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Evidence for crystalline overpressurized Ar clusters in Al and Si

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In the present paper we report an extended x-ray-absorption fine-structure study of Ar ion implanted in Al and Si matrices. The as-implanted samples show the presence of crystalline overpressurized Ar clusters at room temperature. The Ar-Ar nearest-neighbor distance allows us to estimate the presence of an overpressure of 25 and 44 kbar exerted on Ar bubbles by the Al and Si matrices, respectively. The presence of second- and third-coordination-shell signals confirms that the precipitates are in a crystalline phase. The Debye temperatures, calculated from the Debye-Waller factors, are found to be in excellent agreement with the values obtained with use of a thermodynamic equation of state.

In a recent paper[1] Faraci *et al.* have reported an experimental study on the presence of Xe in the form of bubbles in Si single crystals, using extended x-ray-absorption fine-structure (EXAFS) spectroscopy. The rare gas was introduced into the matrix by ion implantation at several hundred kilo-electron-volts and at high doses. In the as-implanted material, Xe was found randomly diffused; after annealing, the presence of Xe clusters was clearly observed.

On the other hand, several electron-microscope investigations on different metals and semiconductors implanted with Ar, Xe, and Kr have shown[2-9] the presence of rare-gas clusters prior to any annealing. For instance, Revesz *et al.*[7] have found that, in amorphous silicon implanted at a dose of 6×10^{15} atoms/cm^2, Ar bubbles with a 170-Å average diameter are present. On samples implanted with a lower dose of 2×10^{15} atoms/cm^2, the same authors did not detect any clusters within the sensitivity of their experimental apparatus (about 50 Å). More recently Rossouw and Donnelly[4] have detected the presence of Ar bubbles with a mean dimension $d=27\pm5$ Å in aluminum implanted with Ar at 50 keV at a dose of 2×10^{16} atoms/cm^2. In this case, the bubbles were found in a crystalline phase. These authors obtained, on the basis of the temperature dependence of diffracted intensities, a Debye temperature of 141.5 K—a value which is consistent with the observed bubbles melting temperature of 730 K. This superheating by 480 K with respect to solid argon is related to the overpressure exerted on the clusters by the host matrix lattice: In fact, it is a solid phase with a contracted lattice parameter.

In the following, we report the presence of Ar clusters prior to any annealing process in a Si and Al matrix implanted with Ar at room temperature. We have used EXAFS spectroscopy[10] because it provides us with high-accuracy, direct structural information on nearest-neighbor distances, coordination numbers, and Debye-Waller factors of the coordination shells surrounding the implanted atom.

Si(111) single crystals and Al polycrystal foils were implanted with Ar ions at 40 and 130 keV. During implantation, the substrate was held at room temperature or at 350 °C. Different doses ranging from 10^{16} up to 10^{17} atoms/cm^2 were used. The doses implanted into the samples were checked by Rutherford backscattering analysis. X-ray-absorption measurements were performed on beam-line EXAFS II at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE)-Orsay, with use of the synchrotron radiation emitted by the Dispositif de Collisions dans l'Igloo (DCI) Storage Ring working at an electron energy of 1.85 GeV and at a current of 250 mA. A double-crystal monochromator, equipped with Si(111) crystals, was used to monochromatize the photon beam. After the monochromator, a two-mirror system was used to reject the harmonics.

X-ray spectra were recorded at the Ar K edge in the energy range 3150–3500 eV. The implanted Ar ions penetrate into the matrix to a depth of a few hundred ang-

stroms under the surface; therefore, the investigated samples behave as very diluted ensembles of rare-gas atoms in a thick layer beneath the matrix surface. For this reason, spectra were recorded in the total-electron-yield mode. An electron detector, developed at LURE (Ref. 11) which works in helium under atmospheric pressure, was used.

