ELSEVIER

Journal of Nuclear Materials 283–287 (2000) 1405–1408

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

XPS and UPS studies on electronic structure of Li_2O

Satoru Tanaka [a,*], Masaki Taniguchi [b], Hisashi Tanigawa [a]

[a] *Department of Quantum Engineering and Systems Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[b] *Naka Fusion Research Establishment, Japan Atomic Energy Research Institute, 801-1 Mukoyama, Naka-machi, Ibaraki-ken 311-0193, Japan*

Abstract

The adsorption behavior of H_2O on Li_2O was studied by X-ray photo electron spectroscopy (XPS) and ultraviolet photo electron spectroscopy (UPS). XPS and UPS spectra of Li_2O single crystals which were exposed to different pressure of H_2O vapor were observed. In O(1s) region, two peaks were observed and they were assigned to O(1s) in precipitated LiOH on the surface and O(1s) in Li_2O. After H_2O exposure, a peak broadening and an appearance of a new peak were observed at the higher binding energy region than O(1s) in Li_2O. They were attributed to surface −OH and H_2O molecule adsorbed on the surface. The adsorption behavior of H_2O was discussed from the observation of electronic structure in Li_2O surface.

1. Introduction

Lithium oxide (Li_2O) has been considered as a potential candidate for the blanket breeding material because of its high lithium atom density. It is required to understand the tritium release behavior from the blanket materials in order to design the fusion reactor fuel cycle. In solid breeding materials, tritium is considered to be released through diffusion in the grain, diffusion along grain boundaries and desorption of surface hydroxyl groups. Among these processes, recent experimental results have suggested the importance of the surface process. The present authors have been conducting quantum chemical calculations about the adsorption and desorption of H_2O and H_2 on the surface of Li_2O [1,2]. It was shown that the charge transfer from the surface to the adsorbate was important in the dissociative adsorption of H_2O and H_2. It is considered that the electronic states of the surface vary largely by the interaction with the adsorbate. Therefore, it is possible to study the adsorption behavior of H_2O and H_2 by observing the electronic state of the surface by X-ray photo electron spectroscopy (XPS) and ultraviolet photo electron spectroscopy (UPS).

From XPS, core-level spectra of oxygen and lithium near the surface are obtained. Different chemical states near the surface lead to a 'chemical shift' of these spectra. Observing this chemical shift gives us important knowledge about surface phenomena such as adsorption of −OH or production of vacancies. UPS enables us to observe valence-band spectra. The energy of the photons in the UPS, 21.2 eV in this study, is much smaller than that of photons in the XPS. Therefore, UPS is more sensitive to variation of electronic states at the surface. Generally, the width of the valence-band spectra is so large that it is difficult to analyze the obtained spectra when more than two kinds of molecules coexist. In such a case, XPS is more useful because core-level spectra localize and are easily separated. In this paper, electronic states of the Li_2O surface were studied by XPS and UPS especially emphasizing the adsorption behavior of H_2O.

2. Experimental

Single crystal of Li_2O was used for investigations. The floating zone growth method has been used for the preparation of Li_2O single crystal rods. The obtained single crystal rods whose diameter is about 8 mm were cut into disk with about 1 mm thick. XPS and UPS spectra were recorded using JEOL, JPS-9800 with ultra violet source (AP-Z7021T). It has the preparation

---

[*] Corresponding author. Tel.: +81-3 3812 2111; fax: +81-3 3818 3455.
E-mail address: chitanak@q.t.u-tokyo.ac.jp (S. Tanaka).

0022-3115/00/$ - see front matter
PII: S0022-3115(00)00251-8

chamber separated from the measurement chamber. In the preparation chamber, samples could be annealed and exposed to H_2 or H_2O gases at controlled pressure. After the pre-treatment, the sample was transferred to the adjacent measurement chamber. XPS and UPS measurements were performed using MgKα X-ray source at 1253.6 eV and He discharge lamp at 21.2 eV (He I), respectively. During the observation, the measurement chamber was kept at 10^{-8} Pa in XPS and 10^{-6} Pa with He gas in UPS. Each spectra of emitted electrons were recorded at the resolution of 0.1 eV.

