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TEM study on the evolution of Ge nanocrystals in Si oxide matrix as a function of Ge concentration and the Si reduction process

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Abstract—**Growth and evolution of germanium (Ge) nanocrystals embedded into a silicon oxide (SiO_2) system have been studied based on the Ge content of co-sputtered Ge-SiO_2 films using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). It was found that when the proportion of Ge relative to Ge oxide is 20%, TEM showed that annealing the samples at 800°C for 60 min resulted in the formation of a denuded region between the silicon/silicon oxide (Si/SiO_2) interface and a band of Ge nanocrystals towards the surface of the film. By introducing a 20-nm thick thermal oxide barrier on top of the silicon (Si) substrate on which the film is deposited, no denuded region in the bulk of this sample is observed. It is proposed that this barrier is effective in reducing both Ge diffusion into the Si substrate and Si diffusion from the substrate into the film. Si diffusing from the Si substrate reduces the Ge oxide into Ge which can subsequently diffuse into the Si substrate. However, the oxide barrier is able to confine the Ge within the oxide matrix so that the denuded region in the bulk of the film cannot form. However the reduction in diffusion should be more significant for Ge as its diffusion coefficient is lower than Si due to its larger size. It is suggested that the denuded region consists of amorphous Ge diffusing towards the Si/SiO_2 interface. When the Ge content is increased to slightly more than 70%, TEM showed that Ge nanocrysyals formed after annealing at 800°C for only 30 min for samples with and without the oxide barrier. There is no denuded region between the Ge nanocrystals band and the Si/SiO_2 interface for both samples but it was observed that coarsening effects were more prominent in the film deposited on top of the oxide barrier. The reduction effect of Si on Ge oxide should not play a significant role in these samples as the Ge content is high..**

Index terms—**Germanium nanocrystals, Silicon reduction, Germanium diffusion**

I. INTRODUCTION

There is an intense interest in germanium (Ge) nanocrystals embedded in silicon oxide matrix as it has potential applications in the electronics [1,2] and optoelectronics [3-5] area. Two of the most frequently used methods for synthesizing Ge nanocrystals in silicon oxide matrix involved conventional furnace annealing [6,7] or rapid thermal annealing (RTA) [4,8] of co-sputtered germanium plus silicon oxide films. However, manipulation of the size and the distribution of the Ge nanocrystals formed by this self-assemble method are found to be relatively challenging.

Recently, we have examined [9] the effect of RTA temperature on the diffusion of Si and Ge and the formation of Ge nanocrystals in co-sputtered Ge plus silicon oxide film. We found that for samples RTA at 800˚C, the nanocrystals were uniform in size and distributed evenly in the bulk of the oxide but became denser nearer to the silicon-silicon oxide (Si-SiO_2) interface. Annealing at 900˚C resulted in the formation of two regions with different nanocrystal densities and size distributions separated by a region void of nanocrystals. For annealing at 1000˚C, nanocrystals were only observed at the Si-SiO_2 interface and these have significant size variation, with the rest of the oxide being void of nanocrystals. The formation of Ge nanocrystals was mainly attributed to the reduction of Ge suboxides by Si diffused from the Si substrate due to the abundance of Si there. The elemental Ge, GeO_2 and GeO_x concentrations were estimated by XPS and found to be about 10%, 30% and 60%, respectively, in the as-sputtered samples. With such an environment, the supply of elemental Ge from the reduction of GeO_2 and GeO_x by Si diffused from the substrate for the formation of Ge nanocrystals should play a dominant role.

In this paper, we prepared co-sputtered samples with different levels of Ge, GeO_2 and GeO_x concentrations. We investigated the effect of Ge, GeO_2 and GeO_x concentrations on the formation of Ge nanocrystals using conventional furnace anneal (i.e. with longer annealing

time). We also examined the influence of Si (diffused from the substrate) on the formation of nanocrystals in these samples by placing a 20 nm thick thermal oxide barrier between the Si substrate and the co-sputtered films. The effect of this barrier on Ge diffusion into the substrate is also discussed.

