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Electronic structure of $CeAl_2$ thin films studied by X-ray absorption spectroscopy

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Abstract

We report X-ray absorption near edge structures (XANES) study of $CeAl_2$ thin films of various thicknesses, 40–120 nm, at Al K- and Ce L_3-edges. The threshold of the absorption features at the Al K-edge shifts to the higher photon energy side as film thickness decreases, implying a decreased in Al p-orbital charges. On the other hand, from Ce L_3-edge spectra, we observed a decrease in the 5d4f occupancy as the surface-to-bulk ratio increases. The valence of Ce in these thin films, as revealed by the Ce L_3-edge spectral results, is mainly trivalent. From a more detailed analysis we found a small amount of Ce^{4+} contribution, which increases with decreasing film thickness. Our results indicate that the surface-to-bulk ratio is the key factor which affects the electronic structure of $CeAl_2$ thin films. The above observations also suggest that charge transfer from Al to Ce is associated with the decrease of the film thickness.

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Keywords: XANES; Mixed valence; Surface; Thin film

1. Introduction

The subject of finite size effects on physical properties of nanoparticles has attracted tremendous interests in the recent years due to their applications in the emerging nanotechnology [1,2]. The concept of surface-to-bulk ratio plays a very important role in understanding these materials. They exhibit physical properties different from those of the bulk, including geometric structure, electronic band structure and magnetism essentially because of a symmetry breaking and/or of a lower dimensionality. The absence of three-dimensional symmetry at the surface changes the electronic structure and the magnetic properties. In many cases, unique properties of nanoparticles arise because of the competition between surface magnetic properties and core magnetic properties. Two major factors determine the electron energy levels of nanoparticles, the increased surface area and the reduced coordination. The former tends to broaden the band while the latter tends to narrow the band [3]. Direct measurement of the electronic structure of nanocrystalline materials using X-ray absorption spectroscopy techniques revealed various interesting effects [3–5]. In a recent work [5], we reported that decrease of 4f occupancy and narrower line-width in 8 nm nanoparticle of $CeAl_2$ was attributed to surface effects caused by the small particle size, including lower coordination number and higher surface pressure. Due to the limitation of sample preparation method, the flash evaporation [6], only 8 nm particles were successfully obtained. In order to verify the effect of different surface-to-bulk ratio on electronic state of $CeAl_2$, thin films of different thickness were investigated. As the thickness of the film enters the nanoscale regime, the electronic structure gets modified which in turn affects the electronic properties of the materials dominated progressively by surface effects. X-ray absorption near edge structure (XANES) is the modulation of

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the absorption signal associated with an electronic transition from an inner level to outer unoccupied electronic states. Therefore, XANES offers as one of the most powerful ways to understand the variation in the electronic structure. In this study, we report the results of XANES study of $CeAl_2$ at various thickness and discuss the changes in the electronic structure as the thickness is varied.

2. Experimental

The bulk samples of $CeAl_2$ used in this study were prepared by arc melting the high-purity constituent elements in an argon atmosphere. Details of the procedure are described elsewhere [6]. The $CeAl_2$ thin films of thickness 40, 65, 80, 100 and 120 nm were fabricated by flash evaporation of the bulk $CeAl_2$ ingot on MgO (1 0 0) substrate, which was attached on a liquid nitrogen cold trap in a 0.1 Torr of high-purity helium. The thickness of these films was monitored by a quartz crystal oscillator during the evaporation process. There were no traces of CeO_2, the commonly formed impurity in Ce-based intermetallics, within the resolution limit of our X-ray diffractometer. Neither did we observe any other impurity compounds due to possible film-substrate interactions. X-ray absorption measurements were performed at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The XANES at Ce L_3-edge spectra were taken at beamline 17C (wiggler beamline) using fluorescent mode at room temperature. The XANES spectra at Al K-edge were recorded at beamline 20A (also known as HSGM) using total electron yield and fluorescent mode, respectively. The energy resolutions of beamline 17C and 20A are better than 0.4 and 0.2 eV, respectively.

3. Results and discussion

Fig. 1 shows the XANES spectra of $CeAl_2$ thin films of different thickness, varying from 40 to 120 nm, along with a piece of pure Al metal foil at Al K-edge. The spectral features of Al K-edge XANES spectra of the $CeAl_2$ films are very similar but differ significantly from that of pure Al. The intensities of the leading features of $CeAl_2$ thin films are significantly enhanced and the inflection point of the threshold clearly shift towards the higher energy relative to that of pure Al. According to the dipole-transition selection rules the leading feature in Fig. 1 is due to transitions from 1s core state to unoccupied Al 3p derived states that hybridize strongly with Ce 4f–5d states in the $CeAl_2$. The intensity of feature A_1, 1555–1563 eV, is significantly reduced and feature B_1 (located at around 1570 eV) is enhanced in the $CeAl_2$ thin films.

Fig. 2 (top panel) shows that the leading edge shifts to higher energy as indicated by the arrow while the intensity of the feature B_1 decreases when thickness is increased from 40 to 120 nm samples. This result suggests that Al loses more p-orbital charge to the Ce and has a more attractive electrostatic potential when the thickness of the thin films are reduced. This reduction of the p-state charge results in lessening the screening of the Al nuclear charge and thus lowers the Al 1s energy level.