3. Results and discussion

3.1. XPS spectra on Li_2O surface

The XPS spectra are shown in Fig. 1 for an Li_2O sample placed into the vacuum system from the air and then sputtered by Ar ions at 500 eV for 10 s. Only this wide range spectra were recorded at the resolution of 1 eV. Besides the peaks from Li and O, the peaks from C and Ar were observed. Observed spectra position was considered to be affected by the charge pile-up because Li_2O is a insulator. Therefore, the peak energy was calibrated by the C(1s) peak.

3.1.1. O(1s) spectra in Li_2O

O(1s) spectra were shown in Fig. 2. Before Ar ion sputtering, a peak was observed at 532 eV. The sample was sputtered by Ar ion with 500 eV for 60 s and XPS spectra were measured again. It was observed that the peak broadened to a lower binding energy region after sputtering. After additional sputtering for 60 s, the peak at 528.5 eV appeared. This shows that several chemical states of oxygen exist near the surface. Two peaks observed at 531 and 528.5 eV were also observed in the annealed samples. O(1s) spectra for the annealed sample at 573 and 873 K for 12 h are shown in Fig. 3. After annealing at 873 K, the peak at 531 eV vanished and only the peak at 528.5 eV was observed.

Li_2O can easily react with H_2O or CO_2 in the air and LiOH or Li_2CO_3 are produced on the surface. These two peaks in O(1s) spectra were observed after C(1s) peak vanished by sputtering. From these results, the peak at 531 eV was attributed to O(1s) in the precipitated LiOH on the surface and the peak at 528.5 eV to O(1s) in Li_2O.

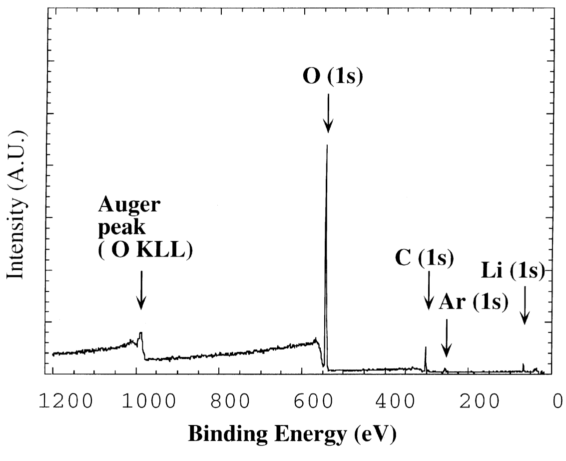

Fig. 1. XPS spectra in Li_2O.

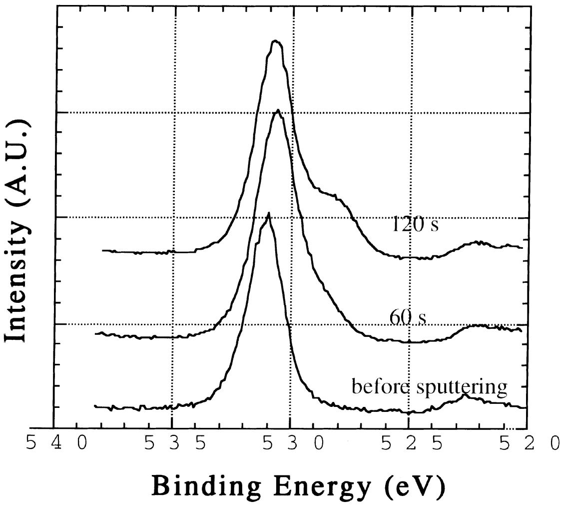

Fig. 2. O(1s) spectra of Li_2O.

