Surface Plasma Oscillations in Copper Films

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Dedicated to Professor Dr. G. Borrmann, on the occasion of his 65th birthday

An energy loss peak at 2 eV in the energy spectrum of electrons transmitted through thin copper films is observed and the variations of the energy value and of the intensity of the peak with film thickness are studied. The cross section for the surface plasmon excitation is calculated from optical data. The observed variations of the energy value and of the intensity of the peak show quantitative and qualitative agreements, respectively, with calculated values. It is concluded that the peak is mainly due to the surface plasmon which does not emit plasma radiation.

1. Introduction

Energy loss spectra of electrons transmitted through thin films of noble metals have been studied by many workers. For silver, it is well known that a sharp peak at 3.7 eV arises from both the volume and surface plasmons. In fact, the peak splits into two peaks if measured with an energy analyser at high resolution power. The observed energy loss values of the peaks on the low and high energy sides agree with the theoretical values for the surface and volume plasmons, respectively. These theoretical values of the energies of the surface and volume plasmons can be determined from the conditions that the real parts of the dielectric constant are equal to minus one and zero, respectively [1].

For gold, several peaks are observed, but the particular peak corresponding to the volume plasmon is not identified. On the other hand, one of the present authors [2] concluded from the concentration dependence of energy loss spectra for gold-silver alloys that the peak at 3 eV may belong to the surface plasmon. Carillon [3] have studied the energy dependence of the 3 eV peak of gold as a function of film thickness and confirmed that this peak is due to the surface plasmon.

In the case of copper, Creuzburg [4] suggested that a peak at 2 eV is caused by surface effects. In the present work, the quantitative dependence of the energy and the intensity of this 2 eV peak on the film thickness is measured. It is expected that the 2 eV peak shows a behavior which is different from the peak produced by surface plasmons in silver and aluminum as explained below.

2. Theory

According to a calculation by Hattori and Yamada [5], the inelastic scattering probability, $P(\hbar\,\omega, \Theta)\, \mathrm{d}\Omega\, \mathrm{d}(\hbar\,\omega)$, of electrons from a solid of dielectric constant ε and thickness a in the energy region $(\hbar\,\omega, \hbar\,\omega + \mathrm{d}(\hbar\,\omega))$ and inside an element of solid angle $\mathrm{d}\Omega$ around the scattering angle Θ is given by

$$P(\hbar\,\omega, \Theta) = (e^2/\pi^2\,\hbar^2\,v^2)\;(V - Q_\mathrm{p} + Q_\mathrm{s} + Q_\mathrm{a}), \tag{1}$$

where

$$V = \frac{a}{\Theta^2 + \Theta_\mathrm{E}^2} \cdot \mathrm{Im}\left[-\frac{1}{\varepsilon}\right], \tag{2a}$$

$$Q_\mathrm{p} = \frac{2\,\hbar}{p}\,\frac{\Theta}{(\Theta^2 + \Theta_\mathrm{E}^2)^2}\left\{\frac{\sin^2(\omega\,a/2\,v)}{\tanh(p\,a\,\Theta/2\,\hbar)} + \frac{\cos^2(\omega\,a/2\,v)}{\coth(p\,a\,\Theta/2\,\hbar)}\right\}\cdot \mathrm{Im}\left[-\frac{1}{\varepsilon}\right], \tag{2b}$$

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$$Q_s = \frac{2\hbar}{p} \frac{\Theta}{(\Theta^2+\Theta_E^2)^2} \frac{\cos^2(\omega a/2v)\{\coth(pa\Theta/2\hbar)+1\}^2}{\coth(pa\Theta/2\hbar)} \times \mathrm{Im}\left[-\frac{1}{\varepsilon+\coth(pa\Theta/2\hbar)}\right] \quad (2\,c)$$

and

$$Q_a = \frac{2\hbar}{p} \frac{\Theta}{(\Theta^2+\Theta_E^2)^2} \frac{\sin^2(\omega a/2v)\{\tanh(pa\Theta/2\hbar)+1\}^2}{\tanh(pa\Theta/2\hbar)} \times \mathrm{Im}\left[-\frac{1}{\varepsilon+\tanh(pa\Theta/2\hbar)}\right]. \quad (2\,d)$$

Here, v and p are the velocity and the momentum of the incident electrons, respectively, and Θ_E is equal to $\hbar\omega/pv$.

