Observation of anharmonicity for copper thin film near room temperatures

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The fluorescence EXAFS spectra for a copper thin film with a thickness of 3000Å measured at 300K, 350K and 400K were analyzed by the regularization method to directly obtain the radial distribution. The pair distribution was almost symmetric for 300K but asymmetric for 350K and 400K. This indicates that the atoms in copper vibrate anharmonically near room temperatures. The anharmonicity and the skewness of the asymmetric distribu-tion increases as temperature increases.

Key words : EXAFS, anharmonicity, thermal disorder, regularization method

1. Introduction

The anharmonicity of atomic vibration has been frequently reported in the extended absorption fine structure (EXAFS) fields since Tranquada pointed out that CuBr has the anharmonicity at a very low temperature (Yokoyama, *et al.*, 1996, Sayers, *et al.*, 1971, Stern *et al.*, 1975, Tranquada & Ingalls, 1983). Recently, studies of anharmonicity have been stimulated to measure the thermal expansion of atoms in solids (Frenkel & Rehr, 1993, Dalba *et al.*, 1993, Tröger *et al.*, 1994, Yang & Joo, 1998).

The commonly used method to measure the anharmonicity was the cumulant expansion method (Koningsberger & Prins, 1988). However, it is very difficult to measure the cumulants because all cumulants vary imultaneously with the measuring temperatures.

In this study, the regularization algorithm (Yang & Bunker, 1996, Babanov *et al.*, 1981) has been introduced into the mea-surement of the anharmonicity. A unnormalized pair distribution is directly obtained by the regularization procedure from the EXAFS spectrum, and the anharmonicity is shown by the asym-metry of the distribution.

2. Experiments

A thin film of copper with a thickness of 3000Å was deposited on the silicon wafer by the RF sputtering system.

EXAFS experiments were carried out at the beam line 3C1 EXAFS of the Pohang Light Source (PLS) in Korea. The PLS operates with an electron energy of 2.5 GeV and a maximum current of 220 mA. X-rays were monochromatized by a Si(111) double crystal monochromator with the energy resolution, $\Delta E/E = 2 \times 10^{-4}$. The higher harmonics were eliminated by a 15 percent detuning of the crystal.

The EXAFS spectrum was measured at about 300K, 350K and 400K in Cu K-edge (8979eV) in the gazing angle fluorescence mode. In order to detect the X-ray intensity, the ionization chamber before the sample was filled with a flowing nitrogen gas and the fluorescence signal was detected by the solid state detector.

3. Regularization method

The EXAFS equation can be expressed in terms of the pair distribution function, $g(r)$,

$$\chi(k) = \frac{NS_0^2(k)F(k,r)}{k} \int_0^\infty \frac{g(r)}{r^2} e^{-2r/\lambda(k)} \times \sin(2kr + \varphi(k,r))dr \tag{1}$$

where $F(k,r)$ is the effective backscattering amplitude, $S_0^2(k)$ is the many electron overlap factor, N is the coordination number, R is the interatomic distance, λ is the mean free path of photo-electron, and $\varphi(k)$ is the phase shift due to the atomic potentials.

Eq. (1) can be simplified and vectorized as follow,

$$\chi = Ag \tag{2}$$

where χ and A are $m \times n$ matrices, g is a column vector made by $g(r)$ multiplied by N, and A is a matrix calculated $K(k,r)$ given by

$$K(k,r) = \frac{S_0^2(k)F(k,r)}{k} \frac{1}{r^2} e^{-2r/\lambda(k)} \times \sin(2kr + \varphi(k,r)) \tag{3}$$

The solution of g^n is obtained from the functional minimum condition

$$\Psi(g, \alpha, \beta) = \| \chi - Ag \|^2 + \alpha \int_0^\infty |g(r)|^2 dr + \beta \int_0^\infty |\frac{d}{dr}g(r)|^2 dr + \gamma \| g - |g| \|^2 \tag{4}$$

where α is a regularization parameter, β a smoothness parameter, and λ is a positivity parameter.

