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In the photon-energy region 1.5–6.5 eV, a size-dependent change in interband transitions associated with the *d* bands of metal particles has been detected directly for the first time by measuring the transmittance spectrum and its derivative of Cu island films. It is shown that the narrowed *d* bands for Cu particles smaller than 70 Å in diameter depart from flatness gradually from the highest to the lowest levels with decreasing particle size. Comparing the *d* bands of bulk Au surface, this *d*-band change is shown to be connected with the reduced coordination number of atoms on the particle surface.

Study of energy bands of metal particles becomes increasingly important in solid-state physics, e.g., it reveals information concerning the transition from the molecular state to the bulky solid. As is well known, optical absorption caused by interband transitions reflects the energy-band structure. If we can observe the change in such absorption due to the decrease in particle size, we shall be able to obtain information about the size dependence of energy bands. The distortion of the top of the *d* bands has been suggested for Au and Ag particles by recent optical studies[1,2] in which interband transitions or energy bands were investigated indirectly through the estimation of dielectric constant spectra. This paper is the first report of direct detection of the size-dependent change in the interband transitions associated with the *d* bands of metal particles. Furthermore, we report the weakening of the optical plasma resonance absorption (OPRA) for small size. Taking account of the *d* bands at the surface layer of bulk Au, we analyze the above change and the weakening and discuss the *d*-band change.

The samples were prepared by vacuum evaporation in conditions similar to those described in a previous study.[3] Cu (purity 99.999%) was deposited both on SiO_2-coated fused-quartz substrates and on SiO_2-coated carbon meshes, which were heated to about 500 °C during deposition in order to obtain highly aggregated island films. The films were then annealed at the same temperature for 3 h. After annealing, the films were coated with SiO_2 to prevent adsorption or chemical reactions on exposure to air. The transmittance of the evaporated SiO_2 film without Cu particles was almost constant in the spectral region of interest here. Transmittance spectra for normal incidence and its derivative were measured at room temperature with a double-beam spectrophotometer in the photon energy region 1.5–6.5 eV. The particle-size distribution was investigated with an electron microscope operating at 200 kV.

For normal incidence of light, the transmittance of island films can be expressed by[4]

$$T=\left[1+\frac{2\pi}{n_0}\frac{d_w}{\lambda}\frac{\Delta g}{(F+g)^2+(\Delta g)^2}\right]^{-1},$$

where n_0 is the refractive index of the medium surrounding the particles, λ is the wavelength, d_w is the weight thickness, and F is the effective depolarization factor. g and Δg are related to the dielectric constant ϵ_i of the particles by the following relation:

$$g+i\Delta g=(\epsilon_i/\epsilon_0-1)^{-1},$$

where

$$\epsilon_0=n_0^2 .$$

ϵ_i consists of two terms,

$$\epsilon_i=\epsilon_f+\delta\epsilon_b ,$$

where ϵ_f is the Drude term contributed by conduction electrons and $\delta\epsilon_b$ is the bound-electron contribution which arises from interband transitions. ϵ_f is expressed as

$$\epsilon_f=1-\omega_p^2/(\omega^2-i\omega\omega_\tau) ,$$

where ω_p is the plasma frequency and ω_τ is the collision frequency. In the classical size-effect theory,[1] ω_τ is given by

$$\omega_\tau=\omega_{\tau,\mathrm{bulk}}+v_F/R ,$$

where $\omega_{\tau,\mathrm{bulk}}$ is the bulk collision frequency, v_F is the Fermi velocity, and R is the particle radius.

In the spectral region 1.5–6.5 eV, the optical absorption of Cu island films is known to contain the OPRA contribution and the interband transition contribution, which is mainly associated with the *d* bands.[5] Using the above transmittance formula and ω_τ and assuming $\delta\epsilon_b$ is equal to the bulk value obtained from the bulk dielectric constant,[6] the transmittance spectrum and its derivative

were computed for particle sizes 20, 30, 50, and 70 Å in diameter. In the computation, the values obtained from the bulk dielectric constant[6] were used for ω_p and $\omega_{\tau,\text{bulk}}$ and the value of 1.51 was used for n_0.

Figure 1 shows an example of the computed results. The scale of the derivative is arbitrary. The structure of the transmittance spectrum is as follows:[5,7] The large absorption at about 2 eV is the OPRA. The dip (labeled A) at about 2.6 eV is generated by transitions from the uppermost d states (band 5) into s,p-like states (band 6) just above the Fermi level. The weak dip (labeled B) at about 3.8 eV originates from transitions between the d-like bands 2, 3, and 4 and the s,p-like band 6. The well-defined dip (labeled C) at about 5.4 eV is due to transitions between the lowest-lying d state (band 1) and the s,p band (band 6) and, with smaller contribution, between the s,p-like states in bands 6 and 7. The sloped parts labeled A', B', and C' in the derivative correspond to the presence of the dips A, B, and C, respectively. All the computed spectra showed the presence of the OPRA and the above interband transitions.