The first term, V, on the right hand side of (1) is the scattering probability due to volume effects; the other terms are the contributions from surface effects. The term Q_p is a correction to V and the terms Q_s and Q_a represent surface effects with symmetric and antisymmetric mode, respectively. In the case of thick films, both the terms Q_s and Q_a are proportional to

$$\mathrm{Im}[-1/(\varepsilon+1)] \quad (3)$$

as given by Kanazawa[6]. The quantity (3) has a large value when

$$\varepsilon_1+1 \approx 0 \quad (4\,a)$$

and

$$\varepsilon_2 \ll 1. \quad (4\,b)$$

Here, ε_1 and ε_2 are the real and imaginary parts of ε, respectively. Equations (4 a) and (4 b) are the usual conditions which determine the position of a peak due to surface plasmon. For aluminum and silver, the peak due to the surface plasmon is observed at the energy satisfying the conditions (4 a) and (4 b) and the intensity is almost independent of the film thickness. The situation in the case of copper is different from the above.

In general, however, the condition (4 a) is not always necessary and can be replaced by

$$\varepsilon_1+\coth(pa\Theta/2\hbar) \approx 0 \quad (5\,a)$$

or

$$\varepsilon_1+\tanh(pa\Theta/2\hbar) \approx 0 \quad (5\,b)$$

as can be seen from (2 c) and (2 d). In the case of metals, ε_1 has the range of value covering one to minus infinity. Especially, large negative values in the low energy region are only found in metals. Therefore, (5 a) and (5 b) are always satisfied, even if interband transitions exist. If the condition (5 a) or (5 b) is satisfied in the energy region with small ε_2, a peak due to the excitation of the surface plasmon must be observed. In this case, the intensity of the peak depends on film thickness and primary electron energy, since Q_a or Q_s is large for certain values of pa only.

According to an optical measurement[7], copper has a small ε_2 in the vicinity of 2 eV, and $-\varepsilon_1$ is large in this region, that is, the condition (5 a) is satisfied. Therefore, it is excepted that only the surface plasmon with a symmetric mode is strongly excited in a thin film, and that its energy increases with film thickness.

The surface plasmon is strongly affected by oxide layers on the film surface. According to our calculation, the scattering probability of electrons in a film of total thickness d, metal layer thickness a, and oxide layer thickness τ on both sides of the film is given by

$$P'(\hbar\omega,\Theta) = (e^2/\pi^2\hbar^2 v^2)\,(V-Q_p+Q_s'+Q_a'), \quad (6)$$

$$Q_s' = \frac{2\hbar}{p} C_s \frac{\Theta}{(\Theta^2+\Theta_E^2)^2} \cdot \mathrm{Im}\left[-\frac{1}{\varepsilon_0\{S\coth(pa\Theta/2\hbar)+\eta\}}\right] \quad (7\,a)$$

and

$$Q_a' = \frac{2\hbar}{p} C_a \frac{\Theta}{(\Theta^2+\Theta_E^2)^2} \cdot \mathrm{Im}\left[-\frac{1}{\varepsilon_0\{S\tanh(pa\Theta/2\hbar)+\eta\}}\right], \quad (7\,b)$$

where

$$C_s = \frac{[\{S\coth(pa\Theta/2\hbar)+1\}\cos(\omega a/2v)-(1-\varepsilon_0)A_s\cos(\omega d/2v)]^2}{\coth(pa\Theta/2\hbar)}, \quad (8\,a)$$

$$C_a = \frac{[\{S\tanh(pa\Theta/2\hbar)+1\}\sin(\omega a/2v)-(1-\varepsilon_0)A_a\sin(\omega d/2v)]^2}{\tanh(pa\Theta/2\hbar)}, \quad (8\,b)$$

$$S = \frac{1+\varepsilon_0\tanh(p\tau\Theta/\hbar)}{\varepsilon_0+\tanh(p\tau\Theta/\hbar)}, \quad (8\,c)$$

$$A_s = \frac{\coth(p\, a\, \Theta/2\,\hbar)}{\sinh(p\,\tau\,\Theta/\hbar) + \varepsilon_0 \cosh(p\,\tau\,\Theta/\hbar)}\,, \tag{8 d}$$

$$A_a = \frac{\tanh(p\, a\, \Theta/2\,\hbar)}{\sinh(p\,\tau\,\Theta/\hbar) + \varepsilon_0 \cosh(p\,\tau\,\Theta/\hbar)}\,, \qquad \eta = \varepsilon/\varepsilon_0\,. \tag{8 e), (8 f}$$

