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Xe bubbles in Si observed by extended x-ray-absorption fine-structure spectroscopy

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We report the first experimental investigation of Xe bubbles in Si single crystals by extended x-ray-absorption fine-structure (EXAFS) spectroscopy. Measurements have been performed on the Xe L_3 edge at 70 and 300 K, on both as-implanted and annealed samples. Implanted doses up to 10^{17} atoms/cm^2 have been investigated. The as-implanted samples did not show any EXAFS structure, revealing that the gas is randomly diffused in the host matrix either in an atomic configuration or in small gaslike aggregates. By way of contrast, annealed samples show an EXAFS structure due to the presence of Xe bubbles in the fcc crystalline phase. The observation of a temperature-dependent average Xe-Xe nearest-neighbor distance in the bubbles is shown to be related to the overpressure on the bubbles due to the host matrix. These results are in excellent agreement with independent thermodynamic calculations.

Rare gases introduced in a metallic or semiconducting solid matrix by ~100-keV ion implantation are not miscible with the matrix and hence tend to agglomerate in clusters or bubbles.[1-12] To date, the properties of these agglomerates have been studied mainly by transmission electron microscopy (TEM),[4-7] energy-loss spectroscopy,[1] small-angle x-ray scattering,[12] and Doppler-shift attenuation[10] techniques, as a function of preparation conditions, implanting dose and energy, annealing temperature, and time. The most investigated rare gases are the lightest ones such as He, Ne, and Ar. In particular, for Ar-implanted samples at a dose of 6×10^{15} atoms/cm^2, bubble formation occurs during the implantation process; the cluster dimensions grow considerably during annealing with microtwins development.[8] At lower doses no bubble formation has been detected even after annealing. For heavier rare gases (Kr) no bubble formation occurs in both as-implanted samples and in samples annealed at 525 °C for 180 min;[7] a higher annealing temperature is necessary before small bubbles become detectable. The fraction of gas in a solid, liquid, or gaslike phase strongly depends on the implanting dose. For Ne implanted in Al, bubbles have been found in liquid phase, while 2 at.% Ar in Al is solid at room temperature.[1] Recent TEM investigations on various metals and semiconductors implanted with Ar, Kr, and Xe show solid fcc noble-gas clusters epitaxially grown in the metal.[1,3-5] Moreover, the Xe lattice parameter has been found to change with the host matrix, and to increase during annealing. Assuming this lattice expansion is related to the pressure acting on the bubble, then the Ronchi equation of state[13] is no longer valid and this implies that there is a large uncertainty on the effective overpressure produced by the host matrix on the cluster.

The large phenomenology associated with these systems strongly motivates us to investigate the conditions under which clusters are formed, their phases, and the relation between their lattice parameter and the size-dependent overpressure on the bubbles.

To clarify this situation we measured the extended x-ray-absorption fine structure (EXAFS) on Xe-implanted Si single crystals. The site specificity and the local structure sensitivity of this technique[14,15] are used to determine the interatomic distances, coordination numbers, and Debye-Waller factors of the Xe atoms. Such a direct measurement of the Xe-Xe first neighbor distance has allowed the temperature-dependent overpressure of the Si host on the Xe bubbles to be determined.

Si(111) single crystals were implanted with Xe at 100 keV or at 300-200-100 keV with doses ranging from 10^{15} atoms/cm^2 up to 10^{17} atoms/cm^2. At the maximum dose the implanted ions penetrate about 400 Å with a spread of about 400 Å. At the implanting temperature $T=300$ K the matrix is amorphized by the projectiles. All samples were studied as implanted and after annealing at 600 °C for 30 min. The doses of samples were checked by using Rutherford backscattering analysis.

X-ray-absorption spectra (XAS) were registered on the

Puls x-ray beam line at the Frascati Synchroton Radiation facility. The radiation was monochromatized with a Si(111) channel-cut crystal. The spectra were recorded in the energy range 4780–5100 eV by monitoring the Xe L_3 fluorescence yield. During the measurements the implanted samples were oriented at a few degrees with respect to the x-ray beam to maximize the area contributing to the absorption. The samples implanted with higher doses were measured both at room temperature (RT) and at 70 K. XAS spectra were also recorded on Xe gas at RT. In what follows a Xe L_3 XAS spectrum recorded at 5 K, reported in the literature,[16] will be used as reference compound in our EXAFS data analysis.

As shown in Fig. 1(a), at all doses the as-implanted samples show no EXAFS signal on the high-energy side of the L_3 edge, thus revealing that the Xe atoms are randomly diffused in the host matrix either in gas-phase bubbles or in atomic form. On comparing Fig. 1(a) with the absorption spectrum of Xe gas [Fig. 1(b)], we note that the characteristic gas-phase multielectron excitation at about 12 eV above the L_3 edge is absent in the Xe-implanted spectra. This suggests that interaction of Xe atoms between one another and/or with the matrix is negligible. By providing extra charge needed to screen the L_3 core hole, this interaction causes disappearance of the multielectron excitation and is also responsible for the broadening of the white line. By way of contrast, at doses higher than 5×10^{16} atoms/cm^2 all the annealed samples present EXAFS oscillations [Fig. 1(c)]. This implies that ordered Xe bubbles are present in a condensed phase, either liquid or solid. At lower doses no significant EXAFS signal could be detected, indicating that at such doses only a small percentage (less than few percent) of Xe atoms are present in the form of condensed-phase bubbles.

