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Influence of hydrogenation on the structure and visible photoluminescence of germanium oxide thin films

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ABSTRACT

Substoichiometric germanium oxide thin films were prepared by evaporation of GeO_2 powder. The as-deposited samples showed a luminescence band in the visible range. Hydrogen was used to passivate the dangling bond defects and therefore to determine the origin of photoluminescence in the germanium oxide films. Hydrogen was introduced in the films from an electron cyclotron resonance (ECR) plasma source during or after the evaporation. The films hydrogenated during evaporation contain little oxygen because of an etching mechanism. In the post-hydrogenated films, the oxygen content is higher. With the hydrogenation treatment, the oxygen dangling bonds are suppressed. It is proposed that the photoluminescence in the visible range is attributed to the structural defects.

1. Introduction

Photoluminescence (PL) of germanium nanocrystals (nc-Ge) embedded in silicon dioxide (SiO_2) or germanium dioxide (GeO_2) matrices has been studied since last decade because of the potential applications in optoelectronics. Many groups have observed visible PL in Ge–SiO_2 [1–5] or Ge–GeO_2 [6] systems or in oxidized Ge films [7]. Takeoka et al. [8] have also measured an infrared (IR) band in Ge–SiO_2 films and the PL shift observed with decreasing of the nc-Ge size was attributed to a quantum confinement phenomenon, in agreement with the theoretical predictions of Niquet et al. [9]. On the contrary, the visible bands, which show practically no shift, were attributed either to defects or to quantum confinement and their origin is still subject of controversy. Different groups have investigated experimentally [10,11] and theoretically [12,13] point defects in pure germanium oxide. They have shown that PL bands can be observed in the ultraviolet (UV), visible or infrared ranges. In fact, as the experimental bands are rather broad, they may have a multi-source origin since several different types of defects can contribute to their formation.

In order to correlate the PL band with the presence of defects, it may be useful to compare the same samples with and without defects. Thermal annealing and hydrogenation are two well-known methods to suppress structural defects. Hydrogenation is nevertheless the more convenient method because it allows us to compare the optical properties of samples hydrogenated and non-hydrogenated having the same atomic structure whereas annealing treatments provoke diffusion and modify the structural characteristics of the films.

Our group has recently prepared amorphous SiO_x [14] and GeO_x [15,16] thin films by the evaporation of SiO or GeO_2 powder. The as-deposited samples are substoichiometric and thermal treatments provoke a decomposition phenomenon with the apparition of silicon or germanium aggregates growing with increasing annealing temperature. These alloys present visible PL, which could be due to a quantum confinement effect in the clusters or to the structural defects. The aim of this study is to identify the origin of this visible band using the hydrogenation of the GeO_x layer.

2. Experiment

GeO_x films were prepared by evaporation of GeO_2 powder in an ultrahigh-vacuum chamber from an electron beam gun onto

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silicon or silica substrates maintained at 100 °C. The base pressure was 10^{-8} Torr. The pressure during the evaporation increases until 3×10^{-6} Torr due to the partial decomposition of GeO_2. The deposition rate of 0.1 nm/s was controlled by a quartz microbalance. The layer thickness was 200 nm. After deposition, the films were annealed in a high-vacuum quartz tube with a heating rate equal to 10 °C/min and they were cooled down immediately after the annealing temperature T_a was reached.

Hydrogenation and deuteration of the films were obtained by hydrogen and deuterium ions bombardment, produced by an electron cyclotron resonance (ECR) plasma source. The flow in the ion gun was regulated by maintaining the total pressure in the evaporation chamber at 4×10^{-5} Torr. The 2.45 GHz microwave energy of the ECR source was 200 W. A 875 G axial magnetic field was used to create the electron cyclotron resonance and to promote efficient coupling of the microwaves to the plasma. The distance between the source and the substrate was 15 cm.

Different series of samples were prepared. The series A corresponds to non-hydrogenated samples. The series B corresponds to samples hydrogenated during the evaporation of GeO_2. The series C corresponds to samples post-hydrogenated during 1 h. For the latter series, the first experiments have shown that the hydrogenation is more efficient when the samples were maintained at 300 °C. At lower temperatures, the diffusion of hydrogen in the film is too slow. At higher temperatures, there is effusion of hydrogen. Moreover, as the annealing treatment at 300 °C can modify the structure, these samples were firstly annealed at 350 °C, and then hydrogenated at 300 °C.

The evolution of the atomic structure was followed by Fourier-transform infrared (FTIR) absorption spectroscopy. The measurements were carried out with a resolution of 4 cm^{-1}. The contribution of an uncoated reference silicon substrate was subtracted from the experimental spectra. The base line of the absorption spectra was also subtracted for clear presentation of the data. The PL measurements were carried out with samples deposited on silica substrates. The signal in the range of 500–1700 nm was analyzed by a monochromator equipped with a 600-grooves/mm grating and by an InAs photomultiplier tube cooled at 190 K. The 325 nm excitation was emitted from a He–Cd continuous laser. The response of the detection system was precisely calibrated with a tungsten wire calibration source.

