Electronic structure in the valence band of molybdenum being bombarded with argon ions

M. Kitajima, Kazutaka Nakamura, M. Fujitsuka, and H. Shinno

Tsukuba Laboratories, National Research Institute for Metals, Tsukuba-shi, Ibaraki 305, Japan

H. Katoh and T. Miyahara

Photon Factory, National Laboratory for High Energy Physics, Tsukuba-shi, Ibaraki 305, Japan

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This paper reports the electronic-structure changes induced in the valence band of molybdenum (110) during argon-ion bombardment. The ultraviolet-photoemission-spectroscopy measurements using synchrotron radiation show that argon-ion bombardment induces a reduction in the intensity of the peak at 4.10 eV below the Fermi energy and a decrease in the work function. In comparison with results of an $X\alpha$ calculation, the reduction in the peak corresponds to a substitution of molybdenum atoms by vacancies. The decrease in the work function also suggests that vacancies are being created in the surface region due to argon-ion bombardment.

I. INTRODUCTION

Direct information on the electronic structure in the valence band of materials modified by ion bombardment can be derived from photoemission spectroscopy. Several types of modifications exist in the photoemission spectra. For example, the peak in the valence-band spectrum for a Cu(111) surface is broadened and becomes asymmetric after ion bombardment.[1,2] This effect of surface disorder on the spectral shape can be explained as a result of the reduced coherence length parallel to the surface and inhomogeneous damping.[2] Recently, Parmigiani and Kay have shown an opposite trend, that the peaks in the valence band of Pd and Cu films that were grown under Ar^+ bombardment become narrower, suggesting more localized $4d$ electrons.[3] Huefner, Wertheim, and Buchaman have reported that ion sputtering also causes a disappearance of detailed structural features in the spectra for Pd, suggesting the amorphization of the surface.[4]

The influence of ion sputtering on the valence band of Mo has been studied recently with x-ray photoemission spectroscopy (XPS) using Al $K\alpha$ as a source.[5] Little difference, however, has been observed between the valence-band photoemission spectra of pure Mo and the one after 2 h of sputtering with 1-keV argon ions.[5] The XPS spectrum of the core levels for Ta is found to change only during ion bombardment, recovering to the initial state after switching off the ion current.[6] This suggests that it is possible to observe the effects of atomic displacement and substitution of host atoms with the implanted atoms on the electronic structure more directly during bombardment than after that. Several experimental studies using uv photoemission spectroscopy (UPS) and XPS as well as theoretical calculations have been made on the molybdenum valence band.[7-18] Little research, however, has been performed on photoemission for the valence band during ion bombardment.

This paper reports a study on the uv photoemission spectroscopy of the valence bands of Mo being bombarded with argon ions of 3 keV by using synchrotron radiation, in order to clarify the disorder effect on electronic structure. The electronic-structure changes induced during the bombardment process will be discussed, by comparing with the results of the molecular-orbital calculation.

II. EXPERIMENTAL

Photoemission experiments were carried out at the Photon Factory of the National Laboratory for High Energy Physics. Angle-integrated uv photoemission spectra were measured with a cylindrical mirror analyzer (CMA) at beam line 11D. The photon energy used was between 84 and 120 eV and the monochromator resolution was 0.06% of photon energy. A chamber was evacuated to around 1.0×10^{-8} Pa using two 400-liter/s turbo molecular pumps, and the working pressure was about 1.5×10^{-5} Pa Ar with an ultimate impurity level of 3×10^{-9} Pa H_2O. Single crystals of a 5-mm-diam molybdenum rod were made by zone melting with an electron beam, and cut to give sheets with a face perpendicular to the [110] direction. The orientation was determined using the Laue technique. The clean Mo surface was prepared by repeated argon sputtering and annealing above 1073 K, and the cleanness of the surface was confirmed by Auger electron spectroscopy (AES) and UPS. The sample was heated by electron bombardment to the backside of the tantalum sample holder. The sample was bombarded at around 1073 K with an Ar-ion beam of 3-keV energy and ~ 2 $\mu A/cm^2$ ($\sim 1 \times 10^{13}$ ions/cm^2 s). The UPS measurements were made at the same temperature (1073 K) during and after argon-ion bombardment, to avoid the temperature effect as an artifact of turning off the electron beam heater and cooling the sample to room temperature. The beam struck the target at an incidence angle of 45°. The angle between the CMA axis and sample normal was 45°. The UPS spectra were analyzed by nonlinear least-squares fitting using the Lorentzian line-shape function.

