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Spectroscopic characterization of phase transformation in Ge-rich Al₂O₃ films grown by magnetron co-sputtering

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Thermally-stimulated evolution of optical and structural properties of Ge-rich-Al₂O₃ films with different Ge contents was investigated. As-deposited films and films annealed at $T_A \leq 550$ °C were found to be amorphous whatever the Ge content. The formation of amorphous Ge clusters occurs at $T_A = 550$ °C, whereas their crystallization is prominent at $T_A = 600$ °C requiring a shorter annealing time for the higher Ge content. The films annealed at $T_A = 550$ °C showed broad photoluminescence spectrum. Its shape and intensity depend on Ge content and excitation energy. Annealing at $T_A = 600$ °C results in the appearance of additional UV bands originated from the formation of GeO_x phase covered Ge clusters. An analysis of excitation spectra was performed to distinguish the mechanism of light emission in these films as well as to discriminate contribution of carrier recombination in the Ge phase (amorphous clusters and/or nanocrystals) as well as via interface or host defects. The concentration and mobility of free carriers was also estimated.

1. Introduction

Size-dependent optical properties of Ge nanocrystals (Ge-ncs) were reported for the first time by Hayashi et al. [1]. However, only recently the attention towards them has been particularly renewed [2,3] because these environmental friendly alternatives are non-toxic, biocompatible and electrochemically stable. Being free standing or embedded in different hosts, Ge-ncs offer opto- and microelectronic applications [4–6]. Silicon oxide and nitride are most used hosts for Ge-ncs, whereas alumina is rarely addressed.

Usually Ge-Al₂O₃ structures and films are considered as gate alternatives, resistive-switching or non-volatile memories [4–7]. At the same time, Al₂O₃ is promising for optical communication because it offers better light confinement than SiO₂ due to higher refractive index ($n = 1.73$ at 1.95 eV). The application of Al₂O₃ doped with Ge and rare-earth ions for waveguides [8] as well as for GeO_x-Al₂O₃ glasses was reported. These latter showed intense

luminescence in ultraviolet-visible spectral range caused by various defects (Ge oxygen deficient centers (Ge-ODC), F-like centers, Al_i⁺, Al-OH, or complexes of such defects) [9,10].

Photoluminescence (PL) from the Ge-ncs can be tuned in a wider spectral range, offering stronger, more easily identified quantum confinement effects in large nanocrystals [1,3,11]. However, most studies were performed for sapphire implanted with Ge, whereas few reports are available for Ge-rich-Al₂O₃ films [12,13]. The purpose of this work is to investigate thermally stimulated evolution of structural and optical properties of Ge-rich-Al₂O₃ films and to determine the role of different phases in light emitting process.

2. Experimental details

Ge-rich-Al₂O₃ films were deposited by radio-frequency magnetron sputtering of separated pure Ge and pure Al₂O₃ targets in argon atmosphere on long (15 cm) quartz substrate (Supplement, Fig. 1S). The co-sputtered films provided samples with a variation of Ge content along the film length (Fig. 2S) [14]. Annealing was

performed in conventional horizontal furnace at $T_A = 500\text{--}600\text{ }^\circ\text{C}$ during 15–50 min in nitrogen atmosphere. The films were analyzed with spectroscopic ellipsometry (SE), Raman scattering, X-ray diffraction (XRD), specular infrared reflection (IRR) and photoluminescence (PL) methods. More details about film deposition and methods of their characterization can be found in the Supplement. All measurements were performed at room temperature.

3. Results and discussion

The SE spectra of as-deposited films were featureless revealing their amorphous structure. The analysis of the SE spectra showed that in our Ge-rich- Al_2O_3 films the refractive index (n), taken at 1.95 eV, changes from $n = 1.81 \pm 0.01$ (Al_2O_3 -rich side) up to $n = 3.85 \pm 0.01$ (Ge-rich side) testifying to Ge incorporation in alumina host (Fig. 1 and Fig. 3S). The Ge content ($[\text{Ge}]$) was estimated using the effective medium approximation and the values of pure Ge ($n_{\text{Ge}} = 4.21 \pm 0.01$) and pure Al_2O_3 ($n_{\text{Al}_2\text{O}_3} = 1.75 \pm 0.01$) that we obtained on the corresponding films. For as-deposited films, $[\text{Ge}]$ variation from 17% (at Al_2O_3 -rich side) up to 85% (at Ge-rich side) takes place (Fig. 1).

