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Growth and characterization of Ge nanocrystals

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We have synthesized Ge nanocrystals of sizes 4, 8, and 12 nm by ion-implanting Ge^+ ions into thermally grown SiO_2 films and subsequent annealing of the films at 830°C for 30 min in nitrogen. These films were characterized by x-ray, transmission electron microscopy (TEM), and Raman spectroscopy. A distribution of particle size was identified by TEM in a 100 nm band below the surface. Particle sizes were estimated by these 3 techniques.

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Ion beam synthesis of semiconductor nanoparticles in thermally grown SiO_2 films has recently drawn a considerable interest because of its ease and simplicity in growing particles of varying size. Both Si [1] and Ge[2-3] nanoparticles have been grown by ion-implanting either Si^+ or Ge^+ ions into thermally grown SiO_2 films and subsequent annealing at temperatures 800°C or higher in a nitrogen environment. Due to their compatibility with microelectronics, both of these group IV compounds in the nanocrystalline phase offer a variety of applications due to their interesting optical [4] and electronic properties[5]. However, the growth of these nanoparticles with a uniform size distribution has been a challenge to the material scientists. A narrow uniform size distribution of these nanoparticles would enhance the physical properties of these materials which would eventually lead to their successful applications to optoelectronic devices.

In this report we describe the synthesis of Ge nanocrystals by ion-implanting Ge^+ ions into 500 nm thick SiO_2 films and subsequent annealing. SiO_2 films were grown by thermally oxidising a 4" Si wafer. These wafers were then cut into a size of 1 cm^2 in which Ge^+ ions were implanted. Three different doses of Ge^+ ions at an energy of 190 keV were used to grow different size nanocrystals. These doses were 1×10^{17} (Ge1), 2×10^{17} (Ge2), and 3×10^{17} (Ge3) ions/ cm^2 . Trim calculations [6] show a projected range of 250 nm below the surface with a maximum atomic density of 16% for Ge1 at a depth of 130 nm. Ge nanocrystals were formed when the as-implanted samples were annealed at 830°C for 30 min in a nitrogen atmosphere. They were annealed at the

same time. We then characterize these samples by x-ray, high-resolution transmission electron microscopy (HRTEM), and Raman spectroscopy.

The XRD pattern from the annealed samples exhibited the (111), (220), and (311) reflections similar to crystalline Ge (c-Ge) diffraction peaks but were broadened due to the random distribution of Ge crystallites. Figure 1 shows the (111) Bragg-diffraction peak from the annealed films and a c-Ge wafer. The mean sizes were determined from the 2θ full-width at half-maximum (FWHM) of the (111) peak. The accuracy of this estimate is about ± 0.5 nm.

Figure 2(a) shows a cross-section (CS) bright field TEM image of an annealed film. The low and high magnification images were obtained with JEOL electron microscopes (Model JEM 300CX and JEM 4000EX). In accordance with the TRIM calculation, Ge clusters were arranged in a band at a depth of 120 nm below the surface. The band boundary toward the surface shows larger crystallites (>10 nm), but smaller sizes were observed at a depth of 150 nm. Figures 2(b) and (c) show HRTEM images of two annealed films. We show only a small (2.1 nm) and a large size (7.8 nm) nanocrystals from these annealed films. The lattice fringe spacings (0.326 nm) match that of the c-Ge. It is not clear why we observed a large precipitation of Ge clusters near the surface. We are currently conducting more investigation of the cluster formation by annealing these films in a temperature controlled high-vacuum furnace.

Figures 3(a) and (b) show a histogram of the particle-counts as a function of particle-size from these samples. These histograms were obtained from plan-view TEM images. The solid line is a fit to the histogram with a log-normal

distribution function [7]. The estimated sizes from CS-TEM images were slightly higher and closer to the values obtained from x-ray (Fig. 1).

Figure 4(a) shows the phonon dispersion [8-9] of the transverse (TO) and longitudinal optical modes (LO) along the (100) direction as a function of the phonon wave vector q in the first Brillouin zone. Note that a is half the lattice constant for the cubic unit cell of a diamond lattice. The neutron data [8] are shown by three different symbols and the solid lines are cubic-polynomial fits to these data. It is important to point out that the phonon dispersion along the (110) and (111) directions are very similar [9] to the (100) direction except at the zone boundary. Figures 4(b) and (c) show the lineshapes of Raman spectra for the two optic modes as a function of particle size. The Raman line shape was obtained from the following formula [10],

$$I = \int_0^q \frac{|c(0,q)|^2 d^3q}{[\omega - \omega(q)]^2 + \left[\frac{\Gamma}{2}\right]^2} \quad (1)$$