V and Q_p are the same as in (2 a) and (2 b), respectively. Here, we assumed that the oxide contributes only with the real part of its dielectric constant ε_0. Q_s' and Q_a' are more complicated than Q_s and Q_a. In the limiting case where τ is infinite, however, Q_s' and Q_a' coincide with Q_s/ε_0 and Q_a/ε_0, respectively, with ε replaced by η. Furthermore, we can conclude that the behaviour of films with and without oxide layers is almost identical.

3. Experiments

Thin films of copper were prepared by vacuum evaporation on faces of cleaved rocksalt crystals. The film thickness was obtained by the standard method employing the calibrated frequency change of a quartz oscillator. The specimens were removed by dissolving the rocksalt in a cold (about 0 °C) aqueous solution of methanol and then mounted on a conventional mesh of an electron microscope. To avoid oxidation, the use of this cold aqueous solution of methanol was much better than that of pure water. However, we always found weak diffraction rings due to cuprous oxide (Cu_2O) besides those from the copper in the electron diffraction patterns. The total thickness of the oxide layers was estimated from the ring intensity in the Debye-Scherrer pattern to about 60 Å.

A Möllenstedt type energy analyser was inserted between the intermediate and projector lenses of a conventional electron microscope. The electron microscope image of the film formed on the slit of the analyser was analysed and recorded on a photographic plate. The diameter of the objective aperture was 20 μm and the incident energy was 25 and 50 keV. The width in energy of the incident beam was about 0.7 eV.

4. Experimental Results

The energy spectra obtained from copper films with various thickness and from a cuprous oxide film of thickness 200 Å are shown in Fig. 1 and 2, respectively, where the intensities are normalized at the 20 eV peak. In Fig. 1, dashed lines indicate the background estimated from spectra of the oxide and thick copper films. It may be noticed from the intensity measurements that the inelastic scattering probability at 20 eV for cuprous oxide is nearly equal to that for copper. Here, the energy of the incident beam was 50 keV. Figure 1 shows that the intensity of the peak at 2 eV depends strongly on the film thickness, and also that the energy at the maximum intensity increases with film thickness. On the other hand, the peak at 2 eV cannot be observed in Figure 2. These facts suggest that the peak at 2 eV belongs to surface effects in copper.

The thickness dependence of the peak energies observed at incident energies of 50 and 25 keV can be seen in Figs. 3 and 4, respectively. In Figs. 5 and 6, intensities due to surface effects are given for 50 and 25 keV incident energy, respectively. On the ordinates the scale is given as a product of the total film thickness d including the thickness of oxide layers and the intensity ratio I_s/I_{20}, where I_s is the 2 eV peak height above the background, and I_{20} is the 20 eV peak height (see Figure 1). I_s is considered to be the intensity from surface effects and I_{20} can be selected as a standard value. The increase of the peak energy and of the peak intensity I_s with film thickness agrees with the theoretical considerations in the previous section.

5. Comparison with Calculations

To compare the experimental results with theoretical considerations the quantity

$$I(\Delta E) = 2\,\pi \int_0^{\Theta_c} P'(\Delta E, \Theta)\; \Theta\, d\Theta \tag{9}$$

was calculated by using the values of ε_1 and ε_2 obtained by Ehrenreich and Philipp [7], taking an aperture angle of the objective aperture, $\Theta_c = 2$ mrad, estimated from the aperture image in the diffraction pattern. The value of ε_0 is assumed to be equal to 8.5 which is the observed value in the vicinity of 2.5 eV [8]. $I(\Delta E)$ corresponds to the energy spectra of the electron microscopic image shown in Figure 1. Figures 7 a, b, c, and d show the results in the cases where $d = 1000$, 400, 200 and 100 Å, respectively,

