Soft X-ray emission spectra of argon atoms doped in solid matrices

Yasuji Muramatsu a,∗, Tomoyuki Yamamoto b, Jonathan D. Denlinger c, Rupert C.C. Perera c

a Kansai Research Establishment, Japan Atomic Energy Research Institute (JAERI), 1-1-1 Kouto, Mikazuki, Sayo-gun, Hyogo 679-5148, Japan
b Faculty of Engineering, Kyoto University, Yoshida Honmachi, Sakyo-ku, Kyoto 606-8501, Japan
c Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

Available online 5 March 2005

Abstract

Soft X-ray emission spectra in the Ar L region of various solid substrates doped with Ar atoms were measured to investigate the chemical states of the Ar atoms in the solid matrices. Ar ions were implanted into the solid matrices of Si(1 1 1), SiO 2 , highly oriented pyrolytic graphite (HOPG), Ti, Cr, Ni, and Cu with an acceleration voltage of 5 kV at room temperature. Soft X-ray emission spectra in the Ar L region were measured using synchrotron radiation. Low-energy tailing was observed at the L3 –M 1 and L 2 –M 1 X-ray emission peaks in Ar-doped transition metals. The density of states (DOS) of the Ar 3s orbitals indicated that the low-energy tailed DOS can be formed by hybridization with 3d orbitals in the overpressurized Ar clusters.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Argon; X-ray emission; Soft X-ray; Synchrotron radiation

1. Introduction

Since the 1980s, the behavior of rare gas atoms in solid matrices has been experimentally investigated with regards to developing nuclear technology and sputtering technology. Especially, studies on bubble formation of rare gases in solid matrices have been intensively examined since vom Felde et al.’s [1] and Templier et al.’s [2] experimental works. Bubble formation of rare gases doped in various solid matrices are typically probed using transmission electron microscope (TEM) with electron diffraction [3,4], electron energy loss spectroscopy (EELS) [5], and X-ray absorption spectroscopy (XAS) [6] using synchrotron radiation to observe direct evidence of overpressurized rare-gas bubbles in solid matrices. Soft X-ray emission spectroscopy (XES) using synchrotron radiation is another promising method for chemical state analysis of bulk materials. However, few studies have investigated bubble formation of rare gases using XES. Thus, we applied XES to analyze rare gas bubbles in solid matrices.

In this study, we measured the Ar L X-ray emission spectra of Ar-doped solid matrices of Si(1 1 1), SiO 2 (quartz), highly oriented pyrolytic graphite (HOPG), Ti, Cr, Ni, and Cu using synchrotron radiation. This paper compares the spectral features among these Ar-doped solid matrices and the chemical state analysis of the Ar atoms with regards to bubble formation using molecular orbital (MO) calculations.

2. Experimental

Ar ion beams were implanted into solid matrices of Si(1 1 1), SiO 2, HOPG, Ti, Cr, Ni, and Cu substrates in the Ar gas pressure of 2 × 10−5 Torr at room temperature with a 5 kV acceleration voltage. The estimated penetration depth of Ar atoms in Si is 15 nm. Spectroscopic measurements of the soft X-ray emission and absorption in the Ar L region were performed at beamline BL-8.0.1 [7] of the advanced light source (ALS). The Ar L X-ray emission spectra were measured using a grating X-ray spectrometer equipped with a 1500-lines/mm grating, a 5 m radius of curvature, and a 50 μm entrance slit. The total electron yield (TEY) and fluorescence yield (FY) X-ray ab-
sorption spectra were also measured using the spectrometer at BL-8.0.1.

