Oxidation Characteristics of Ge Nanocrystals Embedded in an SiO_2 Matrix

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Abstract

An oxide layer of a single crystal wafer grows at the expense of a certain thickness of the wafer being consumed. Similarly, oxidation of a small spherical particle will result in the formation of an outer oxide shell whose thickness increases with a subsequent decrease in the core size of the particle. Ge nanocrystals embedded in a SiO_2 matrix are fabricated by a rf co-sputtering technique. A post-isothermal anneal produces well-formed microcrystals. Oxidation of the nanocrystals is carried out by bubbling oxygen through water. The size reduction induced thereby is studied by Raman and optical absorption spectroscopy.

Introduction

Oxidation of a single crystal wafer proceeds with a certain thickness of the wafer being consumed. Extending this analogy to a spherical nanoparticle, oxidation will proceed with the consumption of a certain outer thickness of the nanoparticle . This will result in the growth of an oxide shell extending to a depth of a few nanometers surrounding the nanocrystal core, thereby leading to a reduction in the core size of the nanocrystal. Oxide layer formation on low-dimensional systems and their characteristics have been sparsely investigated. Hayashi *et* al. have reported that a thermal oxidation at around 1000℃ causes a complete oxidation of silicon microcrystals[1]. In the recent past, some groups have reported oxidation as a technique to fabricate nanocrystals as well as to reduce their sizes. Ge nanocrystals embedded in a SiO_2 matrix has been synthesized by ultraviolet illumination[2] as well as thermal oxidation[3] of SiGe strained layers. Si nanowires of 10 nm diameter have been effectively thinned down to 5 nm by a light oxidation treatment[4]. Another study of oxidation of silicon small particles showed that the rate of oxidation varied with the particle size, with the larger sized particles oxidizing more rapidly than the smaller sized ones[5]. It appears, therefore, that oxidation is effective in reducing the particle sizes as well as narrowing down the size distribution to achieve a uniformity of sizes. These features of oxidation have motivated us to attempt an oxidation of Ge nanocrystals embedded in an SiO_2 matrix. Nanocrystals embedded in a glass matrix form a particularly stable system.We focus on a combination of Raman and optical absorption spectroscopy to study the size changes. The long wavelength optical phonons in ionic crystals show a strong size dependence due to the modification of the long range Coloumb forces. In addition, there will also be a modification of the short-range forces which would be manifested in the Raman spectrum. Therefore, size effects will be observed for the nonpolar optical phonons in covalent crystals like silicon and germanium. The size effect would also be manifested as a blue shift in the optical absorption spectrum.

Experimental

Ge nanocrystals embedded in a SiO_2 matrix were fabricated by the conventional radio-frequency co-sputtering technique. Several small pieces of Ge chips(5 mm×5 mm) were placed on a circular SiO_2 plate. The substrate used was a p-type (100) oriented silicon wafer for Raman and SiO_2 for optical absorption measurements. The sputtering was performed with a rf power of 100 W in pure argon gas of 5×10^{-4} Torr. A post-isothermal anneal in an argon atmosphere was done to grow well developed microcrystals. These samples are hereafter referred to as Ge-doped glass. The formation of nanocrystals was observed by transmission electron microscopy. Oxidation was carried out by bubbling oxygen through water at 800℃ for sixty minutes.

Raman measuremets were carried out at room temperature in a right-angled scattering