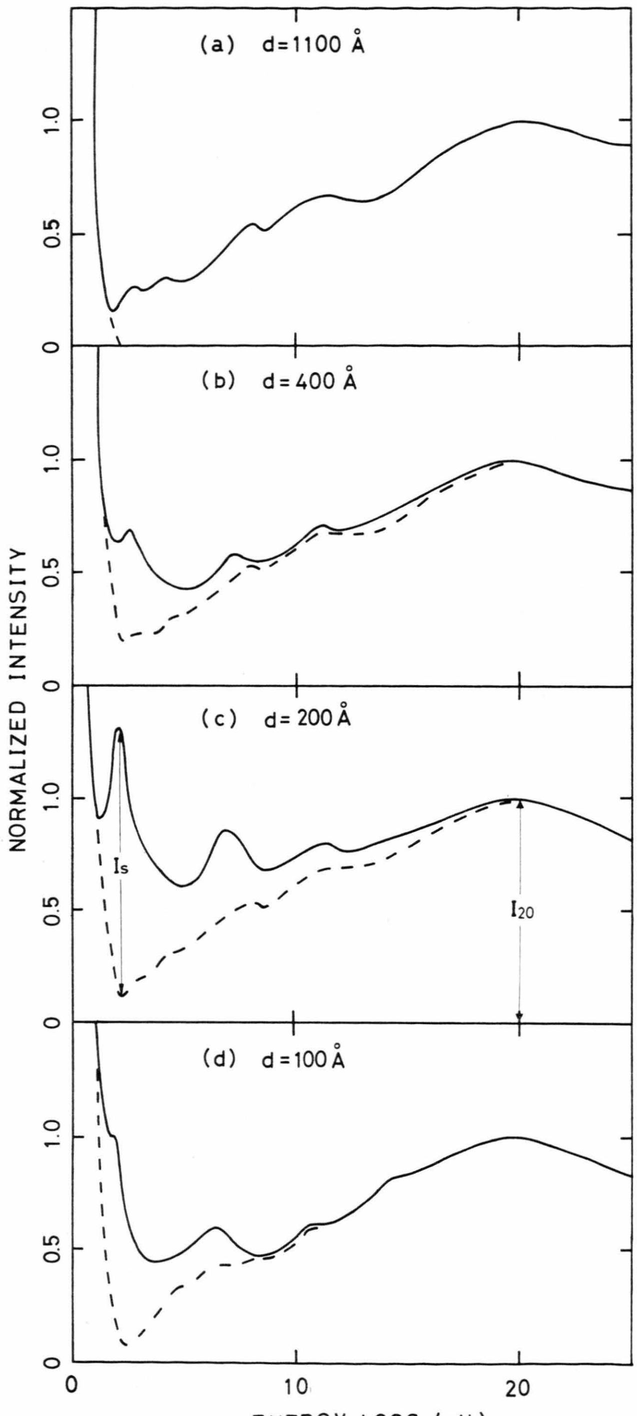

Fig. 1. Electron energy loss spectra from copper films of various thicknesses. The background due to the volume effects of the copper film and of the cuprous oxide layers are shown by dashed lines. In Fig. 1 c, I_S and I_{20} represent intensities from surface effects of copper at 2 eV and volume effects of copper films covered with oxide layers at 20 eV. Primary electron energy 50 keV.

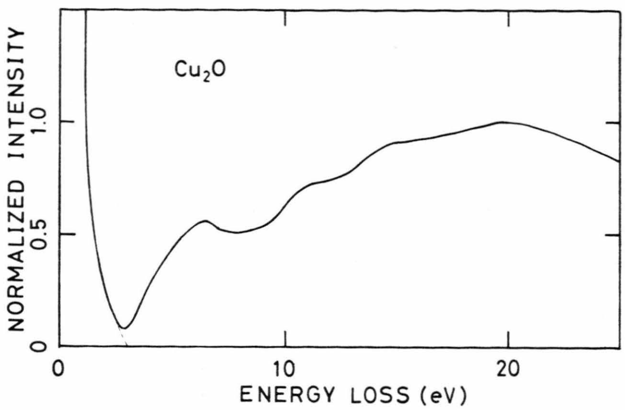

Fig. 2. Electron energy loss spectrum in a cuprous oxide film of thickness 200 Å. Primary electron energy 50 keV.

