Temperature dependence of the photoelectron emission from intentionally oxidized copper

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Abstract

The characteristics of the photoelectron emission (PE), measured by varying the wavelength of incident light, from copper subjected to oxidation treatment in air have been investigated as a function of the measurement temperature between 25 and 300°C using a gas-flow counter. The intensity of PE at a certain measurement temperature decreased with increasing oxidation temperature (100 to 800°C) and the intensity of PE for a given oxidation temperature increased with decreasing measurement temperature. The PE behavior was correlated to the chemical and electrical nature of the surfaces analyzed by X-ray photoelectron spectroscopy and surface potential measurement. A mechanism is proposed for the PE of the untreated sample which exhibited a completely different PE behavior. © 1997 Elsevier Science B.V.

1. Introduction

The measurement of work function changes on well-defined metal surfaces can give a great deal of information about the nature of adsorption and the type of surface bond that forms between the adsorbed molecule and the surface atoms [1,2]. On the other hand, in areas dealing with the surface of real metals such as catalysis, corrosion, adhesion, friction, lubrication, soldering, etc. it is very important to characterize the surface quality due to adsorbed layers and damage from handling and process. Several techniques for monitoring the surface of real metals from the standpoint of work function changes such as surface potential difference and photo-

electron emission have been developed [3,4]. The measurement of these electronic properties gives not only a monitoring technique, but also useful information relevant to the chemical activity of the surface. A photoelectric work function of metal surfaces can be measured by varying the wavelength of the incident light and detecting the threshold photon energy at which the photoelectron emission (PE) is observed. Conrad and Levy [5], Uda [6] and Mori et al. [7] reported the dependence of photoelectric threshold values on the surface pretreatments of metals by the measurement of PE as a function of the light wavelength using a modified Geiger counter. In solid-state physics it is pointed out that little reliable information about the temperature dependence of work function is available because of the temperature dependent surface contamination [8]. However, from a different viewpoint the temperature depen-

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dence of PE from real metals can reflect the surface process such as adsorption and desorption, but little is known about the PE behavior as the temperature is changed.

It is of great interest to obtain information about the electronic properties of copper metal and its oxides in view of the chemical activities in the reactions such as the production of hydrocarbons by the electrochemical reduction of carbon dioxide [9] and the adhesion with polyimides [10]. Therefore, the motivation of the present study is to make clear the PE characteristics of copper sheets due to changes in the surface conditions as the temperature is changed. The purpose of the present work is as follows: (1) to make an apparatus which can be easily handled, with a heating device for measuring PE as a function of the wavelength of incident light; (2) to examine the temperature dependence of PE from copper sheets oxidized in air at different elevated temperatures; (3) to correlate the PE data with those of X-ray photoelectron spectroscopy (XPS) and surface potential (SP) to discuss the emission mechanism.

2. Experiment

2.1. Materials

Rolled copper sheets (NILACO; purity > 99.9%; thickness 0.2 mm; size 30×20 mm^2 (PE and SP),

3×3 mm^2 (XPS)) were used. The metal sheet was polycrystalline, but the X-ray diffraction pattern exhibited only a plane (200). The sheets were ultrasonically degreased twice for 20 min in acetone and then dried in vacuum for 30 min before use. The oxidation treatment was performed by heating the sheet in an electric furnace in air for 30 min at elevated temperatures from 100 to 800°C. The color of the oxidized sheets depending on the oxidation temperature changed as follows: red and lustrous for untreatment and 100°C; brown–black and hardly lustrous for 200–400°C; grey and unlustrous for 500 to 800°C.

