Possible Application of Appearance Potential Spectroscopy (APS) to Studies of Empty Electronic States , Short Range Ordering, and Work Function for Nano-Material Surfaces

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A new soft x-ray appearance potential spectroscopy (SXAPS) apparatus has been developed. SXAPS spectra were measured without differential at low incident electron currents. The spectra are self-deconvoluted and compared with x-ray absorption spectroscopy (XAS) and electron energy-loss spectroscopy (EELS) spectra in which the dipole selection rule is held. It is found that the first-approximate dipole selection rule is held for the self-deconvoluted APS spectra of $TiO_2(110)$ and MgO(100) samples. Application of APS to work function and extended fine structure measurements are described. The possible application of APS to studies of empty electronic states, work function, and short-range ordering of atoms at nano-material surfaces is discussed.

1. Introduction

Appearance potential spectroscopy (APS) has been used as a simple method to investigate empty electronic states of material surfaces, mainly metal surfaces [1,2]. Although it has been thought that the dipole selection rule can not be applied to APS, a calculation suggested that the "first approximate selection rule" is held until incident electron energy exceeds the ionization threshold by at least 500 eV [3]. Since APS intensity (soft x-ray) is very weak, large incident electron currents (mA) were required to obtain the good spectra, leading to damaging surface structures. Auger electron appearance potential spectra (AEAPS) have been measured to overcome the problem because the Auger yield is much higher than the x-ray [4]. However, diffraction effects could be superimposed on the spectra for single crystal surfaces. In general since the differential APS spectra are obtained by a lock-in amplifier using a small AC voltage, the spectral resolution would become larger. We have designed a new APS spectrometer detecting soft x-ray to measure the direct spectra (without differential) at low incident currents. If electron beam is focused at low voltage (0.2 - 1 keV), APS could prove partial empty states of nano-structure surfaces. If a field emission gun is employed for APS, a absolute work function (not work function difference) could be also obtained for the nano-structure surfaces. Furthermore, the surface atomic compositions and surface structures can be studied by installing a cylindrical mirror analyzer (CMA), and fluorescence screen, respectively.

Since APS is a threshold spectroscopy, extended fine structures similar to x-ray absorption spectroscopy (XAS) is expected to be observed. They were first observed on a vanadium surface using AEAPS [5] and the theory was developed [6]. This implies that the short range ordering of atoms at the nano-material surfaces can be determined using APS with a micro-beam electron gun.

In this paper, the theory of APS is described and the results of APS and work function measurement are presented. Two kinds of metal oxides, 3d- and sp-metal oxides, have been studied: Ti 2p and O 1s APS spectra were measured for $TiO_2(110)$, and Mg 1s and O1s for MgO(100). The results are discussed in terms of the first approximate selection rule to compared with XAS and electron energy-loss spectroscopy (EELS) spectra, in which the dipole selection rule is held. The extended fine structures of APS are also mentioned.

2. Experimental

The new APS apparatus was designed and constructed (Fig. 1). A LEED gun was used as an incident electron source. Low energy x-ray was cut by an Al thin film (thickness: about 200 nm) in front of a detector. Emitted x-ray was converted into electrons using a CuI thin film and the electrons were detected by an electron multiplier as a function of the applied voltage. The APS spectra were obtained by about several tens iterations using a computer at sample currents, about 10 μA.

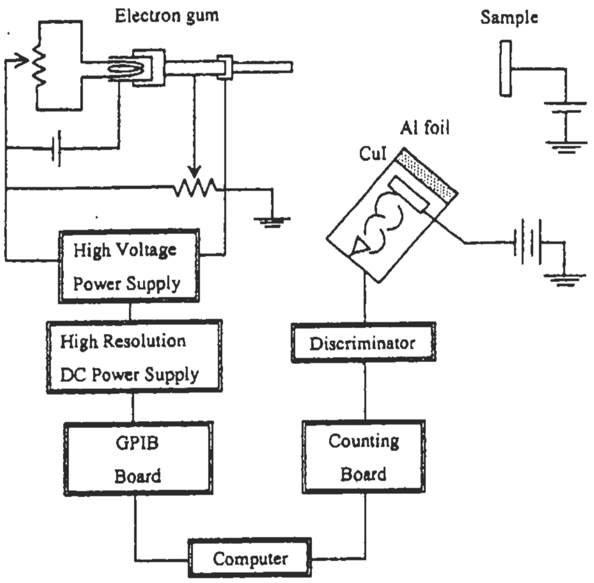

Fig. 1 Schematic diagram of a new APS apparatus.

For the analysis of the spectra, the linear background was subtracted from the direct (non differential) APS spectra obtained in this work and then they were fitted using linear combination of several Gaussians and a linear line. The fitted spectra were self-deconvoluted, yielding density of empty states for one electron system. Those are compared with XAS and EELS spectra.

