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# Infrared luminescence of annealed germanosilicate layers

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## ABSTRACT

In the light of growing importance of semiconductor nanocrystals for photonics, we report on the growth and characterization of annealed germanosilicate layers used for Ge nanocrystal formation. The films are grown using plasma enhanced chemical vapor deposition (PECVD) and post-annealed in nitrogen at temperatures between 600 and 1200 °C for as long as 2 h. Transmission electron microscopy (TEM), Raman scattering and photoluminescence spectroscopy (PL) has been used to characterize the samples both structurally and optically. Formation of Ge precipitates in the germanosilicate layers have been observed using Raman spectroscopy for a variety of PECVD growth parameters, annealing temperatures and times. Ge–Ge mode at $\sim 300\ \mathrm{cm}^{-1}$ is clearly observed at temperatures as low as 700 °C for annealing durations for 45 min. Raman results indicate that upon annealing for extended periods of time at temperatures above 900 °C; nanocrystals of few tens of nanometers in diameter inside the oxide matrix and precipitation and interdiffusion of Ge, forming SiGe alloy at the silicon and oxide interface take place. Low temperature PL spectroscopy has been used to observe luminescence from these samples in the vicinity of 1550 nm, an important wavelength for telecommunications. Observed luminescence quenches at 140 K. The photoluminescence data displays three peaks closely interrelated at approximately 1490, 1530 and 1610 nm. PL spectra persist even after removing the oxide layer indicating that the origin of the infrared luminescent centers are not related to the Ge nanocrystals in the oxide layer.

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## 1. Introduction

There is currently great interest in nanometer sized Si and Ge structures following the observation of the efficient visible photoluminescence (PL) from porous Si [1], since this could open new possibilities for indirect gap semiconductors as new materials in optoelectronic applications. In particular, PL properties of Si nanocrystals (nc-Si) have widely been studied and the relationship between the size of nc-Si and the PL peak energy has been revealed experimentally [2]. Many approaches to the realization of Si nanocrystals in a variety of matrices have been proposed. Si nanocrystals in insulating matrices, such as $SiO_2$, are also considered candidates for future memory devices [3]. Intense work is under way to realize a Si laser [4]. Silicon nanocrystals in $SiO_2$ typically form at relatively high temperatures, such as 1100 °C, when annealed for 1 h or more and exhibit tunable photoluminescence due to size controlled nanocrystals formed by appropriate annealing conditions.

On the other hand, germanium (Ge) also is an indirect band gap semiconductor similar to silicon in many respects except for a smaller band gap. Ge containing $SiO_2$ thin films can be obtained through, among many different techniques, ion implantation or plasma enhanced chemical vapor deposition (PECVD) of germanosilicate layers [5,6] to name a few. However, Ge nanocrystals form at much lower annealing temperatures and durations as opposed to Si nanocrystals. While annealing temperatures of 800 °C and durations of a few minutes is typical to obtain Ge nanocrystals, Ge clusters of 2–3 nm sizes have been claimed to have formed even at annealing temperatures as low as 300 °C when annealed for 30 min [7]. However, lattice fringes of these nanocrystals have not been observed casting shadow on their crystallinity. Both TEM and Raman scattering have been employed to observe the formation of Ge nanocrystals in single and multilayers [8]. Extensive photoluminescence work yielded mixed results. Dutta [9] reported observing blue luminescence from Ge nanocrystals and claimed that PL is due to quantumconfined electronic transitions despite insufficient data. Paine et al. [10] have observed photoluminescence at 580 nm obtained from samples by $H_2$ reduced $Si_{0.6}Ge_{0.4}O_2$ and postannealed 750 °C which they attributed to Ge nanocrystals. Ge nanocrystals prepared by the sol–gel method in $SiO_2$ and three photoluminescence peaks in the range of 2.0–2.3 eV were attributed to Ge nanocrystals [11]. Maeda [7] has studied Ge nanocrystals in $SiO_2$ prepared by the cosputtering method and have observed both blue (3.1 eV) and visible (2.2 eV) photoluminescence and analyzed the data considering the quantum confinement model as well as Ge: E' luminescence centers in glasses