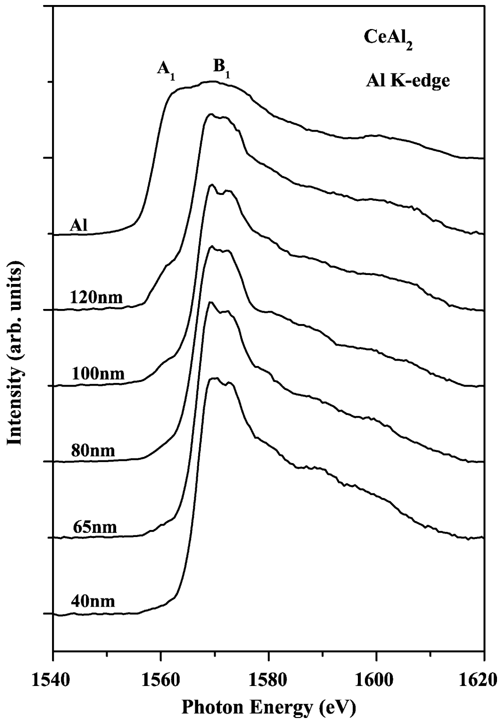

Fig. 1. Normalized XANES spectra of various $CeAl_2$ thin films (40, 65, 80, 100 and 120 nm) at Al K-edge and pure Al metal.

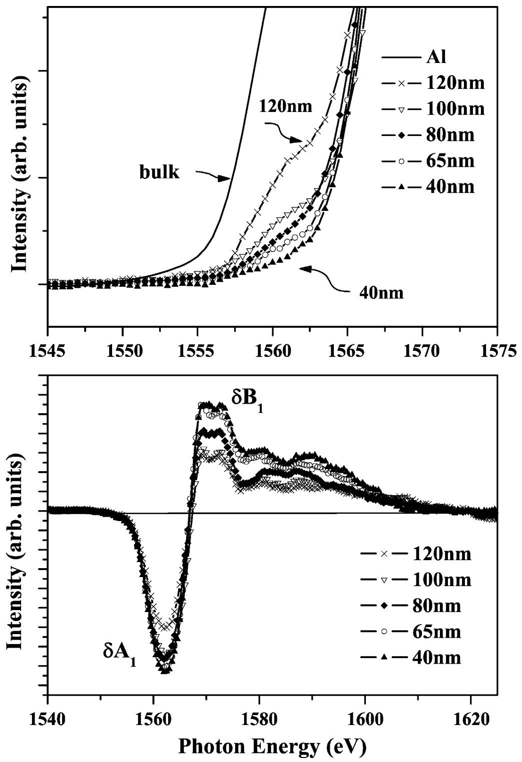

Fig. 2. The magnified leading features at the threshold of XANES spectra at Al K-edge are shown. Note that edges for films shift toward the higher energy side with the decrease in thickness of the films. The lower panel shows the difference spectra of $CeAl_2$ thin films obtained after subtracting pure Al K-edge spectra.

Also observed is the increase of the Al 3p holes with reducing thickness, determined by the difference of the densities of Al 3p states for $CeAl_2$ films and pure Al just above the Fermi level. In the earlier report [7], the density of states (DOS) for Al unoccupied states with s, p and d characters spread up to ~60 eV. Thus, the normalization procedure is conducted by matching the absorption coefficient from below the threshold to 60 eV above in the energy range between 1610 and 1620 eV. The relative intensity of the area under feature A_1 and B_1 with respect to pure Al, which is obtained from the spectral difference ($\delta A_1 + \delta B_1$) between each film and the pure Al, is plotted in the lower panel of Fig. 2. The integrations of the spectral difference (not shown in Fig. 2) increase systematically from 1.56 to 9.32 as the film thickness decreases from 120 to 40 nm. This comparison implies that Al loses p-orbital charge which is in accordance with the proposition indicated by the shift of the edge of spectra. It may be noted that the surface-to-bulk ratio is 0.0250, 0.0154, 0.0125, 0.0100 and 0.0083 nm^{-1} for thickness of 40, 65, 80, 100 and 120 nm, respectively. The relation between the integration ($\delta A_1 + \delta B_1$) and surface-to-bulk ratio as a function of film thickness can be seen in the inset of Fig. 4. This implies the charge transfer is closely related to the surface-to-bulk ratio.