$TiO_2(110)$ and MgO(100) single crystal samples were used for the APS measurements. The clean surfaces of the samples were prepared by Ar^+ sputtering and annealing in oxygen (10^{-6} Torr) at high temperature. Cleanness of the surfaces was checked by AES.

A Cu(111) sample was used for the work function measurement. The surface was cleaned by iterations of Ar^+ sputtering and annealing. A field emission gun was employed for the measurement.

3. Theory of APS

Figure 2 shows a schematic illustration of the energy diagram for APS. E_{FC}, E_{FS}, and $N_V(E)$ represent Fermi level of the cathode and sample, and density of filled states, respectively. When the voltage V is applied on the electron gun using a thermal emitter, the electron energy on the sample is $eV + \phi c$ (work function of the thermal emitter at temperature T) + kT (thermal broadening of the electron energy at T). The electrons impinged into solid samples are captured in an empty level, $\varepsilon 1$ and on the other hand, core electrons are simultaneously excited into the empty states, $\varepsilon 2$. Soft x-ray which is detected in APS is emitted in the relaxation process. This total soft x-ray intensity is measured as a function of the incident electron energy. This is so-called soft x-ray appearance potential spectroscopy (SXAPS).

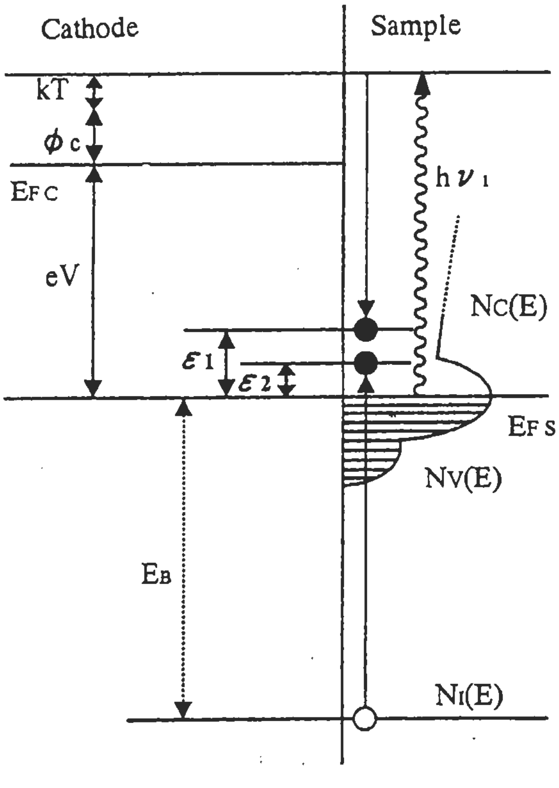

Fig.2 Schematic energy diagram for APS.

Auger electrons are also emitted in the relaxation process and then sample currents are abruptly decreased by the Auger electron emission. Changes in the sample currents at the threshold are measured for AEAPS. When quasi-elastic electrons are measured as a function of applied voltage, the currents would be abruptly decreased at Auger electron emission threshold. This is disappearance potential spectroscopy (DAPS) [7].

Taking into account of the energy conservation and binding energy E_B for the core-level, the following equation,

$$E_V + \phi c + kT = E_B + \varepsilon 1 + \varepsilon 2 \qquad (1)$$

is obtained. At the threshold, $eV + \phi c + kT = E_B$ since $\varepsilon 1 = \varepsilon 2 = 0$. The binding energy E_B can be obtained since ϕc (tungsten) and kT are 4.52 (at 2800 K) [8] and 0.24 eV, respectively.

The transition probability in Fig. 2 is expressed as following:

$$T(E) \propto \int_0^E \int_0^{E'} Nc(E')Nc(E'-E'')dE'' \times N_I(E+E_B-E')dE' \qquad (2)$$

in which Nc(E) and N_I (E) correspond to density of empty states for one electron and that of filled states for excited core-level, respectively. Since the density of states of core-level, $N_I(E + E_B - E')$, is generally expressed as a delta function, the transition rate is described as following:

$$T(E) \propto \int_0^E Nc(E')Nc(E-E')dE' \qquad (3)$$

This means that the rate is proportional to self-convolution of the density of empty states for one-electron system. This is schematically shown for a 3d transition metal in Fig. 3 in which (a) and (b) represent density of states of one electron system (filled states: shaded and empty states: above E_F) and self-convoluted empty states, respectively. Therefore, if the APS spectra measured are self-deconvoluted, the density of empty states for atoms on the samples could be obtained.

