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Structure and photoluminescence properties of evaporated $\text{GeO}_x/\text{SiO}_2$ multilayers

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Amorphous $\text{GeO}_x/\text{SiO}_2$ multilayers were prepared by successive evaporations of GeO_2 and SiO_2 powders onto substrates maintained at 100 °C. The evolution of the structure was investigated by x-ray reflectometry, transmission electron microscopy, infrared-absorption spectrometry and Raman spectrometry for annealing temperatures less than 800 °C. These experiments allowed us to follow the phase decomposition of the GeO_x alloy and to observe the appearance of amorphous and crystallized germanium aggregates. The evolution of the photoluminescence in the range of 0.8–2.2 eV was correlated to the structure of the films. © 2006 American Institute of Physics.

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I. INTRODUCTION

The study of silicon or germanium nanostructures is a very active field of research because of the light-emission properties of the nanostructures which could lead to applications for optoelectronics devices with group IV elements. Indeed the confinement of carriers in such nanostructures leads to the increase of the emitted photon energy and to a strong enhancement of the radiative transition yield.

Silicon or germanium nanocrystals can be obtained in substoichiometric SiO_x (Ref. 1) or GeO_x (Ref. 2) films. In such alloys, the clusters are generated by annealing post-treatments which involve in the demixtion of the film to obtain the stable phases Si and SiO_2 or Ge and GeO_2 . A better control of the nanocrystals size can be achieved with SiO/SiO_2 multilayer structures, which can be prepared by evaporation^{3,4} or by magnetron sputtering⁵ techniques. The advantage of such systems is to accurately control the SiO_x active layer thickness in which the nanocrystals are grown. These layers are separated by stable SiO_2 barriers which limit the nanocrystal size. Similar studies have also been performed in order to form Ge nanocrystals during annealing treatments in Ge-based systems such as $\text{GeO}:\text{H}/\text{SiO}:\text{H}$ (Ref. 6) or Ge/SiO_2 (Ref. 7) multilayers.

Our group⁸ has recently prepared GeO_x films in order to obtain Ge aggregates embedded in a GeO_2 matrix. Photoluminescence (PL) was observed, but the films are not stable because the germanium oxide becomes volatile for annealing temperatures T_a greater than 600 °C and it was not possible to control the size of the Ge nanocrystals. In order to improve the structural stability and to try to control the nanocrystal size, we have prepared $\text{GeO}_x/\text{SiO}_2$ multilayers by successive evaporations of GeO_2 and SiO_2 . This article reports on the stability of the multilayered structure for T_a less than or equal to 800 °C and shows that the evolution of photoluminescence with T_a is similar in single GeO_x layers and in $\text{GeO}_x/\text{SiO}_2$ multilayers.

II. EXPERIMENT

The multilayers were prepared in a high-vacuum chamber with a background pressure equal to 10^{-8} Torr. GeO_2 and SiO_2 were evaporated alternately with electron beam guns for 30 and 50 s, respectively, onto silicon substrates maintained at 100 °C. The deposition rates were controlled by a quartz microbalance system and were equal to 0.1 nm s^{-1} . The thicknesses of the layers were therefore 3 and 5 nm and the total thickness of the layers was 200 nm. In fact, a decomposition of the sources under the electron bombardment may occur so that the obtained films are not stoichiometric. This is why the deposited germanium oxide alloys are noted GeO_x . It will be shown that the silicon oxide films have the composition SiO_2 . After deposition, the films were annealed in a quartz tube with a base pressure equal to 10^{-8} Torr and with a heating rate equal to 10 °C/min . The samples were cooled down immediately after the annealing temperature T_a was reached.

The stability of the multilayers was studied by x-ray reflectometry, using the incident wavelength of the Co $K\alpha$ radiation at 0.1789 nm, and by transmission electron microscopy (TEM). The evolution of the atomic structure was followed by Fourier transform infrared absorption spectroscopy and Raman spectroscopy experiments. The infrared absorption measurements were carried out in the range of $400\text{--}4000 \text{ cm}^{-1}$ with a resolution of 8 cm^{-1} . The base line of the spectra was subtracted. Raman measurements were carried out with a multichannel spectrometer equipped with a 1800 grooves/mm grating. The detector was a charge coupled device camera cooled at 140 K. The 488 nm excitation light source was emitted by an argon laser and the incident power of around 10 mW/mm^2 was chosen so as not to induce any crystallization of the analyzed samples.