3. Results and discussion

Fig. 1 shows the Ar L X-ray emission spectra of the Ar-doped Si(1 1 1) in which the excitation energy was tuned from near the Ar L absorption edge to the higher energy region. A two-peak structure composed of L3–M1 and L2–M1 peaks is clearly observed with excitation energies of 250.6 eV and higher. However, higher-energy satellites are also observed at excitation energies of 399.6 eV and higher. These satellites generally result in the multiple-ionization where the L2,3M2,3 double vacancy is the dominant component by higher energy excitation above ionization threshold energy [8]. From the binding energy of the L2,3 and M2,3 electrons, this double vacancy requires at least 260 eV for excitation. Therefore, the Ar L X-ray emission spectra without the multiple-ionization satellites can be obtained using 256.6 eV excitation. Fig. 2 shows the Ar L X-ray emission spectra of the Ar-doped solid matrices excited by 256.6 eV in which multiple-ionization satellites are not observed. In the spectra of Si, SiO2, and HOPG, L3–M1 and L2–M1 peaks are clearly separated from each other. However, in the transition metal spectra, the peaks appear to overlap. In order to compare their spectral shapes, the spectra of SiO2 and HOPG are drawn on the spectrum of Si and their subtracted spectra of \( \text{SiO}_2 - \text{Si} \) and \( \text{HOPG} - \text{Si} \) are shown in Fig. 3. From this figure, it is confirmed that the spectral shapes of SiO2 and HOPG nearly correspond to that of Si. Fig. 4 compares the spectral feature of the transition metals with Si and their subtracted spectra. Compared to the peak shapes in Si, low-energy tailings are observed in both L3–M1 and L2–M1 peaks of the transition metals. This low-energy tailing in L3–M1 and L2–M1 peaks in metals is clearly confirmed in their subtracted spectra.

To explain the low-energy tailings of the L₃–M₁ and L₂–M₁ peaks in the Ar L X-ray emission spectra of Ar-doped in transition metals, density of states (DOS) of the Ar clusters are calculated by discrete variational (DV)-Xα molecular orbital calculations [9] since bubble formation of Ar atoms is probable in transition metal matrices [10]. The upper panel in Fig. 5 shows the fcc-structured Ar₆₃ cluster model used in the calculations. In the calculations, the lattice parameter (a) of the cluster model varied from 4.5 to 5.1 Å and the basis set of the orbitals is expanded to 1s, 2s, 2p, 3s, 3p, 3d, 4s, and 4p to consider orbital overlapping of the valence orbitals with the outer 4s and 4p orbitals in the overpressurized clusters. The lower panel of Fig. 5 shows the DOS spectra of the centered Ar atom in the Ar₆₃ cluster models with the lattice parameters of 4.5 and 5.1 Å. These spectra are obtained by broadening the DOS with the 0.5 eV wide Lorentzian functions. It can be confirmed that the 3p orbitals are hybridized with 3d orbitals, but the inner 3s orbitals are not hybridized with 3p orbitals in the models. The overpressurized-lattice effects on the DOS are clearly observed; hybridization between the 3p and 3d orbitals can be enhanced by the overpressurized lattice (a = 4.5 Å) and that between the 3s and 3d orbitals can be detected. Consequently, the DOS of the inner 3s orbitals can be affected through the hybridized 3p and 3d orbitals by the overpressurized lattice structure. Fig. 6 shows the lattice-parameter-dependence on the 3s-DOS spectra, which clearly shows that low-energy tailing can be formed on the 3d-DOS in the overpressurized Ar clusters. This low-energy tailing on 3s-DOS is consistent with the observed low-energy tailing of the L₃–M₁ and L₂–M₁ peaks in Ar L X-ray emission spectra of Ar-doped in transition metals.

4. Conclusion

We measured the soft X-ray emission spectra in the Ar L region of Ar atoms doped in various solid matrices (Si, SiO₂, HOPG, Ti, Cr, Ni, and Cu) to investigate the chemical states of the Ar atoms in the solid matrices. Low-energy tailing is observed at the L₃–M₁ and L₂–M₁ X-ray emission peaks in Ar-doped transition metals, but tailings are not observed in the Ar-doped Si, SiO₂, and HOPG. From the spectral analysis by DV-Xα MO calculations using fcc-structured Ar₆₃ cluster models, a probable explanation for the observed low-energy tailing in the L₃–M₁ and L₂–M₁ peaks is the hybridized Ar 3s-DOS of the overpressurized Ar clusters. This spectral anal-
ysis result seems to be consistent with the existence of the overpressurized Ar bubbles in solid matrices.

Acknowledgments

This work has been supported by the grant-in-aid from the Japanese Ministry of Education, Culture, Sports, Science, and Technology under contract no. 15550081 and by the US Department of Energy under contract no. DE-AC03-76SF00098.

References