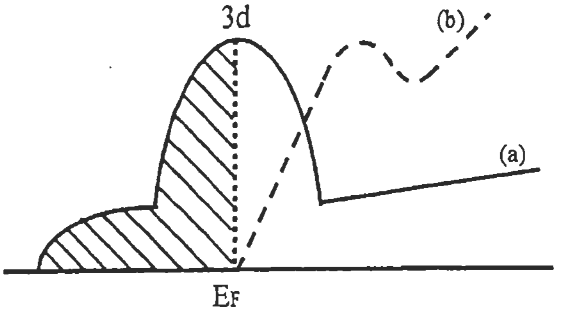

Fig. 3 Schematic illustration of filled and empty bands for a 3d transition metal.

If the field emission gun is employed in Fig.2 and sample currents are measured as a function of applied voltage, the work function of the samples could be obtained with high-resolution since $\phi c = 0$ and $kT = 0.026$ eV at 300 K [9].

The short range ordering of atoms on the surfaces can be obtained using extended appearance potential fine structure (EAPFS) as well as extended x-ray absorption fine structure (EXAFS). The APS data are transformed using an Fourier transform to obtain radial distribution functions, F(r), which represent the interatomic spacings.

$$F(r) = \int_{k1}^{k2} \exp\{-i\delta_\ell(k)\}k^2\chi(k) \times \exp\{-i2kr\}dk \qquad (4)$$

where k1 and k2 are the lower and upper limits of the data range, $\chi(k)$ is the background-subtracted extended fine structure in wave-number space, and $\delta_\ell(k)$ is the energy- and angular-momentum-dependent total phase shift [10]. Thus the nearest neighbor atomic spacing at the surfaces can be obtained from the highest peak in F(r).

4. Results and discussion

(1) APS spectra of $TiO_2(110)$

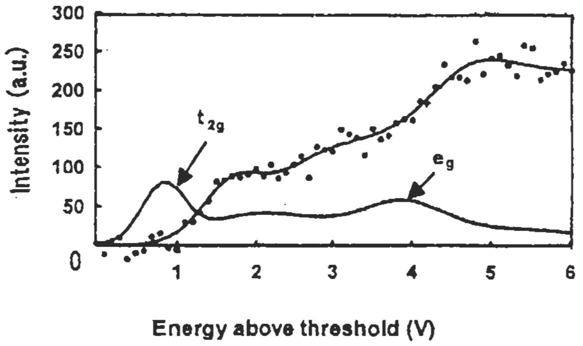

Fig. 4(a) Ti 2p APS spectrum for $TiO_2(110)$.

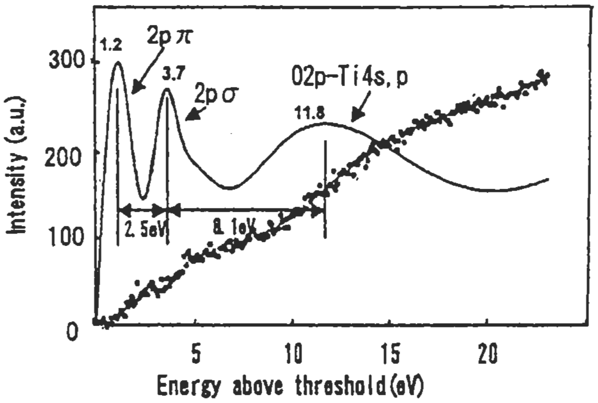

Fig. 4(b) O 1s APS spectrum for $TiO_2(110)$.

Figure 4 shows Ti 2p (a) and O 1s (b) APS spectra of $TiO_2(110)$. The dots and solid line (superimposed on the dots) correspond to the measured and fitted spectra, respectively. The self-deconvoluted spectra are also shown in the solid line. Two peaks at about 0.8 and 4.0 eV above the threshold are found for the Ti 2p spectrum. They could be ascribed to t_{2g} and e_g [11], respectively. For O 1s, three peaks at about 1.3, 3.8, and 11.6 eV above the threshold are found, in which the two formers could be assigned to O 2pπ and O 2pσ, respectively and the latter to O 2p mixed with Ti 4s,p [12]. These spectra are similar to the EELS [11] and XAS [12] spectra, respectively. We also found that the Mg 1s and O 1s spectra (not shown here) for MgO(100) are similar to the corresponding EELS [13] spectra. This implies that the first-approximate dipole selection rule is held for the APS spectra of not only 3d-transition metal but also sp-metal oxides.

(2) Work function measurement

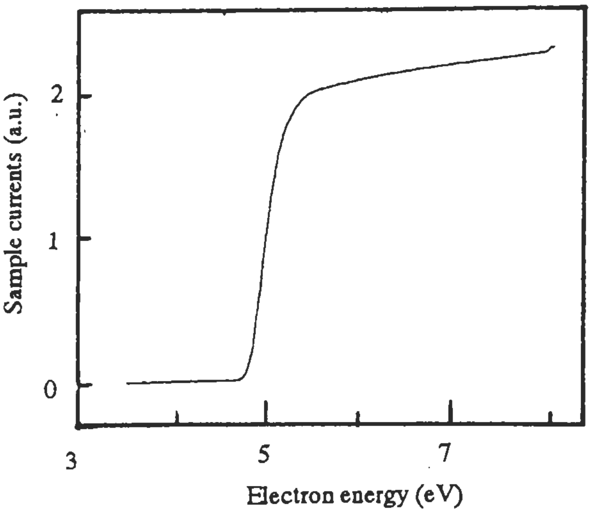

Fig. 5 Work function measurement for Cu(111).