Figure 1 shows some spectra recorded in as-implanted samples. The absorption coefficient shows the same features in all spectra, even though the jump at the edge decreases with the increase of the implantation energy. This is due to the deeper penetration of the Ar projectiles into the matrix at higher energy, which results in a lower detection efficiency. The escape depth of the electrons is only about 300 Å. All the recorded spectra have shown EXAFS oscillations. In a few of them the signal-to-noise ratio was high enough to allow a quantitative EXAFS data analysis.

In Fig. 2 we show the Fourier transform (FT) of the EXAFS spectrum of a typical sample. The position of the first peak in the FT provides the nearest-neighbor (NN) distance after a phase-shift correction has been made. This correction was determined by using the data reported by Malzfeldt *et al.*,[12] who measured EXAFS spectra of solid argon at 5 K; it amounts to $\delta R = 0.50$ Å. In Fig. 2, there is clear evidence for the second and third coordination shell, at R positions typical of fcc crystals: This implies that the Ar clusters are in a crystalline phase.

Table I reports for both supports (Al,Si) quantitative determination of first-coordination-shell position, coordination numbers, and Debye-Waller factors obtained through a quantitative analysis in **k** space.

The Ar-Ar NN distance is clearly contracted with respect to the crystal: For Ar in Al, the contraction amounts to 0.31 ± 0.05 Å, that for Ar in Si, to 0.42 ± 0.05 Å. Using the isotherm equation reported in Ref. 13, which gives the compression of crystalline argon at high pressure and room temperature, we find that the Ar clusters come under an average overpressure of 25 and 44 kbar, respectively, in Al and Si matrices. These values are average values, since transmission-electron-microscope measurements[7] have shown the presence of a quite large spread in cluster sizes.

The ratio N/N_0 between the coordination numbers in the clusters and in the crystal is quite low. This implies that only 6% of argon atoms in Si and 21% of those in Al have the same coordination as in bulk Ar. This is a clear evidence for the existence of a large amount of argon atoms either randomly diffused or in very small gaseous aggregates.

Table I also shows the relative Debye-Waller factors $\Delta\sigma^2 = \sigma^2 - \sigma_c^2$, i.e., the difference between the Debye-Waller factor of the implanted sample, σ^2, and that of solid Ar, σ_c^2 at 5 K. To get the absolute value $\sigma^2(T,\Theta)$, we have calculated σ_c^2 in the Debye approximation.[14] For crystalline Ar at 5 K, a Debye temperature of 93.3 K was used.[15] It resulted in $\sigma_c^2 = 17 \times 10^{-3}$ Å^2. From the values listed in Table I, we obtain

$$\sigma^2(\text{Ar/Al}) = 30.6 \times 10^{-3} \text{ Å}^2$$

and

$$\sigma^2(\text{Ar/Si}) = 16 \times 10^{-3} \text{ Å}^2 .$$

The increase of the Debye-Waller factors is due to the increase of the Debye temperature for solid Ar in the clusters, which is $\Theta = 212$ K for Ar in Al and $\Theta = 300$ K for Ar in Si. This increase is reasonable: The clusters are actually very hard since they are under high pressure.

A check of the reliability of this result is obtained by evaluating the Debye temperature of the Ar bubbles in an independent way. For this purpose, we assume that the Ar in overpressurized clusters can be treated as an Ar crystal at the same pressure.

Holt and Ross[16] have shown that the thermodynamical behavior of pressurized argon is expressed by the following equation of state:

$$P(V,T) = (3RT\gamma/V)D(\Theta/T) ,$$

where R is the gas constant; Θ, the Debye temperature; γ, the Grüneisen parameter; T, the absolute temperature; and D, the Debye function