In Figs. 2–4, the scale of the derivative is the same. Figure 2 shows the experimental result for particles about 160 Å in diameter. The general structures in Figs. 1 and 2 agree very well, which shows that the bulk interband transitions occur at the above size. Figure 3 shows the experimental result for particles about 70 Å in diameter. Obviously, the dip and the sloped part which correspond to those A and A' in Fig. 2 are not found. The dip B and the sloped part B' are found to be ill-defined compared to those in Fig. 2. The positive peak at about 5 eV in the derivative is low in comparison with that in Fig. 2, which shows that dip C is broader than that in Fig. 2. Figure 4 shows the experimental result for particles about 30 Å in diameter. The dips and the sloped parts which correspond to A, B, A', and B' in Fig. 2 are not found. Dip C is broader than that in Fig. 3. From Figs. 2–4, it can be seen that as the particles become smaller, the dips become less and less defined in the order of A, B, C, i.e., in increasing order of energy. On the basis of the size-dependent broadening of dip C, it is reasonable to consider that dips A and B broaden and disappear with a decrease in particle size.

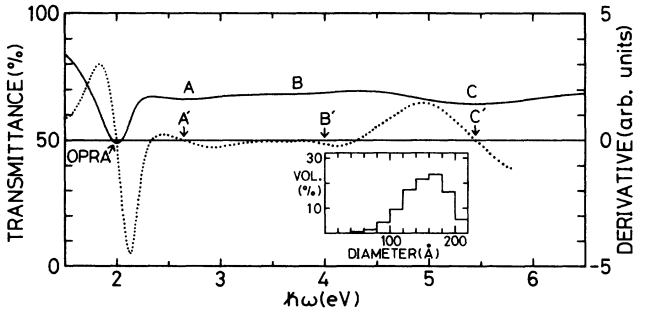

FIG. 2. The transmittance spectrum (solid curve) and its derivative (dotted curve) of the Cu island film with particle diameter of about 160 Å. The weight thickness is about 77.4 Å. The deposition rate is about 0.05 Å/s.

It has been shown[8] that when the d bands depart from flatness, the interband transitions are turned on gradually and $\text{Im}(\delta\epsilon_b)$ becomes broader and smaller. Such a change in $\text{Im}(\delta\epsilon_b)$ broadens and decreases the joint density of states.[2] In this case, the interband-transition absorption is broad and of small amplitude. Therefore, the observed broadening of the dips shows the departure of the d bands from flatness, and from the energy order of the broadening we can see that with decreasing particle size the departure occurs from the highest to the lowest levels. The previously suggested distortion of the top of the d bands for Au and Ag particles[1,2] seems to correspond to the change at the upper part in our results.

The ratio of surface to volume atoms increases with decreasing particle size. Hence, it is obvious to ascribe the change in the d bands to the causes concerned with the surface. The possible causes are lattice contractions and reduction of the coordination number. In a previous paper,[2] the change in the d bands was calculated for Ag particles by assuming 2% lattice contraction. The calculated result showed that the lattice contraction affects mainly the lower part in the d bands and only shifts the interband transitions to the higher-energy region. Thus our experimental results seem not to be interpreted by lattice contractions. From x-ray photoemission spectros-

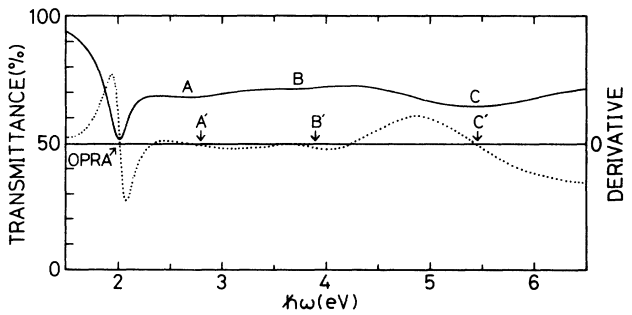

FIG. 1. The computed transmittance spectrum (solid curve) and its derivative (dotted curve) of the Cu island film. The particle diameter is 70 Å. The weight thickness is 40 Å. The effective depolarization factor is 0.083.

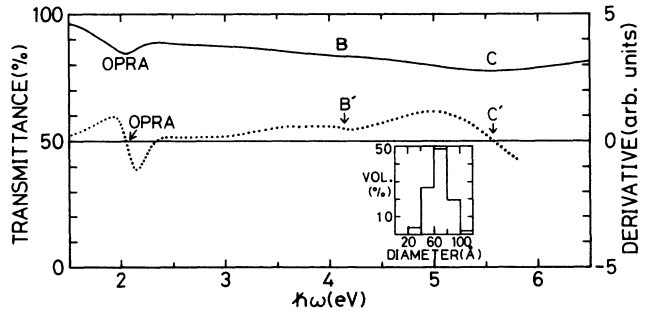

FIG. 3. The transmittance spectrum (solid curve) and its derivative (dotted curve) of the Cu island film with particle diameter of about 70 Å. The weight thickness is about 35.2 Å. The deposition rate was about 0.11 Å/s.