2.2. Photoelectron emission (PE) measurement

Fig. 1 shows the arrangement of PE measurement apparatus. It consists of the following parts: an electron counter with anode, the voltage of which is set at 1400 V, a sample holder with a heater on which the light beam is incident at about 90°C, a monochromator and a UV light source (30 W, D$_2$ lamp). Q gas (He + iso-C$_4$H$_{10}$(ca. 1%)) was used as a counter gas and flowed at a constant rate (about 60 bubbles/min). A -94 V potential relative to the grounded grid of the counter located over the sample was applied to the sample to accelerate and collect the emitted electrons. The intensity (count/min) of PE was measured by varying the wavelength of the light from 300 to 170 nm at the rate of 20 nm/min. A spot of 2×2 mm^2 on the sample was illuminated
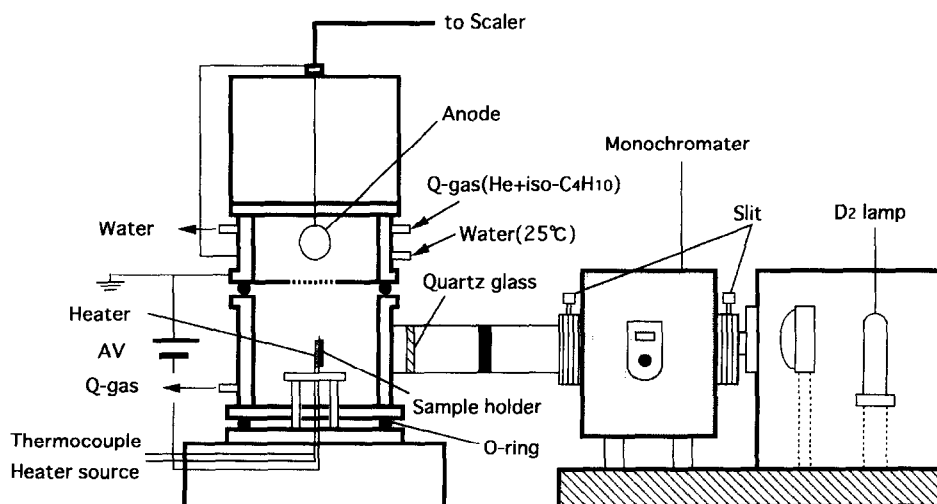

Fig. 1. Apparatus for photoelectron emission (PE) measurement.

by the light. We call the curve of the emission intensity versus the wavelength a PE spectrum. For one sample the PE spectra were repeatedly measured at different temperatures in the two cycles of initial temperature increase and subsequent temperature decrease between 25 and 300°C. The measurement temperature was successively changed at intervals of 50°C as follows: the first cycle (25 → 300 → 50°C) and the second cycle (50 → 300 → 25°C).

2.3. XPS and SP measurement

XPS spectra of Cu2p, O1s, C1s, Cu_{LMM} and Cu3p before and after PE measurement were recorded on a Shimadzu ESCA 750 spectrometer. No attempt was made to correct the binding energy for these peaks. The SP is defined as the contact potential difference between the sheet mounted on the brass holder plated with gold and the reference electrode (a Vycor glass coated with SnO_2). The SP measurement was performed in air at 25°C by vibrating the reference electrode.

3. Results and discussion

3.1. PE

Fig. 2 shows a typical PE spectrum. The intensity of PE increases progressively, reaches a maximum and then decreases with decreasing wavelength of the light. The reduction in the PE on the shorter wavelength side is attributed to the absorption of the incident light by the UV transmission glass used in
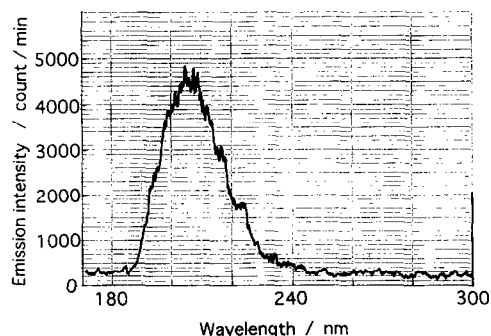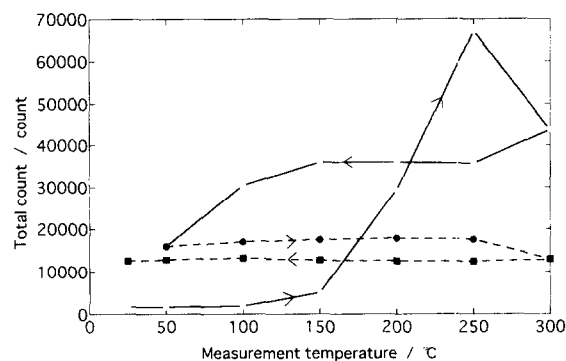
Fig. 3. Relation between the total count of electrons counted for a PE spectrum for an untreated sample and the measurement temperature successively changed: (○, □) the first cycle; (●, ■) the second cycle; (○, ●) temperature-increase process; (□, ■) temperature-decrease process.

the lamp and oxygen in air present in the light beam path and to the lowering of the diffraction efficiency of the grating monochromator. The PE spectrum provides the following characteristics: the total count of electrons emitted during the measurement, the photoelectric threshold wavelength, the maximum emission intensity and the maximum wavelength. The PE data used in the present article does not include the background intensity.