In the following we will concentrate on the EXAFS results obtained for a typical sample (three-step implanting energy 300-200-100 keV; implantation dose of 10^{17} atoms/cm^2), measured as-implanted and after annealing. Standard data analysis was performed for extracting the EXAFS from the spectra.

Figure 2 illustrates the Fourier transform (FT) of the spectrum taken at 70 K [Fig. 2(a)], together with that of crystalline Xe from Ref. 16 [Fig. 2(b)]. Note how at 70 K the sample shows the presence of higher neighbor peaks, which correspond to the second and third coordination spheres of an fcc crystal structure, and therefore indicate that the Xe atoms inside the bubbles are in crystalline phase. Quantitative analysis involved only the first coordination shell using the crystalline Xe spectrum as the standard. The obtained values are reported in Table I.

We shall discuss the obtained results as follows: (i) interatomic distances, (ii) coordination numbers, and (iii) Debye-Waller factor.

(i) We find (see Table I) that the lattice parameter is smaller than that in crystalline Xe, indicating that the Xe bubbles are overpressurized at both temperatures, the host

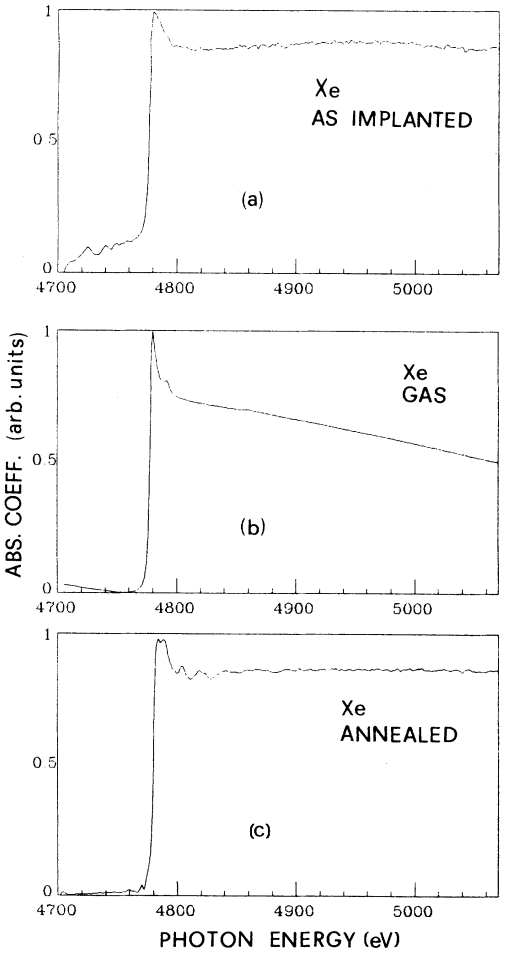

FIG. 1. Absorption spectra of Xe near the L_3 edge: (a) as-implanted sample observed at $T=300$ K, (b) gas at room temperature, and (c) implanted and annealed samples observed at $T=70$ K.

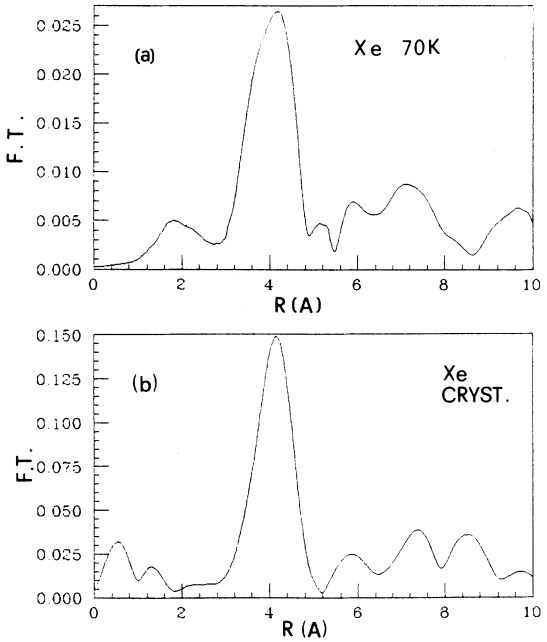

FIG. 2. Magnitude of the Fourier transform of Xe EXAFS spectra: (a) implanted and annealed samples observed at $T=70$ K. The EXAFS spectrum has been weighted by k, and (b) crystalline Xe, as reported in Ref. 16.

TABLE I. First coordination shell R_{NN} distance in implanted and annealed samples compared with the value reported in Ref. 16 for crystalline Xe; coordination number N/N_0 for the first coordination shell of the bubbles compared with that of crystalline Xe; $\Delta\sigma^2=\sigma^2-\sigma_c^2$ is the increase of the Debye-Waller factor at 70 K with respect to crystalline Xe at 5 K.

