Energy Distribution of Secondary Electrons from Copper-Beryllium Alloy by Bombardment of Positive Ions of Inert Gases. II. Activated Copper-Beryllium

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In a previous communication[1], study of the electron ejection from the electro-polished copper-beryllium by the bombardment of the positive ions of inert gases has been reported on. In that work, the energy distribution of secondary electrons was measured, and the mechanism of the secondary electron ejection from the electro-polished copper-beryllium surface was discussed. It was found that the general features of the distribution curves show the kinetic ejection, and that the energy distribution of secondary electrons has a correlation with the ionization potential of the impacted ions. These results indicate that the mechanism of the secondary ejection in that study is not satisfactorily explained by the

1) T. Sugiura, This Bulletin, **34**, 1475 (1961).

simple kinetic ejections; the contribution of the potential ejection must also be taken into consideration. In an earlier communication[2], it has been reported that the secondary electron yield from the copper-beryllium surface impacted by positive ions is markedly increased by the activation treatment of the copper-beryllium surface, and that quite a thick layer of beryllium oxide is newly formed by the activation in the neighborhood of the surface.

It is, therefore, of interest to the present author to investigate the energy distribution of the secondary electrons emitted from the activated copper-beryllium surface, since such an investigation would make possible a comparison with the results reported in the previous communication[1] and with the information on the mechanism of the secondary electron ejection from the activated copper-beryllium surface.

Experimental

Apparatus and Procedure. — The apparatus and the procedure have already been described in the previous communication[1].

Preparation of Ion Target. — The activation treatment of the ion target was carried out in a quartz tube (45 mm. in inner diameter and 500 mm. in length) connected by a water-cooled taper joint to the vacuum system, the reservoir of purified oxygen, and a McLeod gauge. The quartz tube was heated in an electrical furnace, and the temperature was measured with an alumel-chromel thermocouple enclosed in this quartz tube. The shaped and electro-polished ion target was put into the quartz tube and evacuated to lower than 5×10^{-6} mmHg at about 800°C for about three hours. After the evacuation, the temperature in the quartz tube was lowered to the required temperature (400°C in this study), then a known quantity of oxygen was introduced into the quartz tube. The initial pressure of oxygen was about 5×10^{-2} mmHg.

Materials. — The inert gases were the same as those described in the previous communication[1]. Oxygen used for the activation of the ion target was prepared by the thermal decomposition of potassium permanganate and was purified by passing it through a trap cooled by liquid nitrogen.

Results

Contact Potential between Gold and Activated Copper-Beryllium. — The contact potential between gold and activated copper-beryllium was determined for the purpose of the correction of the energy scale for the secondary electrons. Typical results on the retarding potential measured in a manner similar to that described in the previous communication[1] are shown in Fig. 1, in which the circular points indicate the retarding potential curve between the tungsten filament and the gold surface, while the square points show the retarding potential curve between the tungsten filament and the activated copper-beryllium surface. As seen in Fig. 1, the retarding potential portion had been observed to be linear from 0.75 to 1.25 V. for the tungsten~copper-beryllium system, and the value of the retarding potential for the tungsten~gold system well coincides with that obtained in the previous communication. As shown by arrows in each curve in Fig. 1, the point of zero field has beeen determined by the intersection of each extrapolated straight lines with the saturated current and the retarding portion. The observed value of the contact potential difference between gold and activated copper-beryllium is 0.25 eV; namely, the surface potential of activated copper-beryllium is 0.25 eV. more positive than that of gold.