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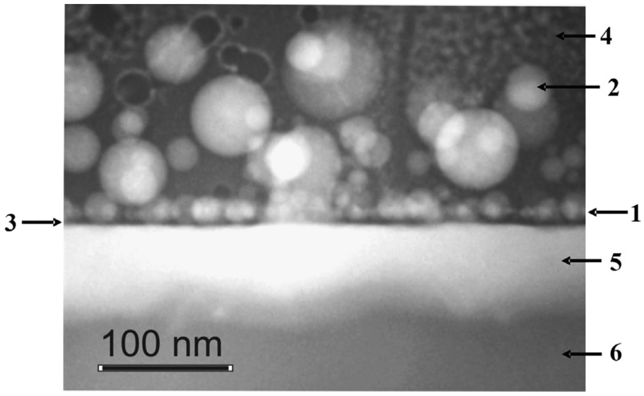

**Fig. 1.** Dark field STEM image of a sample annealed at 1000 °C for 1 h. Ge nanocrystals are formed in the vicinity of the interface (number 1 and 2). Note the presence of two layers with two distinct average sizes of Ge nanocrystals. A nanocrystal free $SiO_2$ interface oxide (number 3) and oxide close to the surface devoid of Ge nanocrystals, (number 4) is observed. Ge diffuses into Si substrate for an average thickness of 50 nm and Si substrate (number 5). Si substrate is also indicated (number 6).

and structural transitions of nanocrystal Ge, favoring the former model. Takeoka [12] has studied the near infrared photoluminescence in the range of 0.88–1.54 eV from Ge nanocrystals prepared by the cosputtering method and concluded that the observed luminescence is due to radiative recombination of electron–hole pair confined in Ge nanocrystals. Torchynska et al. [13] have studied Ge nanocrystals in $SiO_2$ and have concluded that all bands in the range of 1.6–2.35 eV are due to defects in $SiO_x$ whereas PL bands in the range of 0.75–0.85 eV are attributed to excitonic recombination inside Ge nanocrystals. It is thus clear from the literature that origin of photoluminescence from Gedoped silicate layers is still not clear. Much work has been devoted to study the electrical properties of Ge nanocrystals in $SiO_2$ matrices [14]. Charging and discharging of Ge nanocrystals have been studied for flash memory applications. The possibility of charge storage in quantized levels of Ge nanocrystals has been shown [15].

In this work, Ge nanocrystals in $SiO_x$ matrix were prepared by plasma enhanced chemical vapor deposition of $SiO_x$ doped with Ge followed by postannealing of these layers. Both short term anneals as well as prolonged annealing has been carried out in nitrogen environment in the range of temperatures from 600 to 1200 °C. Both the formation of Ge nanocrystals in the oxide matrix as well as diffusion and intermixing of Ge with Si in the substrate and the formation of SiGe alloy have been observed by TEM and Raman spectroscopy. Photoluminescence in the visible as well as in the near infrared is studied both at low and room temperatures. Photoluminescence in the near infrared is studied in detail because of the important optical communication wavelength region of 1.3–1.5 μm. Persistence of the photoluminescence even after the removal of the oxide layer containing the Ge nanocrystals suggests that, Ge islands on the Si substrate and SiGe alloy that forms at the interface of the oxide layer with the Si substrate, should also be considered for the origin of the observed luminescence.