III. RESULTS AND DISCUSSION

Figure 1 shows the observed spectra at around 1073 K with photon energy of 84–120 eV during and after argon-ion bombardment, where the surface is free from impurities such as oxygen and carbon (confirmed with AES and UPS). The spectra consist of four peaks: 0.24 eV (A), 1.32 eV (B), 2.65 eV (C), and 4.10 eV (D) below the Fermi level (E_F), which correspond to the main peaks in the density of states (DOS) calculated by the nonrelativistic augmented-plane-wave method.[18] Decomposed spectra at 100 eV are also shown in Fig. 2. The UPS spectra during bombardment were measured at a dose range of over 1×10^{16} ions/cm^2, and little change in the spectral shape was observed in this dose range. The intensity of peak D increases as photon energy increases. This trend is the same as that for angle-resolved photoemission spectra in a photon energy region of 10.2–21.2 eV.[7] No broadening is observed in the spectra during bombardment. However, it is found that the intensity of
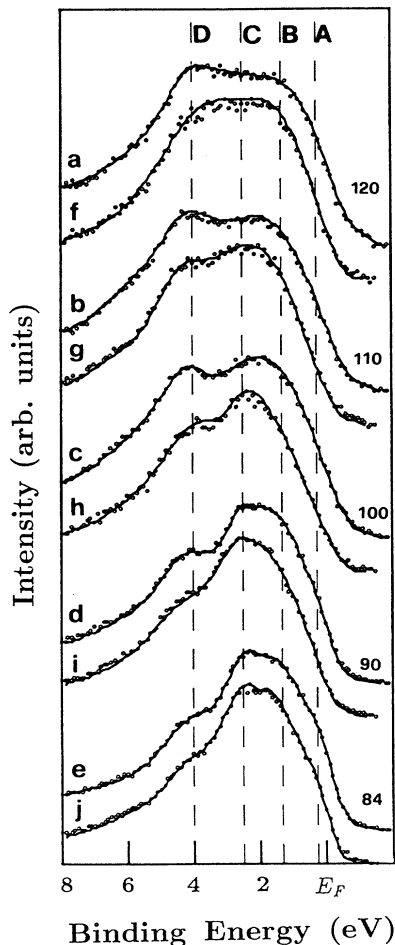

FIG. 1. Photoemission spectra of Mo(110) with photon energy of 84–120 eV (a–e) after (f–j) during argon-ion bombardment with a substrate temperature at 1073 K. Circles are the observed data points and the solid curves are a cubic spline fit. Peak positions are A, 0.24 eV; B, 1.32 eV; C, 2.65 eV; and D, 4.10 eV below the Fermi energy.
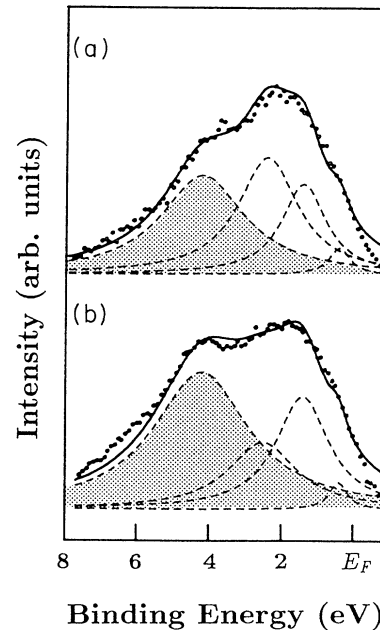

FIG. 2. Decomposition spectra of Mo(110) at a photon energy of 100 eV (a) during and (b) after argon-ion bombardment. The shaded area shows the peak intensity of D (4.10 eV below the Fermi energy).

peak D becomes weaker during ion bombardment than after bombardment, and the total width of the valence band decreases: 4.6 eV during bombardment and 5.3 eV after bombardment. No marked change was induced by bombardment for peaks A, B, and C, which have been assigned to be the Fermi edge and bulk states.[9] Peak positions in energy do not change during bombardment for any peak. The work function was estimated from the kinetic energy of electrons emitted from the Fermi level. The estimated work function of Mo during ion bombardment is 0.3 eV smaller than that after bombardment for all photon energies between 84 and 120 eV. Figure 3 shows the intensity ratio of peak D (the area of the peak D divided by the total area of the valence band) during and after bombardment as a function of photon energy. We can see the reduction in the intensity of peak D more quantitatively.

Argon-ion bombardment reduced the intensity of the peak D of the valence-band photoemission spectra and the total valence-band width of Mo(110) as shown in Figs. 1–3. Peak D, which corresponds to the bottom of the valence band, originated in a surface-state level situated in the s-d hybridization gap.[7,20] The reduction in the peak D may relate to point defects in a crystal lattice produced by ion bombardment in the surface region, or to topography of impact crater formation resulting from collapse of the surface to fill in the vacancies.