The amorphous nature of as-deposited films and those annealed at $T_A = 550\text{ }^\circ\text{C}$ for 50 min was also supported by Raman

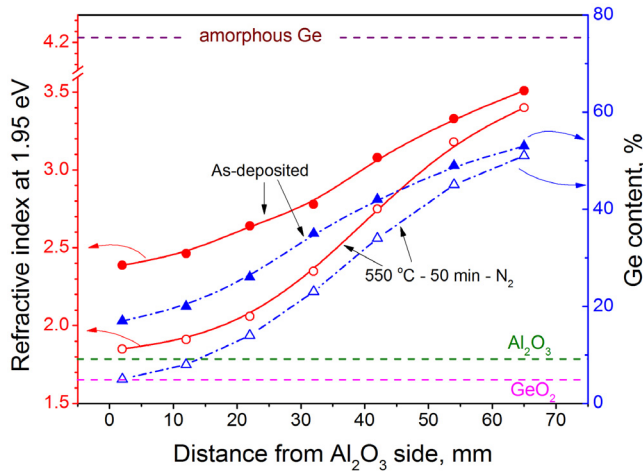


Fig. 1. Variation of the n and $[\text{Ge}]$ along the Ge- Al_2O_3 film length. The values for pure Ge, GeO_2 and Al_2O_3 are shown, for comparison, by the dashed lines.

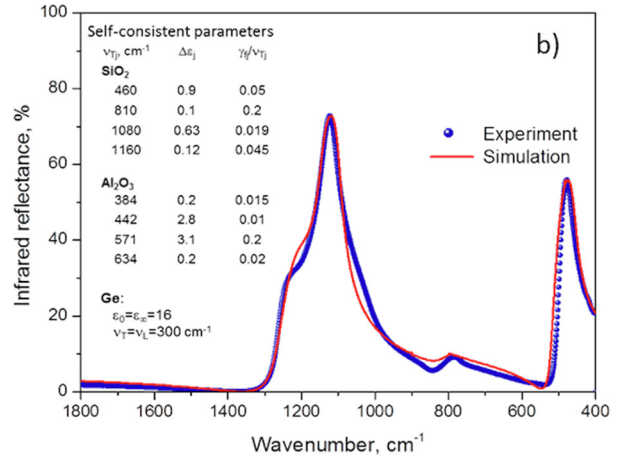
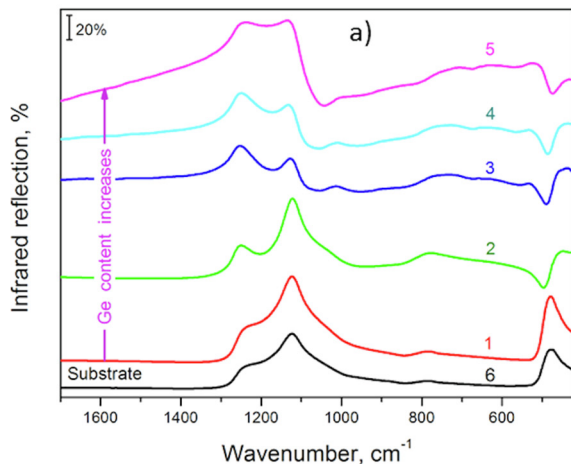


Fig. 2. a) Specular IRR spectra for the films with $[\text{Ge}] = 20(1), 24(2), 30(3), 36(4), 42(5)$. Curve 6 corresponds to the quartz substrate; b) simulation of specular IRR spectrum for the film with $[\text{Ge}] = 20\%$.

scattering and XRD experiments (Fig.4S). The films keep amorphous structure, showing the formation of amorphous Ge clusters (Fig.4S,a). This has to results in the n increase. Contrary to this expectation, a significant n decrease (Fig. 1) accompanied by film transparency rise (Fig. 2S) occurs. This can be explained by important contribution of phases with lower refractive index (Al_2O_3 , Ge oxide and/or cavities) that can cause $[\text{Ge}]$ underestimation (Fig. 1). The analysis of Raman scattering spectra revealed formation of GeO_2 phase (Fig.4S) that was also evidenced by specular IRR spectra.

