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W. S. Liu, J. S. Chen, M.A. Nicolet, V. ArbetEngels, and K. L. Wang

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Nanocrystalline Ge in SiO₂ by annealing of $Ge_xSi_{1-x}O_2$ in hydrogen

W. S. Liu, J. S. Chen, and M.-A. Nicolet California Institute of Technology, Pasadena, California 91125

V. Arbet-Engels and K. L. Wang University of California, Los Angeles, California 90024

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We have synthesized nanocrystalline Ge in vitreous SiO_2 by annealing amorphous $Ge_{0.38}Si_{0.62}O_2$ in hydrogen at 700 °C. The germanium dioxide in $Ge_{0.38}Si_{0.62}O_2$ is thermodynamically unstable in the presence of hydrogen and thus precipitates out as elemental Ge. Elemental Si is not needed in this reduction process. Cross-sectional transmission electron microscopy reveals that the nucleation process is homogeneous, leading to a uniform distribution of small Ge crystallites imbedded in the remaining vitreous SiO_2 .

When $Ge_x Si_{1-x}O_2$ is in contact with unoxidized Si or $Ge_x Si_{1-x}$, the system is thermodynamically unstable. The germanium dioxide can be reduced to elemental Ge by Si or $Ge_x Si_{1-x}$ due to the large negative free energy of the reaction

$$\operatorname{GeO}_2 + \operatorname{Si}(\operatorname{or} \operatorname{Ge}_x \operatorname{Si}_{1-x}) = \operatorname{SiO}_2 + \operatorname{Ge}.$$
 (1)

Experiments with a $\text{Ge}_x \text{Si}_{1-x} O_2$ film on a $\text{Ge}_x \text{Si}_{1-x}$ layer (x=0.28 and 0.36) have shown that this reaction indeed occurs, but that the process is limited kinetically to the close vicinity (<10 nm) of the $Ge_xSi_{1-x}/Ge_xSi_{1-x}O_2$ interface, even after annealing at 900 °C for 3 h.¹ Paine et al.² investigated the system with a 451-nm-thick layer of Ge_{0.1}Si_{0.9}O₂ on top of an 8-nm-thick SiO₂ on a Si substrate. They find that the Ge precipitates throughout the entire thickness of its oxide after a 1-h, 800 °C annealing and attribute that precipitation to the reaction (1) despite the presence of an 8-nm-thick SiO₂ between the Ge_{0.1}Si_{0.9}O₂ layer and the Si substrate. It is well established that Si is essentially immobile in pure SiO₂ at 800 °C.² To explain a uniform distribution of Ge precipitates according to the reaction of Eq. (1) thus demands a very large hypothetical enhancement of Si diffusivity in SiO2 whose origin remains unknown.2

In this letter, we report that by annealing $\text{Ge}_x \text{Si}_{1-x} O_2$ (with x=0.38) in a H₂ ambient, Ge is also reduced from its oxidized state and precipitates in the form of nanometer-size Ge crystals that nucleate homogeneously throughout the oxide matrix. The process is driven by the reaction

$$GeO_2(in Ge_{0.38}Si_{0.62}O_2) + 2H_2 = Ge + 2H_2O.$$
 (2)

It is conceivable that this reaction also explains the results of Paine *et al.*'s experiment, thereby removing the necessity to invoke unexplained mechanisms if some H_2 was still present in the annealer. That this second pathway exists has also been pointed out by these same authors.³ A reduction reaction of type (2) is conceivable with other species, such as CO. In principle, the reaction pathway may also depend on the structure of the oxide.

A 540-nm film of $\text{Ge}_{0.38}\text{Si}_{0.62}$ was first grown epitaxially on a (100)Si substrate by molecular-beam epitaxy. Some samples from the wafer were then oxidized in a tube