In the latter case the possibility exists that the roughness causes a breakdown in the selection rules, leading to new transitions which results in the spectral shape change. Ion impact craters have been observed on ion-
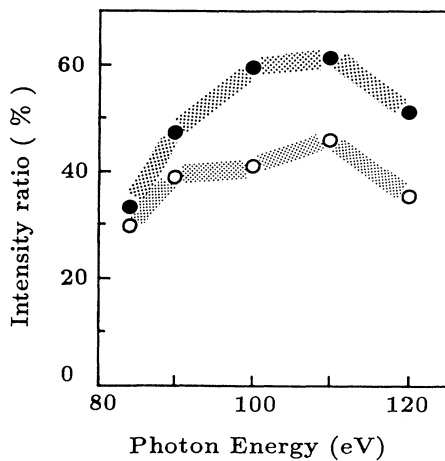
FIG. 3. The intensity ratio of the peak D (the area of peak D divided by the total area of the valence band) as a function of photon energy, during ($\bigcirc$) and after ($\bullet$) argon-ion bombardment.
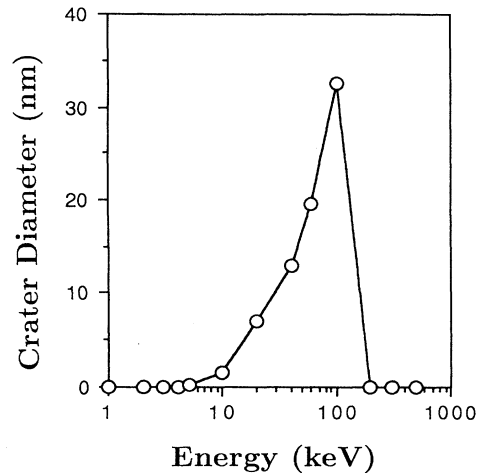

FIG. 4. Crater diameter vs ion energy in molybdenum bombarded with argon ions calculated by using TRIM-85 code based on an energy-deposition cutoff at 900 eV/nm (Ref. 21). Circles show the calculated points.

bombarded surfaces of SiO_2/Si, PbS, and graphite using scanning tunneling microscopy (STM).[21–24] Wilson et al.[21] have found that the crater diameter which was measured with STM as a function of implant-ion energy agrees well with theoretical estimates of the lateral extent of the cascade due to nuclear energy deposition. We calculated the crater diameter of Mo bombarded with Ar ions by a Monte Carlo calculation for the ion range and damage distribution using TRIM-85 (Transport of Ions in Matter, 1985) code.[19] The TRIM-85 calculation showed that in this condition the range is 2.3 nm and the energy deposition decreases from the maximum value at the surface with an increase in depth. Figure 4 shows the crater diameter as a function of Ar-ion energy, where 900 eV/nm was used as a critical energy-deposition value below which the effects of damage are negligible for the formation of the impact crater.[21] The crater diameter increases as argon-ion energy increases to the maximum of around 100 keV. We can see that only a slight impact crater grows below an ion energy of about 5 keV. Therefore the topographical effect on UPS may be very weak.

Sheludchenko et al. calculated the change in the electronic states of Mo with the $X\alpha$ scattered-wave molecular-orbital method when the central atom of a body-centered-cubic Mo_9 cluster was replaced by an argon atom or a vacancy.[25] In their calculation, the d electrons around the central atom and corner atom contribute to the bottom and top of the valence band of Mo, respectively. The replacement of the central Mo atom with an Ar atom or a vacancy leads to a reduction in d electrons around the center of a body-centered-cubic cluster and absence of a structure near the bottom of the valence band. The observed reduction in the peak D, therefore, may correspond to the effects of the ion implantation and/or creation of vacancy. No peak indicating the presence of Ar was observed at a deeper energy than the

valence band of Mo in UPS during bombardment: 11.3 eV is the binding energy expected for Ar $3p$ by the calculation[25] (Fig. 5). This shows that the reduction in the peak D is not attributable to the implanted argon. The decrease of 0.3 eV in the work function of Mo during Ar-ion bombardment also corresponds to the decrease derived from the cluster calculation for containing the vacancies.[25]

IV. CONCLUSION

We measured UPS of the valence band for a Mo(110) single crystal during bombardment with argon ions by using synchrotron radiation. The results showed that
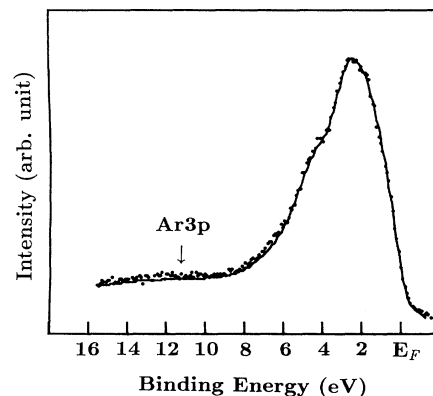

FIG. 5. Photoemission spectrum of Mo(110) during 3-keV Ar-ion bombardment (photon energy 90 eV). No peak indicating the presence of Ar is observed.

argon-ion bombardment induced a reduction in the peak intensity at 4.10 eV (D) below the Fermi energy. The Monte Carlo calculation showed that the surface topographical change is very small in Mo bombarded with an argon-ion beam in the keV range. The reduction in the peak D can be attributed to the substitution of a molybdenum atom by a vacancy, as predicted by the $X\alpha$ scattered-wave molecular-orbital method.[25] The decrease in the work function also suggests that the vacancy is being created in the surface region by argon-ion bombardment.

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