The sample current intensity on Cu(111) as a function of applied voltage is displayed in Fig. 5. In general this is the measurement of work function difference between an electron-gun filament and the sample when the thermal electron gun is used. However, since the field emission gun is used in this experiment, the threshold for the the Cu(111) sample corresponds to the work function. It is found to be 4.86 eV which is close to the previous result (4.65 eV) [14].

(3) Extended appearance potential fine structures (EAPFS)

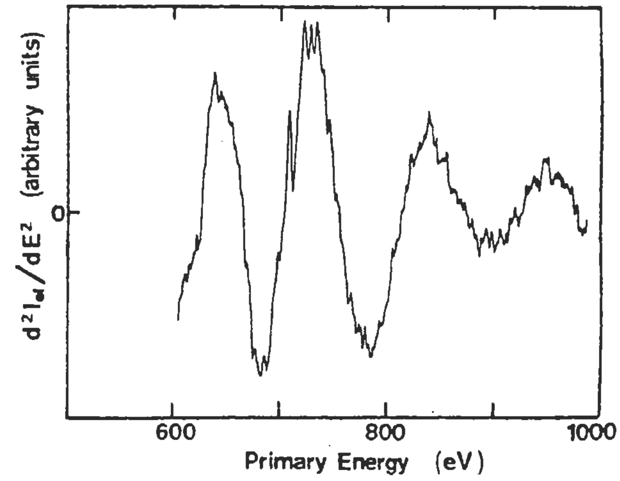

Fig. 6(a) EAPFS spectrum for O-adsorbed Al(100).

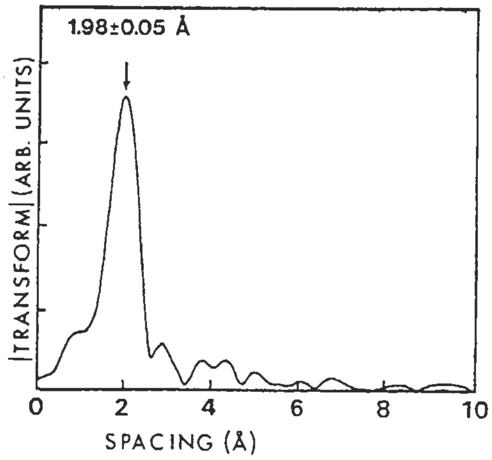

Fig. 6(b) Fourier transform of the EAPSF spectrum.

The EAPFS spectrum for an oxygen-adsorbed Al(100) surface (the oxide layer: about 1.5 monolayers) is shown in Fig. 6(a), where it was measured above the O 1s threshold [15]. Fourier transform of the data is also shown in Fig. 6(b) [15]. It was found a peak is located at 1.98 ± 0.05 Å which corresponds to the nearest distance between oxygen and aluminum atoms. Since the longer Al-O spacing in bulk Al_2O_3 is 1.97 Å, which corresponds to that for Al-O-Al and on the other hand the shorter one is 1.86 Å [16], this result supports the idea that the adatoms go under rather than on top of the first Al layer. The EXAFS result for the thick layer was 1.91 Å [17], the average of the two bulk spacing, and thus was insensitive to this surface-related feature.

The above results were obtained using the normal electron-gun but not micro-beam e-gun. It is necessary to use the micro-beam e-gun for studying the nano-structure materials. If the e-gun generally used for electron microscopy is employed for the APS measurements in ultrahigh vacuum, the empty electronic states and short range ordering of the atoms at the nano-structure surfaces could be measured. For the work function measurements, a cold field emitter is definitely required. Since high electron energy is generally used for electron microscopy, the energy should be varied by biasing on the sample for the APS measurements.

In summary, we have developed the new soft x-ray appearance potential spectroscopy (SXAPS) apparatus. SXAPS spectra were measured without differential at low incident electron currents (about 10 μA). The spectra are fitted by linear combination of several Gaussians and a linear line, then self-deconvoluted. The self-deconvoluted spectra are compared with XAS and EELS spectra in which the dipole selection rule is held. It is found that the first-approximate dipole selection rule is held for the self-deconvoluted APS spectra of the TiO_2(110) and MgO(100) samples. Application of APS to work function and extended fine structure measurements are described. The possible application of APS to studies of empty electronic states, work function, and short range ordering of atoms at nano-material surfaces is discussed.

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