From the minimum condition of Eq. (4), we obtain,

$$\left(\sum_m A_{mn}^* A_{mn} + \tau(\alpha + 2\lambda S^n)I + \beta \sum_m B^{mn} \right)g^n = \sum_m A_{mn}^* \chi^m \tag{5}$$

where

$$S^n = \begin{pmatrix} 0, \ if \ g^n \geq 0 \\ 2, otherwise \end{pmatrix} \tag{6}$$

and

$$B = \begin{pmatrix} 2h & -h & 0 & \cdots & 0 \\ -h & 2h & -h & \cdots & 0 \\ 0 & -h & 2h & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & 0 & \cdots & 2h \end{pmatrix} \tag{7}$$

with $\tau = \Delta r / \Delta k$ and $h = 1/\Delta r \Delta k$. The radial distribution, $g(r)$ is obtained by the matrix form in Eq. (5).

4. Results and Discussion

The EXAFS data were taken by the glazing incidence fluore-scence EXAFS experimental set up. The glazing angle was about

5° and the temperatures were about 300K, 350K and 400K for each scan, respectively. The temperature was controlled within ±5K while a scan was completed.

EXAFS spectra obtained by the standard precedure (Koningsberger & Prins, 1988) from the florescence specta were transformed by Fourier transformation. Fig. 1 is the Fourier transformed spectra for the indicated temperatures. As shown in Fig.1, the magnitude of the spectrum decreased significantly as the temperature increased. However, the positions of the first shell are unchanged.

The reduction of the magnitude in the Fourier transformed spectra can be interpreted by both the harmonic and the anharmonic effects of the interatomic motion. Unfortunately, it is hard to see the anharmonic effect only from the Fourier transformed spectra shown in Fig. 1.
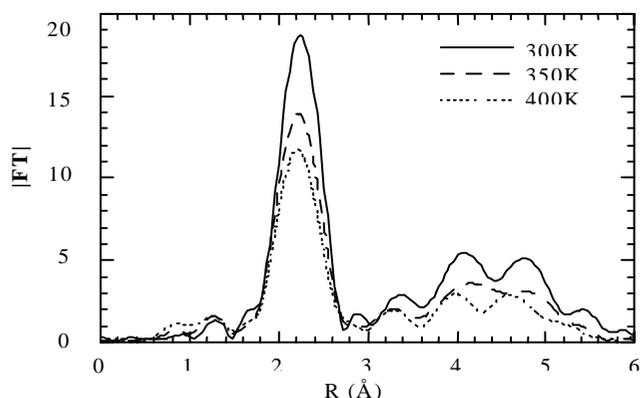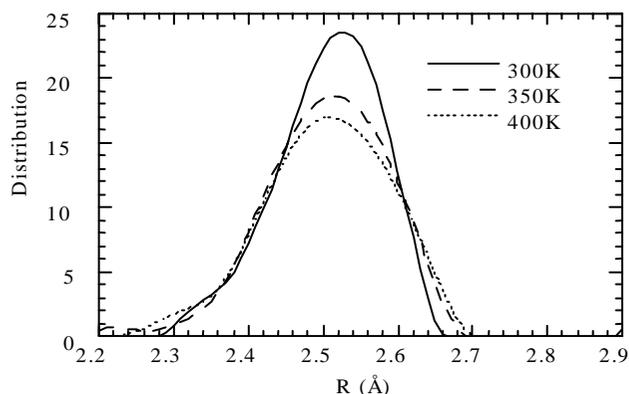

Figure 1
Fourier transformed spectra of the fluorescence EXAFS spectra measured at 300K, 350K and 400K

