Influence of the multilayer system on the structure and photoluminescence of GeO$_x$ thin films

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Abstract
Amorphous GeO$_x$/SiO$_2$ multilayers (1<x<2) were prepared by successive evaporation of GeO$_2$ and SiO$_2$ powders onto the Si substrates maintained at 100°C. Structural study by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared-absorption (FTIR) spectrometry, and transmission electron microscopy (TEM) was carried out. These techniques allowed us to follow the structural evolution, and phase decomposition due to annealing in the GeO$_x$ thin films and the multilayers annealed up to 900°C, and appearance of amorphous and crystallized germanium aggregates. For Ta ≥ 400°C, the photoluminescence band around 1eV attributed to confinement effect in amorphous germanium aggregates was observed. Comparison of the luminescence in multilayer and GeO$_x$ thin film showed that in multilayer, although the control of the nanocrystals size isn't complete, the SiO$_2$ barriers tend to enhance the intensity and reduce FWHM of the luminescence bands. This means that the confinement effect in the germanium aggregates in GeO$_x$ matrix is enhanced in multilayer system.

Keywords: Germanium, photoluminescence, multilayer

1. Introduction
Silicon (Si) is the base of the microelectronics industry and the study of Si nanostructures is a very active field of research [1]. This is because of its light-emission properties [2] which could lead to applications for optoelectronics devices. On the other hand, germanium (Ge) is a good candidate for MOSFET transistors thanks to higher mobility of charge carriers [3]. Furthermore, Ge has a higher Bohr excitonic radius which allows the excitons to confine in the higher sizes of nanostructures [4]. Therefore, study of the photoluminescence (PL) effect on Ge nanostructures is a new field of research [5]. Although most of the results consist of visible PL [6,7], there are few results in near-IR range [5,8,9]. It is theoretically predicted that 2% tensile strain will decrease the energy between r and L valleys to near zero [10]. There are some results attributed to quasi direct transition in tensile strained Ge [5]. Recently, we have observed the visible and near-IR PL band in sub-stoichiometric GeO$_2$ thin films for different annealing temperatures [9], with the near-IR PL attributed to amorphous Ge nano-grains. While for higher annealing temperatures, PL energy shifted to lower energies and intensity decreased due to enlargement of nano-grains and loss of the quantum confinement effect. Trying to control the Ge nano-grains size and increase of quantum confinement effect in the GeO$_x$ layers, the GeO$_x$/SiO$_2$ multilayer (ML) was prepared; it is shown that the Si nanocrystals sizes are well controlled in SiO/SiO$_2$ multilayers [11]. In GeO$_x$/SiO$_2$ multilayer, the PL spectra are similar to GeO$_x$ thin films [11]. In our last paper we discussed the enhancement of the stability of the GeO$_x$ thin films. In this paper, we present the new structural demonstrations about the evolution in the multilayer structure due to annealing and generation of the Ge nano-grains and discuss the influence of multilayer system on the PL band energy, intensity and FWHM by comparing GeO$_x$ thin films and GeO$_x$/SiO$_2$ multilayers.

2. Experiment
GeO$_x$/SiO$_2$ multilayers were prepared by alternative evaporation of GeO$_2$ and SiO$_2$ with electron beam guns in a high-vacuum chamber, at a partial pressure equal to 10$^{-5}$ Torr. The (001) silicon substrates were maintained at 100 °C. The deposition rates were controlled by a
quartz microbalance system and were equal to 0.1 nm s⁻¹. By changing the evaporation time for two different layers, we were able to change the thickness of the layers. For the involved sample, the thicknesses of the layers were chosen 3 and 5 nm for GeO₂ and SiO₂, respectively, and the total thickness of the samples was 200 nm consisting of 25 double layers; the alternative structure and thickness of the layers was verified by TEM images [11]. For comparing the evolution in the structure of active GeO₂ layers in the multilayer and GeO₂ thin films, the GeO₂ thin films were prepared in the same conditions; also for comparing the stability of GeO₂ and SiO₂ molecules against electron bombardment, two separate GeO₂ and SiO₂ thin films were prepared; During evaporation a mass spectrometer was attached to the chamber for detecting the exit of the materials. The samples were annealed after deposition up to 900°C in a quartz tube; the heating rate was equal to 10 °C/min and the base pressure was equal to 10⁻⁶ Torr. The samples were cooled down immediately after the annealing temperature T_a was reached. The evolution of the atomic structure was followed by Fourier transform infrared spectroscopy (FTIR) spectroscopy. The infrared absorption spectra were carried out in range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. The baseline of the spectra was subtracted. Since the composition of the SiO₂ layers is stable enough; we can follow the evolution in the composition of the GeO₂ active layers by investigation of the GeO₂ thin films.

Chemical structure and composition of the GeO₂ thin films were studied by X-ray photoelectron spectroscopy (XPS), instrument (VG instrument Escalab MKII) with an AlKα source (1487.6 eV); the photoelectrons emitted from Ge₃d orbital was recorded using a hemispherical analyzer with 1 eV resolution. The instrument was calibrated by measuring the binding energy of C₁s (284 eV) photoelectrons. The surface of the samples was cleaned by 2 keV Ar⁺ ion bombardment during 10 minutes.