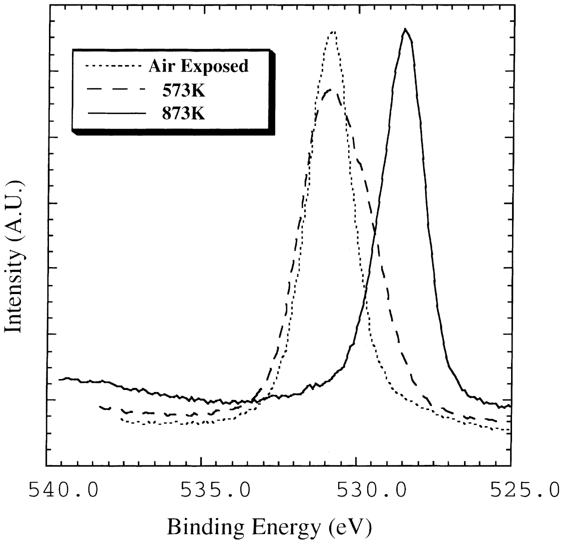

Fig. 3. O(1s) spectra in annealed samples.

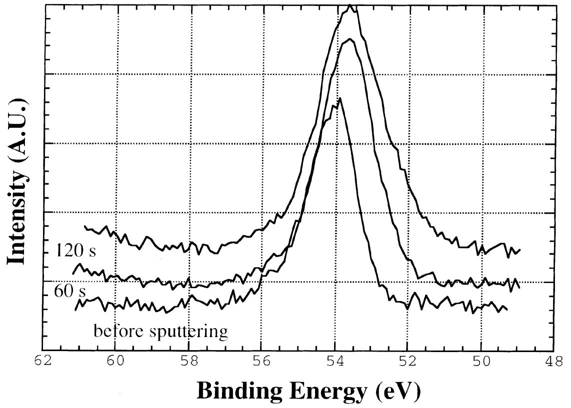

Fig. 4. Li(1s) spectra of Li_2O.

3.1.2. Li(1s) spectra in Li_2O

Li(1s) spectra are shown in Fig. 4. The condition of sputtering is the same as that for observation of O(1s). Before sputtering, a symmetrical peak was observed at 54 eV. After sputtering for 60 s, the peak at 53.5 eV appeared and the spectra broadened to lower binding energy region. After an additional 60 s of sputtering, the peak at 53.5 eV became dominant compared with the peak at 54.0 eV. The peak for lithium metal, which exists as Li^0, is reported in the lower energy region than that for Li^+. The peak for Li^0 is observed at 54.6 eV and the peak for Li^+ at 55.8 eV [3].

3.2. Electronic structure of Li_2O surface covered by –OH

Based on the results described above, adsorption behavior of –OH was studied. The sample was annealed in the preparation chamber at 873 K and 10^{-5} Pa for one day in order to decompose the precipitated LiOH. After the evacuation of the sample, controlled H_2O gas was introduced to the preparation chamber. After H_2O gas exposure, surface hydroxyl groups exist on Li_2O and the coverage is considered to vary with the pressure of H_2O vapor.

3.2.1. O(1s) spectra observed by XPS

The O(1s) spectra of Li_2O which were exposed to varying pressure H_2O gas are shown in Fig. 5. Before the exposure of H_2O, a symmetric peak from Li_2O was observed at 528.5 eV. For the sample exposed to 10^{-6} Pa of H_2O, a peak broadening was observed at the higher binding energy region: 529–532 eV. By exposing the sample to higher pressure of H_2O vapor, the peak at 531.2 eV appeared. After the exposure of 10^{-5} Pa H_2O, the sample was annealed in the preparation chamber at different temperature and the observed spectra are shown in Fig. 6. The peak at 531.2 eV decreased during annealing at 323 K and disappeared when annealed at 373 K.

