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Visible photoluminescence from nanocrystalline Ge formed by H_2 reduction of $Si_{0.6}Ge_{0.4}O_2$

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Samples of nanocrystalline Ge embedded in SiO₂ that display visible photoluminescence were synthesized from chemical vapor deposition-grown Si_{0.6}Ge_{0.4} in a two step process of hydrothermal oxidation using steam at 25 MPa and 475 °C followed by annealing at 750 °C in flowing forming gas ($80/20:N_2/H_2$). A broad photoluminescence band, peaked at 2.14 eV (580 nm) with a full width at half maximum of 0.3 eV, was observed in samples that were annealed at 750 °C in flowing forming gas for 10, 30, and 60 min. As-oxidized (i.e., unprecipitated) samples show no photoluminescence peak when excited under identical conditions.

The optical properties of nanometer-sized indirect band-gap semiconductors is an area of great fundamental and practical interest. Visible photoluminescence (PL), for example, has been reported from porous Si,¹ from nanocrystalline Ge,^{2,3} and from lithographically patterned planar Ge structures.⁴ To date, the bulk of the PL data on nanocrystalline Ge come from samples formed using cosputtering of Ge and SiO₂.^{2,3,5,6} To demonstrate that PL in the Ge-based system is independent of the synthesis method we have used the following alternative technique for the formation of Ge nanocrystals. Compositionally congruent oxide alloys of $Si_{1-x}Ge_xO_2$ can be formed by oxidizing $Si_{1-x}Ge_x$ alloys grown epitaxially on (001) Si substrates using either dry O₂ at 550 °C and 70 MPa⁷ or steam at 25 MPa and 475 °C.8 In the as-oxidized condition the Ge in the oxide is present in the SiO₂ network as GeO₂ and, to a lesser extent, GeO.⁷ The chemically incorporated Ge in these alloy oxides can be reduced by a variety of species, including Si⁸ and H₂.^{9,10} In this letter we describe the H₂ reduction approach to Ge nanocrystalline materials synthesis and show that materials formed by this method display PL spectra that are similar in peak position and shape to those reported in the earlier nanocrystalline Ge work.^{2,3}

Alloys of Si_{0.6}Ge_{0.4} were grown on $\langle 100 \rangle$ Si by chemical vapor deposition (CVD) to a thickness of approximately 400 nm. Before oxidation the wafers were RCA cleaned after which they were immediately loaded into a high pressure oxidation chamber. The oxidation was carried out in a silica lined high pressure reactor vessel constructed of Rene 41 alloy. The volume of water required to generate a pressure of 25 MPa at 475 °C was calculated from P-V-T data for water above the critical temperature. The reactor was heated in a 10 cm diam tube furnace and temperature control was maintained by means of a thermocouple attached to the outside of the reactor. A set of samples were produced in which the entire 400 nm thick alloy layer, and part of the underlying Si substrate, were consumed by oxidizing for 1.5 h. These samples were annealed in flowing forming gas $(80/20: N_2/H_2)$ at 750, 800, and 850 °C for times ranging between 1 and 120 min. After each run the samples were characterized using Raman spectroscopy and selected samples were evaluated using cross-sectional transmission electron microscopy (TEM). Photoluminescence from as-oxidized and annealed samples was investigated using the 488 nm line of an Ar⁺ laser.

In these reduction experiments the N_2 in the forming gas plays no known role while the H_2 causes precipitation in the oxide via the following reaction,

$$GeO_2(In solution with SiO_2) + H_{2(v)} = Ge + H_2O_{(v)}$$
.

Using Gibbs free energy of formation data¹¹ for hexagonal GeO_2 , the standard Gibbs free energy of reaction for the H_2 reduction is estimated to be about -5 kJ/mole at 750 °C. From this it is straightforward to calculate that, at this temperature, this reaction will not proceed if the H_2O/H_2 activity ratio is above 0.9. A similar calculation for the reduction of SiO₂ by H_2 reveals that the H_2O/H_2 activity level necessary for the reduction of SiO₂ at 750 $^{\circ}$ C is of the order 10⁻¹⁰ which is well below the H₂O purity level of the forming gas (99.99%) used in this work. Consequently, the H₂O/H₂ ratio in the gas phase is set well above that which is necessary for the reduction of SiO₂ but far below that which is needed to reduce GeO₂. Based on these thermodynamic considerations it is expected that pure Ge (rather than an alloy of Si and Ge) will precipitate out of the oxide as a result of the H2/GeO2 reaction. As stated above, the oxidation potential (given by the H_2O/H_2 activity ratio) of the gas phase is easily set, however, within the oxide it is determined by the rate at which the reaction product (i.e., H₂O) can diffuse out of the oxide. Since diffusion of H₂O species¹² is significantly slower than the diffusion of H₂ species¹³ in silicon oxide this suggests that the reaction is rate limited by outdiffusion of H_2O . This is supported by TEM studies⁹ that show that the precipitation reaction proceeds via the passage of a moving boundary which starts at the top surface of the

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FIG. 1. Raman spectra showing the Ge $\Gamma_{25'}$ phonon mode in (a) the as-grown condition and after (b) 10, (c) 30, (d) 60, and (e) 120 min at 750 °C in N₂/H₂.

oxide and passes through the oxide thickness. The velocity of this moving boundary is probably determined by the rate of diffusion of H_2O out of the oxide.