Fig. 3 shows the dependence of the total count on the two cycles of the measurement temperature for an untreated sample. A remarkable feature in Fig. 3 is as follows: for the temperature increase process in the first cycle the total count is very small at initial stage, increases sharply above 150°C, reaches a maximum with a markedly increased level at 250°C and then decreases at 300°C with increasing temperature; in the subsequent temperature decrease process the total count is constant and then decreases with decreasing temperature; for the second cycle the temperature dependence of the total count exhibits a completely different trend from that for the first cycle; that is, the total count is maintained nearly constant independent of the temperature, although the total count is slightly smaller in the temperature decrease process than in the temperature increase process. From the difference in the behavior of the PE total count of the first and second cycles it is suggested that a relaxation process being accompanied by a chemical change took place at the surface

Fig. 2. A typical PE spectrum.

during the first cycle measurement. Here, it should be pointed out that no emission of electrons can be observed even at a high measurement temperature such as 250°C unless the light is incident.

Fig. 4 shows the relationship between the total count and the measurement temperature for the 400°C oxidation sample. The total count changes similarly for the temperature increase and decrease processes in the first and the second cycles. A remarkable feature in Fig. 4 is that the total count slowly decreases with increasing temperature. The PE behavior shown in Fig. 4 strikingly differs from that in Fig. 3. This suggests that the PE measurement is a useful technique for characterizing the surface conditions.

The data of PE spectra measured for the temperature decrease process in the second cycle, where the chemical changes at the surfaces are thought to have almost stopped, was employed below to compare the dependence of the PE characteristics on the oxidation temperature. PE spectra for untreated and 100°C oxidation samples were almost the same (the threshold wavelength: 270–280 nm, the maximum wavelength: 205–210 nm and the maximum intensity: 5500–7000 count/min) and were independent of the measurement temperatures. On the other hand, for the oxidation temperature higher than 100°C the threshold wavelength and the maximum wavelength in the PE spectra shifted to 245–250 nm and 195–200 nm, respectively, and interestingly the intensity in the PE spectra for each oxidation temperature strongly depended on the measurement temperature.

Fig. 5. Dependence of PE spectra for 400°C oxidation sample on the measurement temperature in the temperature-decrease process of the second cycle: (a) 25°C; (b) 100°C; (c) 200°C and (d) 300°C.

Fig. 5 shows the variation of the PE spectra for 400°C oxidation with the measurement temperature. The intensity in the maximum emission increases with decreasing measurement temperature, although the emission starts to rise at nearly the same threshold of about 240 nm, resulting in a great difference in the intensity between 25 and 300°C. This situation has already been indicated by the change in the total count in Fig. 4. The PE trend shown in Fig. 5 was typical for the samples of the oxidation temperatures from 200 to 400°C.

Fig. 6 shows the relationship between the maximum intensity at the measurement temperatures of 25 and 300°C and the oxidation temperature. The intensity at the measurement temperature of 25°C
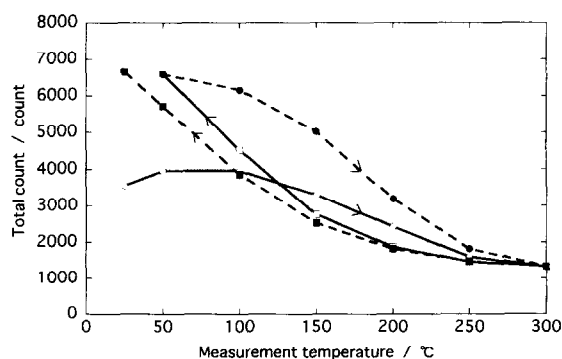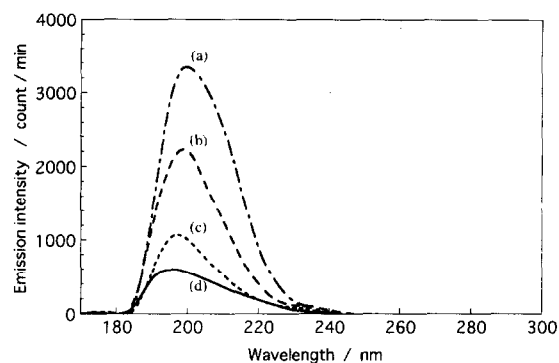