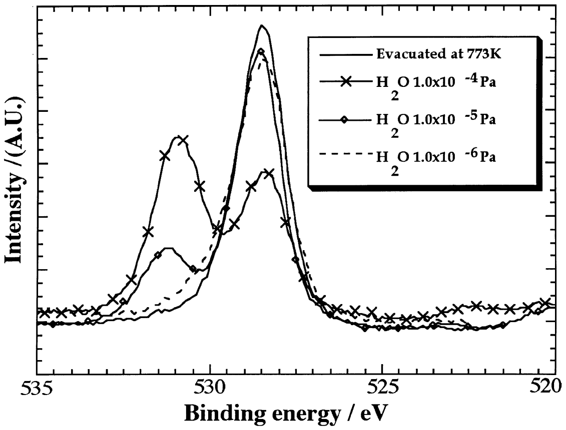

Fig. 5. O(1s) spectra of Li_2O covered by –OH.

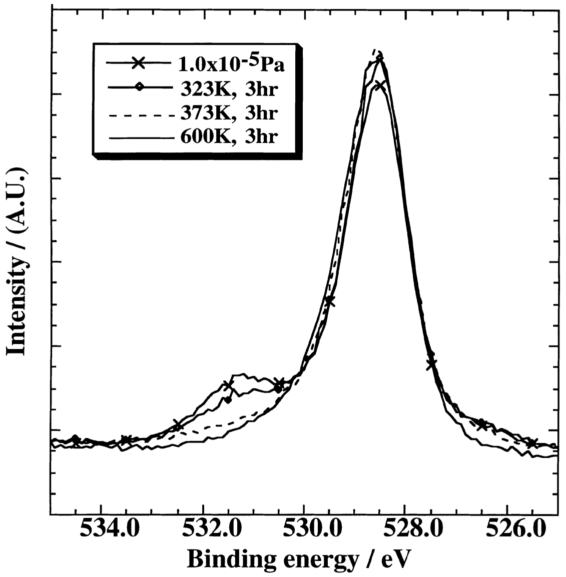

Fig. 6. O(1s) spectra of annealed sample.

For other oxides, a peak broadening and appearance of multiple peaks by exposure of –OH, have been reported. Wang et al. [4] reported XPS spectra of TiO_2 exposed to H_2O vapor. They attributed the peak broadening, which was observed at higher binding energy, to the surface –OH. Hugenschmidt et al. [5] also reported XPS spectra of TiO_2 with similar condition in temperature range 185 K to room temperature. They observed the peak at the binding energy of 3 eV higher than O(1s) of TiO_2. They concluded that this peak was from H_2O molecules adsorbed on the surface.

In this study, the spectra were recorded at room temperature where H_2O molecules could be dissociatively adsorbed. The peak broadening observed at higher binding energy region was considered to be ascribed to –OH on the surface. The region where the broadening was observed was about 4 eV wide and this shows that –OH is located on different sites on the crystal. Our infrared absorption spectroscopy study showed that several adsorption sites of –OH exist on the Li_2O surface [6]. The peak that appeared after exposure to higher H_2O vapor vanished by annealing at 373 K. This suggests that this adsorbate bonds weakly to the surface. This peak was observed at about 3 eV higher binding energy than O(1s) in Li_2O. Comparing with the peak from H_2O molecule observed by Hugenschmidt et al. the peak observed at 531.2 eV was considered to be attributed to the H_2O molecule adsorbed on the surface. Both a peak broadening and appearance of the new peak were observed at higher binding energy region than O(1s) of Li_2O.

3.2.2. Valence-band spectra observed by UPS

The valence spectra of Li_2O were also observed using UPS. UPS spectra are considered to be affected by the charge pile-up within the samples. This effect is larger in UPS than XPS because the flux of photons is larger in UPS. When the sample has positive charge, emitted electrons are decelerated and spectra are shifted to the higher binding energy region (lower kinetic energy region). As our UPS instrumentation has no equipment for charge neutralization, only the peak from secondary electron was observed at room temperature. However, a peak considered as valence-band of Li_2O began to be observed by heating above 573 K. This is probably caused by decrease of positive charge at the surface because electric conductivity became larger with temperature increasing. Hidden by the peak from secondary electrons, the spectra were not observed under 573 K.

