

Bond length contraction in Au nanocrystals formed by ion implantation into thin SiO₂

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Au nanocrystals (NCs) fabricated by ion implantation into thin SiO₂ and annealing were investigated by means of extended x-ray absorption fine structure (EXAFS) spectroscopy and transmission electron microscopy. A bond length contraction was observed and can be explained by surface tension effects in a simple liquid-drop model. Such results are consistent with previous reports on nonembedded NCs implying a negligible influence of the SiO₂ matrix. Cumulant analysis of the EXAFS data suggests surface reconstruction or relaxation involving a further shortened bond length. A deviation from the octahedral closed shell structure is apparent for NCs of size 25 Å.

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Nanocrystals (NCs) have received increasing attention in recent years due to their unique structure and properties and their wide range of prospective applications. Metallic NCs embedded in a dielectric matrix are particularly interesting because of their nonlinear optical properties with a high potential for application in optical filters, memories, or switching devices.¹ Generally, the unique properties of NCs result from the limited number of atoms incorporated therein and the considerable influence of surface atoms due to the increased surface-area-to-volume ratio. These factors can lead to a significant deviation of the crystallographic structure compared with bulk material.² Both the synthesis technique, often dominated by kinetic processes, and the supporting material can have equally important influences on the structural evolution of NCs.^{3,4}

The structure of Au NCs has been extensively studied, both theoretically and experimentally, over the last decades.^{5,6} A variety of techniques has been used to resolve their structure, including extended x-ray absorption fine structure (EXAFS) spectroscopy, transmission electron microscopy (TEM), and x-ray diffraction (XRD). EXAFS provides a powerful tool for analysis of particles of nanometer dimensions, giving unique information about the local atomic environment of the absorbing atom.^{7,8} The technique is particularly sensitive to interatomic distances and local disorder. A bond length contraction of up to several percent with respect to bulk material has been observed in Au NCs fabricated using evaporation⁹⁻¹¹ or chemical synthesis techniques.^{5,12,13} Conversely, only a very small contraction was reported for ligand-stabilized, chemically synthesized NCs¹⁴ and little or no reduction of the interatomic distance was found for Au NCs produced by ion implantation.^{15,16} Commonly, an increase in the mean square relative displacement with decreasing NC size was observed and attributed to

either the increased surface-area-to-volume ratio or bulk disorder.

In the present letter, we have used EXAFS and TEM to investigate the size-dependent bond length and disorder of Au NCs formed by ion implantation into thin SiO₂. One difficulty associated with performing EXAFS measurements on ion-beam-synthesized NCs is the sample preparation. The limited amount of material implanted into the matrix and scattering from the substrate material can yield a high noise level in the fluorescence spectra. Our sample preparation method enables us to obtain a superior signal-to-noise ratio over a high photoelectron momentum (k) range. We find our high-resolution results contradict previous investigations of Au NCs formed by ion implantation.

For our experiments we implanted 4.5 MeV ¹⁹⁷Au ions into 2- μ m-thick SiO₂ thermally grown on Si (100) substrates. The samples were maintained at liquid nitrogen temperature during implantation. Four different ion doses (1×10^{16} , 3×10^{16} , 1×10^{17} , and 3×10^{17} at/cm²) were used to generate different NC size distributions. Subsequently all samples were annealed in forming gas (95% N₂ and 5% H₂) at 1100°C for 1 h in a conventional quartz furnace to promote further precipitation and reduce irradiation-induced damage of the host material. Essential information about shapes and size distributions of the NCs was extracted from TEM analysis. Figure 1 shows representative high-resolution TEM micrographs as a function of ion dose. The NCs were spherical and single crystalline. Decreasing ion doses lead to decreasing NC sizes. These observations are in good agreement with previous studies.¹⁷ The corresponding size distributions were evaluated from micrographs covering the extent of the ion range. Mean particle diameters shown in Fig. 1 were calculated by averaging over the particle volume through cubic weighting of the extracted NC diameters. This is essential for comparison with the EXAFS results given this technique represents a volume probe.

To prepare the samples for EXAFS measurements, the thin SiO₂ layer containing the NCs was isolated by removing

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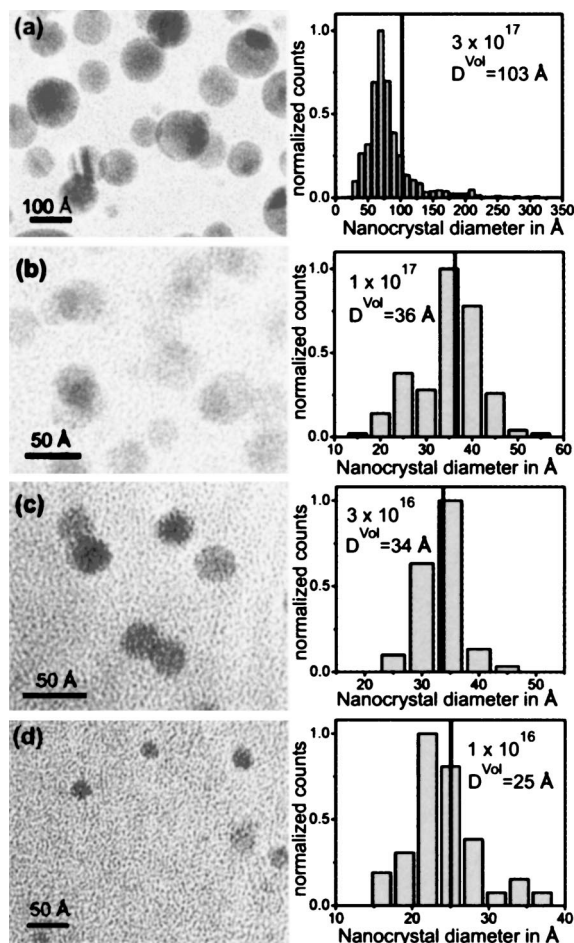


