Vibrational Properties of Au and Cu Nanocrystals Formed by Ion Implantation

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Abstract. Au and Cu Nanocrystals (NCs) were fabricated using ion implantation into SiO₂ and subsequent thermal annealing. Vibrational properties were studied using extended x-ray absorption fine structure (EXAFS) spectroscopy at measurement temperatures between 15 and 300 K. Einstein temperatures were extracted and show a significant decrease for 3.3 nm Cu NCs as compared to bulk Cu. Au NCs, however, show no significant change in the Einstein temperature even at a size of 2.5 nm. The influence of the competing processes of softening of the vibrational density of states due to under-coordinated surface atoms and stiffening of the NC core atoms due to surface tension effects are discussed.

Keywords: Metal nanocrystals, ion implantation, EXAFS, vibrational properties
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INTRODUCTION

Metallic nanocrystals (NCs) embedded in a dielectric matrix show interesting nonlinear optical properties with potential application in optical memories or switching devices [1]. Ion implantation is a very versatile technique, well suited for fabrication of embedded NCs. High particle densities of extremely pure particles can be fabricated at a defined depth and location. A detailed understanding of the structure of such NCs as a function of the synthesis conditions is essential for an efficient utilization in advanced device applications and will also broaden the fundamental understanding of nano-materials.

The properties of NCs are generally governed by finite size effects, i.e. the limited number of atoms and the considerable surface to bulk ratio (SBR). These as well as the synthesis process itself can lead to structural perturbations in the NCs compared to the corresponding bulk materials. Extended X-ray absorption fine structure spectroscopy (EXAFS) has emerged as a valuable tool to study structural and vibrational properties of nano-materials as no long-range order is required. Generally, metallic NCs show increased disorder, manifested in an increased Debye-Waller factor, and a bond-length contraction which can be explained in terms of surface tension effects [2-4].

In this paper, we report results of EXAFS measurements of ion implanted Au and Cu NCs performed at temperatures between 15 and 300 K. We focus our discussion on the vibrational properties of the NCs compared to bulk material.

EXPERIMENTAL

NCs were synthesized by ion implantation of Au and Cu into 2 and 5 μm thick SiO₂, respectively. The SiO₂ was thermally grown on Si substrates. Au implantation was performed at an energy of 4.5 MeV with fluences of 1×10¹⁶ and 1×10¹⁷ ions/cm² corresponding to Au peak concentrations of approximately 0.4 and 4 at.%, respectively. Subsequently, samples were annealed at 1100°C for 1 h in forming gas (95% N₂ / 5% H₂) to promote NC growth. Cu implantations were performed to peak concentrations of 1.0 and 8.3 at.%. Multiple implantation energies and fluences were used to achieve these Cu concentrations[3]. The samples were annealed at 800°C for 1 h in forming gas. Cross-sectional transmission electron microscopy images of (a) Au and (b) Cu NCs are shown in Figure 1. Generally, we observe single crystalline, spherical NCs as apparent from the high resolution image of a Cu NC in (b).

To prepare the samples for EXAFS measurements, the thin SiO₂ layer containing the NCs was isolated by removing the Si substrate using mechanical polishing and selective wet chemical etching in a KOH solution. Multiple layers of the thin SiO₂/NC layer were then stacked together in a sample holder. Using this preparation method, we enhance the relative NC
abundance to yield an improved fluorescence signal and eliminate scattering from the substrate.

FIGURE 1. Cross-sectional transmission electron micrographs of (a) Au NCs and (b) a Cu NC in high-resolution.

Fluorescence EXAFS measurements were performed at the Au L₃ edge (11.919 keV) and the Cu K edge (8.979 keV) at the Australian National Beamline Facility (BL 20 B) at the Photon Factory, Japan. Data were collected using a 10-element Ge solid-state detector. The 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 performed at temperatures between 15 and 300 K.

The spectra were analyzed using the FEFFIT program package[5]. Structural parameters were extracted from the first coordination shell by fitting to the EXAFS equation including the first three moments of the inter-atomic distance distribution[6]. The amplitude reduction factors (S₀²) and threshold energies (E₀) were determined from the metal foils and kept constant for fitting all spectra. The photoelectron scattering-path amplitudes and phases were calculated ab initio using FEFF8[7].