Fig. 4. Relationship between the total count for 400°C oxidation sample and the measurement temperature. The meaning of the symbols is the same as in Fig. 3.
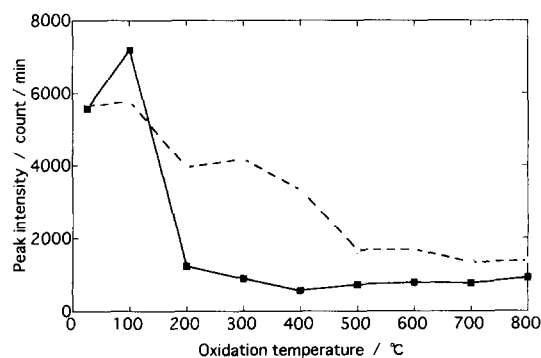

Fig. 6. Plots of the intensity of the maximum emission of PE spectra in the temperature-decrease process of the second cycle versus the oxidation temperature: the measurement temperature: (■) 300°C; (○) 25°C.

slowly increases with decreasing oxidation temperature; on the other hand, the intensity at the measurement temperature of 300°C is nearly constant at higher oxidation temperatures, but rapidly rises at 200°C. A remarkable point in Fig. 6 is that at the oxidation temperatures from 200 to 400°C there is the greatest difference between the maximum intensity at the measurement temperatures of 25 and 300°C. An enhancement of PE at 25°C can be explained by the adsorption of iso-C_4H_{10}, which was used as a quenching gas in the counter gas, on the surface, because the optically stimulated exoelectron emission (OSEE) is strongly influenced by the adsorption of organic molecules [11].

Bouwman and Sachtler [12] indicated the following approximate equation for the analysis of PE according to Fowler:

$$I = M(E - \phi)^2/2k^2, \quad \text{for } (E - \phi)/kT \gg 1 \quad (1)$$

where I is the photoelectric yield in electrons emitted per photon, M is the emission constant expressed in electrons photon^{-1}degree^{-2}, $E = h\nu$ is the energy per photon, ϕ is the work function, k is Boltzmann's constant and T is Kelvin temperature. By plotting $I^{1/2}$ against the energy, E, of the light the values of ϕ and $(M/2k^2)^{1/2}$ are obtained from the intercept on the abscissa and the slope of the straight line, respectively. In the present experiment the samples were prepared in air and exposed to the counter gas during the measurement and were therefore covered with adsorbed layers. Accordingly we call the minimum photon energy necessary for the emission to occur the threshold value instead of the work function. We obtained the threshold value from the plotting the square root of the emission intensity (count/min) for the photoelectric yield, I, against the photon energy [6,7] in the application of Eq. (1). Fig. 7 shows typical plots of (count/min)$^{1/2}$ against the photon energy ($h\nu$) at the measurement temperature of 25°C for several oxidation temperatures. We employed the approximately linear part of the plotted lines in the lower photon energy region of about 0.6 eV [6,7]. Here it can be seen that the threshold value becomes high and the slope tends to become gentle with increasing oxidation temperature.

Fig. 8 shows the relationship between the threshold values obtained for the measurement temperatures of 300, 200, 100 and 25°C and the oxidation
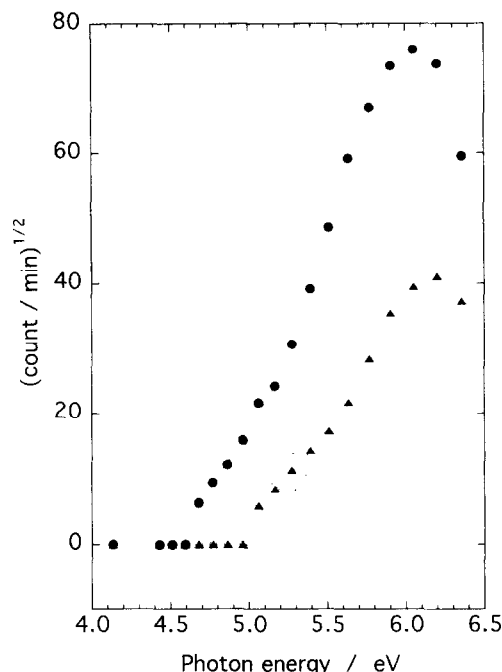