Figure 1 shows a series of Raman spectra that were acquired from the unannealed oxide alloy (part a) and after annealing at 750 °C in N₂/H₂ for 10, 30, 60, 120 min (b-e) respectively. These data were acquired using the 514.5 nm line of an Ar⁺ laser, a step size of 0.2 cm⁻¹ and a sampling gate time of 6 s. Note that the unannealed sample shows no evidence of the Ge $\Gamma_{25'}$ phonon mode around 300 cm⁻¹ but that after 10 min at 750 °C in the H_2 reducing environment it is clearly visible above the background. The peak breadth in Fig. 1 was estimated from the full width at half maximum (FWHM) and was seen to decrease with increasing time at temperature. With increasing time at temperature the peak intensity increase due, in part, to increased coupling efficiency between the incident light and the larger particles and to an increase in Ge precipitate volume in the oxide. A qualitative relationship between particle size and the peak breadth associated with the Ge $\Gamma_{25'}$ phonon mode has been reported by Fujii et al.⁶ The basis for this estimation of the average particle diameter comes from phonon localization within nanometer sized crystallites which results in partial breakdown of the Raman selection rule and hence causes peak broadening. Figure 2(a) shows the Ge Raman peak FWHM measured from samples annealed at 750, 800, and 850 °C for time ranging between 1 and 120 min. In Fig. 2(b), the method of Fujii et al.⁶ was used to relate peak breadth (FWHM) to the average Ge particle size. Although this relation provides only a qualitative estimate of average particle size, the trends can be clearly seen; longer times and



Annealing Time (minutes)

FIG. 2. (a) Full width at half maximum of the Raman Ge $\Gamma_{25'}$ phonon peak as a function of time at 750, 800, and 850 °C, and (c) estimated average particle size as a function of time at temperature calculated from (a) using the approach of Fujii *et al.* (Ref. 6).

higher temperatures result in larger average particle size.

Figure 3 shows a cross-sectional TEM image of a sample that has been reacted in flowing N_2/H_2 gas for 120 min at 750 °C. The annealed microstructure of the Si_{0.6}Ge_{0.4}O₂



FIG. 3. Cross-sectional TEM image of the oxide alloy after annealing in N_2/H_2 for 120 min. The precipitate size distribution varies through the oxide thickness and is described in the text in using labeled regions (a)-(e).



FIG. 4. A high resolution TEM image showing 5 nm diam Ge precipitates (left-hand side) as well as region of smaller crystalline contrast (right-hand side).

consists of five regions [labeled (a-e)] which vary in average precipitate size and numerical density. Latticeresolution TEM studies reveal no evidence of small (<5 nm) precipitates in region (a) while regions (c) and (e) were seen to contain particles that range in size from 3 to 5 nm. A representative lattice resolution image from region (e) is presented in Fig. 4 and shows areas of crystalline contrast that are 4–5 nm in size as well as regions, less well defined, that are about 3 nm in size. In agreement with the Raman results presented in Fig. 1, cross-sectional TEM shows no evidence of Ge (either amorphous or crystalline) in the unannealed oxides.

Photoluminescence studies were performed on the unannealed material and on samples that were annealed at 750 °C in forming gas for 10, 30, and 60 min. Figure 5 shows PL spectra for these samples due to excitation by the 488 nm line of a 100 mW Ar⁺ laser focused to a 0.1 cm diam spot. Samples in the as-oxidized condition [Fig. 5, curve (a)] showed no PL peak whereas after 10 min at 750 °C in flowing forming gas the samples show strong orange luminescence which is easily visible to the unaided eye and which, as shown by curve (b) Fig. 5, is centered at 580 nm (2.14 eV) with a peak breadth of 0.3 eV. The same broadband PL is observed for samples annealed for 30 min [curve (c)] and 60 min [curve (d)] but with much lower intensity. The observation that PL intensity decreases with increasing N2:H2 annealing time and increasing average particle size (as indicated by Fig. 2), suggests that particles above maximum size do not contribute to the PL peak. Although the exact physics of the photoluminescence process that we have experimentally observed currently remains unclear, it is important to note that our PL results are similar in peak position and breadth to the results presented by others^{2,3} for Ge nanocrystalline materials formed by a completely different process.

We have demonstrated photoluminescence from samples that contain nanocrystalline Ge embedded in a SiO_2





Photon Energy (eV)

FIG. 5. PL spectra excited with the 488 nm line of a 100 mW Ar⁺ laser taken from (a) the as-oxidized sample, and after annealing for (b) 10, (c) 30, (d) 60 min at 750 °C in N_2/H_2 .

matrix formed using a new technique that uses H_2 reduction of $Si_{0.6}Ge_{0.4}O_2$. The average precipitate size was controlled through adjustment of post-oxidation forming gas annealing temperature and time. Samples prepared by this new method show a PL peak located at 2.14 eV (580 nm) with a FWHM of 0.3 eV similar to that seen by others.²

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