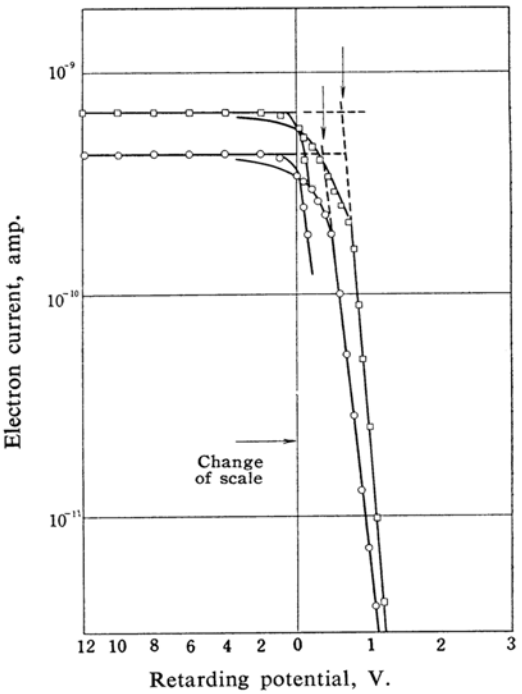

Fig. 1. Retarding potential curves of thermo-ionic electron from the heated tungsten used to determine the contact potential difference between gold and activated Cu-Be. The circular devices show the Au~W system, the square devices show the activated Cu-Be~W system. The vertical arrows on each curve indicate the values for the zero field in each systems.

Energy Distribution of Secondary Electrons. — The distribution curves of the kinetic energy of secondary electrons by singly-charged argon ions are shown in Fig. 2. In this figure, the results obtained for the incident ion energy of 1240, 840 and 540 V. are indicated by circular,

2) T. Sugiura and T. Hayakawa, ibid., **34**, 58 (1961).

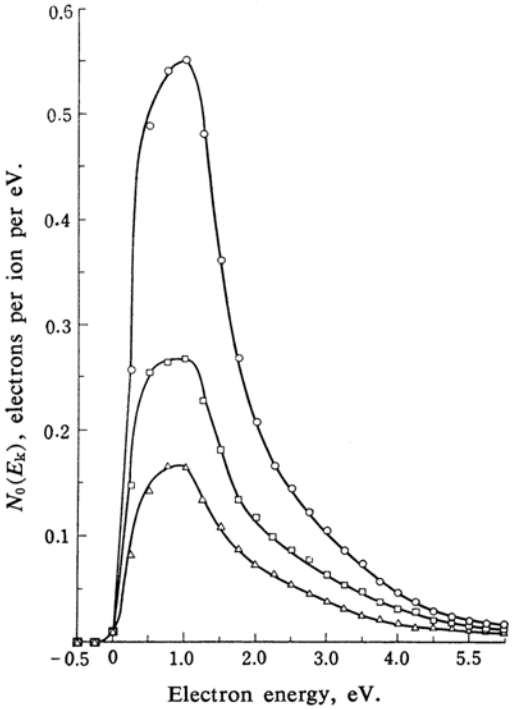

Fig. 2. Energy distributions of electron ejected from activated Cu-Be by singly charged argon ions of 1240, 840 and 540 V. incident kinetic energies, indicate by circular, square and triangular devices, respectively.

square and triangular devices respectively. The electron energy scale (V_r) in this figure was corrected to the contact potential difference between the ion target and the electron collector, as described above. The distribution curves of the kinetic energy of secondary electrons by doubly-charged argon ions, singly- and doubly-charged neon ions and singly charged helium ions have been also obtained; these distribution curves, which have been abbreviated in this paper, have a shape similar to and have the same tendency as the curves in Fig. 2. The distribution of the kinetic energy of the secondary electrons obtained in this study represented by half the width of each distribution curve and the yield of secondary electrons are summarized in Table I. As seen in Fig. 2, these distribution curves show no low energy tail, the fringing field of the analyzing magnet of the mass spectrometer having no observable influence on low energy electrons.