Fig. 7. Typical plots of (count/min)$^{1/2}$ versus incident photon energy: the oxidation temperature: (●) 100°C; (○) 300°C; (▲) 500°C; (△) 700°C.

temperature. For untreated and 100°C oxidation samples the threshold value is nearly the same (4.4–4.5 eV), which is in good agreement with the value for copper (4.40 eV) in the literature [13] and the value measured in air (4.45 eV) [6]. For the oxidation temperatures higher than 100°C the threshold value increases to 4.9–5.1 eV, which corresponds to the
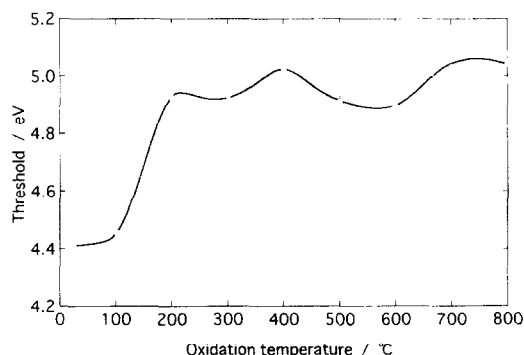

Fig. 8. Relationship between threshold and the oxidation temperature. The measurement temperatures for each oxidation temperature were 25, 100, 200 and 300°C.

value for Cu_2O (4.9 or 5.15 eV) in the literature [13]. On the other hand, surprisingly, there is little dependence of the thresholds (Fig. 8, open circles) on the measurement temperature for each oxidation temperature. Allen and Gobeli [14] reported that the low photoelectric yield of the oxide covered silicon surface compared to the clean surface cannot be accounted for merely by the higher threshold of the oxidized surface, but can be explained by the scattering or trapping action of the oxide film upon the electrons incident upon it from inside. This situation is considered to hold in the present system: the reduction in the slope of the plotted lines with increasing oxidation temperature shown in Fig. 7 suggests a restriction in the transmission of photoexcited electrons in the oxide film, which can be associated with a decrease in the square root of $(M/2k^2)$ in Eq. (1).

3.2. XPS and SP

Figs. 9 and 10 show the Cu2p, O1s, C1s, Cu_{LMM} and Cu3p XPS spectra before and after PE measurement, respectively. According to Evans [15] and Wandelt [16], we can distinguish between all the three oxidation states for copper (Cu^0, Cu^+, and

Fig. 10. Variation of XPS spectra after PE measurement with the oxidation temperature: (a) untreated; (b) 200; (c) 400; (d) 600 and (e) 800°C.