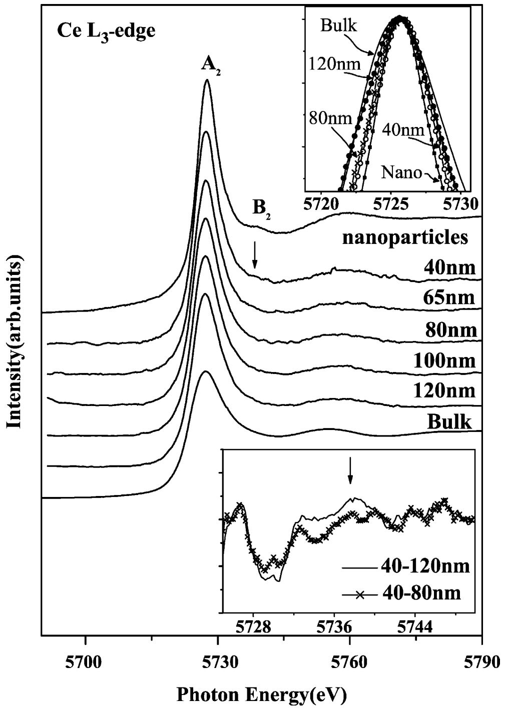

Fig. 3. XANES spectra at Ce L_3-edge for various thickness of $CeAl_2$ thin films along with bulk and nanoparticles. Note that the intensity of the feature assigned to Ce^{4+} is significantly high (marked as B_2) in nanoparticles compared to thin films of $CeAl_2$.

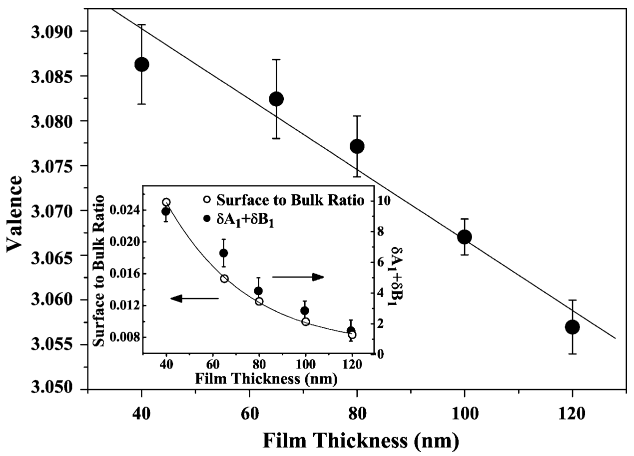

Fig. 4. The average valence of Ce as a function of the film thickness is shown. The inset shows the relation between the integration area under Al K-edge and surface-to-bulk ratio as a function of film thickness.

Fig. 3 plots the series of Ce L_3-edge spectra for different thickness of $CeAl_2$ thin films, together with the bulk and nanoparticles as reference samples. The main peak A_2 near 5727 eV corresponds to trivalent Ce in $CeAl_2$ with a $4f^1(5d6s)^3$ configuration, and a small and unclear feature B_2 on the higher energy side of this peak near 5738 eV corresponds to tetravalent Ce in $CeAl_2$ with a $4f^0(5d6s)^4$ configuration [8] marked by an arrow is observed in nanoparticles and rather unclear in 40 nm film. The general line shapes in Ce L_3-edge of thin films display similar profiles. It is obvious that all films show strong trivalent peak, whereas the tetravalent peak has much lower intensity and it is almost merged into the trivalent peak, the variation of the $4f^0$ contribution is rather obscure. At a closer inspection, two consequences are revealed. First, the line-width reduces as the film thickness decreases, as shown in upper inset of Fig. 3. This effect of reduced line-width, which is similar to the effect observed from the nanoparticles [5], may due to the lower density of states at the Fermi level as a result of the higher surface-to-bulk ratio [9]. Second, the evolution of Ce^{4+} features can be extracted by subtracting the spectrum for each film from the thinnest one (40 nm), as can be seen in the lower inset in Fig. 3. The variation of $4f^0(5d6s)^4$ state marked by an arrow shows that Ce^{4+} contribution is increased as thickness decreased. In general, by a standard procedure [10], the A_2 and B_2 features can be isolated by fitting two Lorentzians curves for the peaks corresponding to Ce^{3+} and Ce^{4+} after subtracting the arctangent edge jump from the XANES spectrum. The average Ce valence for the sample can be calculated by summing the weighted 3+ and 4+ contributions $(v = 3 + (I_{\mathrm{Ce}^{4+}}/(I_{\mathrm{Ce}^{3+}} + I_{\mathrm{Ce}^{4+}})))$ [10]. Fig. 4 plots the average valence as a function of the film thickness. The valence change is interpreted as due to the surface pressure becomes significant. This surface pressure may raise the 4f level relative to the Fermi level and give rise to promote 4f electron to the conduction band [5]. Moreover, the inset shows the integration ($\delta A_1 + \delta B_1$) as a function of the film thickness. An important point which should be noted is that in thinner film, the Al loses more p-orbital charges and exhibits higher valence. The valence change may also correlate with Ce–Al charge transfer behavior.

4. Conclusion

Based on our XANES study we have confirmed that Ce is mixed valent in $CeAl_2$ thin films. The spectral features assigned to Ce^{4+} increases with the decrease of thickness. This variation in the electronic state of Ce is attributed to the charge transfer from Al due to the increased surface-to-bulk ratio. Additionally, the valence change evidenced by Ce L_3-edge is due to transfer the 4f electrons to the conduction band. The variation in the electronic structure (from $4f^1$ to $4f^0$ configuration) of Ce can be understood as the charge transfer from Al 3p state to Ce 4f state, which reduces the energy difference between 4f and 5d orbitals, followed by the promotion the 4f electron to 5d state.

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