## 2. Experimental procedure

The $SiO_x$:Ge films were grown in a PECVD reactor (PlasmaLab 8510C) on Si substrates using 185 sccm $SiH_4$ (2% in $N_2$), 45 sccm $NH_3$ and 120 sccm flow rate of $GeH_4$ (2% in He) as precursor gases, at a substrate temperature of 350 °C, a process pressure of 1000 mTorr under an applied RF power of 10 W. The samples were then annealed under nitrogen environment in a quartz oven at temperatures ranging from 600 to 1200 °C as long as 2 h. Raman scattering experiments were carried out using a 1-m double monochromator with GaAs photomultiplier and photon counting electronics. Various lines of an Ar ion ($Ar^+$) laser and a 35 mW He–Ne laser at 632.8 nm were used to excite the samples. Photoluminescence spectroscopy in the infrared is carried out at low temperatures with a 50 cm single pass monochromator equipped with a large area InGaAs detector. A closed cycle refrigerator is used down to 15 K.

Cross section of the samples was observed with a transmission electron microscopy (TEM). The samples for the TEM observations were prepared by standard procedures in cross-section orientation and view edge on. Mechanical and $Ar^+$ thinning techniques were used to thin down the samples. $Ar^+$ at 5 keV incident at 9–12° was used. To minimize $Ar^+$ damage, the accelerating voltage was lowered down to 1 keV in the final stages of the thinning process. The structural characterization was carried out with a JEOL 2010F field-emission transmission electron microscope operated at 200 keV.

## 3. Results and discussion

Fig. 1 shows a crosssectional dark field STEM image for a typical PECVDgrown $SiO_x$:Ge films annealed at 1000 °C for 1 h. Upon annealing, crystallization of Ge is observed in the samples. TEM image shows that these nanocrystals fall into two groups. These two groups are composed of small nanocrystals with an average size of 15 nm and large nanocrystals that have an average size of 50 nm. From the TEM micrography, a 3–5 nm thick layer of oxide on the Si substrate is observed to be free of Ge nanocrystals (number 1). Furthermore, Ge is observed at the Si/$SiO_x$ interface mixed with Si forming SiGe alloy. Thin layers or islands of Ge may also be present at the interface. It is suggested that Ge nanocrystals from $GeO_2$ form due to an exchange reaction with Si diffusing in from the substrate into the oxide layer forming $SiO_2$ and leaving elemental Ge behind [9]. The fact that Ge nanocrystals form only in the vicinity of the Si substrate seems to corroborate this mechanism. EDAX analysis of the substrate close to the Si/$SiO_x$ interface as well as the narrow band of contrast with the Si substrate at the interface seen in the TEM images suggest the presence of Ge on and in the Si substrate. All this is indicative of diffusion of Ge through the oxide layer and the formation of the SiGe layer at the silicon substrate–oxide interface.

Fig. 2 displays the results of Raman measurements from the same samples displaying the evolution of Ge nanocrystal formation upon annealing at temperatures in the range of 600–1200 °C. As an example, we show the spectra for samples in the annealing temperature ranges of 600–1200 °C for 45 min. The spectrum remains virtually unchanged for the annealing temperatures less than 600 °C. We observe a very broad ($\sim$40 $cm^{-1}$) asymmetric peak centered around 291 $cm^{-1}$ indicative of the quasiamorphous nature of the Ge for samples annealed at 600 °C dominates the spectrum. We also note that the sharp rise on the right culminates in a very small peak at 299.27 $cm^{-1}$ mixing into the quasi-amorphous peak. Presence for this peak suggests that 600 °C is the onset of Ge crystallization as observed by Raman spectroscopy. Si substrate is observed at 520.4 $cm^{-1}$. If the annealing temperature is raised to 700 °C, a sharp peak at 299 $cm^{-1}$, now 10 $cm^{-1}$ in width, (not shown) is accompanied by a wide shoulder on the low frequency side. The sharp peak is a clear sign of Ge nanocrystal formation accompanied by a range of smaller Ge nanostructures. We note that this peak is at a lower frequency than the Ge mode in bulk Ge. This is most likely due to phonon confinement in small crystals. This peak becomes stronger at 299.8 $cm^{-1}$ and narrower (5.3 $cm^{-1}$) and the broad quasi-amorphous structure disappears

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