FIG. 1. Cross-section TEM images and size distributions of Au NCs for the four different ion doses: a) 3×10^{17} ions/cm², b) 1×10^{17} ions/cm², c) 3×10^{16} ions/cm², and d) 1×10^{16} ions/cm². The mean NC diameters are indicated by the solid line (averaged over NC volumes).

the Si substrate via mechanical polishing and selective wet chemical etching in a KOH solution. To obtain an improved fluorescence signal in the EXAFS measurements, multiple layers of the thin implanted SiO₂ were mounted on the sample holder. Using this sample preparation method, we enhance the relative Au concentration and eliminate scattering from the substrate. The reduced noise levels yield excellent data over a high k range as reflected in the k^2 -weighted spectra in Fig. 2. The extended k range is necessary to reveal

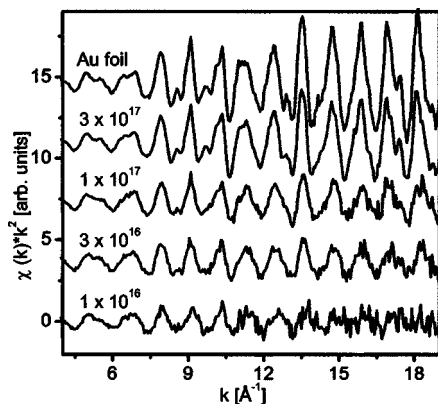


FIG. 2. k^2 -weighted EXAFS spectra at 10 K of Au foil and NCs for different ion doses (in units of ions/cm²).

important structural details, particularly disorder and anharmonicity in the first coordination shell.¹⁸ The fluorescence EXAFS measurements at the Au L_3 edge (11.919 keV) were performed at the Photon Factory, Japan (beamline 20-B) in an energy range between 11.70 and 13.48 keV, the latter corresponding to a k value of 20 \AA^{-1} . Data were collected using a ten element Ge solid-state detector. The Au L_3 fluorescence signal comprised between 10% and 50% of the incoming count rate, with the latter maintained well within the linear region of the detector. Measurements were carried out at a temperature of 10 K to reduce thermal vibrations. A 1000- \AA -thick Au foil was used as a reference standard.

The spectra were analyzed using the FEFFIT program package.¹⁹ EXAFS spectra were Fourier transformed over a k range of $4.7\text{--}18.3 \text{ \AA}^{-1}$. Structural parameters were extracted from the first coordination shell which was isolated by inverse transforming over a non-phase-corrected radial distance range of $2.2\text{--}3.2 \text{ \AA}$. The spectra were then fitted to the standard EXAFS equation including third-order cumulants.⁷ The amplitude reduction factor (S_0^2) and threshold energy (E_0) were determined from the reference standard and kept constant for fitting the NC spectra. The photoelectron scattering-path amplitudes and phases were calculated *ab initio* using FEFF8²⁰ for a fcc structure of Au with a first nearest neighbor distance of 2.8850 \AA . The refined fitting parameters are given in Table I.

The phase corrected, k^2 -weighted, Fourier-transformed EXAFS spectra are shown in Fig. 3. The Au foil spectrum is consistent with the fcc structure with the first to fourth nearest neighbors apparent. This pattern is present for all NC samples representing octahedral closed shell structures with the exception of the lowest ion dose. The reduced amplitudes of the peaks reflect the decreasing average coordination number and the increasing Debye–Waller (DW) factor with decreasing NC size. Both factors result from the increasing surface-area-to-volume ratio. The increasing DW factor is consistent with surface relaxation or reconstruction of the NC surface atoms. An asymmetric deviation from a Gaussian bond length distribution is manifested in the third cumulant C_3 . A negative value of C_3 indicates a bond length distribution skewed to shorter bond length. A possible explanation for the observed negative values of C_3 for the three largest NC sizes would be a surface relaxation or reconstruction of atoms at the NC surface involving a shortened bond length. This agrees with observations of the reconstruction of planar Au surfaces.²¹ For the lowest ion dose, a considerable distortion of the higher neighbor shells with respect to the fcc pattern is apparent from the Fourier-transformed spectrum in Fig. 3. A concomitant change to a positive value for C_3 as well as a deviation of the bond length contraction from a $1/D$ dependence (see the following), however, indicate a deviation from the octahedral closed shell structure.