furnace at 700 °C for 30 min in a wet ambient. The treatment transforms the top 120 nm of the Ge_{0.38}Si_{0.62} layer to amorphous Ge_{0.38}Si_{0.62}O₂ and leaves 420 nm of the Ge_{0.38}Si_{0.62} layer unoxidized. These samples shall be referred to as the "partially oxidized" samples. We also prepared some samples whose Ge_{0.38}Si_{0.62}O₂ film rested on a thick SiO₂ layer. The procedure was as follows: In order not to produce too thick a $Ge_{0.38}Si_{0.62}O_2$ layer, we first removed about 360 nm of the 540-nm-thick Ge_{0.38}Si_{0.62} film by oxidizing the sample at 700 °C in a wet ambient for 6 h and dissolving the oxide with a diluted HF solution afterwards. The etched sample was again oxidized at 700 °C for 2 h and then at 900 °C for 2 h. The treatment at 700 °C fully oxidizes the remaining Ge_{0.38}Si_{0.62} layer, and that at 900 °C produces about 360 nm of SiO₂ by oxidizing the Si substrate. We refer to these samples as the "fully oxidized" samples. The purpose of using these two types of samples is to see if the presence of elemental Si in immediate contact with the Ge_xSi_{1-x} oxide, or in its vicinity with a SiO₂ barrier in between, plays a role during the hydrogen annealing. Both sample types were then annealed in a hydrogen tube furnace at 700 °C for 1 h. The purity of the hydrogen gas used was about 99.95%. The pressure of hydrogen was initially 1 bar above atmospheric pressure and rose to 1.5 bar above atmospheric pressure at 700 °C. This rise is less than that of the absolute oven temperature because the furnace heats up only part of the tube. Some partially oxidized samples were also annealed in vacuum for comparison.

Figures 1(a) and 1(b) show the cross-sectional transmission electron micrographs of the partially oxidized sample before and after the hydrogen annealing. The corresponding electron diffraction patterns derived from illumination of both the oxidized and unoxidized $\text{Ge}_x \text{Si}_{1-x}$ layers are included. After the hydrogen annealing, the thickness of the unoxidized GeSi is about 420 nm, almost unchanged. The thickness of the oxide, however, decreases from about 240 to 210 nm. Only diffraction rings from amorphous but no polycrystalline material are seen in the pattern before the hydrogen annealing. Some rings of crystalline material appear in the diffraction pattern after the annealing. We identify them as belonging to polycrystalline Ge. Under high magnification, small, elongated precipitates are seen throughout the oxide (Fig. 2). Some of these



FIG. 1. Cross-sectional bright-field transmission electron micrographs of the partially oxidized sample: (a) before and (b) after the 700 °C/h hydrogen annealing. The corresponding diffraction pattern obtained from an illumination of both the oxide and the unoxidized GeSi layer are shown in (c) and (d).

precipitates show very clear lattice fringes of crystalline structure. No voids are observed in the oxide. We conclude from Figs. 1 and 2 that small Ge crystallites precipitate out of the oxide upon annealing in hydrogen. A similar conclusion is also drawn from the fully oxidized sample after the hydrogen annealing by virtue of the facts that polycrystalline Ge peaks are also found in its x-ray diffraction spectrum and that only absorption peaks belonging to SiO_2 , but none belonging to GeO_2 are observed in the infrared spectrum. Both peaks are present before the hydrogen anneal-



FIG. 2. Cross-sectional bright-field transmission electron micrograph of the partially oxidized sample after the hydrogen annealing. Small precipitates are clearly seen. The precipitates show clear lattice fringes of a crystallite, some of which are indicated by the arrows.



FIG. 3. 2-MeV He⁺ backscattering spectra of the partially oxidized sample before and after annealing in hydrogen at 700 °C for 1 h. (scattering angle of detected particles: 170 °C, beam incident at 7° from sample normal.)

ing. The size of these precipitates in the fully oxidized sample estimated from the x-ray peaks' width is about 7 nm, which is similar to that in the partially oxidized sample.

It is thus clear that Ge is reduced from its oxide state, and embedded in the silicon dioxide matrix after the hydrogen annealing in both samples. The thick SiO₂ between the Ge_{0.38}Si_{0.62}O₂ layer and the Si substrate in the fully oxidized sample evidently does not inhibit the precipitation of Ge. This proves that the elemental Si has nothing to do with the precipitation of Ge observed here and that Ge does not precipitate via reaction (1) after the hydrogen annealing, unless one accepts the possibility that the diffusivity of the moving species in the SiO₂ (Si and/or the oxidant) required to complete reaction (1) is much enhanced by the presence of hydrogen. If this is the case, that is, that reaction (1) is still the main one, several consequences should be observed. First, the total amount of oxygen in the sample should be conserved. Second, additional Si should be oxidized after the hydrogen annealing. In the partially oxidized sample, this additional oxidation of Si should also result in a decrease of the unoxidized layer thickness and possibly the pileup of Ge near the unoxidized Ge_{0.38}Si_{0.62} layer.