Discussion

General Features of Energy Distribution Curves. — As seen Fig. 2, the general features of the distribution curves of the secondary

TABLE I. VARIATION OF THE HALF WIDTH OF THE ENERGY DISTRIBUTION CURVES AND YIELDS OF SECONDARY ELECTRONS FROM ACTIVATED Cu-Be SURFACE WITH ION ENERGIES OF INERT GAS IONS

	Half width of distribution curves of secondary electron energy in eV.			Yields of secondary electrons γ_1 in electrons per ion		
Ion energy / ion	1240	840	540	1240	840	540
A^+	1.50	1.55	1.60	1.08	0.56	0.32
A^{2+}	1.55	1.60	1.65	1.02	0.67	0.42
Ne^+	1.70	1.80	1.90	1.18	0.83	0.49
Ne^{2+}	2.00	2.20	2.40	1.86	1.45	1.00
He^+	2.40	2.50	2.70	2.40	1.74	1.07

electrons from the activated copper-beryllium surface are similar to those obtained for those of non-activated copper-beryllium surface already reported on in the previous paper[1]. But, as seen in Table I, the half-widths of the distribution curves increased about 10 to 50% by the activation of the copper-beryllium in each case, together with the increase in the secondary electron yield

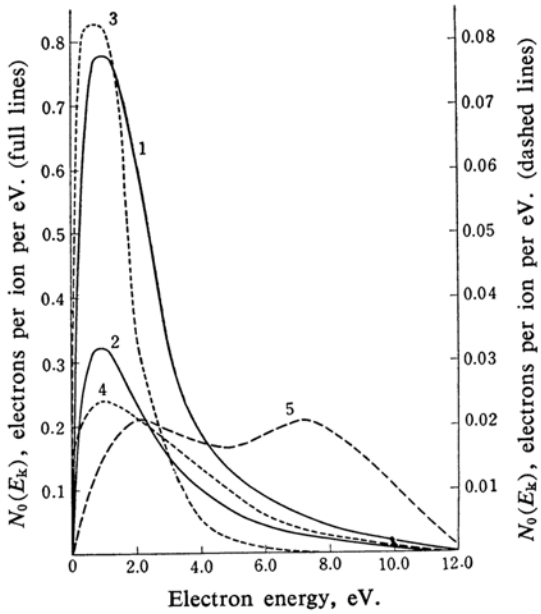

Fig. 3. Energy distributions of electrons ejected from activated Cu-Be by singly-charged helium ions of 1240 (curve 1) and 540 eV. (curve 2), and energy distributions of electrons ejected by 10 eV. helium ions from germanium (111) surface in various cleaning conditions obtained by Hagstrum[3] (curves 3, 4 and 5), the cleaning conditions of germanium surface described in the text.

3) H. D. Hagstrum, *J. Phys. Chem. Solid*, **14**, 33 (1960).

Recently, Hagstrum et al. have reported investigations into the interaction between the slowly moving helium ion and the germanium[3] and the silicon[4]; he was interested to find the procedures necessary for the preparation of clean semiconductor surfaces. In Fig. 3, the energy distribution curves 1 and 2 of secondary electrons ejected from activated copper-beryllium by 1240 and 540 eV. helium ions obtained in the present study are compared with the results of Hagstrum (curves 3, 4 and 5) with 10 eV. helium ions from the (111) face of germanium. Curve 3 in Fig. 3 was obtained for the face of etched germanium, and curve 4 was obtained for the germanium surface treated in the following manner: after being heated to 1125°K for 4 hr., the target was exposed with dry nitrogen at atmospheric pressure and successively repumped for about 100 hr. without any target heating. As seen in Fig. 3, the energy distribution curves of the secondary electrons are gradually broadened from curve 3 to curve 4 by target heating, but the area of the distribution curve is markedly decreased by the heat treatment i. e., the electron yield decreases as a result of target heating. Curve 5 in Fig. 3 was obtained for the germanium surface after heating at 940~1170°K for about 180 hr. and subsequent sputtering of about 100 layers of germanium at a 4 mA/cm^2 current intensity for 90 min.; Hagstrum has considered that curve 5 is the distribution curve of a secondary electron emitted from the atomically clean germanium surface. Hagstrum has obtained similar results for a silicon surface[4].

