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Letter to the Editor

Influence of metal surface structure on the anisotropic XPS

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The intensive distribution of photoelectrons as a function of X-ray beam with variable angle of incidence was investigated. Diffraction caused by the structure of surface was observed in the following metal samples: Al with face-centered cube, Ta and W with body-centered cubes. No effect was observed in Fe and Cu samples. The effect is closely related to the anode high voltages and X-ray energy. There was a range of threshold values in which the surface structure effects could be defined in experimental high voltages of anode. The possible mechanism of this effect was discussed.

Keyword: high voltage of anode, structure of surface, X-ray photoelectron spectroscopy (XPS).

1. Introduction

The surface and interface have been extensively studied in the past years since experimental ways to detect them were found. X-ray photoelectron spectroscopy (XPS) is one of the methods extensively applied. The signal of elements in the surface phase, chemical bond, the structure of valence band as well as their distribution in depth, shake-up, *etc*., can be obtained by using XPS. Unfortunately, when surface with a single crystal is measured via XPS, the intensity of photoelectrons can be increased in some spectral direction because of the diffraction effect caused by crystal lattice [1–3]. Of course, such a phenomenon is of much significance to the analysis of the structure of surface through XPS. But it is to the disadvantage of information in which the effects of structure on surface should be avoided.

In this work, the angular anisotropy due to metal surface was measured by the XPS; attention has been focused on changes of the photoelectron emission created by crystal lattice and high voltage of anode. The experimental results demonstrated that there existed such diffraction caused by the structure of surface and high voltage of anode, and some possible mechanisms to explain the experimental results have been suggested.

2. Experimental

In this work, Al, Fe, Cu, Ta and W foils with 99.99% purity (mass fraction) were selected, all being prepared at Beijing Institute of Metals (China).

XPS measurements taken at a variable angle were carried out via a KRATOS XSAM800 electron spectrometer. In order to reduce the error induced by analytical parameters of XPS maximally, all the parameters were the same for each record. An Ar^+ ion beam with energy of 4.0 keV and about 2×10^{-5} Acm^{-2} of current density was used to etch the surface of each sample for 30 min. The vacuum during the cutting was better than 2.6×10^{-4} Pa. The samples were excited by 4510.0 eV Ti–K_α-line X-ray. The sweep range was 20 eV for every sample, and other parameters of measurement,

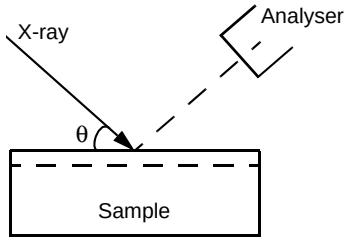

Fig. 1. Schematic diagram of angle changing for XPS.

such as current of filament, step, dwell and scan number were the same for each measurement. Under conditions described above the angle of incidence and high voltage of anode were adjusted. The vacuum during the detecting was less than 2.6×10^{-6} Pa. The experimental arrangement used for measurement is shown in Fig. 1. Every spectrum was calibrated to C at bonding energy (BE) 285 eV, and each peak was stimulated from original spectrum by code DS300X Data System.

3. Results and discussion

Figure 2 displays the angular distribution of normalization intensity from XPS as a function of anode voltages and metal surface (plotted on log-linear paper).

The results of measurements of intensities shown in Fig. 2 confirm that diffraction was caused by Al at any anode voltages within experimental range, the most remarkable effect due to the structure of the surface being the line at 13 kV anode voltage, while the weakest one being the curve at 15 kV. Observation of the angular distribution shows that Ta generated diffraction at any anode voltages, except for 15 kV within experimental range, the most distinct one appearing at 13 kV anode voltage once more. The effect induced by the structure of surface for W only emerged slightly at 13 kV anode voltage. Neither Fe nor Cu created any diffraction within the experimental range of anode voltage.

The results of anisotropic XPS produced by Al with low atomic number to W with higher atomic number demonstrate that the clearest diffraction from lattice is at 13 kV

