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Synthesis and size differentiation of Ge nanocrystals in amorphous SiO_2

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ABSTRACT Germanosilicate layers were grown on Si substrates by plasma enhanced chemical vapor deposition (PECVD) and annealed at different temperatures ranging from 700–1010 °C for durations of 5 to 60 min. Transmission electron microscopy (TEM) was used to investigate Ge nanocrystal formation in SiO_2:Ge films. High-resolution cross section TEM images, electron energy-loss spectroscopy and energy dispersive X-ray analysis (EDX) data indicate that Ge nanocrystals are present in the amorphous silicon dioxide films. These nanocrystals are formed in two spatially separated layers with average sizes of 15 and 50 nm, respectively. EDX analysis indicates that Ge also diffuses into the Si substrate.

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1 Introduction

The charge storage property of semiconductor nanocrystals embedded in an amorphous silicon oxide matrix is currently under intense investigation due to its potential application in future non-volatile memories. As charge loss through lateral paths in nanocrystal based memory devices are suppressed by the oxide isolation between nanocrystals, these devices exhibit superior charge retention characteristics compared with conventional floating-gate memory devices [1–5]. Recently, Choi et al. demonstrated the existence of memory effect in rf sputtered Ge nanocrystal devices [6]. For memory device applications, it is also crucial to control the thickness of the SiO_2 tunnel oxide underneath the nanocrystal layer, as well as the density and size of the Ge nanocrystals.

Nanocrystals that are formed by precipitation from a non-uniform concentration profile often display an average size that is a function of depth [7]. Also, germanium nanoparticles formed in a Ge doped oxide layer on a silicon substrate will generally display a variation in size and concentration with depth as a result of diffusion of Ge towards the Si/SiO_2 interface [8, 9]. Techniques, such as co-sputtering and ion implantation are typically used to obtain embedded Ge nanocrystals, the matrix usually being SiO_2 [10–13]. In this letter, we report on the formation of Ge nanocrystals, with two different average sizes in two separate layers in SiO_2 after single step annealing of the germanosilicate layers. Germanosilicate films deposited by PECVD have some advantages due to low temperature of deposition, excellent step coverage characteristics, a high blocking effect against moisture and alkaline ions, and relatively high dielectric constant values [14]. We used TEM to determine size and crystallization. TEM is a powerful technique for the structural and chemical investigation of a wide range of materials.

Ge nanocrystals has been obtained by ion beam synthesis in SiO_2 and post annealing TEM characterization showed Ge nanocrystal formation with a mean diameter of few nm's depending on implantation dose and annealing time and temperature [15]. The Ge nanocrystal size distribution of samples, rapid thermally annealed at 800 and 1000 °C for 300 s, has been obtained from TEM images and the best photoluminescence (PL) response was obtained with samples that exhibit uniform nanocrystal size [16]. Rapid thermal annealing at 800 and 1000 °C for 300 s resulted in uniform size distribution of Ge nanocrystals, with an average size of 6.0 nm at 800 °C, and 20–28 nm with multiple twinnings close to the interface when annealed at 1000 °C [16]. In samples prepared with rf magnetron sputtering nanocrystalline Ge embedded in a SiO_2 matrix was obtained and examined by X-ray photoelectron spectrometry, Raman spectrometry and high resolution TEM [11, 17].

The precipitation and growth of Ge nanocrystals is found to be related to thermodynamical reduction of GeO and the diffusion of Si atoms from the Si substrate into the glassy matrix, with an aggregation of small sized Ge nanocrystals. Ge nanocrystals were also obtained by ultrahigh vacuum chemical vapor deposition (CVD) of $Si_{0.75}Ge_{0.25}$ on Si followed by high temperature oxidation. TEM studies showed that large nonspherical Ge crystallites were formed at the substrate interface [18]. On the other hand, nanoscale heterogeneity was found by TEM observation in the distribution of Ge ions in SiO_2:GeO_2 glass preforms and fibers prepared by the vapor phase axial deposition method [19]. Formation of Ge nanocrystallites were also studied in other matrices such as a-SiN_x deposited by the PECVD technique and followed by an annealing treatment at 800 °C. It has been found that substrate temperature is a critical parameter for the formation of Ge clusters and the diffusion limited growth model was used to explain the crystallization mechanism of this mate-

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rial [20]. Ge nanocrystal size was uniform with an average size of 20 nm in a single layer with no distinct size separation.

In this work, the size distribution of Ge nanocrystals in SiO_2 was determined from high-resolution transmission electron microscopic (HRTEM) observations. Samples for the cross-sectional HRTEM observations were prepared by standard procedures including mechanical thinning and low temperature (200 K) Ar-ion milling techniques.

We found that Ge nanocrystals form in two average sizes in two spatially separated layers. The size dependent spatial separation of Ge nanocrystals has been observed.