$$D(z) = 3z^{-3}\int_0^z \frac{x^3}{e^x - 1} dx .$$

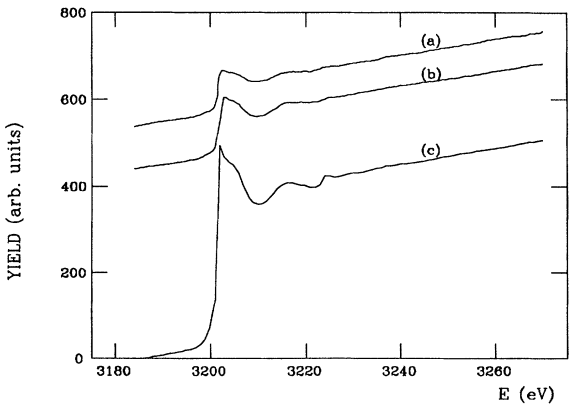

FIG. 1. Absorption spectra of Ar implanted on (a) Al at an energy $E = 130$ keV, (b) Si at an energy $E = 130$ keV, and (c) Si at an energy $E = 40$ keV.

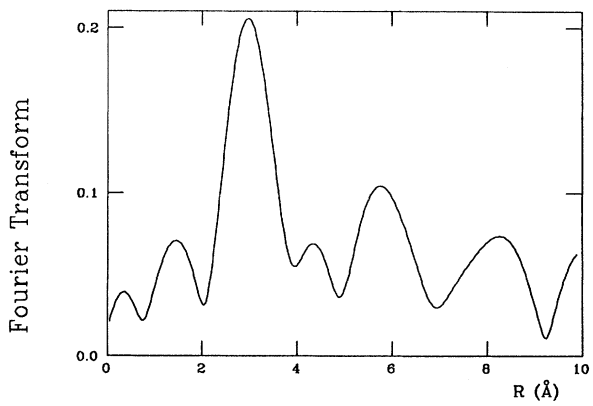

FIG. 2. Magnitude of the Fourier transform of the EXAFS spectrum of Ar as implanted in Al.

TABLE I. First-coordination-shell distance R_{FT} and relative first-shell coordination number of solid Ar and of two samples ion implanted on Al and Si substrates. $\Delta\sigma^2=\sigma^2-\sigma_c^2$ is the increase of the Debye-Waller factor of the samples with respect to the solid Ar; the pressure deduced from the contracted lattice parameter is also reported.

Samples	R_{FT} (Å)	N/N_0	$\Delta\sigma^2$ (Å^2)	P (kbar)
Solid Ar	3.26 ± 0.01	1	0	...
Ar in Si	2.84 ± 0.05	0.058 ± 0.03	-0.0010 ± 0.0005	44
Ar in Al	2.95 ± 0.05	0.208 ± 0.03	$+0.0136\pm0.0005$	25

In the previous equation, the Grüneisen parameter is given by $\gamma=(V/V_0)\gamma_1+0.5$, with $\gamma_1=2.2$, independent of volume. Moreover, it has been shown that the Debye temperature[13] can be written as

$$\Theta(V)=\Theta_0(\sqrt{V_0/V})(1-V/V_0)e^{\gamma_1}.$$

Using the values of the overpressure deduced from the contracted lattice parameter in the previous equation, we have calculated that (i) for Ar in Al, $\Theta=207$ K and (ii) for Ar in Si, $\Theta=300$ K. These values are in excellent agreement with the values deduced from the EXAFS Debye-Waller factors. It is to be emphasized that the two procedures used to calculate the Debye temperatures are completely independent. In fact, in one case we have used the amplitudes of the EXAFS spectra and in the other we have used the phases. This independence of the two methods that we have used gives good reliability to the interpretation presented in this paper.

In conclusion, we have shown clear evidence for the presence, prior to any annealing, of overpressurized Ar clusters in samples of Si and Al implanted with Ar. The clusters are in a crystalline fcc phase.

Our results show that the crystal phase does not grow epitaxially on the matrix, as a consequence of the amorphization of the substrate caused by the ion implantation.

Based on the lattice contraction, we have deduced the mean pressure exerted on the bubbles by the matrix and the Debye temperature for these overpressurized clusters. We want to emphasize that, in this EXAFS investigation, we have studied the structural and vibrational properties of a system at high pressure (of the order of 50 kbar), getting information on its thermodynamical behavior.

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