Cu^{2+}) by the combined use of the photoelectron and Auger spectra. A comparison of the main Cu2p signal of copper oxides (Cu_2O and CuO) and metallic copper shows that there is no chemical shift between Cu^0 and Cu^+ (932.5 eV), but Cu^{2+} is shifted to higher binding energy by about 1.0 eV. A strong shake-up satellite structure appears between 6 to 10 eV above the main Cu2p line in Cu^{2+} (d^9) compounds, which is completely absent in the spectra of the Cu^+ (d^{10}) materials. This correlation between oxidation state and shake-up structure is similarly, but less pronounced, observed with the 3s and 3p core level spectra. Also, the X-ray induced Cu_{LMM} Auger spectra of both Cu_2O and CuO deviate from that of metallic copper. In Figs. 9 and 10 the main Cu2p line appears at the binding energies of 934 eV (Cu^0 and Cu^+) and 935 eV (Cu^{2+}) and the Cu_{LMM} line peak appears at the binding energies of 337 eV (Cu^{2+} and Cu^+) and 335 eV (Cu^0). From these it can be seen in Fig. 9 that there are present metallic copper and CuO for the untreated sample (this situation was also observed for 100°C oxidation sample), but for the oxidation temperatures higher than 100°C CuO only is observed and a difference in the Cu2p, Cu_{LMM} and Cu3p spectra cannot be distinguished between the oxidation temperatures. In Fig. 10
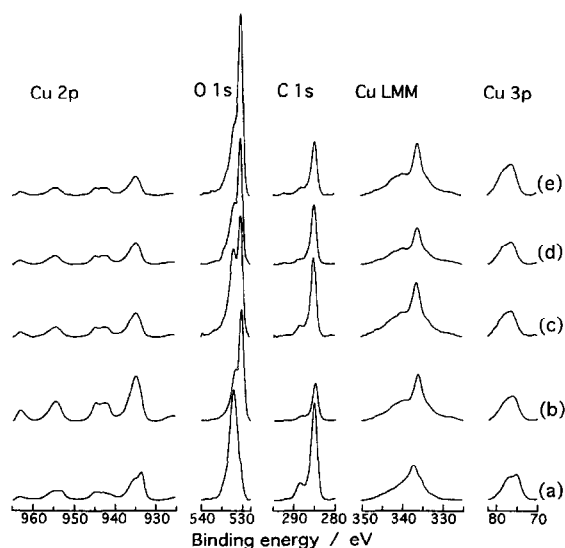
Fig. 9. Variation of XPS spectra before PE measurement with the oxidation temperature: (a) untreated; (b) 200°C; (c) 400°C; (d) 600°C and (e) 800°C.
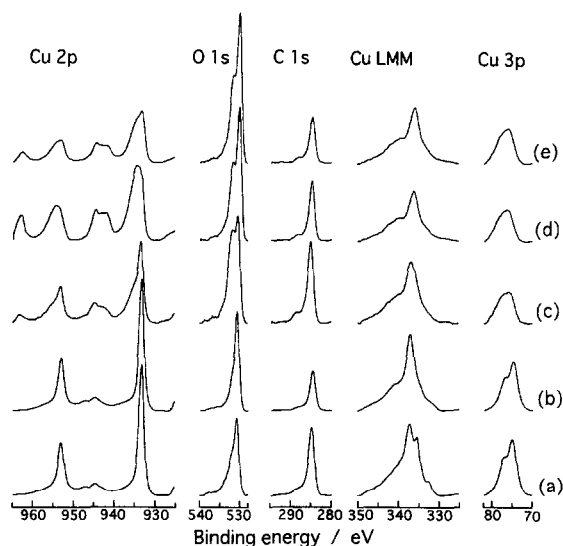
metallic copper and Cu_2O develop for all the samples, although CuO is still present for the oxidation temperatures above 400°C. The analysis of the Cu XPS spectra suggests that the adsorbed oxygen at the oxidized sample surfaces can be removed to a certain degree after PE measurement. This removal of the adsorbed oxygen can be attributed to the reduction by iso-C_4H_{10} in the counter gas and to thermal desorption from the surface.

We consider the adsorbed oxygen in detail. Evans [15] proposed a two-stage mechanism for the room temperature chemisorption of oxygen on copper: a dissociative process leading, for up to about a monolayer uptake, to a Cu^+ surface oxide, which is converted to a Cu^{2+} surface oxide as a further oxygen overlayer builds up; the split of O1s peak, on further exposure to oxygen, from initially one at 530.5 eV into two components, one at 529.9 eV and the other at 532.5, the former being assigned to oxygen bonded directly to copper and the latter oxygen adsorbed onto the initial Cu–O structure, the adsorbed overlayer accompanying the involvement of Cu3d electrons in the bonding between the copper surface and the initially chemisorbed oxygen, that is, the production of Cu^{2+}. Applying this mechanism to the present system shown in Figs. 9 and 10, two components appearing at ca. 530 and ca. 532 eV in the O1s peak can be assigned to oxygen directly bonded to copper, i.e., oxide ion and oxygen adsorbed on the initial Cu–O, respectively. A striking observation in Figs. 9 and 10 is that for the untreated sample before PE measurement the adsorbed oxygen develops predominantly, but this is converted to the oxide ion after PE measurement. Concerning the assignment of the higher binding energy component in O1s peak to the adsorbed oxygen, it should be noted that the existence of OH species and non-stoichiometric oxygen, which has been reported about the O1s lines for oxygen–nickel interaction system [16,17], may be involved in the component since the preparation of the sample surfaces in the present experiment was performed in air.