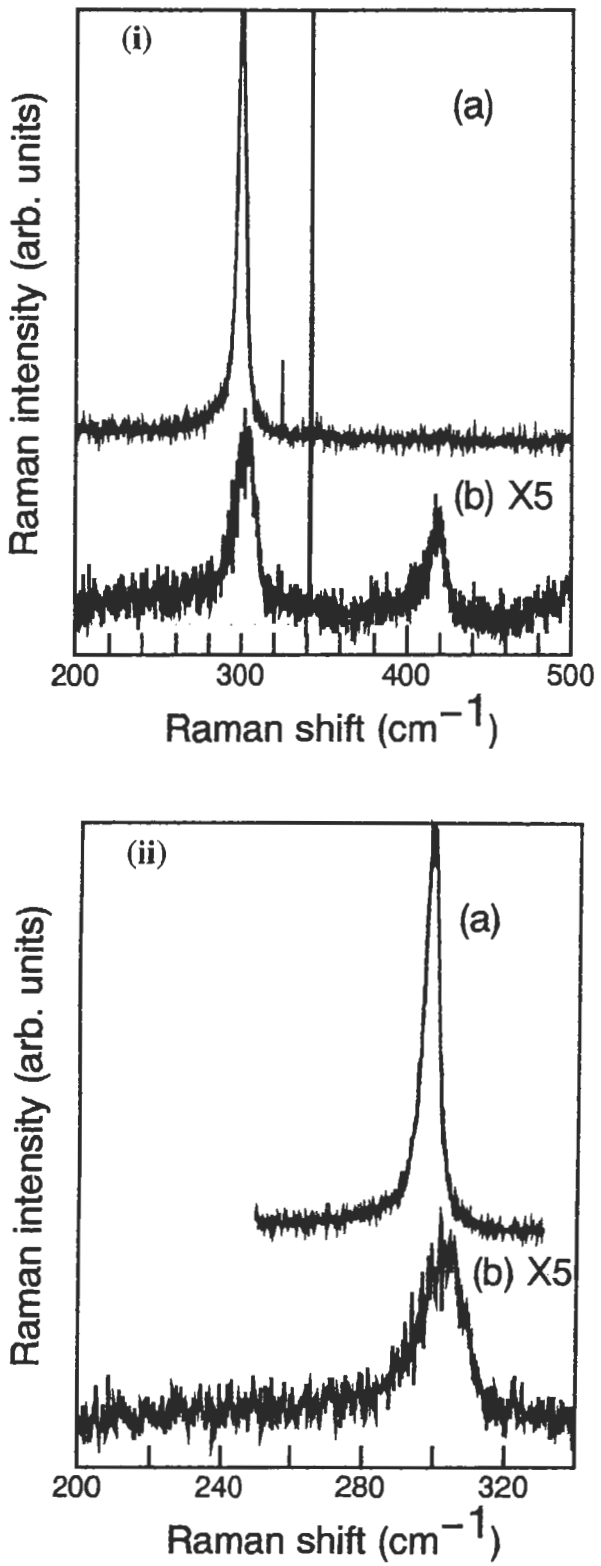

Fig.1 Raman spectra of Ge-doped glass (a) annealed in Ar atmosphere at 800℃ and (b) same sample subjected to a wet oxidation at 800℃ for one hour. (i) shows the appearance of the oxide peak and (ii) is the extended spectra in the region of the optical phonon mode of Ge.

geometry. The 514.5 nm line of the Ar-ion laser was used for exciting the sample and low laser powers were used to avoid sample heating. The scattered light was analyzed with a double monochromator and detected by a PMT. The data was recorded using photon counting electronics.

Optical measurements were performed with a Shimadzu UV-VIS spectrometer.

Result and discussion

The Raman spectra of Ge-doped glass annealed at 800℃ prior to and post oxidation is shown in Fig. 1. The peak at 300 cm^{-1} is the degenerate one-phonon diamond-like Raman mode of bulk germanium. Oxidation of the Ge-doped glass is confirmed by the occurence of the peak at around 420 cm^{-1} in the oxidized sample. This peak corresponds to the formation of quartz-type GeO_2[6], which is trigonal with Ge atoms located in the center of linked GeO tetrahedra.

We analyzed the spectral changes of the optical phonon at 300 cm^{-1} mode before and after oxidation. The changes in the particle size can be understood from the lineshape changes of this mode. The modifications include:(i) a decrease in the peak intensity (ii) an increase in the FWHM (iii) a shift in the peak frequency towards higher value and (iv) an asymmetry on the lower energy side of the peak. The Raman spectral modifications are indicative of a difference in the particle size. This can be understood in terms of the phonon confinement theory which describes the Raman lineshapes of low-dimensional materials. The confinement of the phonon to a finite volume, for instance, to the size of the nanocrystal, causes a relaxation of the normally allowed $\bar{q}=0$ selection rule and phonons with $\bar{q}$ within a region $2\pi/d$, where d is the size of the nanocrystal, participate in the Raman scattering process. This leads to an asymmetric lineshape of the optical phonon. This theory is used to estimate the particle sizes of semiconductor nanocrystallites.

The Raman lineshape of the first-order optical phonon is given by[7]

$$I(\omega)=\int \frac{d^3q|C(0,\bar{q})|^2}{(\omega-\omega(\bar{q})^2+(\Gamma_0/2)^2}$$

where $\omega(\bar{q})$ is the phonon dispersion relation chosen appropriately to agree with the neutron scattering data, Γ_0 is the natural linewidth of

bulk germanium and $C(0,\bar{q})$ is the Fourier transform of a phonon confinement function chosen to be $\exp(-q^2L^2/4)$, where L is the diameter of the microcrystal.