2 Experimental procedure

The 460 nm thick germanosilicate film was grown in a PECVD reactor (model PlasmaLab 8510C) on Si substrates using 180 sccm SiH_4 (2% in N_2), 225 sccm NO_2 and 90 sccm GeH_4 (2% in He) as precursor gases, at a sample temperature of 350 °C, a process pressure of 1000 mTorr under and an applied rf power of 10 W. The composition of the grown film was determined as $Si_{1.0}Ge_{0.54}O_{3.4}$ from X-ray photoelectron spectroscopy measurements. Pieces cut from the same sample were annealed in nitrogen atmosphere in a quartz oven at different temperatures ranging from 700–1010 °C for durations of 5 to 60 min. During annealing, the samples were loaded and unloaded slowly, resulting in ramp times of 1 min. The film was grown on *p*-type silicon substrates with resistivity of 55 Ω cm.

Samples were prepared in cross-section orientation, so that the film layers were viewed edge-on. This preserves the information about the position of the nanocrystals with respect to the surface. Samples were then glued onto a Cu grid using M-Bond 600/610 and the glue was cured at 150 °C for 2 hours. Both sides of the samples were polished and mechanically ground down to 20 μm. To obtain samples of the right thickness for TEM observations, an ion Ar^+ beam of 5 kV and incidence angle of 9–12° was used. The acceleration voltage of the beam was lowered down to 1 kV during the final stages of the thinning process in order to further minimize the Ar^+ induced impact damage in the area of interest. The structural characterization was carried out with a JOEL 2010F field-emission transmission electron microscope operated at 200 kV.

3 Results and discussion

High-resolution micrographs and selected area diffraction confirm that Ge nanocrystals are formed in our samples. As a representative example, Fig. 1 shows the dark field STEM image of a sample annealed at 1010 °C for 1 h. It can clearly be seen that Ge nanocrystals with well-defined spherical shapes are formed. Similar results are obtained for samples annealed between 850 °C and 1010 °C. The crystallinity of the Ge nanoclusters was identified by selected area diffraction. The sizes of the crystalline particles were determined from the TEM images. For some nanocrystals, the actual size may be larger than the apparent size in TEM micrographs, due to cross sectioning at different sections of the particles. Nanocrystal sizes are estimated to vary in the range of 5–70 nm. It can be seen from the TEM image that these nanocrystals fall into two groups. The first group is

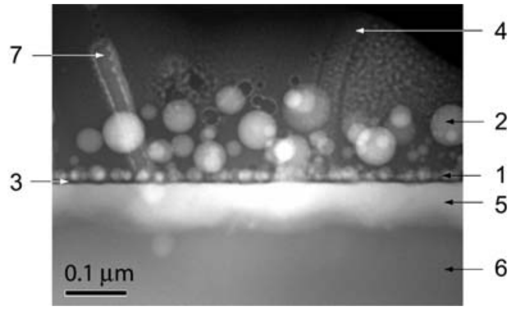

FIGURE 1 Dark field STEM image of a sample annealed at 1010 °C for 1 h. Ge nanocrystals are formed in the vicinity of the interface (1 and 2). Note the presence of two layers with two distinct average sizes of Ge nanocrystals. A nanocrystal free SiO_2 interface oxide (3) and oxide close to the surface devoid of Ge nanocrystal formation, (4) is observed. Ge diffuses into Si substrate for an average thickness of 50 nm, (5). Si substrate (6) and the electron damage during EDX study (7) is also indicated

composed of small nanocrystals that have an average size of 15 nm and a second group of large crystals that have an average size of 50 nm. Following a 3–5 nm thick layer of oxide on the Si substrate, free of Ge nanocrystals, the smaller nanocrystals occupy an oxide layer of about 15 nm. Larger nanocrystals are located in an oxide layer of 150 nm next to the smaller nanocrystals. The top 310 nm of the oxide layer is devoid of Ge nanocrystals, but not of Ge as observed by secondary ion mass spectroscopy (SIMS). From the TEM micrograph, a narrow band of contrast on the Si substrate side of the Si/SiO_2 interface is observed. Upon closer analysis using EDX, we find that this layer is composed of a Ge rich mixture of Si and Ge. This indicates that during the 1 h annealing time at 1010 °C, Ge diffuses into Si substrate for an average depth of 70 nm. Ge is known to be a fast diffuser in SiO_2 beyond 800 °C [21]. Since the annealing temperature of 1010 °C is significantly above the bulk melting point of Ge, rapid diffusion of Ge is to be expected. Diffusion of Ge may be further enhanced by built-in strain effects during high temperature annealing processes.

In Fig. 2, we present a statistical analysis of the size distribution of Ge nanocrystals. We obtained a very good modified log normal fit to the data [22]. We note the absence of nanocrystals near the interface for a narrow band of oxide layer. Small nanocrystals with a mean size of 15 nm are crowded into a relatively narrow band in the 15 nm thick oxide layer. Larger nanocrystals are found in a wider band of 150 nm in thickness. We did not find Ge nanocrystals or clusters beyond 150 nm away from the interface, suggesting that oxide close to the surface is devoid of Ge nanocrystal formation. The inset of the figure shows a summary of the number of nanocrystals as a function of their location from the oxide–substrate interface. Clustering of Ge nanocrystals into two layers is clearly observed.