II. EXPERIMENT

The samples were co-sputtered in argon at ambient temperature. The target was a 4-inch. SiO_2 disk with pieces of Ge (99.999% pure, 5 mm×10 mm×0.3 mm) attached. An increase in the Ge concentration in the oxide matrix was achieved by having more Ge pieces attached to the target. The argon pressure and rf power for the sputtering were fixed at 3×10^{-3} mbar and 100 W, respectively. The thickness of the sputtered film in our samples was varied from 270 nm to 320 nm. The furnace annealing was carried out in nitrogen ambient at a temperature of 800˚C for a duration from 30 to 60 minutes.

The formation of Ge nanocrystals in the oxide matrix was observed using TEM. The TEM experiments were carried out using a field emission gauge system with an operating voltage of 300 kV. The information on the composition of elemental Ge, GeO_2 and GeO_x was obtained from XPS measurements. The XPS depth profiling was carried out at a sputtering rate of 140 nm/min. The XPS spectra of our furnace annealed samples showed prominent Ge 2*p* (1217.2 eV) and GeO_2 (1220.6 eV) peaks. These peaks were fitted with Gaussian-Lorentzian functions and the background was removed using the SpecSurf Version 1.7.2.15 software. To achieve best fit, the full widths at half maximum of the Ge 2*p* and GeO_2 peaks were allowed to vary from 0.8 to 1.1 eV. We assigned the area outside the two fitted peaks as germanium suboxides.

III. RESUTLTS & DISCUSSIONS

Two set of samples with different concentrations of elemental Ge, GeO_2 and GeO_x were prepared to investigate the influence of Ge and germanium oxides on the formation of nanocrystals. Samples A (6 cm^2 of Ge) and B (12 cm^2 of Ge) represent the two cases in which the concentrations of Ge, GeO_2 and GeO_x were 20%, 10% and 70% (for sample A) and 75%, 5% and 20% (for sample B), respectively.

The nanocrystal formation process [9] can be described by the following steps: (1) GeO_2 (or GeO_x) reduction leading to the creation of elemental Ge atoms; (2) diffusion of liberated Ge in the oxide matrix; (3) nucleation due to Ge-Ge collisions causing the formation of immobile Ge clusters; (4) growth, whereby diffusing Ge atoms bond to existing Ge clusters; and (5) coarsening of nanocrystals due to Ostwald ripening.

A typical TEM image of Sample A that has been annealed at 800˚C for 60 minutes is shown in Fig. 1(a). It is observed from this figure that there exists a region (i) of ~55 nm from the oxide surface that is void of nanocrystals, followed by region (ii) of nanocrystals of bigger and varying sizes, and region (iii) that is again void of nanocrystals. From our previous estimation [10] of Si from the substrate diffusing into the silicon oxide matrix to activate the reduction process, GeO_2 (or GeO_x) + Si → Ge + SiO_2 (or SiO_x), a duration of 60 minutes at 800˚C is more than sufficient for Si to traverse the whole oxide layer. As sample A contains a high content of GeO_x of 70%, most of the Ge that is responsible for the formation of nanocrystals should come from the reduction of GeO_x by the Si atoms originally present in the silicon oxide matrix and those diffused from the substrate.

The existence of a region that is void of nanocrystals (i.e. region (i)) is similar to our previous TEM results on a RTA sample with similar Ge, GeO_2 and GeO_x concentration [10]. We suggest that the Ge atoms in region (i) had outdiffused to the ambient and left behind a layer void of nanocrystals. Heinig *et al.* [11] reported that the few ppm of impurities (mainly H_2O) present in high-purity annealing gases N_2 and Ar act as an oxidant of Ge at 950 to