Photoluminescence excitation at 355 nm was performed using a frequency-trippled YAG (yttrium aluminium garnet):Nd laser. Optical emission was analyzed by a monochromator equipped with a 600 grooves/mm grating and by a near-infrared photomultiplier tube cooled at 190 K. The response of the detection system was calibrated with a tungsten

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FIG. 1. X-ray reflectometry patterns of the $\text{GeO}_x/\text{SiO}_2$ multilayers as deposited and annealed at different temperatures T_a .

wire calibration source. For PL measurements, the films were maintained at 77 K. A small PL band at 1.1 eV due to the silicon substrate was subtracted from the spectra.

III. RESULTS AND DISCUSSION

The x-ray reflectometry pattern collected from the as-deposited multilayers exhibits three diffraction peaks and thus gives evidence of the layered structure of the sample (Fig. 1). The wavelength of the modulation, i.e., the width of the bilayers, as calculated from the position of the peaks, is equal to 8.7 nm, which is slightly greater than the nominal thickness of the bilayer because the layers are less dense than the corresponding crystalline compounds. With annealing treatments until 600 °C, the intensity of the peaks remains nearly constant. For T_a equal to 700 °C, only the first peak is visible, and for T_a equal to 800 °C, the peaks have disappeared, due to the interdiffusion between the germanium oxide and silicon oxide layers. These results are in agreement with those of Williams *et al.*⁹ who have mentioned that the layered structure of Ge/SiO multilayers is still present after annealing at 760 °C.

Figure 2(a) shows a cross-section TEM view of the multilayer annealed at 700 °C. The contrast between the GeO_x layers and the SiO_2 layers is well visible. It is also possible to observe the Ge nanocrystals in the dark lines. This image confirms the high stability of the multilayers. The

FIG. 2. Cross-section (a) and bright-field (b) TEM micrographs from the $\text{GeO}_x/\text{SiO}_2$ multilayer annealed at 700 °C.

FIG. 3. Infrared absorption spectra of the $\text{GeO}_x/\text{SiO}_2$ multilayers as deposited and annealed at different temperatures T_a .

Ge nanocrystals embedded in the GeO_2 matrix are also well visible in the bright-field micrograph [Fig. 2(b)], with sizes varying between 5 and 15 nm.

Figure 3 presents the infrared absorption spectra of the multilayers as deposited and annealed at different temperatures T_a . The represented domain of 400–1300 cm^{-1} contains the main absorption bands, except a small band around 3400 cm^{-1} which is due to Ge–OH or Si–OH bonds. For the as-deposited sample, two intense bands are observed at 836 and 1052 cm^{-1} , which are assigned to the Ge–O–Ge (Ref. 10) and Si–O–Si (Ref. 11) symmetric stretching vibration modes, respectively. The positions of these bands give information about the chemical environment of the atoms since the frequency of the Si–O–Si vibration mode increases with the oxygen composition in homogeneous films,^{12,13} due to the strong electronegativity of the next-nearest-neighbor oxygen atoms. The observed values are lower than those corresponding to the compounds GeO_2 and SiO_2 , around 870 and 1075 cm^{-1} , respectively, which indicates that the layers are not perfectly stoichiometric.

This is confirmed by mass spectrometry experiments carried out during evaporation, which shows that the electron beam induces a partial decomposition of GeO_2 with effusion of oxygen, so that the deposited germanium oxide films are substoichiometric. This is not the case for the evaporation of SiO_2 , and a 200 nm single layer obtained by evaporation of SiO_2 shows an absorption band located at 1072 cm^{-1} , which does not shift with annealing treatments and which corresponds practically to SiO_2 . In fact, in the multilayer, a great number of silicon atoms are in contact with the germanium oxide layers and, if silicon atoms have germanium atoms as first neighbors, the group Si–O–Si must vibrate at lower frequencies than those observed in pure silicon dioxide, which can explain the 20 cm^{-1} shift of the absorption band.

For T_a equal to 400 °C, the germanium oxide band shifts toward higher wave numbers. As the average chemical composition remains unchanged, it can be concluded that a phase separation occurs and that germanium-rich areas appear in the layers, following the reaction $\text{GeO}_x \rightarrow \text{Ge} + \text{GeO}_2$.

For T_a equal to 500 and 600 °C, the germanium-oxide band has shifted with a maximum at 871 and 877 cm^{-1} , respectively, which corresponds to the complete decomposition

FIG. 4. Raman spectra of the $\text{GeO}_x/\text{SiO}_2$ multilayers as deposited and annealed at different temperatures T_a . The substrates are silicon wafers.

of the alloy. As the evaporated SiO_2 layers are stable, the shift of the corresponding band with annealing treatments can be explained by the fact that, during the decomposition process which forms pure germanium aggregates, there occurs a diffusion of the oxygen atoms which break the Si–Ge bonds at the interfaces to form Si–O–Ge groups. Thus, the silicon atoms recover an environment close to silica with four oxygen neighbors and the absorption band of the Si–O–Si groups presents a maximum at 1072 cm^{-1} with a shoulder at 1150 cm^{-1} , typical of SiO_2 . This is confirmed by the appearance of a third absorption band around 1000 cm^{-1} which comes from the Ge–O–Si symmetric stretching vibration modes.¹⁴

For T_a equal to 800°C , the intensity of the silicon oxide peak decreases; the band at 1000 cm^{-1} becomes more and more visible while the germanium oxide peak shifts again towards higher wave numbers with a decreasing intensity. These behaviors correspond to the interdiffusion between the GeO_2 and SiO_2 layers, which is in agreement with the x-ray reflectometry experiments.