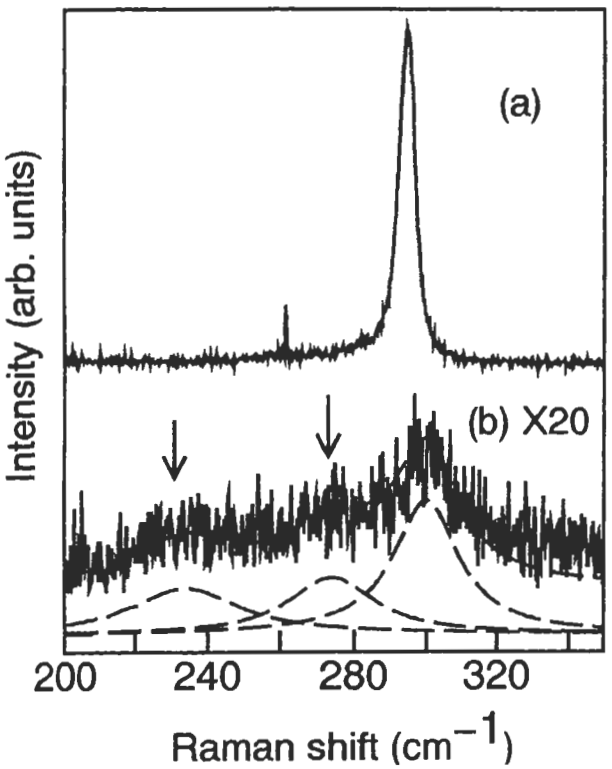

Fig.2 Raman spectra of Ge-doped glass :(a) annealed in Ar atmosphere at 700℃and (b) d to a wet oxidation at 800℃ for one hour. Peaks marked by arrows are representative of a tetragonal form of Ge.

Figure 2 depicts the Raman spectra of Ge-doped glass annealed in an argon atmosphere at 700℃ and then oxidized at 800℃ for one hour. The optical phonon mode shows lineshape changes similar to the previous sample. New features,at around 240 and 270 cm^{-1},also appear in addition to the diamond-like mode. The frequency positions of these modes agree with those of ST-12 [8],which is a high pressure form of germanium having a

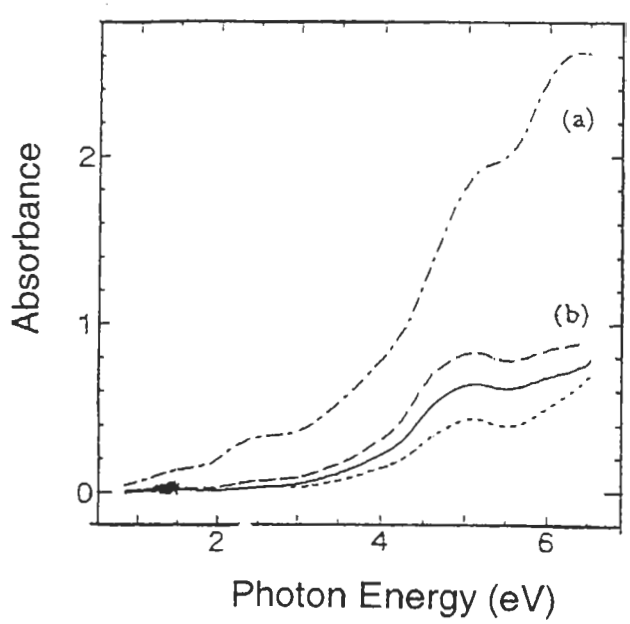

Fig.3 Absorption spectrum of Ge-doped glass:(a) unoxidized and (b) oxidized at 600℃ (···),700℃ (—) and (- -) 800℃.

tetragonal structure. The occurence of these new modes upon oxidation also support a particle size decrease. There are theoretical [9] and experimental [10] reports of a crystal phase transformation from a diamond to a tetragonal structure for sizes in the range of 4-5 nm. The size estimated from PCM calculations is close to this value. A summary of the changes in the FWHM and the particle size are tabulated in Table 1.

The absorption characteristics upon progressive oxidation is illustrated in Fig.3. The unoxidized Ge-doped glass exhibits a behaviour almost similar to bulk Ge. The absorption in the low energy region (1-2 eV) is rather flat and begins to increase for photon energies larger than 2 eV. The onset of absorption in the oxidized sample as compared to the unoxidized sample appears to shift to higher energies by 1 eV. Bulk Ge has an indirect bandgap of 0.67 eV and is highly absorbing in the visible region.

Table 1:Summary of changes in the FWHM of the optical phonon mode and particle size of Ge-doped glass induced by oxidation

Annealing temperature (℃)	FWHM of the optical phonon mode (in cm^{-1})		Size estimated from phonon confinement model(in nm)	
	before oxidation	after oxidation	before oxidation	after oxidation
800	4.7	11.5	14.0	8.0
700	5.2	14.0	12.0	6.0

Small particles,on the other hand,are nearly transparent in this region. This blueshift of the absorption spectrum indicates a reduction in size occuring due to quantum confinement of carriers

Conclusion

Ge nanocrystals were fabricated by a rf co-sputtering technique and oxidized in an attempt to reduce their sizes further. Raman spectral changes of the optical phonon mode show evidence of a reduction in the particle sizes. The change in the absorption spectra of the oxidized sample also supports an oxidation-induced decrease in the particle sizes.

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