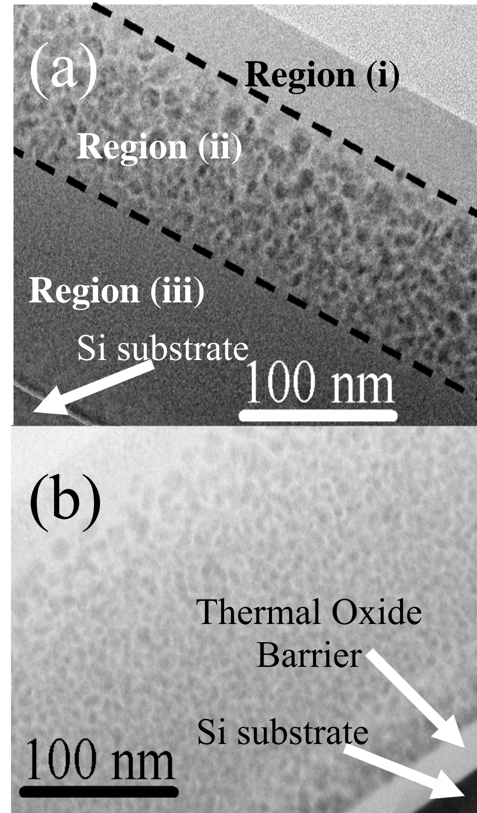

Fig. 1. Sample A: XTEM of co-sputtered Ge plus SiO_2 sample that was furnace annealed at 800˚C in N_2 ambient for 60 minutes, (a) without barrier and (b) with a thermal oxide barrier (20 nm) inserted between the Si substrate and the co-sputtered layer.

1100˚C, and reacts with Ge in a zone between the surface and the cluster band to form GeO_2 which is built homogeneously into the glassy SiO_2 network. As our annealing temperature is relatively lower at 800˚C, we believe the outdifussion of Ge would be more dominant than the re-oxidation of Ge. The reduction of GeO_x should result in evenly populated nanocrystals in region (ii) and (iii) with the number of nanocrystals increasing as one approaches the SiO_2-Si interface. This can be explained by the fact that a higher rate of reduction should take place near the SiO_2-Si interface due to the presence of more Si atoms at this region as compared to deeper into the bulk of the oxide. However, due to the low solubility of Ge in Si oxide, there exists a driving force for Ge to diffuse away from the Si oxide matrix, and coupled by the fact that Ge and Si are completely miscible, there is a tendency for Ge, once reduced, to diffuse towards the Si substrate. As the annealing duration is 60 minutes, Fig. 1(a) suggests that Ge atoms reside within 120 nm from the SiO_2-Si interface would diffuse into the Si substrate which resulted in region (iii) void of nanocrystals. Note that within region (ii), the smaller nanocrystals located near region (iii) is due to lesser Ge available for nanocrystal formation as some Ge would have diffused into the Si substrate. The bigger and unevenly sized nanocrystals/nanoclusters in region (ii) are a result of Ge obtained mainly from the reduction of GeO_x that subsequently nucleated and coarsened.

Fig. 1(b) shows the TEM picture of a sample prepared with exactly the same conditions as sample A, but with a thermal oxide layer (20 nm) grown by dry oxidation at 900˚C inserted between the Si substrate and the co-sputtered layer. This oxide barrier layer will reduce the diffusion of Si atoms from substrate to the co-sputtered layer and Ge from the co-sputtered layer to Si substrate. The reduction in diffusion should be more significant for Ge as it has a lower diffusion coefficient and it is much larger than Si. Novikov *et al.* [12] has also stated that for dissolved Ge produced by reduction of GeO_2, the Ge diffusion coefficient is lower than that of Si. With 60 minutes of annealing, there should be enough Si diffused from substrate to the co-sputtered layer to reduce the germanium oxides, as evident from the rather dense nanocrystals shown in Fig. 1(b). The diffusion of Ge to the Si substrate is, however, significantly reduced, resulting in bigger nanocrystals near the SiO_2-Si interface. The denuded zone (c.f. region (iii) of Fig. 1(a)) is also absent as the oxide barrier layer is able to confine the Ge within the matrix so that nucleation of the nanocrystals can take place.

We have also annealed sample A for 30 minutes at 800˚C but failed to observe nanocrystals in the silicon oxide matrix. We believe that a duration of 30 minutes is sufficient for Si atoms to diffuse across the whole oxide and therefore would have reduced all the germanium oxides. It means that with furnace annealing, a duration of 30 minutes is insufficient for the formation of Ge nanocrystals at this concentration (20%). This is in contrast to our earlier results of Ge nanocrystal formation at 800˚C for 300s using RTA. It basically shows that RTA is more efficient in transferring thermal energy to Ge atoms for the formation of nanocrystals.

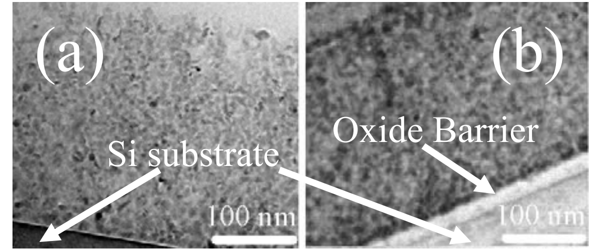

Fig. 2. Sample B: XTEM of co-sputtered Ge plus SiO_2 sample that was furnace annealed at 800˚C in N_2 ambient for 30 minutes, (a) without barrier and (b) with a thermal oxide barrier (20 nm) inserted between the Si substrate and the co-sputtered layer.

