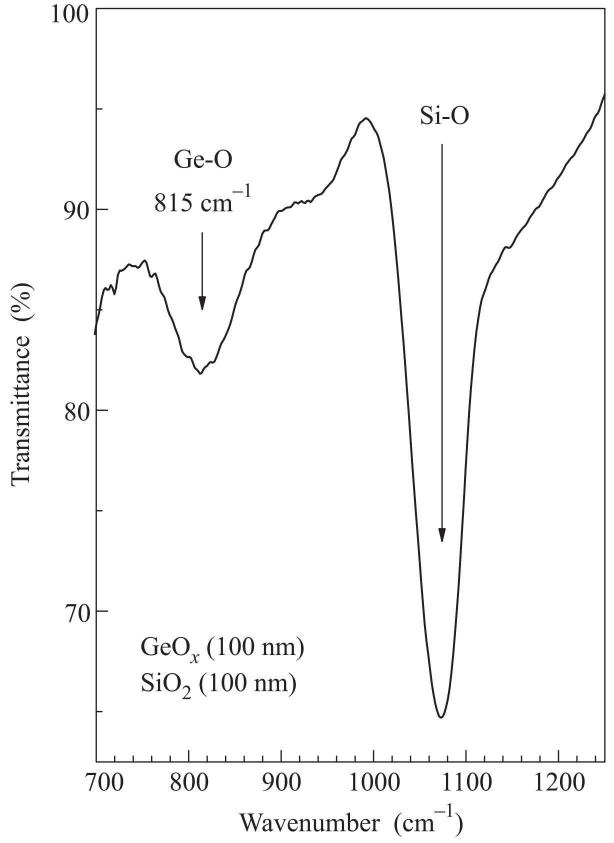

Fig. 2. IR transmission spectrum of the 100 nm GeO$_x$ film

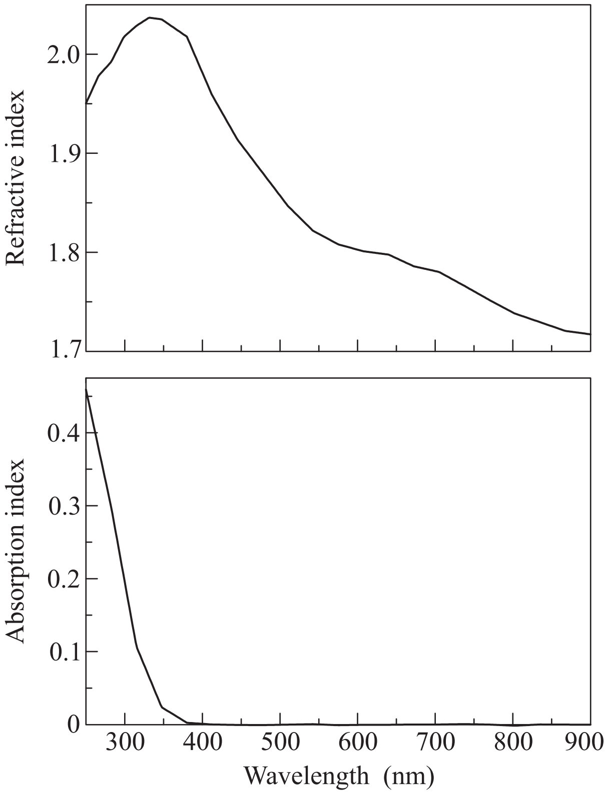

Fig. 3. Optical constants of the 115 nm GeO$_x$ film. The film was covered by SiO$_2$ (100 nm) cap layer

timated from deposition rate (100 nm). Comparing the refraction index of the GeO$_x$ film with refractive index of GeO$_2$ film [18], one can conclude that our film is substoichiometric, and close to germanium monoxide, as it was already obtained from analysis of IR spectroscopy data.

The PL spectra in visible and near-IR diapason of the studied samples are shown in Fig. 4. One can see broad peak with the maximum at 680 nm from relatively thick (100 nm) GeO$_x$ film. The broad PL band at 800 nm was observed earlier from GeO$_x$ films [10]. Ardyanian et al. have interpreted origin of this band to optical transitions conditioned by with O-deficiency-related defects or oxygen dangling bonds [10]. Some shift of this band in our case can be caused by a little difference in GeO$_x$ stoichiometry of the studied film, compared with the films studied earlier [10]. It is known, that optical gap of sub-stoichiometric oxides strongly depends on stoichiometry. One can see that PL peaks from GeO$_x$/SiO$_2$ multilayer structures are blue-shifted. Note that in spite of 4 time difference in total thickness of GeO$_x$ in GeO$_x$(4 nm)/SiO$_2$(4 nm) and GeO$_x$(1 nm)/SiO$_2$(4 nm) samples, the PL intensities do not differ much. One can assume that, in the case of thin GeO$_x$ layers, the PL is mainly originated by optical transitions conditioned by interface O-deficiency-related defects or oxygen dangling bonds. The PL intensities for all case were relatively low, so, we assume that rate of nonradiative recombination is much higher than rate of radiative recombination. To elucidate the role of radiative and nonradiative processes in defect induced PL of GeO$_x$ films and GeO$_x$/SiO$_2$ multilayer heterostructures, temperature dependence of PL was studied.