Figure 3 indicates that distribution curves 1 and 2 show a great similarity to distribution curves 3 and 4 rather than to the distribution curve of the kinetic ejection obtained by Waters[5]. These results imply that the emission of secondary electrons from activated copper-beryllium is followed by the Auger ejection in spite of the fact that the surface is not atomically clean. Further comparison reveals that the yields of secondary electrons in the present experiments are about one order greater than the results of Hagstrum, and distribution curves 1 and 2 are both broader than curve 3, though narrower than curve 4. These results suggest that the cleanliness of the target in the present study may correspond to that about the middle of curve 3 and of curve 4 in Fig. 3. In the present study, the ion target was heated to about 800°C by electron bombardment of the background pressure of 1×10^{-6} mmHg for about 10 min. It is clear that this treatment did not result in an atomically clean surface, but some adsorped layers of residual or foreign gases were removed. Allen[4] has studied the nature of the silicon surface by means of the field emission microscope connected with the investigations of Hagstrum; he has observed that the high intensity random spots from the unheated surface and the secondary electrons emitted by ions from this surface have an energy similar to that shown on curve 3 in Fig. 3. These high intensity spots were eliminated by heating of the silicon, and this surface then emitted secondary electrons having an energy similar to that shown on curve 4 in Fig. 3. Allen has described how these high intensity spots are emitted from the cluster of adsorption layers. From this study, the difference between curves 3 and 4 in Fig. 3 is considered to arise from the fact that the respective surface have and do not have the cluster of adsorption layers. In a comparison of the curves shown in Fig. 3, the energy of each secondary electron shown by curves 3 and 4 is considered to shift to a low energy compared with the energy of the secondary electrons shown by curve 5, and it is supposed that secondary electrons emitted from the ion target lose their kinetic energy in collisions with the adsorbed molecules or atoms. In these surfaces, it is supposed that the influence of the surface characteristics on the energy of the secondary electrons emitted by ions is obscured by the action of the adsorption layers. From the consideration described above, it may be considered that the cluster on the ion target in the present study is removed by the heating of the electron bombardment.

The influence of the ion kinetic energy, the ion species and the ionic charge on the distribution curves of the electron energy has a tendency similar to the results on the electro-polished surface reported on in the previous paper[1].

Influence of Target Activation of the Energy Distribution Curves. — By the activation of copper-beryllium, the yield of secondary electrons was greatly increased. For the purpose of obtaining information about the emission characteristics of the secondary electrons emitted from activated copper-beryllium, the energy distribution curves of the secondary electrons increased by target activation were plotted from the results both of the present study and of the previous communication[1].

Figures 4, 5 and 6 show the plot of the difference in the energy distribution $\Delta N_0(E_k)$ of secondary electrons at each electron energy E_k obtained for the activated and electro-polished

4) F. G. Allen, J. Eisinger, H. D. Hagstrum and J. T. Law, *J. Appl. Phys.*, **10**, 1563 (1959).
5) P. M. Waters, *Phys. Rev.*, **109**, 1053 (1958); **111**, 1466 (1958).

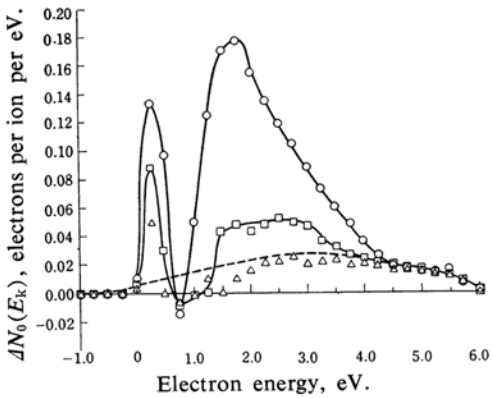

Fig. 4. Plots of the differences between energy distribution ejected from activated and electro-polished Cu-Be impacted by singly-charged argon ions. Circular, square and triangular devices indicate the kinetic energy of incident ions of 1240, 840 and 540 eV., respectively. The dashed curve shows the distribution curve of Auger electron ejected by singly charged argon ions of 10 eV. from atomically clean W surface obtained by Hagstrum[6].