The variation of UPS spectra by heating is shown in Fig. 7. This sample was placed at the preparation chamber and kept at 10^{-5} Pa for one day at room temperature. Therefore, some impurities such as –OH exist at the surface. The sample was moved to the measurement chamber and UPS spectra were observed at temperature ranging from 573 to 873 K. As the temperature increases, the spectra became sharp at the lower kinetic energy side and shifted to higher kinetic energy region. It was considered that the observed spectra consist mainly of O(2p) in Li_2O. The O(2p) peak from surface –OH could also be observed in this region. Therefore, the sharp peak at the higher temperature could be explained by the decrease of the contribution from the surface –OH.

Because of the peak shift by charge pile-up, binding energy for observed peaks were not determined in this study. The neutralization of sample is required for the next stage.

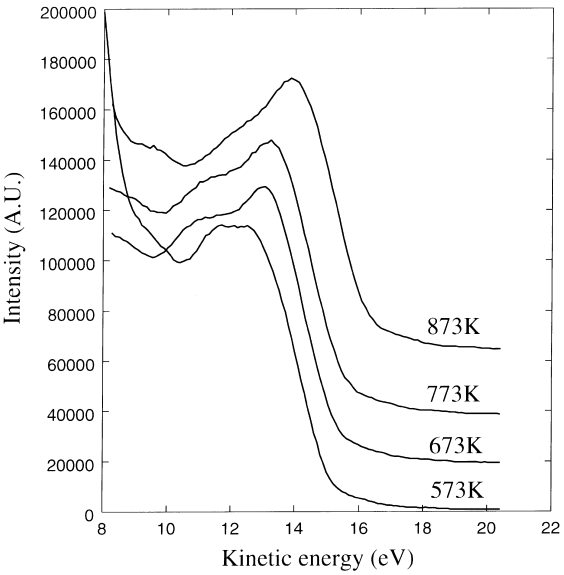

Fig. 7. Valence-bond spectra of Li_2O by UPS.

4. Conclusions

In order to study the adsorption behavior of H_2O on Li_2O, we observed the electronic states of the Li_2O surface by XPS and UPS.

In O(1s) region, two peaks were observed and they were attributed to the O(1s) in LiOH: 531 eV, O(1s) in Li_2O: 528.5 eV, respectively. The variation of O(1s) spectra of the Li_2O surface was observed with different pressure of –OH exposure. Observed tail and peak were attributed to O(1s) from surface –OH and H_2O molecule adsorbed on the surface. The broadening of the peak was considered to show that –OH with several chemical states exit at the surface.

The variation of the valence-band spectra was also observed by UPS. The observed spectra were considered to consist of O(2p) in Li_2O and surface –OH.

References

[1] M. Taniguchi, S. Tanaka, Fus. Eng. Des. 39&40 (1998) 707.
[2] M. Taniguchi, S. Tanaka, J. Nucl. Mater. 531 (1998) 258.
[3] J.P. Contour, A. Salesse, M. Froment, M. Garreau, J. Thevenin, D. Warin, J. Microsc. Spectrosc. Electron. 4 (1979) 483.
[4] L.-Q. Wang, D.R. Baer, M.H. Engelhard, A.N. Shultz, Surf. Sci. 344 (1995) 237.
[5] M.B. Hugenschmidt, L. Gamble, C.T. Cambell, Surf. Sci. 302 (1994) 329.
[6] M. Taniguchi, S. Tanaka, Y. Nose, V. Grishmanov, Fus. Technol. 28 (1995) 1284.