Fig. 11 shows the relationship between the O1s/Cu2p ratio before and after PE measurement and the oxidation temperature, obtained from the spectra shown in Figs. 9 and 10. Clearly the ratio before PE measurement is remarkably high for untreated and 100°C oxidation samples and drops at
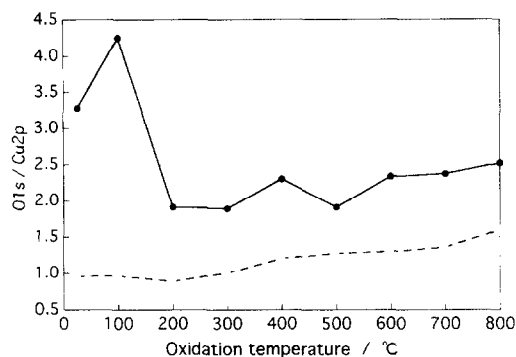
Fig. 11. Relationship between the ratio of O1s/Cu2p and the oxidation temperature: (●) before PE measurement; (□) after PE measurement.

200°C, but subsequently tends to increase and become constant with increasing oxidation temperature. After PE measurement the ratio is markedly reduced; particularly the adsorbed oxygen for untreated and 100°C oxidation samples is easily removed, although the ratio level is still higher than the stoichiometric ratio for Cu_2O; the ratio slowly increases with increasing oxidation temperature. Concerning the oxide film for untreated and 100°C oxidation samples it should be noted that as shown in Figs. 9 and 10 the adsorbed oxygen at higher binding energy in the O1s peak was changed to the oxide oxygen at lower binding energy after PE measurement, but the former was nearly completely removed by 5 min Ar ion etching (2 kV and 5×10^{-6} Torr), suggesting that the former was weakly bonded on the surface.

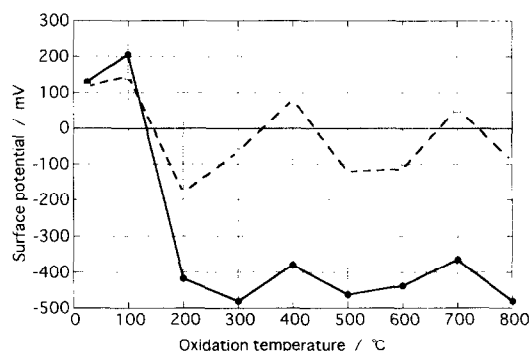Fig. 12 shows the relationship between the SP

Fig. 12. Relationship between the surface potential and the oxidation temperature: (●) before PE measurement; (□) after PE measurement.

before and after PE measurement and the oxidation temperature. The SP for untreated and 100°C oxidation samples exhibits an entirely different trend from that above 100°C. The SP for these samples is positive (+130 to +200 mV) before PE measurement regardless of an increased ratio of O1s/Cu2p (Fig. 11) and slightly lowers after PE measurement, but with a still positive level. A positive SP value implies a decrease in the work function of the metal. Spitzer et al. [18] reported that upon water adsorption on clean Cu(100) surface the work function decreases, depending on the desorption when the sample is warmed up. This suggests that the O1s peak for untreated ((a) in Fig. 9) and 100°C oxidation samples may contain not only adsorbed oxygen, but also a contribution from adsorbed water which plays a dominant role in the SP. In Fig. 12, for the samples above 100°C oxidation temperature the SP before PE measurement becomes remarkably negative to a level of −400 to −500 mV, almost independent of the oxidation temperature. The fact that the oxidation of the metal in air at high temperature produces a negative SP was also observed for nickel [19]; therefore this observation appears to be a characteristic nature of metals. The negative SP is considered to originate from the formation of the lower binding energy component (oxide ion) of the O1s peak shown in Fig. 9 as well as the increased ratio of O1s/Cu2p indicated in Fig. 11. It was reported by Quinn and Roberts [20], Delchar [21], Wagner and Spicer [22] and Evans [15] that the interaction of oxygen with a clean copper surface leads to a work function increase: oxygen exposures $(5 \times 10^{-4}$–10^{-3} Torr s) for polycrystalline copper at ordinary temperatures produced a work function increase of ca. 0.45 eV; greater exposures resulted in a larger increase, ca. 0.9 eV, from the value appropriate to the clean metal [15]. Therefore there seems to be little difference in the work function change between the clean copper subjected to oxygen exposures and the copper oxidized in air at high temperature in the present experiment. In Fig. 12 the SP after PE measurement shifts to a positive direction by +200 to +400 mV. This can be attributed to the reduction of the surface oxide film. The change in the thresholds indicated in Fig. 8 can be correlated to the ratio of O1s/Cu2p and the SP after PE measurement shown in Figs. 11 and 12, respectively. From the comparison of these
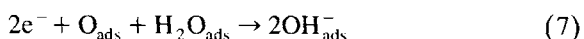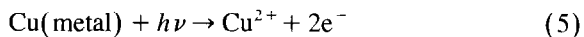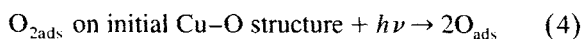
data it is suggested that the SP with a high positive value plays a significant role for the thresholds of untreated and 100°C oxidation samples, but the ratio of O1s/Cu2p, which gradually increases with oxidation temperature, is responsible for the thresholds for 200 to 800°C oxidation samples.