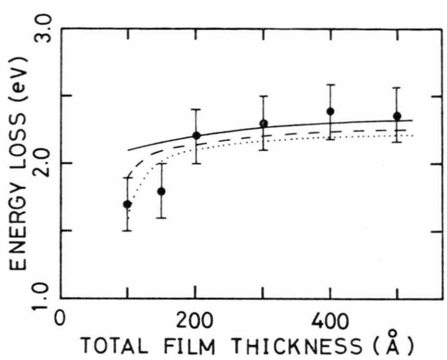

Fig. 3. Experimental (●) and theoretical values of the surface energy loss peaks versus total foil thickness. The solid, dashed, and dotted curves represent theoretical values for $\tau=0$, 20, and 30 Å, respectively. Primary electron energy 50 keV.

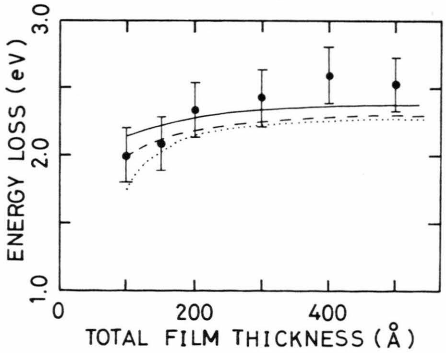

Fig. 4. Experimental (●) and theoretical values of the surface energy loss peaks versus total foil thickness. The solid, dashed, and dotted curves represent theoretical values for $\tau=0$, 20, and 30 Å, respectively. Primary electron energy 25 keV.

the incident energy being 50 keV. Here, the curves (1), (2), and (3) represent $I(\Delta E)$ for $\tau=0$, 20, and 30 Å, respectively. Curves (4), (5), and (6) are due to Q_s' for $\tau=0$, 20, and 30 Å, respectively; (7) arises

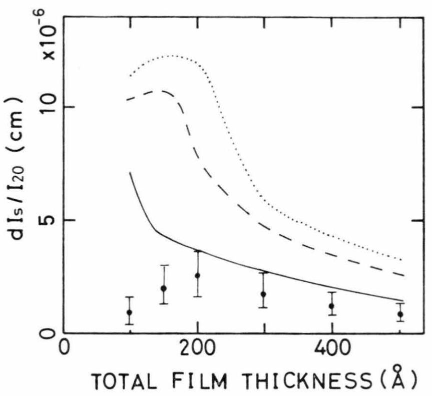

Fig. 5. Experimental (●) and theoretical values of intensities due to surface effects versus total foil thickness. The solid, dashed, and dotted curves represent theoretical values for $\tau=0$, 20, and 30 Å, respectively. Primary electron energy 50 keV.

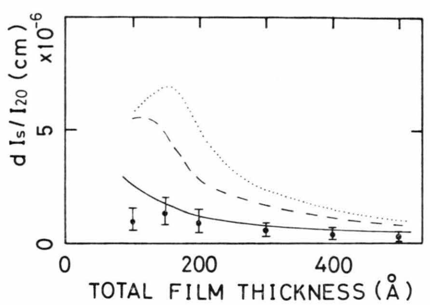

Fig. 6. Experimental (●) and theoretical values of intensities due to surface effects versus total foil thickness. The solid, dashed, and dotted curves represent theoretical values for $\tau=0$, 20, and 30 Å, respectively. Primary electron energy 25 keV.