The results of temperature dependence of PL intensities are shown in Fig. 5. The intensity is presented in logarithmic scale. The PL intensity from excited electron-hole pairs (excitons) is defined by the competition between a thermally dependend radiative process and nonradiative relaxation of photoexcitations [11]:

$$I(T) = \frac{I_0}{1 + e_{\mathrm{rad}}^{-1}(T) e_{\mathrm{nr}}(T)}, \qquad (2)$$

here, e_{rad} and e_{nr} are the radiative and nonradiative recombination rates, and I_0 do not depend on temperature, and depend on concentration of radiative centers, the excitation photon flux and transition coefficient of the emitted photon from the film to air. We have assumed that in our temperature range the dependence of radiative recombination rate on temperature is negligi-

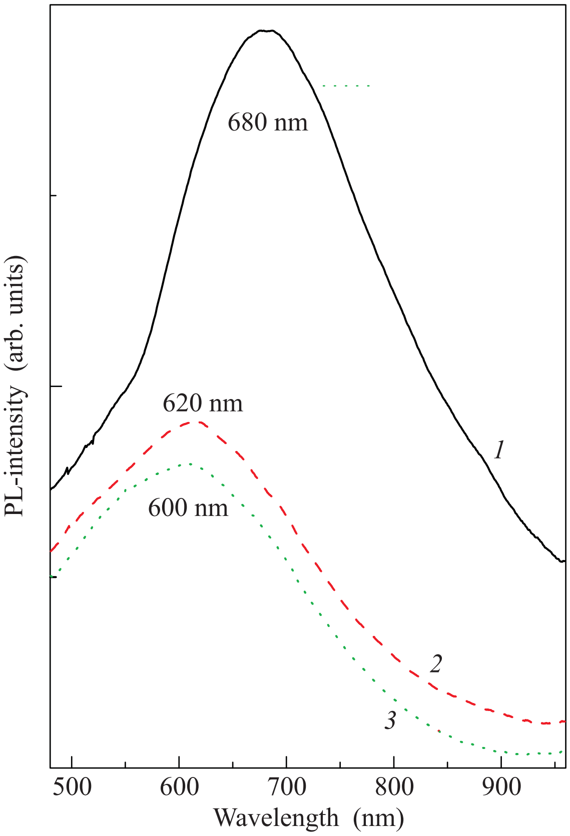

Fig. 4. PL spectra at 83 K: *1* – 100 nm GeO$_x$ film; *2* – multilayer film GeO$_x$(4 nm)/SiO$_2$(4 nm); *3* – multilayer film GeO$_x$(1 nm)/SiO$_2$(4 nm)

ble. According to our estimation, the quantum efficiency of PL is low, so the nonradiative recombination rate is high, and one can neglect unity in the denominator in (2). If we approximate the temperature dependence of the nonradiative recombination rate using Arrhenius-like activation dependence $e_{\rm nr}(T) \propto \exp(-Ea/kT)$, no agreement with experimental and calculated dependencies was observed. So, we used the modified temperature dependence of the nonradiative recombination rate using Berthelot type function $e_{\rm nr}(T) \propto \exp T/T_{\rm B}$, where $T_{\rm B}$ is Berthelot temperature [19, 20]. The modification was assumption of the possibility of changing the degree of $T/T_{\rm B}$. So, the approximation formula is:

$$I(T) = I_0 \exp[-(T/T_{\rm B})^{\beta}]. \qquad (3)$$

In Fig. 5 one can see, that calculated temperature dependencies are in good correlation with experimental ones. According to approximation of calculated data Berthelot temperature ($T_{\rm B}$) is 36 K for GeO$_x$ film, and 9 K for GeO$_x$/SiO$_2$ multilayer heterostructures. The proposed parameter β is close to 1 for GeO$_x$ film (as it should be in Hurd theory [20]), but for GeO$_x$/SiO$_2$ multilayer heterostructures it is close to 0.4.