3.3. Mechanism of PE

We consider the reason why the PE intensity for the untreated sample was very high, particularly at the measurement temperature of 250°C during the temperature increase process in the first cycle (Fig. 3). It is pointed out that the PE in this case is strongly related to the increase in the measurement temperature and the irradiation of the light with a shorter wavelength around 205–210 nm at the same time. From the XPS and SP data before PE measurement it is also suggested that the amount of oxygen adsorbed on the initial Cu–O structure is considerably larger than that of oxygen directly bonded to copper and that the surface layer contains adsorbed water, resulting in a positive SP. The wavelength of the photon energy necessary for the dissociation of O_2 and H_2O is known as follows [23]:

$$O_2 + h\nu \rightarrow 2O(^3P) \quad < 242 \text{ nm} \tag{2}$$

$$H_2O + h\nu \rightarrow H + OH(X^2\Pi)(^3P) \quad < 190 \text{ nm} \tag{3}$$
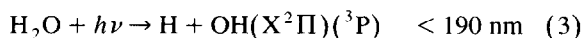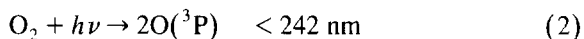
Enomoto and Hashimoto [24] reported that the photo-stimulated exoelectron emission from metals abraded in atmospheric conditions can be closely associated with the standard free energy of formation of metal oxides and metal hydroxides. Taking these into consideration, the PE for the untreated sample can be accounted for to be the electron emission accompanying the formation of the oxide and hydroxide of copper at the surface. The involved chemical reactions are thought to be as follows:

$$O_{2ads} \text{ on initial Cu–O structure} + h\nu \rightarrow 2O_{ads} \tag{4}$$

$$Cu(\text{metal}) + h\nu \rightarrow Cu^{2+} + 2e^- \tag{5}$$

$$2e^- + O_{ads} \rightarrow O_{ads}^{2-} \tag{6}$$

$$2e^- + O_{ads} + H_2O_{ads} \rightarrow 2OH_{ads}^- \tag{7}$$

Here, the dissociation of H_2O by the incident

light is not taking place since the photon energy required is much higher than that corresponding to the peak in the PE spectrum. The electron released from the metal following Eq. (5) is considered to act in the PE process and in the formation of the oxide and the hydroxide ions bonded to Cu^{2+}. The metal oxide and metal hydroxide are little by little removed by the reduction and the thermal desorption during the subsequent measurements of PE spectra.

4. Conclusion

The temperature dependence of PE from intentionally oxidized copper exhibited a markedly different behavior depending on the presence of adsorption layer and oxide film on the surfaces. The results are summarized as follows.

(1) The PE characteristics represented by the total count, the threshold wavelength and the maximum emission intensity greatly depended on the oxidation treatment temperature and the measurement temperature.

(2) The total count and the maximum intensity remarkably changed with the measurement temperature, probably due to the effect of the adsorption of iso-C_4H_{10} used as a quenching gas in the counter gas.

(3) The threshold value was sensitively influenced by the presence of oxide film depending on the oxidation temperature, but nearly independent of the measurement temperature.

(4) A completely different PE behavior for untreated and 100°C oxidation samples can be associated with the presence of contaminants such as adsorbed oxygen and water.

(5) The XPS analysis after PE measurement revealed that the reduction of CuO to Cu and Cu_2O, being accompanied by the desorption of oxygen at the surface occurs.

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