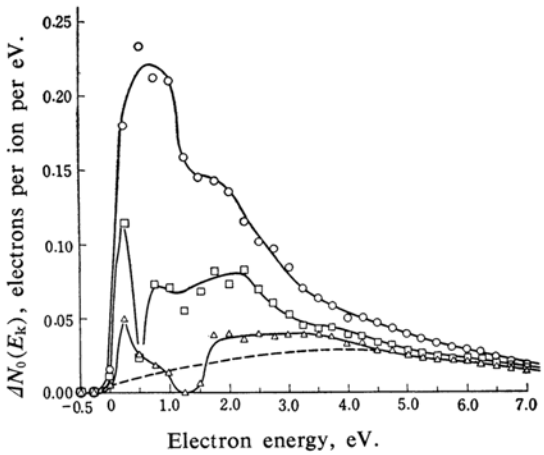

Fig. 5. Plots of the differences between energy distribution ejected from activated and electro-polished Cu-Be impacted by singly-charged neon ions. Circular, square and triangular devices indicate the kinetic energy of incident ions of 1240, 840 and 540 eV., respectively. The dashed curve shows the distribution of Auger electron ejected by singly neon ions of 10 eV. from atomically clean W surface obtained by Hagstrum[6].

copper-beryllium target impacted by the singly-charged argon, neon and helium ions respectively. In these figures, circular, square and triangular devices indicate the energy distributions by the incident ions of 1240, 840 and 540 eV. kinetic energy respectively. For comparison, the energy distribution curves of secondary electrons from an atomically clean tungsten surface impacted by 10 eV. inert gas ions obtained by Hagstrum[6] are shown by dashed lines in Figs. 4, 5 and 6.

The distribution curves of $\Delta N_0(E_k)$ were very different from that obtained from activated copper-beryllium. The distribution curves of the singly-charged ions, especially in the case of the slow ions shown in the figures, have two maxima, and the peak of the lower energy side is very narrow, while the distribution of the higher energy side is relatively broad and has a high energy tail. The emission processes of secondary electrons shown in these distributions must thus be considered separately in three parts.

The distribution curves higher than about 4 eV. in electron energy show a great similarity to the distribution curves of Hagstrum indicated by dashed line in each figure, and this distribution is independent of the kinetic energy of the incident ions. From this similarity, the distribution curve under the dashed line may be considered that of the secondary electrons emitted by the Auger

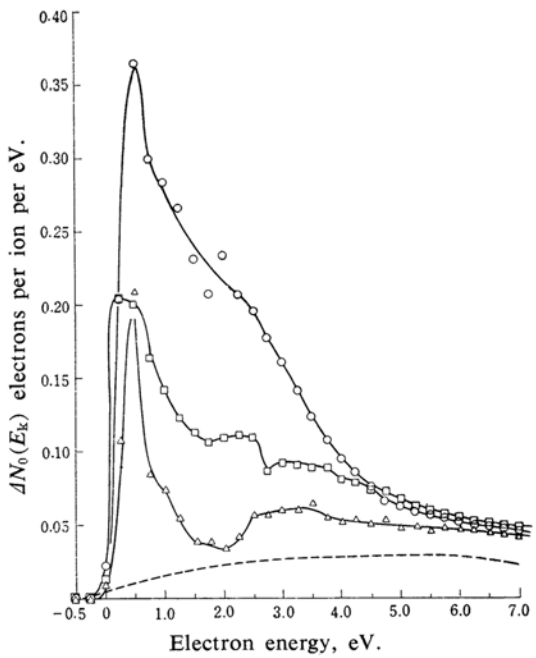

Fig. 6. Plots of the differences between energy distribution ejected from activated and electro-polished Cu-Be impacted by singly-charged helium ions. Circular, square and triangular devices indicate the kinetic energy of incident ions of 1240, 840 and 540 eV., respectively. The dashed curve shows the distribution of Auger electron ejected by 10 eV. singly-charged helium ions from atomically clean W surface obtained by Hagstrum[6].

6) H. D. Hagstrum, ibid., **104**, 317 (1956).

