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Comments on the Energy Calibration in X-Ray Photoelectron Spectroscopy

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Synopsis. The change of the contact potential difference between the sample and spectrometer was examined on the adsorbed carbon/Au system by observing the low kinetic energy limit of the X-ray photoelectron spectrum. Discussions are given on the use of the contamination carbon for energy calibration.

In X-ray photoelectron spectroscopy (XPS) of solid materials, the observed kinetic energies of photoelectron peaks are affected not only by the contact potential difference between the sample and spectrometer, but also by the charge-up of sample caused by X-ray irradiation. The latter, called "charging effect", is known to be particularly significant in the case of insulating samples. There are two methods most widely used to calibrate the energies of photoelectron peaks; the one is to use the C 1s peak of "contamination carbon" as the reference, and the other to use the Au $4f_{7/2}$ peak of a very thin gold film deposited on the sample surface.

It has been pointed out by Ascarelli and Missoni[1] that the contact potential difference between the spectrometer and sample under the condition of the measurement of XPS spectrum can be directly known by observing the low kinetic-energy limit of the photoelectron spectrum. This low energy limit can be observed if an appropriate potential difference is externally applied between the sample and spectrometer. When a voltage $V_{\text{ext.}}$ is externally applied on the sample against the spectrometer, the following relation is expected,

$$E_{\text{k}}^{0} = (\Phi - \Phi_{\text{sp}}) - eV_{\text{ext.}} \qquad (1)$$

where E_{k}^{0} is the observed kinetic energy of the low-energy limit of the photoelectron spectrum, and Φ and Φ_{sp} are the work functions of the sample and spectrometer, respectively. This method provides another way to calibrate the energies of photoelectron peaks.[2]

In the present study, we have examined if the above three calibration methods do provide results consistent with each other. We carried out experiments with McPherson ESCA 36 electron spectrometer employing Al$K\alpha_{1,2}$ (1486.6 eV). We prepared a gold film by evaporating gold onto an aluminum plate within the sample chamber of the spectrometer, and observed the changes in the Au $4f_{7/2}$ peak of the film and the C 1s peak of "contamination carbon".[3] At the same time, we observed the low kinetic energy limit of photoelectron spectrum by applying −50 volt on the sample against the spectrometer. The low kinetic energy limit appeared as a sharp edge, of which position was able to be determined with an accuracy of ±0.03 eV. Throughout the experiment the vacuum of the sample chamber was kept at about 10^{-8} Torr by means of the combined action of a turbomolecular pump and a cryopump.

As shown in Fig. 1, the intensity of C 1s peak of contamination carbon gradually increased with time, which being accompanied by a decrease of the intensity of Au $4f_{7/2}$ peak. These changes ceased after about two hours, and thereafter, the intensities of both peaks remained constant. On the other hand, no trace of C 1s peak was observed during the measurement. Accordingly, the saturation of the growth of C 1s peak is likely to correspond to the complete coverage of the sample surface with adsorbed hydrocarbon. Thus we took the ratio of the C 1s intensity observed at a given time to the intensity at the saturated state as a measure of surface coverage.

From the low kinetic energy limit of photoelectron spectrum, we estimated the contact potential difference $\Delta\Phi$ according to Eq. 1. The change of $\Delta\Phi$ from the initial value is plotted in Fig. 2 against the surface coverage by adsorbed carbon. We note that the

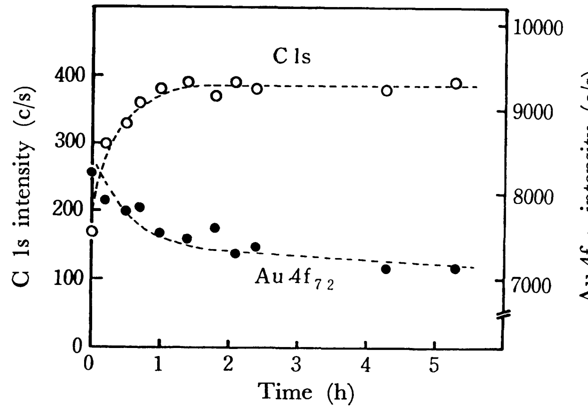

Fig. 1. The variations of the intensities of C 1s and Au $4f_{7/2}$ peaks with time.