Vibration bands peaked at about 460 cm^{-1} , 1080 cm^{-1} , 1160 cm^{-1} and 1260 cm^{-1} originate from Si-O vibrations (curves 1–5) of the quartz substrate (curve 6) (Fig. 2,a). The low Al_2O_3 signal for $[\text{Ge}] < 30\%$ (curve 1 and 2) is governed by the presence of GeO_2 phase. Its range of “residual rays” ($400\text{--}900\text{ cm}^{-1}$) overlaps significantly with that of Al_2O_3 ($400\text{--}1000\text{ cm}^{-1}$), but due to the higher force constant of Ge-O oscillators, the GeO_2 absorption dominates the spectra by masking the reflection from Al_2O_3 . For the films with higher Ge contents, the Al_2O_3 signal increases due to lower GeO_2 signal contribution accompanied by the enhancement of the minimum at about 500 cm^{-1} linked with the Ge phase (Fig. 2,a).

The simulation of the IRR spectra allows the estimation of the free carrier concentration (n_0), the mobility (μ) and the film conductivity (σ). As an example, the simulation of the spectrum for $[\text{Ge}] = 20\%$ was performed using the approach developed in [15,16] and the self-consistent parameters for SiO_2 , Al_2O_3 and Ge, taking the electron effective mass value of $0.16m_e$. A good agreement was achieved between the experimental and simulated spectra (Fig. 2,b). The parameters extracted were: $n_0 = 2.50 \times 10^{17}\text{ cm}^{-3}$, $\mu = 2.08 \times 10^3\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $\sigma = 83.5\text{ }\Omega^{-1}\text{cm}^{-1}$. The Ge- Al_2O_3 films with high Ge content, subjected to the low annealing temperature, show promising electrical properties while keeping an amorphous structure.

It should be noted that our as-deposited films showed weak PL emission peaked at $\sim 2.1\text{--}2.2\text{ eV}$ for Al_2O_3 -rich side only. It can originate either from Ge-ODCs [13] or F^{2+} centers in Al_2O_3 host [17]. Annealing at $T_A = 550\text{ }^\circ\text{C}$ results in the appearance of broad PL band (Fig. 3) the shape of which depends on the excitation light energy (Fig. 3a,b) and the Ge content (Fig. 3a,c). The most broad spectrum was registered for $E_{\text{exc}} = 4.43\text{ eV}$ showing PL components centered at 1.8 eV, 2.0 eV, 2.84 eV, 2.96 eV, 3.38 eV and 4.0 eV (Fig. 3a). PL excitation spectra of near-infrared PL components (peaked at 1.6–1.8 eV) differ from those of all other PL bands (Fig. 3b) showed that

