Local structure of Ge nanocrystals embedded in SiO_2 studied by X-ray absorption fine structure

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Local structure of Ge nanocrystals embedded in SiO_2 has been studied by X-ray absorption fine structure on the Ge K-edge. The XANES and EXAFS results indicate that Ge atoms in samples with the Ge concentration x=25-40 mol. % are coordinated with oxygen atoms, while they exist as amorphous Ge clusters in samples with x=60 mol. %. Upon annealing, completely relaxed crystalline Ge phase is formed for samples with x=60 mol. %, in contrast to the x=25-40 mol. % sample, which show little or no indication of Ge cluster formation. A possible mechanism of Ge nanocluster formation is discussed.

1. Introduction

Recent years have witnessed growing interest in Ge and Si nanostructures. This interest is to a large extent due to the possibility that radiative efficiency of indirect optical transitions can be significantly increased if the size of the semiconductor is in the nanometer-scale range (Takagahara and Takeda, 1992). Intense visible photoluminescence from porous silicon is a typical example. It was also argued, based on a comparison of the electronic properties of Ge and Si, that it is likely to be even easier to change the electronic structure around the band gap of Ge (Maeda, 1995). A number of groups have reported the formation of Ge nanocrystals embedded in SiO_2 by different methods and intense photoluminescence around 2.3 eV has indeed been observed (Maeda, 1995, Okada and Kanemitsu, 1996).

In this paper, we report the results of an X-ray absorption study of the formation of Ge nanocrystals embedded in a SiO_2 matrix.

2. Experimental details

The samples were prepared by co-deposition of Si and Ge oxides onto Si(001) substrates with about 3-5 nm thick native oxide by radio-frequency (rf) magnetron sputtering. Two kinds of substrates, namely Si(001) and quartz glass have been used. The thickness of the samples was in a 500 nm to 1 mm range and Ge concentration varied from 25 to 60 mol.%. After deposition, the samples were annealed for 1 h at 800°C in an argon atmosphere which produced nanocrystals with a characteristic size of 6-8 nm. More details on the sample preparation can be found elsewhere (Maeda, 1995).

X-ray absorption experiments were performed at BL 13B of the Photon Factory. A double crystal Si(111) monochromator designed for a high heat-load wiggler (Oyanagi H, Haga K, and Kuwahara Y, 1996) was used. The measured energy resolution at the Cu K-edge (8.980 keV) was 2.0 eV with a partially limited vertical beam size. Extrapolating the function, the energy resolution is expected to be ca. 4 eV at the Ge K-edge energy.

The stability of energy position was monitored by the independent XANES measurements of reference materials, i.e., copper foil and bulk c-Ge, the former being the calibration point. It was found that the energy scale was stable during the experiment extending to 6 days within ± 0.0002 degrees in Bragg angle, which amounts to ca. 0.57 eV in uncertainty.

All measurements were performed in a fluorescence mode at room temperature. As a fluorescence X-ray detector, we have used a 19-element pure Ge detector. The output of single-channel analyzer for each detector channel was recorded in 12-channel CAMAC counters and normalized by the incident beam intensity measured by an ionization chamber filled with dry nitrogen gas.

Data analysis was carried out utilizing FEFF-8 and UWXAFS-3 packages.

3. Results

Figure 1a shows the Ge K-EXAFS oscillations for as-made and annealed samples with 60 mol.% Ge content after subtraction of smooth backgrounds due to the atomic absorption from the fluorescence yield spectra. The EXAFS oscillations multiplied by k [$k\chi(k)$] were Fourier-transformed (FT) using the region extending from 3 to 16 $Å^{-1}$ (Fig. 1b).

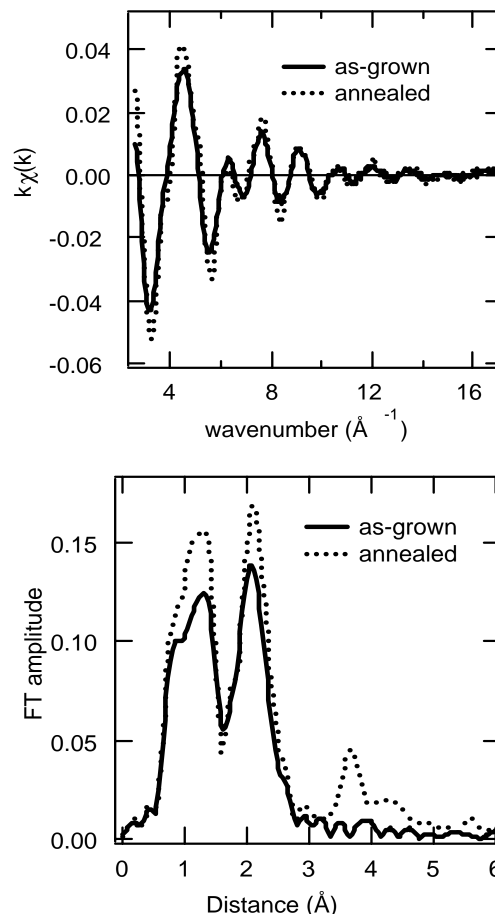

Figure 1
Raw EXAFS oscillations (top) and their Fourier transforms (bottom) for as-grown and annealed samples (60 mol.% Ge)