Figure 3 shows HRTEM image of a Ge nanocrystal with a size of 25 nm formed in the germanosilicate thin film. The micrograph shows clear lattice fringes of Ge nanocrystal. The Ge nanocrystals are spherical and single crystalline. No twinnings were observed in the nanocrystals studied. We have carried out the EDX study in the STEM mode. In this mode we have used a probe size of 1.0 nm. This probe size is much

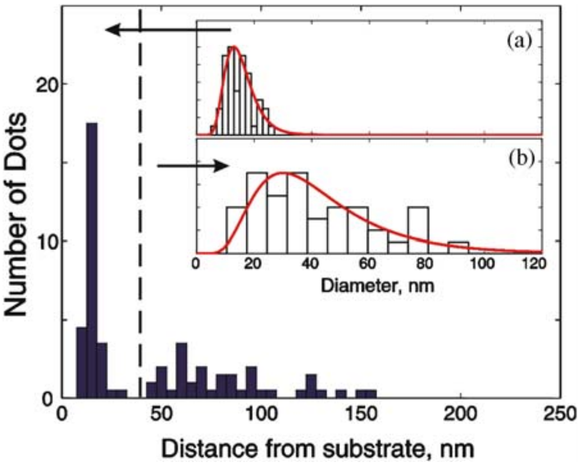

FIGURE 2 Distribution of Ge nanocrystals as a function of distance from the Si interface. It can be seen that a band of nanocrystals forms close to the interface, and another band forms further away from the interface. *Inset*: Size distributions of the two individual bands of Ge nanocrystals, (a) smaller nanocrystals are formed in the band close to the substrate, (b) larger nanocrystals form further away from the substrate

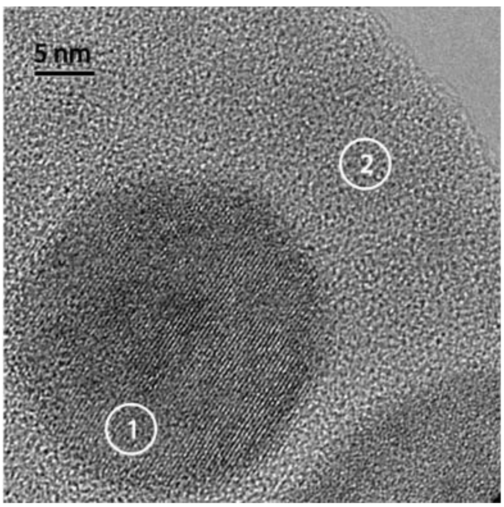

FIGURE 3 HRTEM image of a well separated Ge nanocrystal (1) with a size of 25 nm formed in the SiO_2 matrix (2). Note the perfect alignment of crystalline planes throughout the Ge nanocrystal. No twinnings were observed

smaller than the large Ge balls in the SiO_2 matrix and the Ge layer over the Si substrate.

From the results of the observations described above, a preliminary picture of Ge nanocrystal formation emerges. Highly mobile Ge under compressive strain [11] diffuses toward the silicon substrate forming spherical Ge nanocrystals in the oxide layer [8]. This is common to all samples annealed between 850 and 1010 °C. For samples annealed for 1 h, Ge diffuses into the Si substrate as well. Small Ge nanocrystals form at the interface while larger Ge nanocrystals form further away from the interface. While the mechanism of formation is not clear to us, the separation of Ge nanocrystals with different sizes into two layers is a crucial result of this study. If the separation between the different sized nanocrystal bands and size distributions can be controlled and reduced to a few nanometers, such a double band formation can be especially important for flash memory applications. In a recent study, Ohba et al. [23] has studied the affect of double stacking of two different Si nanocrystal sizes on the retention properties of flash memory devices. They used Si nanocrystals of 5 and 10 nm in diameters, in two separate layers of SiO_2 matrix. They found that inclusion of a double layer of nanocrystals in the oxide improves the retention time and decreases read-write voltages significantly. Our work indicates that such bilayers with small and large nanocrystals may be formed in single step annealing of PECVD grown Ge rich oxides. Further investigation of the dynamics of this bilayer formation may shed light into ways of controlling the size of the nanocrystals. It should also be noted that small nanocrystals at the interface are distinctly separated from the interface by a layer of SiO_2 with an average thickness of 3.6 nm, suitable for tunneling of injected carriers in a memory device.

4 Conclusions

In summary, HRTEM analysis of SiO_2:Ge thin films prepared by PECVD technique has revealed the formation of Ge nanocrystals with two different sizes in the SiO_2 matrix. In addition to Ge diffusing into the Si substrate for an average thickness of 70 nm, large Ge nanocrystals with an average size of 50 nm, form in a 150 nm thick layer above the lower layer with smaller Ge nanoballs, with an average size of 15 nm, in a layer that is 15 nm thick. These small nanocrystals are separated from the Si substrate by a 3.6 nm thick layer of oxide. This self organized stacking of Ge nanocrystals into two size in two layers separated by an oxide layer from the Si substrate is observed for the first time and promises to be a candidate for improved flash memory applications.

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