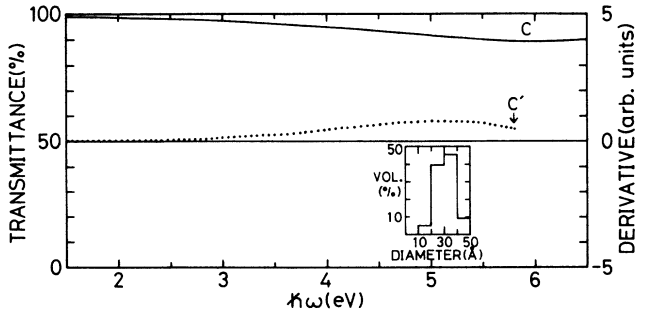

FIG. 4. The transmittance spectrum (solid curve) and its derivative (dotted curve) of the Cu island film with particle diameter of about 30 Å. The weight thickness is about 14.1 Å. The deposition rate was about 0.11 Å/s.

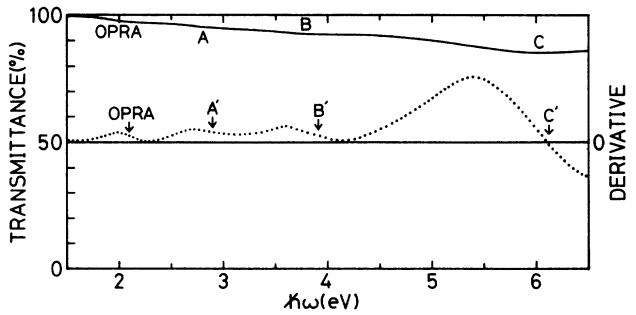

FIG. 5. The computed transmittance spectrum (solid curve) and its derivative (dotted curve, arbitrary scale) of the Cu island film. The size distribution and the weight thickness in Fig. 4 were used. The effective depolarization factor is 0.165.

copy (XPS) measurements for bulk noble metals, Citrin *et al.*[9,10] have reported that at the surface layer the *d* band is narrowed due to the reduced coordination number of atoms on the surface. For the case of Au, they reported the surface and the bulk density of states (DOS) also. On relative comparison of these DOS, the surface DOS is found to be appreciably low at the upper part of the *d* bands, which shows that when the coordination number is reduced, the DOS decreases at the lower-energy region. The XPS result agrees with our results with respect to the change at the upper part in the *d* bands. Thus, the change in the *d* bands can be connected with the reduced coordination at the particle surface. This connection is supported by the weak OPRA as follows.

In Fig. 4, the transmittance is almost constant in the OPRA region 1.9–2.3 eV, which shows that in contrast to the computed results mentioned above, the actual OPRA for small size is very weak. In the case of thin island films such as in Fig. 4, the possible causes of the damping of the OPRA other than the size effect are the particle-size distribution, the overlap with the interband-transition absorption,[11] and the increase in ω_τ due to the high concentration of lattice defects.[4] As shown in Fig. 5, however, the OPRA was found clearly in the spectrum computed by taking account of the above causes. In the computation, the size distribution in Fig. 4 was taken into account by weighting the absorption with the particle volume,[4] and the overlap was increased for the bulk interband-transition absorption by using the large F, and the value which is 15% larger than the value by the classical size effect was used as increased ω_τ by referring to the experimental value[4] for Ag particles about 30 Å in diameter.

The narrowing of the *d* bands is achieved by a combined reduction of *d* delocalization and *s*-*d* hybridization, giving an overall net increase in the localized *d* states at the expense of the delocalized *s* and *d* states.[9,10] As a result, the narrowed *d* band is atomiclike and the electronic configuration of surface atoms is intermediate between those of the free and bulk atoms.[9,10] Thus the surface layer is less metallic than the bulk. An analogous electronic reconfiguration should occur for the surface atoms of the particles. In this case, presumably, the particles become less and less metallic with decrease in particle size because the ratio of surface to volume atoms increases with decreasing particle size. Thus the OPRA is considered to weaken with a decrease in particle size because the OPRA is based on plasma resonance of conduction electrons, i.e., on one of the primary characteristics of metals.[1] The very weak OPRA can be interpreted by such weakening. Therefore, the very weak OPRA also supports the above connection.

In this study, the narrowing of the *d* bands was not detected directly. However, since the interband-transition change was found for particle sizes smaller than about 70 Å in diameter, the *d* bands for Cu particles smaller than this size are considered to be narrower than that of the bulk.

The main conclusion is that the narrowed *d* bands for Cu particles smaller than about 70 Å in diameter depart from flatness from the highest to the lowest level with a decrease in particle size, and that this change in the *d* bands can be connected with the reduced coordination number of atoms on the particle surface.

It has been predicted by simulated calculations[11] that the presence of an interband transition in the vicinity of the OPRA may split the OPRA into a free-electron-like and an interbandlike doublet. The correspondence between the structures in Figs. 1 and 2 is good. In the spectral region in this study, therefore, we concluded that such a split does not occur.

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