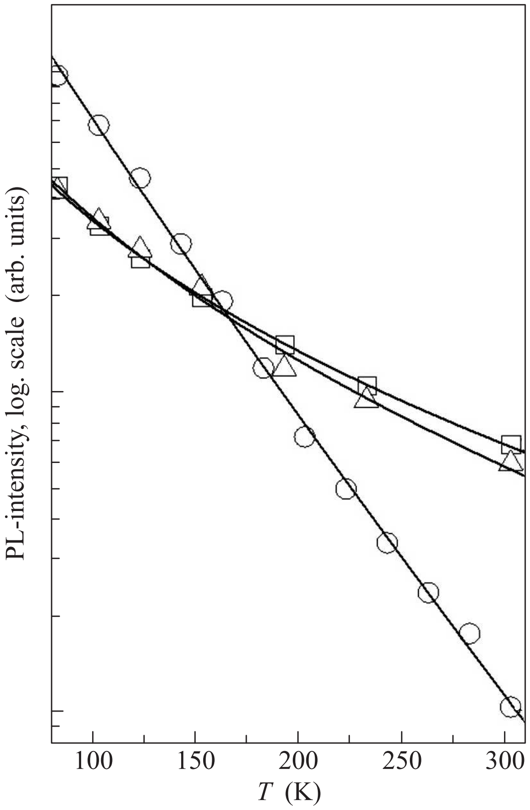

Fig. 5. Temperature dependence of PL intensities, figures are experimental data, lines are approximations. Circles – 100 nm GeO$_x$ film; squares – multilayer film GeO$_x$(1 nm)/SiO$_2$(4 nm); triangles – multilayer film GeO$_x$(4 nm)/SiO$_2$(4 nm)

The Berthelot temperature dependence can appear not only in experimental dependencies of PL intensity [11, 21–24], but also in experimental dependencies of conductivity of materials with low conductivity [20, 25]. If there is possibility of electron tunneling between two point states (centers), the probability for tunneling should depend on temperature. Wave function of an electron localized near one of the centers, $\psi(r) \propto \exp(-r/a)$, where a is parameter of localization. Hurd have calculated [20], that if these centers vibrate with frequency ω, then at relatively high temperature ($kT \gg h\omega$) the standard deviation of them from equilibrium is proportional to the temperature. In adiabatic (or Born–Oppenheimer) approximation the time of tunneling much lower than period of vibrations, probability for tunneling is highest when both centers are closest to one another position. The closest distance between them depends on the standard deviation, consequently, the probability for tunneling depends on temperature as $\exp(T/T_{\rm B})$. So, if one assume that electron is tunneling to center of nonradiative recombination, the rate of nonradiative recombination should be proportional to $\exp(T/T_{\rm B})$, and if one can neglect unity in the denominator in (2) and also neglect the temperature dependence of radiative recombination rate, temperature dependence of PL will be approximated by (2) with $\beta = 1$. If one estimate localization parameter a using approaches of Hurd [20] and Calcott [11], this parameter in our case is close to 1.5 nm for GeO_x film. The dependence of Berthelot temperature on vibration frequency ω is inverse quadratic dependence [20], so, it is quite reasonable that Berthelot temperature for $\text{GeO}_x/\text{SiO}_2$ multilayer heterostructures is lower than that for GeO_x film. Frequency of Ge-O-Ge bonds vibration in GeO_x is 815 cm^{-1} (see Fig. 2). As it was assumed above, the PL from $\text{GeO}_x/\text{SiO}_2$ multilayer heterostructures is interface defect induced. The vibration frequency of Ge-O-Si or Si-O-Si bonds is higher than that of Ge-O-Ge bonds. Decrease of the parameter β for $\text{GeO}_x/\text{SiO}_2$ multilayer heterostructures is not yet fully clear. It can be connected with that Hurd theory taken into account "isotropic" vibrations, but the interface $\text{GeO}_x/\text{SiO}_2$ has anisotropy. One can assume that tunneling take place mainly along the interface, but atomic displacement due to vibrations have both directions – along and normal to the interface. It can be a subject for further analysis.

The optical properties of GeO_x film and $\text{GeO}_x/\text{SiO}_2$ multilayer heterostructures were studied, the defect induced PL was observed. In the case of $\text{GeO}_x/\text{SiO}_2$ multilayer heterostructures we suppose that it is interface related defect induced PL. From temperature dependence of PL intensity, it was found that rate of nonradiative transitions in GeO_x film has Berthelot type. According to estimation, localization parameter for wave function is about 1.5 nm for GeO_x film. Some anomalous deviations from Berthelot type temperature dependence were observed in temperature dependences of PL intensities for $\text{GeO}_x/\text{SiO}_2$ multilayer heterostructures.

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