The Continuum Wave (CW) PL in range of 500–1700 nm was analyzed by a monochromator equipped with a 600 grooves/mm grating and by a photomultiplier tube cooled at 190 K. The sample was excited by a 30 mW He–Cd laser using the 325 nm line. The response of the detection system was precisely calibrated with a tungsten wire calibration source. PL experiments were conducted at 77K, in a cryostat cooled by liquid nitrogen.

3. Results and discussion
3.1. Structure
The spectrum of the mass spectrometer ion current versus the m/q fraction (Figure 1) shows a strong peak corresponding to oxygen (m/q=32) for GeO₂ evaporation. This means that GeO₂ is less stable than SiO₂ during evaporation; hence contrary to SiO₂ layers, GeO₂ layers should be sub-stoichiometric (we call them GeOₓ) in mono and multilayer samples.

Chemical evolution in GeO₂ layers was studied by XPS spectroscopy (Figure 2). For as-deposited sample the binding energy of Ge₃d photoelectrons is 32 eV; for annealing at T_a=500°C a new shoulder appears in the spectrum. Deconvolution of the spectrum shows a new band at 29.5 eV as the characteristic of pure Ge. For T_a=600°C, the shoulder becomes stronger and the main band shifts toward 32.5 eV. The binding energies of Ge₃d orbital in stoichiometric GeO₂ (Ge⁴⁺) and pure Ge (Ge⁰) are centered at 32.5eV and 29.5eV, respectively [12]; the binding energy of Ge₃d orbital in sub-stoichiometric oxide is placed between the two energies [13]. In as-deposited sample, the binding energy is about 32 eV the characteristic of the sub-stoichiometric oxide; for T_a=500°C creation of the new shoulder suggests the decomposition phenomenon in GeO₂ thin films leading to the generation of Ge nano-grains. However, the binding energy of the main band is not still shifted toward 32.5 eV; For T_a=600°C the shoulder becomes stronger, and the main band shifts toward 32.5 eV. This suggests that the decomposition is completed at T_a=600°C and the composition of samples is reached to GeO₂ following the next chemical reaction:

![Figure 1. Mass spectrometer Spectra of the chamber atmosphere during the SiO₂ (up) and GeO₂ (down) evaporation.](image1)

![Figure 2. XPS spectra corresponding to GeO₂ thin films as a function of annealing temperatures.](image2)
It is also concluded that in the multilayers system for annealing down to 500°C, the new phase of Ge nanostructures could be generated in the active GeO\textsubscript{x} layers. Raman spectroscopy results show that in the GeO\textsubscript{x} thin films, Ge nanostructures are amorphous for annealing at \( T_a=500^\circ C \) and crystallize for \( T_a=600^\circ C \) [9]. Similar results are also obtained for the multilayers [11].

For investigating the structure of multilayer and its evolution due to annealing, FTIR spectroscopy was utilized. The FTIR spectrum of as-deposited multilayer is compared with as-deposited SiO\textsubscript{2} and GeO\textsubscript{x} thin films (Figure 3). In multilayer Spectrum (No.1), four main absorption bands about 830, 450, 500 and 1050 cm\(^{-1}\) are observed. The first two bands are attributed to the stretching and bending vibration of Ge-O-Ge group respectively (No.3), and the last two bands correspond to the same vibration of Si-O-Si groups (No.2). Wide absorption band around 3400 cm\(^{-1}\) corresponding to Si-OH bonds was also observed (not shown in figure). This band disappears at \( T_a=400^\circ C \). A red-shift compared to as-deposited SiO\textsubscript{2} thin films (No.2) at 1072 cm\(^{-1}\) is observed. This could be due to influence of the heavier Ge atoms bonded to Si-O-Si group as second neighbours in the interface with the adjacent layers, which reduces its vibration frequency. On the other hand, the blue-shift of the other band about 800cm\(^{-1}\) in the multilayer compared to the same band in GeO\textsubscript{x} thin films (No.3) could be explained by the same argument for lighter Si atoms bound to Ge-O-Ge group. Since the characteristic band of GeO\textsubscript{2} is placed about 870 cm\(^{-1}\) [14], absorption at 830 cm\(^{-1}\) demonstrates the sub-stoichiometric structure of germanium oxide layers in conformity with XPS results.

FTIR [9] and XPS results of GeO\textsubscript{x} thin film describe that the chemical structure of GeO\textsubscript{x} thin film is modified and its composition reaches GeO\textsubscript{2} for annealing at \( T_a=500^\circ C \). We have already shown that contrary of volatilization of GeO\textsubscript{2} thin films at \( T_a=700^\circ C \) [9], in GeO\textsubscript{x}/SiO\textsubscript{2} multilayer system GeO\textsubscript{x} layers remain stable until \( T_a=800^\circ C \) [11].