Figure 2 shows FT spectra of as-grown samples with the Ge concentration varying from 25 to 60 mol. %. One can see the

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spectra consist essentially of two peaks, one at ~ 1.4 Å and another one at ~2.2 Å. Figure 3 shows XANES spectra for as-grown samples with the Ge concentration from 25 to 60 %. The

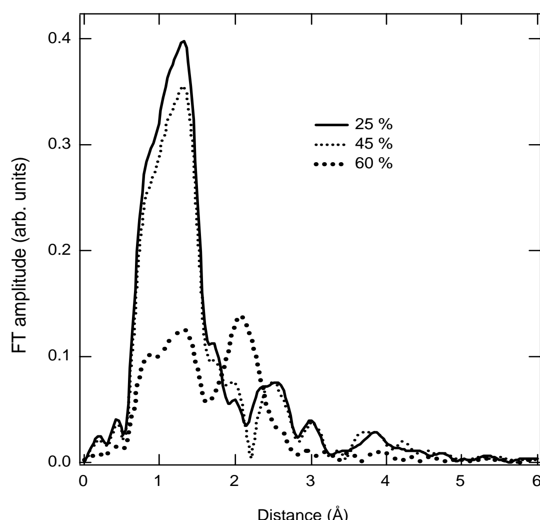

Figure 2
FT spectra for as- grown samples with different Ge concentrations

as-made samples with low and intermediate Ge concentration are characterized by a strong white line characteristic of Ge-

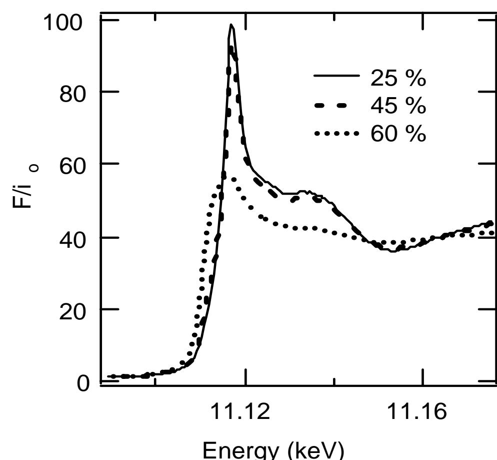

Figure 3
XANES spectra for as-grown samples

oxide, while that for the high Ge concentration sample resembles that of bulk Ge.

4. Discussion

Presence of the two peaks in the FT spectra indicate that Ge has two different nearest neighbours. The peak located at 2.2 Å is due to Ge-Ge interactions while that at 1.4 Å represents Ge-O interaction. The spectra are dominated by the Ge-O peak in the samples with low and intermediate Ge concentration while the sample with high Ge concentration also possesses a peak corresponding to Ge-Ge correlation but only the first-nearest peak is observed in the as-grown sample.

For quantitative data analysis, we performed the curve fitting assuming that the total number of the first-nearest neighbours around Ge equals 4, the neighbour being either Ge or O. Our Raman scattering study has shown that no Ge-Si mixing was taking place in nanocrystals and for this reason we did not include the Ge-Si correlations in the curve fitting procedure. A typical example of a two-shell fit for the annealed sample containing 60 mol. % Ge is shown in Fig. 4.

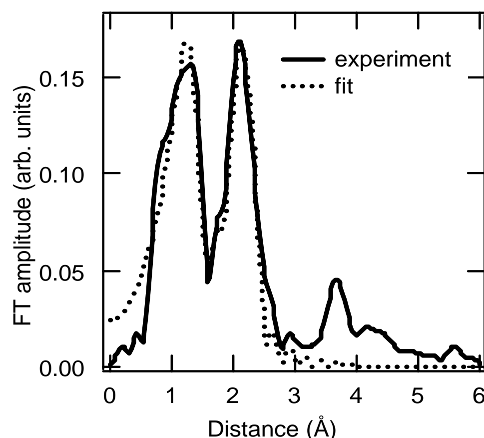

Figure 4
Fitting of the first shell (Ge-O and (Ge-Ge) for the annealed sample (60 mol.% Ge)

The results of the curve fitting for various samples are summarised in Table 1. The table uses the following notations. *N* stands for the partial coordination number, *i.e.* N_{GeGe} = 1.8 means that Ge atoms have on the average 1.8 Ge neighbours and 4 - *N* oxygen neighbours. *BL* is the bond length and *MSRD* is the mean-square relative displacement for the Ge-Ge and Ge-O bonds.