Fig. 2 is the filtered EXAFS spectra of the first shells in the Fourier transformed spectra. The filtered spectrum is obtained by the inverse Fourier transformation. As shown in Fig. 2, the amplitude decreases while the phase increases slightly as the temperature increases. In general, the harmonic vibration causes only the reduction of the amplitude. The simultaneous variations, which are the reduction of the amplitude and the increases of the phases, can be interpreted by the anharmonic vibrational effect. However, the changes of phases in Fig. 2 are so small that the anharmonic effect cannot be shown clearly.
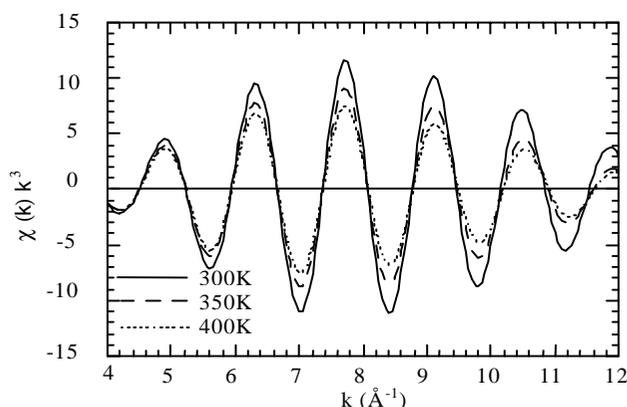
Figure 2.
The first shell EXAFS spectra filtered by the inverse transformation from the Fourier transformed spectra

The unnormalized pair distribution was directly obtained by the regularization procedure. The unnormalized pair distribution does not match the real pair distribution but gives useful information such as the shell position (interatomic distance) and the width of the distribution. Fig. 3 showes the unnormalized pair distribution of atoms in the first shell. As shown in Fig. 3, the distribution is not realistic because it is not symmetric and there are big tails in low R region. It could be a systematic error due to the regularization process. However, the spectra in the region beyond R=2.4Å in Fig. 3 give interesting results

Figure 3
Radial distribution extracted by the regularization method from the filtered spectra.

In the process of regularization, the parameters for the regularization were $\alpha=10^{-5.5}$, $\beta=10^{-6.5}$ and $\gamma=10^{-2.5}$. As shown in Fig. 3, the radial distribution of the spectrum measured at 300K is almost symmetric but the distribution for 350K is slightly asymmetric. The skewness of the asymmetric distribution increa-ses as temperature increases.

The asymmetric pair distribution can be related to the anharmonic vibrations of atoms. In a rough approximation, the distribution can be expressed by Boltzmann's distribution,

$$g(r) = g(r_0)e^{-\frac{V(r)}{k_B T}} \qquad (8)$$

where $g(r)$ is the pair distribution function, $V(r)$ is the atomic potential and k_B is Boltzmann's constant. The asymmetric pair distribution can be expressed by the anharmonic potential,

$$V(r) = \frac{1}{2}k_0(r - r_0)^2 - k_3(r - r_0)^3 \qquad (9)$$

where k_0 is the force constant and k_3 is the anharmonic parameter due to the mutual repulsion of atoms. As shown in previous work (Yang & Joo, 1998), the pair distribution in Eq. 8 can be expressed in terms of the parameters of anharmonic potential as

$$g(r) = g(r_0)\left(\frac{r - r_m}{\delta}\right)^s e^{-\left(\frac{r - r_m}{\delta}\right)} \qquad (10)$$

where r_m is the closest distance and

$$s = \frac{k_0^3}{9k_3^2 k_B T}, \; \delta = \frac{3k_3}{k_0^2} k_B T.$$

The skewness of the distribution in Eqs. 8 and 10 increases as the anharmonic term in Eq. 9 increases.

Even trough the distribution in Fig. 3 is not a real pair distribution, we can see a systematic changes of the distribution. The distribution at 350K is already asymmetric. This indicates that the anharmonic vibration occurs at low temperature and the anharmonicity can be measured at a much lower temperature than the melting temperature.

5. Summary

In this work, the asymmetric pair distribution due to the anharmonic vibration of atoms in a copper thin film is directly observed by the EXAFS analysis with the regularization method in relatively low temperatures.

This showed that the anharmonicity can be measured at a much lower temperature than the melting temperature.

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