**Figure 3.** Comparison of the FTIR spectrum of the as-deposited GeO\textsubscript{x}(3nm)/SiO\textsubscript{2} (5nm) multilayer (1) with the as-deposited SiO\textsubscript{2} (2) and GeO\textsubscript{x} (3) thin films.

\[
2\text{GeO}_x \Rightarrow \text{xGeO}_2 + (2-x)\text{Ge} \tag{1}
\]

Now we present the FTIR results corresponding to the samples annealed at 600°C and 900°C for studying the influence of annealing on the multilayer structure (Figure 4). In deconvoluted spectra, an absorption band about 1000 cm\(^{-1}\) is observed in which the absorbance increases for \( T_a=900^\circ C \). We attribute this band to the vibration of the Ge-O-Si groups in the interface of the adjacent layers. Furthermore, the absorbance of the band around 900 cm\(^{-1}\) attributed to GeO\textsubscript{x} layers decreases strongly. This behavior could be attributed to the interdiffusion of the GeO\textsubscript{2} and SiO\textsubscript{2} layers and extension of the interface zone due to annealing at high temperatures which leads to increasing the density of the Ge-O-Si and decreasing the density of the Ge-O-Ge bonds.

Transmission electron microscopy (TEM) images corresponding to the GeO\textsubscript{x} thin film annealed at 600°C and the multilayer annealed at 700°C are presented in figure 5. The Ge nano-crystals were not observed at lower temperatures [11], hence in multilayer system the crystallization temperature of Ge nano-grains increases. This could be due to the constraint of the SiO\textsubscript{2} layers which leads to elevating the crystallization temperature similar to Ge/SiO\textsubscript{2} multilayer [15]. We expected to observe the smaller grains in multilayer sample because of the size control by SiO\textsubscript{2} barrier layers.

We have already reported the Ge nanocrystals size between 11-16 nm [9] in thin films. In multilayer sample,
containing 3nm GeO$_x$ layers, the size distribution is centered about 10 nm (Figure 6) which suggests the partial size control of the nanocrystals. At lower annealing temperatures, when the Ge nano-grains are amorphous the size control could lead to a blue-shift in the energy of the PL spectra [16].

### 3.2 Photoluminescence

We already presented the PL results of GeO$_x$ thin films [9] and GeO$_x$/SiO$_2$ multilayers [11]; the visible PL for $T_a<400^\circ$C was attributed to the defects in the structure of sub-stoichiometric oxide. For $T_a \leq 550^\circ$C, the new NIR PL bands were observed and attributed to the confinement effect in amorphous Ge nanograins, the red-shift of the PL energy for annealing at the higher temperatures was attributed to the enlargement of the nano-grains. For $T_a>500^\circ$C, disappearance of the PL band was attributed to the loss of the confinement effect in oversized Ge nanograins. According to TEM results and thanks to SiO$_2$ barrier layers, we expect to have the smaller nano-grains and the more effective confinement effect which leads to increase the PL intensity and making blueshift in PL energy in similar multilayer samples for the same annealing temperature.

Comparison of the PL intensity between thin film and multilayer annealed at $T_a=400^\circ$C and 450°C for the same total thickness of GeO$_x$ layer is presented in figure 7. The PL intensity in multilayer is stronger by factor 6 and 3 than GeO$_x$ thin film for $T_a=400^\circ$C and 450°C, respectively. This result could be interpreted by the more effective confinement effect in Ge aggregates in multilayer system, it could also be attributed to tensile strain of GeO$_x$ layers by SiO$_2$ barriers that can imply quasi direct inter-band transition in tensile strained Ge [1]. The PL energy is also compared for the normalized samples annealed at $T_a=400^\circ$C and 450°C (Figure 8). As seen, the PL in multilayers blueshifs with respect to thin films. Moreover, the FWHM of the PL bands in multilayers is reduced. These results suggest the more effective confinement and partial size control of the nanostructures in multilayer samples, because according to confinement effect model, the PL energy blueshifts by reducing the nano-grains sizes [17].

The TEM result suggested that the multilayer structure not only increases the stability of GeO$_x$ layers, but also partially controls the nanograins sizes. The PL results confirm our interpretation; however in spite of the partial size control of nanostructures, TEM results show that for $T_a> 500^\circ$C the grains sizes are so large for confinement effect that it is lost.

Since the atomic structure of the Si and Ge oxide are so similar and the interdiffusion occurs between the two adjacent layers, as a new perspective we propose to change the barrier layer with the other compositions to avoid this phenomenon.
4. Conclusion
It is concluded that the GeO$_x$/SiO$_2$ multilayer is an efficient structure for increasing the stability of the GeO$_x$ layers against de volatilization due to annealing. Comparing the thin films and multilayer system, we discovered that the demixtion in the GeO$_x$ active layers occurs almost at the same temperature and crystallization of Ge nanostructures occurs at higher temperature (almost 100°C) in ML system. The SiO$_2$ barrier layers do not have the negative influence on the structure of the GeO$_x$ layer below Ta=800°C. On the other hand, they not only partially control the Ge nanograins sizes, but also imply the better confinement effect on Ge nanostructures, which leads to the increasing of the PL intensity and reducing of the FWHM of PL band. These results make us to use the multilayer system for benefitting from its advantages.

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