Raman spectroscopy is a very efficient method to observe the presence of germanium or silicon aggregates on their crystalline or amorphous forms. Bulk crystalline germanium and silicon are characterized by intense and thin bands at 300 and 520 cm^{-1} , respectively, which correspond to the transverse optic (TO) modes of phonons. In the case of amorphous phases, the disorder induces changes in the vibrational density of states. The Raman spectra of germanium and silicon are characterized by broad bands at 270 and 480 cm^{-1} , respectively, corresponding to the TO modes of phonons.

Figure 4 shows Raman shifts of the multilayers annealed at different temperatures T_a . For T_a less than 400°C , the spectra only show very weak bands which correspond to the vibrational modes of the crystalline silicon substrate. This means that the films do not contain Ge aggregates. For T_a equal to 500°C , the spectrum shows the signal of the film, i.e., a broad band at 270 cm^{-1} , corresponding to the presence of an amorphous phase of germanium. For T_a equal to 600°C , the amorphous peak is no longer visible and a sharp peak appears at 300 cm^{-1} , which corresponds to the formation of crystalline germanium. The peak presents a low-frequency asymmetric broadening, as is usually the case for

FIG. 5. PL spectra of the $\text{GeO}_x/\text{SiO}_2$ multilayers annealed at different temperatures T_a .

nanocrystals.¹⁵ The presence of a crystallized GeO_2 phase,^{16,17} characterized by a Raman shift at 440 cm^{-1} , was not observed in these multilayers. In complement of the infrared spectrometry study, these results strongly suggest that a phase separation process occurs in the films to form Ge aggregates in an amorphous GeO_2 matrix. For T_a greater than 600°C , the germanium phase is crystallized but the GeO_2 phase and the SiO_2 layers remain amorphous.

Figure 5 presents PL spectra of the multilayers annealed at different temperatures T_a . The films as deposited and annealed at 300°C show identical spectra, with a very broad band between 1.24 and 2.1 eV (600 and 1000 nm). For T_a greater than 400°C , the large band disappears and another broad band appears at higher wavelength. This band redshifts from 1060 nm (1.17 eV) for 400°C to 1240 nm (1 eV) for 500°C . It was verified that the bands were not due to the SiO_2 phase since thin films prepared by the evaporation of SiO_2 practically do not show any PL.

The PL evolution is similar to that observed in single GeO_x films. The broad band observed in the samples as deposited and annealed at 300°C is rather similar to the bands generally attributed to the defects in the oxide phase.¹⁷ With annealing at temperatures higher than 400°C , infrared absorption experiments have shown that there is a modification of the structure, characterized by an important shift of the stretching vibration band. This structural change could be the origin of the defect suppression and therefore of the disappearance of the high-energy PL band for T_a equal to 400°C . After this structural modification, a weak band with a maximum near 1.17 eV appears for T_a equal to 400°C . This band redshifts with increasing T_a with an energy slightly higher than the band gap of germanium (0.66 eV at 300 K). Its observation corresponds to the phase decomposition of the alloys and to the appearance of the amorphous germanium aggregates, as shown by the infrared absorption and Raman spectrometry experiments. Its redshift with increasing T_a and therefore with increasing aggregate size could be due to the quantum-confinement effect. This PL band could then be attributed to the germanium aggregates. But, although the multilayered structure is more stable than the single layer, it was not possible to keep the PL signal for T_a greater than 500°C ,

certainly because the size of the aggregates, not limited inside the GeO_x layers, becomes too large to produce luminescence.

IV. CONCLUSION

In conclusion, $\text{GeO}_x/\text{SiO}_2$ multilayers were prepared by evaporation. X-ray reflectometry and transmission electron microscopy have shown that the multilayered structure is visible till 700 °C, although some interdiffusion can be detected at 500 °C. The evolution of the structure, studied by infrared absorption and Raman spectrometries, was correlated to the PL experiments. It is deduced that visible PL originates in the presence of defects in the oxide matrix for T_a less than 300 °C and that infrared PL originates in the germanium aggregates for T_a in the range of 400–500 °C.

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