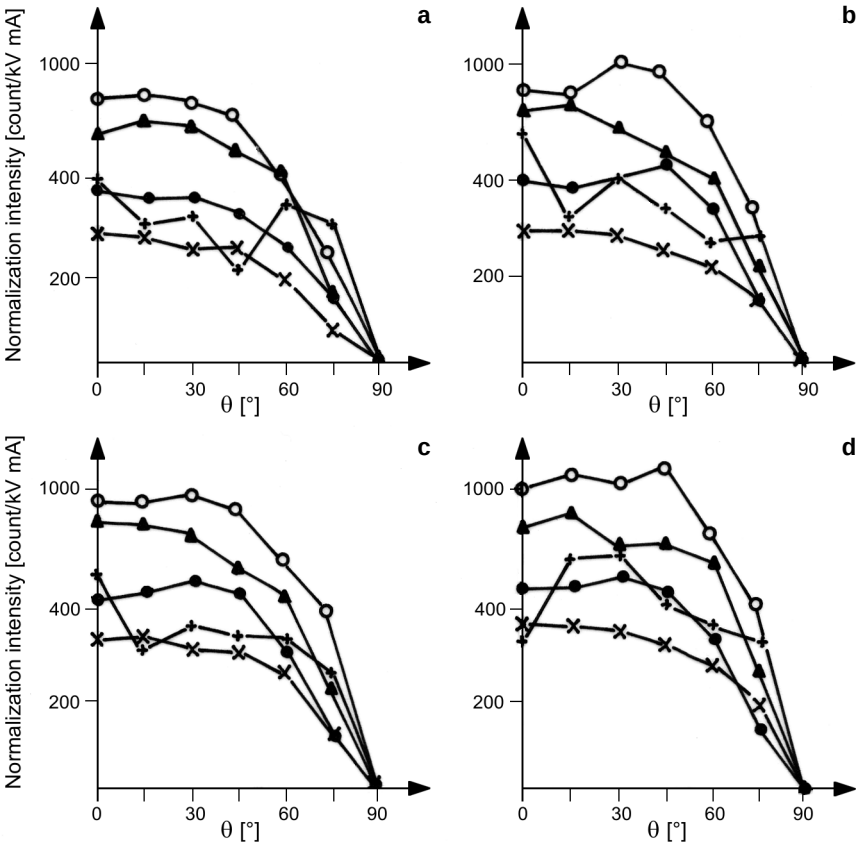

Fig. 2. Angular distribution of normalization intensity by XPS as a function of anode voltages and metal surface (**a**, **b**, **c** and **d** correspond to anode voltages at 12, 13, 14 and 15 kV, and the symbols –○–, –●–, –×–, –▲– and –+– refers to results obtained for Ta, W, Cu, Fe and Al samples).

anode voltage and the dimmest constructive effect is at 15 kV. Based on the present discussion, one may say that there exists one range of threshold value in which the effects of surface structure can be defined very clearly in experimental high voltage of anode. Diffraction will be decreased if the high voltage of anode is either higher or lower than the threshold value.

In this work, a typical kinetic energy of photoelectron excited by X-ray from Al is 5.73×10^{-10} m (De Broglie wavelength). While the grating constant of aluminum whose structure is that of a face-centered cube is 8.10×10^{-10} m, the former is much lesser than the latter. Therefore, there is no doubt that diffraction is generated very easily. In the case of iron, the kinetic energy of photoelectron excited by X-ray from Fe is typically 6.16×10^{-10} m. But as to the grating constant of iron whose structure is that of a body-centered cube being 5.72×10^{-10} m, the former is bigger than the latter.

The chance of diffraction occuring may be smaller. The kinetic energy of photoelectron excited by X-ray from copper with structure of face-centered cube is 6.37×10^{-10} m and the grating constant of Cu is 7.22×110^{-10} m, typically. Although the former is shorter than the latter, the difference is still small (it is 0.85×10^{-10} m only). What has been described above does not comply with the condition that the shorter wavelength of electron is to produce diffraction in Cu because the face-centered cube is characterized by a higher density of lattice, which is probably one reason why there is not constructive effect in cooper foil. The kinetic energy of photoelectron excited by X-ray in both tantalum and wolfram are less than their grating constant. Furthermore, the body-centered cube is characterized by a low density of lattice, thus diffraction can be observed in both Ta and W. However, the differences between grating constant and kinetic energy of photoelectron excited by X-ray are $(6.32–5.82)\times10^{-10}$ m in W and $(6.6–5.81)\times10^{-10}$ m in Ta, so the more constructive effect may be generated in tantalum than in wolfram.

The collision obeyed the Bragg equation is elastic scatter. If such collision takes place between X-ray and atom at lattice, there will not be any photoelectron emission because energy is not absorbed by atom at lattice. Thus the higher the intensity of photoelectron is, the lower the intensity of diffraction of X-ray arise. In other words, Fig. 2 is in contrast to the X-ray intensity as a function of angle, anode voltages and metal surface. The calculation of X-ray diffraction in accordance with Bragg condition shows that the first order diffraction peak of Al is located at 22°30' diffraction angle and the second order diffraction maximum of Al is located at 49°57' diffraction angle. The same calculation illustrates that there is only one peak of diffraction of Fe, Cu, Ta and W, being located at 44°56', 63°3', 54°34' and 51°17' diffraction angle. Once more the phenomenon that the most observable diffraction is caused by Al can be explained based on the data provided here.

The degree of effect caused by the structure of the surface of Al, Fe and Cu in this work agrees with the studies made by VALERIA *et al.* [4] using the Auger electron spectroscopy in which the kinetic energy of electron is 2.0 keV. Because the mechanism of Auger electron spectroscopy used to investigate the structure of surface is dependent on remarkable scatter between incident electron beam and lattice [5], the effects of the structure of surface detected by the Auger electron spectrometer are more observable than those through XPS with variable angle in Al, Fe and Cu.

4. Conclusions

The constructive effects on the surface of metal foils have been observed using XPS with variable angle. The comparison of results obtained for particular foils suggest that there exist one range of threshold values in which the surface structure effects can be defined very clearly in experimental high voltage of anode. When XPS with variable angle is selected to look into the structure of surface, the high voltage of anode should be scanned until the best image arises. On the other hand, if the least error induced by diffraction is expected, the high voltage of anode should be such that there would be neither any diffraction phenomenon nor the minimum constructive effect.

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