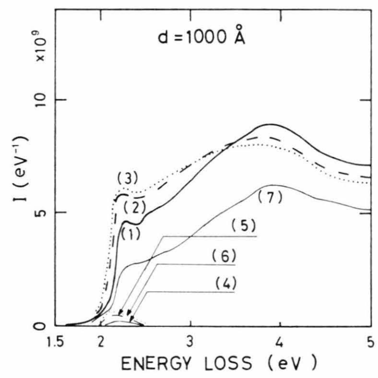

Fig. 7 a

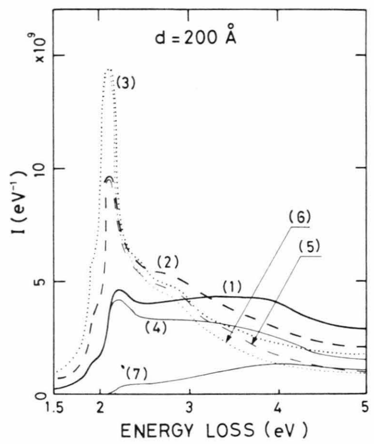

Fig. 7 c

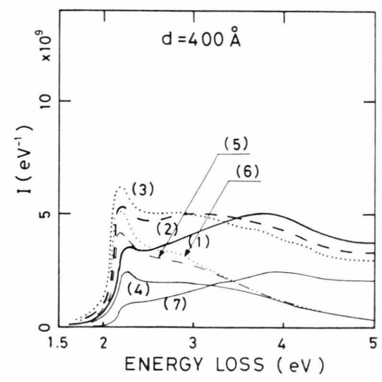

Fig. 7 b

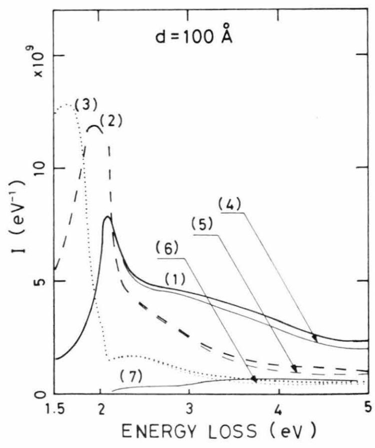

Fig. 7 d

Fig. 7. Theoretical electron energy loss spectra of copper foils of various thicknesses. Curves (1), (2), and (3) represent total intensities for $\tau=0$, 20, and 30 Å, respectively. Curves (4), (5), and (6) are contributions from Q_s' for $\tau = 0$, 20, and 30 Å, respectively. Curve (7) shows the contribution from V for $\tau=0$.

from V for $\tau = 0$. As can be seen in Fig. 7, in the case of a thin film, the 2 eV peak is mainly due to the surface plasmon with a symmetric mode. The peak intensity obtained from the film covered with the oxide is stronger than that from the film without oxide. The variations of the theoretical peak energies with total film thickness for $\tau = 0$, 20, and 30 Å are indicated by the curves in Figures 3 and 4. The theoretical values given by

$$d(I_s/I_{20}) = d\left[\int_0^{\Theta_c} Q_s' \, \Theta \, d\Theta\right]_{\text{peak}} \Big/ \left[\int_0^{\Theta_c} V \, \Theta \, d\Theta\right]_{20 \text{ eV}} \tag{10}$$

are illustrated in Figures 5 and 6. Here V is the value for $\tau = 0$, since the scattering probability at 20 eV for cuprous oxide is almost equal to that for copper. Figures 3 and 4 show a good agreement between the observed and the theoretical values obtained by taking into account the oxide layers. Concerning the intensity variations seen in Figs. 5 and 6, the observed and the theoretical values behave identically. However, the magnitude of the observed peak heights are much lower than theoretically expected. This discrepancy may come from the fact that the incident beam has an energy width of 0.7 eV; this width is neglected in the theoretical calculations. Furthermore, the film and oxide thickness may not be uniform and contaminations may strongly affect surface effects.

Other difficulties in comparing experimental and theoretical results are that the theoretical values vary with the choice of the employed optical data. For instance, when we use the optical values by Spencer and Givens [9], the energy value at the peak maximum increases by $0.1 \sim 0.3$ eV and the peak height becomes higher than that obtained from the Ehrenreich and Philipp optical data.

6. Discussion

From the above results and the considerations in section 2, we can conclude that the energy loss peak at 2 eV in copper is due to the excitation of a surface plasmon with symmetric mode. According to the free electron model, the energies of volume plasmons, $(\hbar\,\omega_p)$, in silver and copper are 9.2 and 9.3 eV, respectively, and those of surface plasmon are given by $\hbar\,\omega_p/\sqrt{2}$. For silver, the energies of volume and surface plasmons are reduced by the transition from the d-band to the Fermi surface. Their values of about 3.7 eV are near the edge of such a transition. For copper, the surface plasmon is found at the edge of the interband transition analogue to silver. However, contrary to silver, the volume plasmon of copper is not clearly identified, although several peaks in thick films can be observed. Furthermore, for the surface plasmon, the oscillations of the antisymmetric mode at long wavelengths are very weakly excited, since ε_2 has a large value in the energy region where ε_1 satisfies the condition (5 b). Therefore, in the case of copper plasma radiation cannot be observed. This is quite different from the surface plasma oscillations in silver, aluminum, and other metals.

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