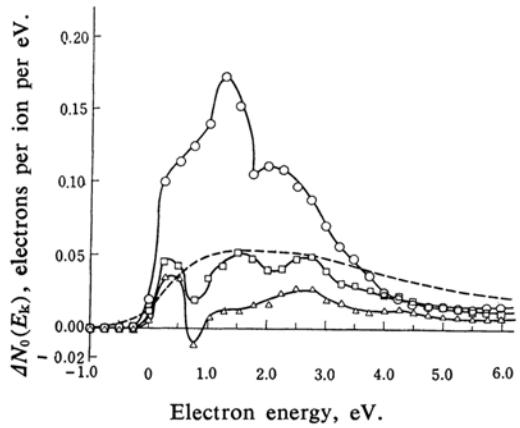

Fig. 7. Plots of the differences between energy distribution ejected from activated and electro-polished Cu-Be impacted by doubly-charged argon ions. Circular, square and triangular devices indicate the kinetic energy of incident ions of 1240, 840 and 540 eV., respectively. The dashed curve shows the distribution of Auger electron ejected by 200 eV. doubly-charged argon ions from atomically clean W surface obtained by Hagstrum[7].

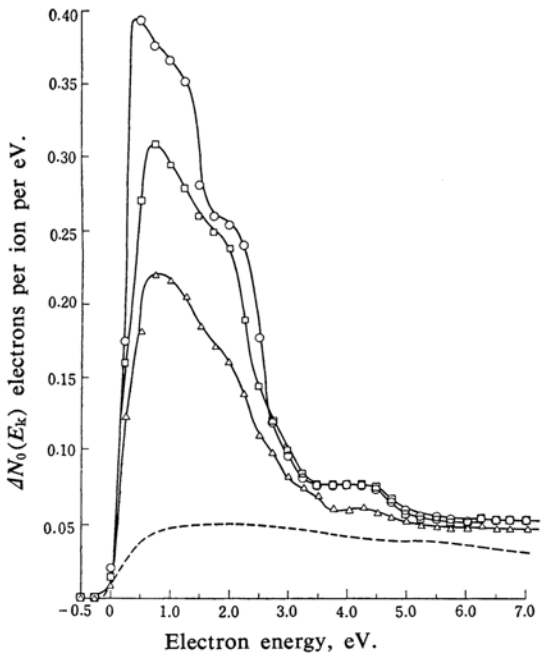

Fig. 8. Plots of the differences between energy distribution ejected from activated and electro-polished Cu-Be impacted by doubly-charged neon ions. Circular, square and triangular devices indicate the kinetic energy of incident ions of 1240, 840 and 540 eV., respectively. The dashed curve shows the distribution of Auger electron ejected by 200 eV. doubly-charged argon ions from atomically clean W surface obtained by Hagstrum[7].

process described by Hagstrum[7]. According to the earlier study by electron diffraction analysis of the activated and electro-polished copper-beryllium surface[2], the quite thick layers of the beryllium oxide were formed on the surface, replacing the copper oxide, by the activation treatment, and the results of the surface configuration suggested that the Auger ejection from activated copper-berillium might be contributed by the beryllium oxide layers mentioned above.

As seen in Figs. 4, 5 and 6, electron distributions exist above the dashed curve in each figure, and these distributions have relatively high energy as compared with distributions obtained from activated surface; the quantity of $\Delta N_0(E_k)$ depends on the kinetic energy of the incident ions. These phenomena show that secondary electrons emitted from activated copper-beryllium have a relatively a higher energy than those emitted from an electro-polished surface. Consequently, higher energy electrons markedly increased by the target activation may be formed relatively near the surface of the ion target. It is also supposed that the stopping cross-section of beryllium oxide for low speed ions in the present study may be greater than that of cupric oxide, although it is difficult to evaluate the values of the stopping cross-section of low energy ions.