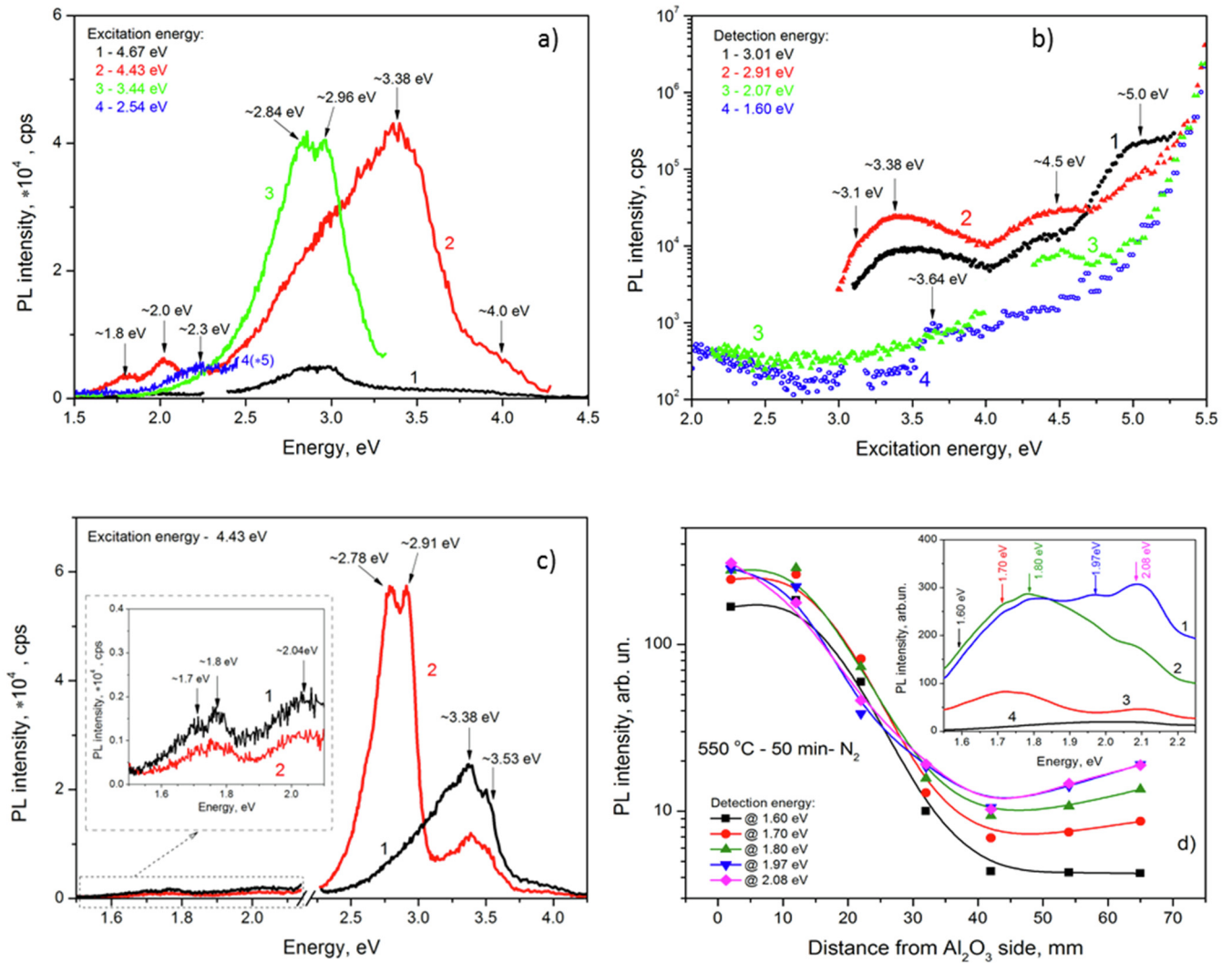


Fig. 3. PL (a) and PLE (b) spectra of the films with $[Ge] = 20\%$, $T_A = 550\text{ }^{\circ}\text{C}$; c) PL spectra of the film with $[Ge] = 30\%$ annealed at $550\text{ }^{\circ}\text{C}$ -50 min (1) and $600\text{ }^{\circ}\text{C}$ -15 min (2); d) Variation of PL intensity of different components along the film length. The inset shows the PL spectra of annealed films for different distances from the Al_2O_3 end (12 (1), 22 (2) 32(3) and 42 (4) mm) that corresponds to the increase of Ge content from 20 up to 40% according to Fig. 1. $E_{exc} = 2.33\text{ eV}$. This excitation is used to prevent the contribution of Al_2O_3 defects in PL spectrum.

both UV and visible light can provide an effective excitation (Fig. 3b,d).

The 2.84-eV and 2.96-eV PL bands can originate from Ge-ODCs or Ge-ncs/ Al_2O_3 interface defects [13] because these components are enhanced for higher T_A (Fig. 3.c) when Ge-ncs are formed (Fig.4S). PL emission at 3.38 eV and 4.0 eV can be due to as F_2^+ and F_2 centers in Al_2O_3 [9,10], while the PL band near 2.0–2.2 eV can be due to F_2^{2+} centers [3,12]. All these bands in the interval 2.0–4.5 eV show similar behavior with the $[Ge]$ rise being detected for all the samples (Fig. 3).

Near-infrared PL components (at 1.6 eV and 1.7–1.8 eV) are similar to those reported for isolated Ge-ncs with the same sizes [18] and for Ge-ncs embedded in Al_2O_3 host [5,19]. However, since the carriers confined in the Ge-ncs are under a finite potential [5], the surrounding host affects them via band offsets as well as via polarization of interface charge due to the difference in dielectric constants of the Ge-ncs and the host matrix.

4. Conclusions

The evolution of optical and structural properties of Ge-rich- Al_2O_3 films was studied. It was observed that the formation of

the Ge and Al_2O_3 phases as well as the Ge oxide that contribute to light emission process. The Ge phase crystallizes at $600\text{ }^{\circ}\text{C}$ requiring shorter annealing time for the films with higher Ge content. Estimation of the film stoichiometry as well as the free carrier concentration and mobility was performed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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