To look for the above consequences, the partially oxidized sample was analyzed by 2-MeV ⁴He backscattering spectrometry. The spectra before and after the hydrogen annealing for 1 h is shown in Fig. 3. Within the resolution of backscattering spectrometry, no germanium or silicon is lost after the H₂ annealing, as should obviously be the case according to both reactions (1) and (2). About 40% of the oxygen is lost, however. Because the signals of the oxygen and the Si substrate overlap, we estimate the error of this loss to about $\pm 20\%$. It is therefore evident that a significant fraction of the oxygen is gone after the annealing. The original oxide composition derived from the backscattering spectrometry is uniform and has the composition Ge_{0.37}Si_{0.63}O_{2.1} with an error of $\pm 5\%$. This result is consistent with our previous oxidation study.⁴ After the

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annealing the oxide is still compositionally uniform but has changed to about $Ge_{0.36}Si_{0.64}O_{1.28}$ with an error of $\pm 5\%$. This composition is equivalent to 0.36 Ge+0.64 SiO₂ and strongly suggests that the layer is a mixture of elemental Ge and silicon dioxide. Such a composition is consistent with the conclusion drawn from the transmission electron microscopy which indicates that the Ge is reduced from its oxide state after the hydrogen annealing (Fig. 1). Furthermore, the unoxidized portion of the GeSi layer remains unchanged in composition and in thickness during the hydrogen annealing within the resolution of the backscattering spectra. No pileup of the Ge in the unoxidized GeSi laver is observed. None of the consequences enumerated above are thus observed. Instead, we find further evidence in support of reaction (2). Finally, a partially oxidized reference sample annealed in vacuum instead of hydrogen at 700 °C for 1 h has indistinguishable backscattering spectra before and after the heat treatment in vacuum. This outcome is consistent with our previous stability study¹ and shows that the reaction of Eq. (1) cannot explain a uniform reaction of $Ge_xSi_{1-x}O_2$ throughout the film thickness at 700 °C since such a significant precipitation only occurs in the hydrogen ambient but not in vacuum. The composition change of the oxide observed in Fig. 1 is thus due to the hydrogen ambient.

Since none of the consequence of reaction (1) is observed here, we conclude that the elemental Si is not needed for the precipitation of the Ge observed here. The formation of essentially all of the Ge is thus due to reaction (2).

The standard free energy, G^0 , of reaction (2) is indeed negative, and is about 2.3 kcal/mol after a solid-solution correction of the value of 4.2 kcal/mol for pure GeO₂ at 700 °C.⁵ This standard free energy is small. The partial pressure ratio of H₂ and H₂O is therefore the key factor controlling the free energy and the way this reaction goes (reduction or oxidation). It can be simply calculated that under H₂ partial pressure, P_{H_2} , and H₂O partial pressure, P_{H_2O} , the free energy of reaction (2) is given by $G^*=G^0$ $+2RT \ln(P_{H_2O}/P_{H_2})$. The partial pressure of H₂ in our system is about 2.5 atm; that of H₂O is unknown, but certainly extremely small as a result of preannealing with Ti getters and multiple purges with H₂ of the high-vacuum tight system. This $P_{\rm H_2O}/P_{\rm H_2}$ ratio thus makes the free energy very negative and greatly drives reaction (2) to the reduction direction. The diffusivity of hydrogen in SiO₂ is high even at 700 °C (about $10^{-6} \text{ cm}^2/\text{s}$).⁶ A high diffusivity of hydrogen probably also exists in the GeSi oxide. This large diffusivity of hydrogen coupled with a large driving force makes the critical radius (the smallest stable precipitate) of the germanium precipitates small and causes the Ge to nucleate homogeneously in the oxide, resulting in nanocrystalline Ge precipitates throughout the oxide.

In conclusion, we have shown that hydrogen reduces GeO_2 to Ge via reaction (2) when a film of the GeSi dioxide is annealed in a hydrogen ambient. Such a hydrogen annealing also provides a new alternative to synthesize the nanocrystalline precipitates of Ge in an amorphous SiO_2 matrix. These precipitates show interesting optical properties and strong photoluminescence.

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