The lower energy side of the distribution curves of $\Delta N_0(E_k)$ greatly depends on the kinetic energy of the incident ions, as seen in Figs. 4, 5 and 6; the low energy part of these distribution curves may imply the following interpretation. Part of the secondary electrons are produced in the deeper layer of the ion target by penetrated ions, and these secondary electrons thus produced pass through the considerable length of beryllium oxide produced near the surface of the ion target by target activation, and that part of these secondary electrons with sufficient energy may be ejected from the ion target. Assuming that the stopping power for the electrons of the beryllium oxide is greater than that of the copper oxide, the ejected electrons from the activated copper-beryllium may lose their energy more than those from the electro-polished copper-beryllium surface, as has been suggested by Sternglass[8]. A part of the ejected electrons from activated copper-beryllium may be shifted to the low energy side, in contrast to those from the electro-polished surface.

The distribution curves of $\Delta N_0(E_k)$ for doubly-charged argon and neon ions are shown in Figs. 7 and 8 respectively. As seen in Fig.

7) H. D. Hagstrum, ibid., **96**, 336 (1954).

8) E. J. Sternglass, ibid., **108**, 1 (1957).

7, for the doubly-charged argon ions the high energy tail in the present distribution curve is smaller than that of Hagstrum indicated by the dashed line in Fig. 7, and the separation of the distribution curve is not clear. In the case of the doubly-charged neon ions as seen in Fig. 8, the separation of the distribution curve is not clear for any incident ion energy. As seen from the results of Hagstrum[9] on the 200 eV. doubly-charged argon and neon ions shown by the dashed line in Figs. 7 and 8 respectively, the distribution curve by the Auger ejection processes of the doubly-charged inert gas ions has shifted to the lower energy side as compared with the distribution curves of singly-charged ions. Hagstrum has considered that the faster electrons may be ejected by highly charged ions in the Auger process and that the mean energy of the ejected electrons is practically independent of the ionic charges; he has explained his results by saying that the Auger neutralization of the highly charged ions by the metal surface occurs in steps. From the fact that this explanation may also be fitted to apply to the present result of the doubly-charged ions, it is considered that the distribution of $\Delta N_0(E_k)$ results from the shift of electron energy to the low energy side.

The phenomena in this study can not be attributed to the surface of the ion target not being atomically clean, but it is not unreasonable to consider that the secondary electron emission from activated copper-beryllium includes the contribution of the Auger ejection together with the kinetic ejection.

Summary

The distribution curves of the kinetic energis of secondary electrons from the activated copper-beryllium surface impacted by inert gas ions were together with the yield of the secondary electrons, measured by the retarding potential method. The contact potential difference between the ion target (activated copper-beryllium) and the electron collector (gold) was also measured by the retarding potential method for the thermal electrons from tungsten, and the correction to the kinetic energies of secondary electrons by this contact potential difference was made. For the purpose of obtaining information about the emission characteristics of the increase in the yield of secondary electrons by target activation, the distribution of $\Delta N_0(E_k)$, which is the difference in the secondary electrons emitted from activated and from electro-polished copper-beryllium, was plotted by electron energies. The main results obtained are as follows:

(1) The contact potential difference between activated copper-beryllium and gold is 0.25 eV. (gold, negative).

(2) The general features of the distribution curves of the secondary electrons emitted from activated copper-beryllium show a tendency similar to that of the secondary electrons emitted from electro-polished copper-beryllium, and they also show a great similarity to the distribution curves obtained from the not atomically clean semiconductor surface (germanium or silicon) by Hagstrum.

(3) The distribution of $\Delta N_0(E_k)$ show a remarkable difference from the distribution curves for activated copper-beryllium. Distribution curves of $\Delta N_0(E_k)$ higher than about 4 eV. in electron energies showed a great similarity to the distribution curves of the Auger electron obtained by Hagstrum. Moreover, the distribution of $\Delta N_0(E_k)$ for singly-charged ions shows clearly a separation in the electron energy scale; this result was explained by the fact that the stopping cross-section of the beryllium oxide is greater than that of the cupric oxide.

(4) From the explanation of the distribution of $\Delta N_0(E_k)$, it is considered that the increase in the yield of secondary electrons by target activation depends on the stopping cross-section of beryllium oxide and on the Auger process of electron emission.

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9) H. D. Hagstrum, ibid., **96**, 325 (1954).