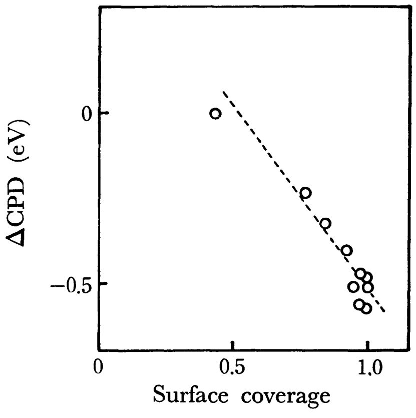

Fig. 2. The relation between the contact-potential-difference change (ΔCPD) and the amount of adsorbed carbon.

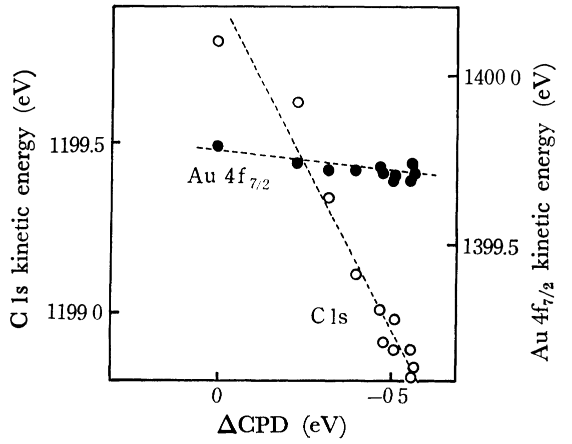

Fig. 3. The dependences of the energies of Au $4f_{7/2}$ and C 1s peaks on the contact-potential-difference.

contact potential difference decreases on increasing the surface coverage. This is consistent with the reported effect of hydrocarbon adsorption on the surface potentials of metals.[4]

In Fig. 3, we have plotted the observed kinetic energies of the C 1s and Au $4f_{7/2}$ peaks against the change of the contact potential difference (CPD). We found that the C 1s peak was shifted to lower kinetic energy linearly depending on the decrease of contact potential difference, whereas the Au$4f_{7/2}$ peak remained almost at the same position.

The above result seems quite reasonable since the Fermi level of the gold film must be little affected by the adsorption of hydrocarbons on its surface while the carbon atoms of the adsorbed layer are under the strong influence of the electrical double layer formed on the surface by the adsorption.

Several conclusion may be derived from the present result. First, the energy of the C 1s peak of "contamination carbon" adsorbed on metal surface can vary depending on the amount of adsorption, consequently its use as the reference of energy calibration seems to be dubious in some cases, especially for metallic samples. Second, the contact potential difference determined from the low kinetic energy limit of photoelectron spectrum, sensitively reflects only the very surface properties, and not necessarily useful to calibrate the energies of the photoelectron peaks associated with the bulk material. One could expect that it might be useful at least for the calibration of the energies of the peaks associated with the adsorbed layer. In this respect, however, it should be noted that, although the observed energy of the C 1s peak of adsorbed carbon was found to be linearly dependent on the change of contact potential difference, its shift was about two times of the value expected from the latter change. This indicates the difficulty in employing the average contact potential difference determined from the low energy limit of photoelectron spectrum even for the purpose of energy calibration of the photoelectron peaks of adsorbed layer. Finally, we wish to point out the possibility that the photoelectron peaks of the bulk material can be distinguished from those of the surface by examining their dependence on the change of contact potential difference as demonstrated by the results shown in the present paper.

References

1) P. Ascarelli and G. Missoni, *Discuss. Faraday Soc.*, **54**, 298 (1972).

2) S. Evans, *Chem. Phys. Lett.*, **23**, 134 (1973).

3) We do not know its exact origin. One of the possible origins could be the oil seal of the turbomolecular pump.

4) R. V. Culver and F. C. Tompkins, *Adv. Catal.*, **11**, 67 (1959).