Sample	N_{GeGe}	BL_{GeGe}, Å	BL_{GeO}, Å	MSRD $_{GeGe}$, Å	MSRD $_{GeO}$, Å
25 %, as-grown	0.3	2.55	1.70	0.031	0.044
25 %, annealed	0.5	2.53	1.69	0.030	0.044
45 % as-grown	0.5	2.52	1.69	0.030	0.045
45 % annealed	0.5	2.44	1.69	0.029	0.043
60 % as-grown	1.8	2.46	1.71	0.047	0.082
60 % annealed	1.9	2.46	1.70	0.034	0.058

Upon annealing, the intensities of the peaks (both Ge-O and Ge-Ge) grow in the sample with 60 % Ge and peaks at higher distances come out (Fig. 1) indicating the formation of the crystalline phase. No change was detected in samples with the lower Ge concentration. Interestingly, in the sample with 60 mol. % Ge did not find any increase in the Ge-Ge coordination number upon annealing. This result suggests, that the nanocrystalline (nc-) Ge phase is not formed from the Ge-Si-O matrix upon annealing but rather the pre-existing amorphous Ge phase crystallises. This conclusion agrees with the result for the samples with the lower Ge concentration where Ge species predominantly have oxygen as the first-nearest neighbours: annealing does not lead to a detectable appearance of the nc-Ge phase.

The fitting of the second Ge-Ge shell in the nanocrystalline Ge yielded the values for the coordination number of 3.0 ± 0.5 while the corresponding value in bulk Ge equals 12. The much lower coordination number in the second shell is typical for nano-meter size clusters and is usually attributed to a purely geometrical factor. The found value of the coordination number would correspond to the cluster radius of the order of several Ångstroms. Our TEM studies have demonstrated that in the sample under investigation much larger nanocrystals are formed,

typically of about 15 - 20 nm with roughly spherical shape. The coordination number in nanocrystals of this size should be very close to that in the bulk solid.

We thus conclude, that the observed much lower coordination number in the second Ge-Ge shell is not related to the nanometer-size of the crystals but is due to the fact that not all amorphous phase in transformed into nanocrystals. In such a case. both the amorphous and the crystalline phases will have effect on the amplitude of the first-shell peak but only the crystalline phase will contribute into the second-shell peak.

The bond length in nc-Ge of 2.46 Å, very close to that in bulk Ge demonstrates that the nanocrystals are relaxed. Most likely this is due to the fact that nc-Ge is embedded in an amorphous SiO_2 matrix which is softer than the c-Si substrate and as a result the amount of stress accumulated in nc-Ge is negligible.

The observed values for the Ge-Ge coordination number in the samples with the lower Ge content is close to the accuracy of the measurement, In addition, the obtained MSRD values are also smaller than for the 60 mol. % Ge sample and are suspiciously similar. We believe that no reliable conclusion about the structure of Ge nanocrystals can be made in this group of samples. While the formation of the nanocrystals with the size of ~ 6-10 nm has been demonstrated by TEM, in EXAFS we do not observe any clear Ge-Ge peak. We believe that this results from the fact that majority of Ge atoms remain within the Ge-Si-O matrix and the observed Ge-related signal is dominated by those atoms. Whilst species selective, EXAFS is unable to distinguish between chemically identical atoms located in different crystallographic positions. A modification of EXAFS such as DAFS would, probably, be a more promising technique to study a mixture of amorphous and crystalline phases.

5. Conclusion

The local structure of Ge in an amorphous Ge-Si-O matrix strongly depends on the Ge composition. In as-grown samples with the Ge content within 25 - 45 mol. % Ge is mainly coordinated by oxygen atoms while at higher concentrations (60 mol. %), the amorphous Ge phase is formed.

Annealing does not result in any significant changes in EXAFS for the samples with the lower Ge concentration: Ge is still mainly surrounded by oxygen. In the sample with high Ge concentration, the annealing results in the formation of nanocrystals. The nanocrystals are relaxed and their fraction is ~ 25 % of the total Ge phase, the rest remaining in the amorphous phase.

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