3. Results and discussion

3.1. Non-hydrogenated GeO_x thin films (series A)

During evaporation, there is a partial decomposition of the GeO_2 source by the electron beam, which explains the increase of the pressure in the chamber, and the deposited films are substoichiometric. The IR absorption spectrum of the as-deposited sample (Fig. 1) shows two intense Ge–O bands at 530 and 825 cm^{-1}, which are assigned to the bending vibration mode and to the stretching vibration of the Ge–O–Ge group, respectively [17]. With annealing treatment above 400 °C, the absorption intensity of these bands increases and their frequency shifts towards higher wave numbers [15]. Such a shift shows that the suboxide evolves into the Ge dioxide phase. As the average composition remains unchanged, it can be concluded that a phase separation appears in the film and that pure Ge and Ge-rich areas appear in the samples, following the reaction $GeO_x \rightarrow Ge+GeO_2$.

Another weak absorption band is visible near 700 cm^{-1} for the as-deposited film. As proposed by Skuja et al. [11] and Busani et al. [18], this band could be due to a stretching mode of Ge–O-bonds, also called non-bridging oxygen (NBO) atoms or oxygen dangling bonds. The attribution of this band to a defect is in agreement with our experiments, which show that the intensity of this band is a decreasing function of the annealing temperature. The disappearance of this band appears for annealing temperatures greater or equal to 550 °C. This behaviour generally corresponds to a densification of the atomic structure, which involves in the disappearance of the dangling bonds. However, the exact origin of this infrared absorption band is still an open question.

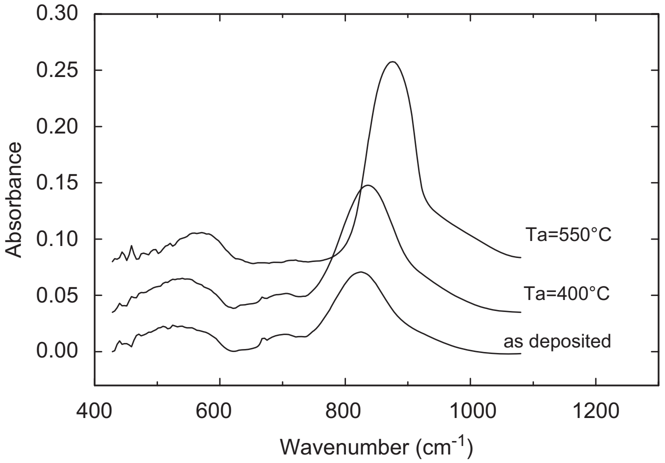

Fig. 1. IR absorption spectra of GeO_x films annealed at different temperatures T_a.

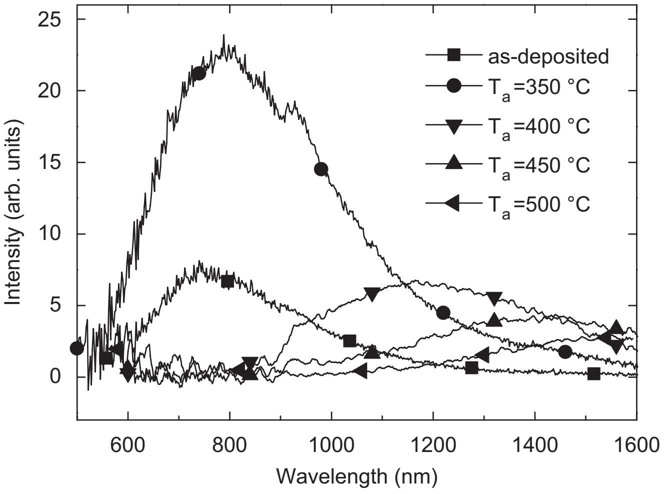

Fig. 2. PL spectra of GeO_x films annealed at different temperatures. The measurement temperature is 77 K.

Fig. 2 presents PL spectra of GeO_x films annealed at different temperatures. For the films as-deposited and annealed at 350 °C, the PL spectra show a very broad band centered at 800 nm. The PL intensity increases with the annealing at 350 °C, but its shape and its position remain unchanged. For annealing at 400 °C, the visible peak disappears and another weaker and broader peak appears near 1200 nm in the infrared range. This band redshifts near 1500 nm for T_a equal to 500 °C and there is no more PL for T_a equal to 550 °C.

The broad band observed for the as-deposited sample and for the sample annealed at 350 °C is rather similar to the bands generally attributed to the defects in the oxide phase, as O-deficiency-related defects or oxygen dangling bonds. With annealing at temperatures higher than 400 °C, this band disappears. The other PL band in the IR range appears for annealing at 400 °C. With increasing T_a, this band redshifts with energy slightly higher than the band gap of Ge. Its observation