where $\omega(q)$ is obtained from either the LO or the TO phonon dispersion curve shown in Fig. 4(a). The wave vector q is expressed in units of $2\pi/a$ where a (5.6 Å) is the Ge lattice constant. The parameter $c(0,q)$ is estimated from the relationship:

$$|c(0,q)|^2 = \exp\left(-\frac{q^2 L^2}{4a^2}\right) \quad (2)$$

where L is the average size of a Ge nanocrystal. For a particle size of 300 Å or higher, we fit the lineshape of the c-Ge phonon spectra by choosing ω and Γ as 300.6 cm^{-1} and 7.5 cm^{-1} , respectively. We then vary L to obtain several Raman lineshapes shown by Figures 3(b) and (c).

The red shift of the Raman spectra as a function of particle size is caused by the decrease in phonon frequency (ω) as a function of q . Near the zone boundary the LO phonon frequency decreases considerably as compared to the TO phonon frequency. As a result one observes a considerable broadening of the LO spectra for smaller particles. The shift of the LO phonon frequency for a 20 Å particle is about 7 cm^{-1} from the bulk phonon frequency, while that for the TO_1 mode is 12.6 cm^{-1} .

Figure 4 (a) shows the Raman spectra from the three annealed samples along with a c-Ge sample. The shift of the phonon mode is about $2\text{-}3 \text{ cm}^{-1}$ for all samples as compared to the phonon frequency (300.6 cm^{-1}) of c-Ge. The Raman spectra were taken with a cooled CCD array of resolution of $1.7 \text{ cm}^{-1}/\text{pixel}$ at an excitation wavelength of 488 nm. The uncertainty in the measurement of the peak position is roughly 1 pixel. The resolution of our spectrometer [10] is about 6 cm^{-1} . With this kind of instrument resolution, it is difficult to estimate the particles sizes between 40 and 100 Å by probing the shift and broadening of the phonon band of Ge nanocrystals. According to the theoretical model, the peak positions vary between 297 and 300 cm^{-1} when the sizes were varied between 40 and 100 Å. For Si nanocrystals [10], the phonon frequency was found to shift by about 10 cm^{-1} from the bulk phonon frequency

(521 cm^{-1}) for a particle of size 40 Å and that's why Raman spectroscopy was useful in estimating the particle size of Si nanocrystals.

Figures 4(b) and (c) show a fit to the lineshape of the Raman spectra of samples Ge1, Ge2, and Ge3. A shoulder at 280 cm^{-1} was observed in all samples that we attribute to amorphous Ge phonon band [9]. The lineshape (solid line) was obtained from the theoretical model using Eqn. (1). As we anticipated, we measure approximately the same size for the three annealed samples since we found the shift and broadening of the spectra identical in all three samples. The only explanation that we can offer for measuring the same sizes in all samples is the instrument resolution. The shift and broadening of the phonon band are not large enough to be discerned by our instrument resolution. Note that in reference 11, significant shift and broadening of the phonon spectra were only observed for particles of size less than 15 Å.

In summary, we have synthesized three sizes of Ge nanocrystals grown by ion-implanting Ge^+ ions into SiO_2 films and subsequent annealing. We estimated the mean particle size of the annealed samples to be 4, 8, and 12 (± 1 nm) by x-ray diffraction and HRTEM.

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Figure Caption

Figure 1. x-ray diffraction spectra of three annealed and a c-Ge samples. The peak at 26.5° has been identified as the GeO_2 phase. The broad peak at 27.35° has been identified as the cubic phase of Ge.

Figure 2. (a) Cross-section TEM image of the SiO_2 layer of an annealed sample. The Ge clusters can be identified by the dark spots. HRTEM images of samples (b) Ge1 and (c) Ge2. The (111) lattice planes of Ge clusters can be easily seen.

Figure 3. Histograms (shaded areas) of size distributions from the plan-view images of two annealed samples. The solid line is a fit with a log-normal function. The mean diameters of particles are expressed as D_1 and D_2 .

Figure 4. (a) Dispersion curves for the three optic modes of c-Ge. Selective neutron datapoints are shown by the symbols, while the solid line is a cubic polynomial fit to the data. Raman lineshapes for the (b) LO and (c) TO modes were calculated for different sizes.

Figure 5. (a) Raman spectra of three annealed and a c-Ge sample in a backscattering geometry. A vertically polarized incident laser beam with laser power of 10 mW was focused into a $300\ \mu$ spot. The scattered beam was unpolarized. (b) and (c) Theoretical fits to the experimental Raman data. Note that a similar 50 Å fit is also obtained for the TO_2 mode and is not shown.

Raman Shift (cm^{-1})