A significant bond length contraction with decreasing NC size is observed from the fitting results (see Table I). This agrees with previous observations of nonembedded Au NCs.^{5,9–13} The inset in Fig. 3 shows the relative lattice contraction with respect to the reference standard plotted as a function of the inverse NC diameter D . The data for the three highest implanted ion doses are clearly linearly dependent on $1/D$ (the smallest NC size was excluded due to the apparent structural change). A macroscopic explanation for this behavior can be found in terms of surface stress due to the high surface-area-to-volume ratio. The relative contraction ΔR

TABLE I. Refined fitting parameters from EXAFS analysis of the first coordination shell as a function of ion dose (in units of ions/cm²). N , R , σ^2 , and C_3 are the coordination number, bond length, Debye–Waller factor, and third-order cumulant, respectively.

	Au foil	3×10^{17} Au	1×10^{17} Au	3×10^{16} Au	1×10^{16} Au
N	12 (fixed)	10.3 ± 0.5	9.3 ± 0.8	9.9 ± 0.8	8.4 ± 0.9
$R(\text{\AA})$	2.858 ± 0.006	2.854 ± 0.002	2.839 ± 0.004	2.838 ± 0.002	2.836 ± 0.005
$\sigma^2(10^{-3} \text{\AA}^2)$	1.8 ± 0.1	2.0 ± 0.1	3.4 ± 0.2	3.8 ± 0.2	5.0 ± 0.4
$C_3(10^{-4} \text{\AA}^3)$	-0.4 ± 0.3^a	-0.7 ± 0.1	-0.9 ± 0.3	-0.8 ± 0.3	1 ± 0.5

^a C_3 was included in the fit for the Au foil to provide a reference for the following fits of the NC samples and can be interpreted as a small offset (Ref. 23).

due to the surface tension f can be expressed by a liquid drop model⁹ given by $\Delta R = -\frac{4}{3}KR_b f(1/D)$, where K is the bulk compressibility, and R_b the bulk metal bond length. Using a bulk compressibility K of $5.99 \times 10^{-3} \text{ GPa}^{-1}$ for Au, we obtain a surface tension f of $3.6 \pm 0.8 \times 10^{-4} \text{ J/cm}^2$, similar to the value of $3.46 \pm 0.42 \times 10^{-4} \text{ J/cm}^2$ reported by Balerna *et al.*¹⁰ for evaporated Au NCs. The similarity of our results compared with those of Balerna *et al.* implies a small or negligible influence of the SiO₂ matrix on the bond length in the Au NCs. Our results also agree with the value of $4 \times 10^{-4} \text{ J/cm}^2$ obtained from TEM analysis by De Marchi *et al.* for ion-beam-synthesized Au NCs in SiO₂.²²

Fukumi *et al.*¹⁶ did not observe a contraction of the Au–Au interatomic distance in ion-beam-synthesized Au NCs using annealing temperatures similar to those of the present study. These results contradict our data. Given their mean NC diameter of 85 Å extracted from XRD measurements,¹⁵ a bond length contraction of approximately 0.01 Å would be expected from the inset in Fig. 3. However, their EXAFS spectra show significantly higher noise levels and as a consequence a considerably lower k -range. This might lead to unresolved details in the first coordination shell.

In conclusion, we have studied size-dependent bond length and disorder in ion-beam-synthesized Au NCs using EXAFS and TEM. We have observed a bond length contraction which can be explained by surface tension in a liquid drop model. Our results are in good agreement with those achieved by others on nonembedded NCs which suggests a negligible influence of the SiO₂ matrix. NCs of diameter

$\geq 33 \text{ \AA}$ retain the fcc structure where increasing disorder with decreasing NC size is attributed to atoms at the NC surface. A negative third cumulant is consistent with a surface reconstruction involving a shortened bond length. In NCs with a diameter of 25 Å a significant deviation from the octahedral closed shell structure was apparent.

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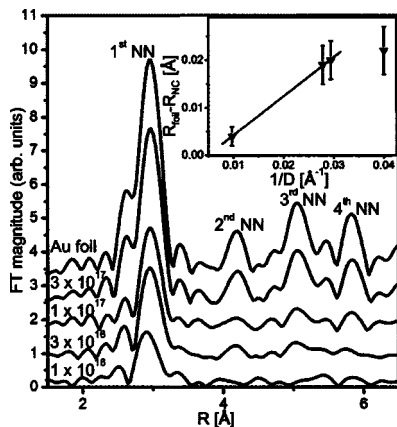


FIG. 3. Phase corrected Fourier transforms of bulk (Au foil) and NC EXAFS spectra in a k range of 4.7–18.7 Å⁻¹, k^2 -weighted, as a function of ion dose (in units of ions/cm²). The inset shows the relative first nearest neighbor bond length contraction as a function of the inverse NC diameter $1/D$. The solid line represents the mean-square linear fit for the three highest ion doses.