Figures 2(a) and (b) show the TEM pictures of sample B with and without the oxide barrier (20 nm) annealed at 800˚C for 30 minutes, respectively. Both figures show two regions in the oxide with a region void of nanocrystals (near the surface of the film) and a region densely populated with nanocrystals (in the bulk of the film above the Si substrate). As the Ge concentration of sample B is significantly higher than sample A (75% c.f. 20%), the contribution of Si reduction reaction is less important in the formation of nanocrystals. The abundance of Ge atoms means that nucleation can bypass the Si reduction process to supply the elemental Ge atoms and it can occur at the same time throughout the oxide resulting in the rather uniform distribution of Ge nanocrystals in the bulk of the film for both samples as shown in Fig. 2(a) and (b). This explains why the nanocrystals can form in a shorter annealing time of 30 minutes. The absence of the denuded zone in region (ii) of Fig. 2(a) could be explained by the presence of the numerous and evenly sized nanocrystals. It is more favorable for the Ge to form numerous and small nanocrystals as they are easier to nucleate. This becomes possible as the high Ge content leads to an increase in Ge supersaturation and reduced the barriers to nucleation resulting in a smaller critical nucleus size. The nucleation rate would also increase. Once formed, the Ge attains a dynamically stable configuration and it requires a driving force to result in the dissolution of these nanocrystals that is not sufficiently provided by the relatively low annealing temperature of 800˚C. When the nucleation rate is faster than the rate of diffusion of Ge into the Si substrate, the denuded region mentioned would not form.

Extending the annealing time on samples shown in Fig. 2(a) and (b) allowed coarsening to take place as shown by the TEM micrographs in Figs. 3(a) and (b). The nanocrystals for samples shown in Fig. 3(a) at the SiO_2-Si interface become larger due to coarsening and a significant Ge diffusion into the Si (indicated by a stratified layer at the Si surface). For the sample shown in Fig. 3(b), the

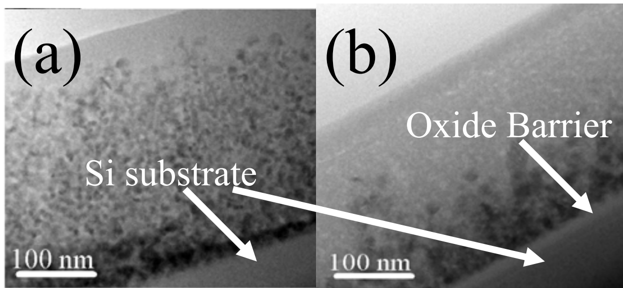

Fig. 3. Sample B: XTEM of co-sputtered Ge plus SiO_2 sample that was furnace annealed at 800˚C in N_2 ambient for 60 minutes, (a) without barrier and (b) with a thermal oxide barrier (20 nm) inserted between the Si substrate and the co-sputtered layer.

increase in annealing time to 60 minutes has resulted in extremely dense nanoclusters at the SiO_2-Si interface due to the blockage of Ge diffusion to Si substrate by the oxide barrier.

IV CONCLUSION

It is found that when the Ge concentration is low, relative to Ge oxides concentration, in co-sputtered Ge plus silicon oxide film, the effect of Si reduction on the Ge oxides plays an important role in the growth and evolution of the Ge nanocrystals. A denuded region is observed in the bulk of the film when the film is annealed. The insertion of a 20-nm thick oxide barrier between the Si substrate and the co-sputtered film reduces the diffusion of both Si from the substrate into the film and the diffusion of Ge into the substrate. The denuded region in the bulk of the film cannot be observed because the barrier is able to confine the Ge within the oxide matrix. When the Ge concentration is high relative to the Ge oxides concentration, Ge nanocrystals can form at a shorter annealing time due to the increase in supersaturation of Ge. The reduction effect of Si on Ge oxides does not play a significant role in these samples as the concentration of elemental Ge is high. Coarsening effects were more prominent in the film deposited on top of the barrier as the barrier helps to confine more Ge in the oxide matrix by reducing the diffusion of Ge into the Si substrate.

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