RESULTS

The Debye-Waller factor or mean square relative displacement of the bond length distribution measured by EXAFS can be described as a superposition of a static and a dynamic component σ²=σₛ²+σₕ². The static component σₛ² originates from inherent crystallographic disorder in the sample and the dynamic component σₕ² from thermal vibrations of the atoms around their equilibrium position. For quantification of the thermal component, an anharmonic, correlated Einstein model is often used, which assumes a single frequency to approximate the mean value of the local vibrational density of states (VDOS). The EXAFS Debye-Waller factor can then be written as[8]:

$$
σ² = \frac{h}{2ωμ} \times \frac{1+\exp(-θₜ/E)}{1-\exp(-θₜ/E)} + σₛ², \quad (1)
$$

where $μ$ is the reduced mass, $θₜ$ the Einstein temperature, and $ω=θₑk_B/h$ the corresponding Einstein frequency. Figure 2 shows the temperature dependence of the Debye-Waller factor for the metal film standard and the two different NC sizes of each metal for (a) Au and (b) Cu. The dotted lines show the corresponding fits to equation (1). Values for $θₜ$ and $σₛ²$ are listed in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$θₜ$ [K]</th>
<th>$σₛ² \times 10^{-3} \text{Å}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au foil</td>
<td>133.1±2.4</td>
<td>-0.2±0.2</td>
</tr>
<tr>
<td>Au NCs 3.6 nm Ø</td>
<td>136.6±2.2</td>
<td>2.4±0.1</td>
</tr>
<tr>
<td>Au NCs 2.5 nm Ø</td>
<td>131.0±3.9</td>
<td>3.9±0.2</td>
</tr>
<tr>
<td>Cu foil</td>
<td>236.4±2.8</td>
<td>-0.4±0.2</td>
</tr>
<tr>
<td>Cu NCs 14 nm Ø</td>
<td>231.3±3.6</td>
<td>-0.3±0.2</td>
</tr>
<tr>
<td>Cu NCs 3.3 nm Ø</td>
<td>205.5±8.2</td>
<td>0.5±0.4</td>
</tr>
</tbody>
</table>

The experimental Einstein temperatures for both standards agree very well with previously obtained values[9]. Only a small deviation of the Einstein temperatures for the Au NCs compared to the Au foil is apparent. These deviations, however, are of similar magnitude as the associated fitting errors. The values for Cu NCs show a decrease with NC size. 14 nm NCs already show a decrease in $θₜ$ despite the fact that at such sizes the Cu NCs show near bulk like behavior in the structural parameters[3]. The 3.3 nm NCs show a significant decrease of more than 10% as compared to the foil standard. The static components $σₛ²$ of the Debye-Waller factor increase with decreasing NC size and are virtually zero for the standards and the large Cu NCs. We note that the small negative values given in Table 1 carry no physical meaning and have to be considered as small, negligible offsets.

DISCUSSION

In metallic NCs, simulations[10] show a broadening of the VDOS at low and high frequencies as the result of two main effects: (i) undercoordinated surface atoms lead to a softening of the VDOS at low frequencies and (ii) surface tension effects lead to a bond-length contraction and thus stiffening of the bonds in the NC interior. In previous experiments, we have observed a significant size dependent bond-length contraction for both NC systems under investigation[2, 3] consistent with surface tension effects, and as such we expect stiffening of the bonds in the NC interior.
However, the single frequency Einstein model we use here yields an average of the VDOS. Both effects described above can thus be seen as competing and the Einstein frequency evaluated from our EXAFS measurements can give an indication which of these effects dominates. For the Cu NCs a net softening of the VDOS is clearly apparent indicating that the contribution of the surface atoms governs the change in the VDOS. The Au NCs show no clear deviation compared to bulk, although the 2.5 nm Au NCs show some indication of a change in cluster structure. This suggests a balance between the two effects.

Previous investigations on metallic NCs (Pt[8], Ag[11], Pd[11]) have reported a decrease in the Einstein temperature which has been attributed to the vibration of the surface atoms. For Au NCs both a decrease[4] and an increase[12] of the Einstein frequency have been observed. Intuitively one would expect that surface termination of the NCs (for example embedded or ligand stabilized NCs), and as such the fabrication method, can have a profound influence on their mean vibrational properties. This could be one factor for the small variation in the Einstein temperature observed for Au NCs in this work.

CONCLUSIONS

In conclusion, we have investigated vibrational properties of Au and Cu NCs formed by ion implantation in SiO₂. We observed a size dependent decrease of the Einstein temperature for Cu NCs whereas only slight variations are apparent for the Au NCs. The decrease can be explained by softening of the VDOS due to the undercoordinated surface atoms.

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REFERENCES