Samples	R_{NN} (Å)	N/N_0	$\Delta\sigma^2$ (Å^2)
Xe (300 K)	3.94 ± 0.05	0.08	. . .
Xe (70 K)	4.23 ± 0.05	0.28	0.008 ± 0.001
Xe (crystalline)	4.35 ± 0.01	1	0

pressure being larger at 300 K than at 70 K. The nearest-neighbor distance (NN) of the sample at RT is 0.41 ± 0.06 Å shorter than in the crystal due to the nonnegligible overpressure on the bubbles. At 70 K the NN distance contraction is reduced to 0.12 ± 0.06 Å since the mean pressure acting on the condensed bubbles decreases at lower temperature. Using diffraction results of Zisman, Alehsandrov, and Stishov,[17] and Asaumi[18] on pressurized Xe crystals and our Xe-Xe measurements, we can determine the average pressure acting on the bubbles to be 3.5 GPa at 300 K and 0.55 GPa at 70 K.

(ii) Table I also lists the values of the relative coordination number N/N_0, N and N_0 being the coordination number of the Xe atoms in the bubbles and in the crystal, respectively ($N_0=12$ since Xe crystallizes in the fcc structure). We believe that the low-N values obtained constitute evidence that only a fraction of the total Xe atoms are in condensed phase, the most being still present in the form of gas-phase bubbles. In fact, a mixture of gaseous Xe and solid Xe bubbles will both contribute to the absorption coefficient but only the latter will show an EXAFS signal. Accordingly, the apparent coordination number measured by EXAFS, i.e., $N/N_0=\alpha_c$, is closely related to the atomic percentage of Xe in the condensed phase. We recall that even in the crystalline phase, small clusters have a high surface-to-volume ratio and this may considerably reduce the number of Xe atoms with bulk coordination. The fact that at 70 K the relative intensities between the first, second, and third shells are comparable to those of crystalline Xe indicates that the distortion introduced by the surface atoms is small. The size distribution of the bubbles in the matrix does not allow an absolute determination of the real percentage of atoms in crystalline phase, but the relative increase of α_c at 70 K clearly indicates that only a small fraction of Xe is crystalline at room temperature. On lowering the temperature from RT to 70 K, the number of Xe atoms in crystalline phase increases, even though the pressure of the Si host decreases.

(iii) The data quality of the spectrum recorded at 70 K is good enough to allow reliable evaluation of the difference $\sigma^2-\sigma_c^2=(8\pm1)\times10^{-3}$ Å^2 between the Debye-Waller factors of the implanted sample, σ^2, and that of 5-K Xe crystal, σ_c^2. To find the absolute value σ^2, we have estimated σ_c^2 in the Debye approximation, using the known Debye temperature for crystalline Xe ($\Theta_D=64$ K): the value obtained is $\sigma_c^2=7.5\times10^{-3}$ Å^2, and therefore $\sigma^2=(15.5\pm1.0)\times10^{-3}$ Å^2. This value is almost a factor of 2 lower than that expected for Xe at atmospheric pressure and $T=70$ K, which in the Debye approximation is 24×10^{-3} Å^2.

This last result gives a measure of the hardening of the Xe lattice due to the overpressure. The experimental value of σ^2 can be accounted for by increasing the Debye temperature of the overpressurized bubbles: for a $\Theta_D=80$ K the calculated Debye-Waller factor (15.7×10^{-3} Å^2) is in fact in agreement with the experimental one [$(15.5\pm1.0)\times10^{-3}$ Å^2]. Such an increase in Θ_D is also in agreement with previous work on Ar in Al, by Rossouw and Donnelly,[2] who found that the Debye temperature is increased by the overpressure from the bulk value of 70 K to one of about 140 K due to the overpressure.

A quantitative estimate of our increased Θ_D is obtained by using the thermodynamic relation

$$-\gamma_G=\frac{\partial\ln\Theta_D}{\partial\ln V},$$

where γ_G is the Grüneisen constant and V the volume; the isothermal compressibility β with respect to the pressure P is given by

$$-\beta=\frac{\partial\ln V}{\partial P}.$$

Resolving these two equations for Θ_D, we obtain

$$\Theta_D(P)=\Theta_D(P_0)\exp\left[\int_{P_0}^{P}\gamma_G\beta\,dP\right],$$

where P_0 is the atmospheric pressure and $\Theta_D(P_0)=64$ K.

Assuming the values reported by Asaumi[18] of $\beta=0.13$ GPa and $\gamma_G=2.61$, we get $\Theta_D=78$ K for Xe bubbles at 0.55 GPa, in very good agreement with $\Theta_D=80$ K estimated from the NN distance.

We emphasize that in calculating Θ_D for the bubbles, two uncorrelated experimental quantities (NN distance and Debye-Waller factor) have been used. Such internal consistency gives us confidence in the reliability of our interpretation.

In conclusion, we have used EXAFS spectroscopy to extract clear evidence that crystalline Xe bubbles are present in a Si matrix. We have shown that these bubbles are overpressurized; from the lattice parameter contraction we have calculated the mean value of the pressure acting on them. Using thermodynamic relations, we have also shown that the overpressure on the bubbles causes an increase in their Debye temperature.

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