Optical absorption of fcc Co particles: Properties of conduction electrons of fcc Co

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Optical plasma-resonance absorption of fcc Co island films consisting of fcc Co particles smaller than about 300 Å in diameter was measured in the photon energy region from 0.5 to 6.5 eV. Comparison of the broadening and the location of this absorption with those of Ni island films shows that the *d* character of conduction electrons of fcc Co is stronger than that of Ni, and that the number of conduction electrons per atom of fcc Co is large compared to that of Ni. The difference in the character can qualitatively be attributed to the difference in the *s*-*d* hybridization, which is larger in fcc Co than in Ni. The difference in the number may be due to the difference in the *s*-*d* hybridization.

I. INTRODUCTION

Recently there has been interest in the electronic properties of fcc Co because of its importance in both fundamental research and applications.[1–4] Theoretical and experimental studies of these properties have been made, but a detailed understanding is still lacking. In particular, the properties of the conduction electrons are less well understood.

Optical plasma-resonance absorption (OPRA) of metal island films, consisting of small metal particles, arises from the plasma oscillation of conduction electrons.[5] Information about the OPRA is useful in understanding the properties of conduction electrons. For example, from the particle-size- and particle-shape-independent broadening of the OPRA of Ni and Pd island films, the strong *d* character of conduction electrons of these metals can be seen,[6] and from the location of the OPRA, we can study the number of conduction electrons per atom because the location reflects the density of these electrons.[5,7,8]

Small Co particles have a fcc structure.[9] In this study, the OPRA of fcc Co island films is reported. The broadening and location of this OPRA are compared with those of Ni island films,[6] and the *d* character of conduction electrons and the number of conduction electrons per atom of fcc Co are discussed qualitatively.

II. EXPERIMENT

The samples were prepared by vacuum evaporation in conditions similar to those described in a previous paper.[6] Co (purity 99.96%) was deposited both on a SiO_2-coated fused-quartz substrate and on SiO_2-coated carbon meshes, which were heated to about 500 °C during deposition. The films were then annealed at the same temperature for 1 h. After annealing, the films were coated with SiO_2 to prevent adsorption or chemical reactions on exposure to air. The weight thickness and the deposition rate were monitored with a quartz-crystal oscillator. The transmittance of the evaporated SiO_2 film without Co particles was almost constant in the spectral region of interest here.

Optical and electron-microscopic investigations were carried out after exposure of the samples to air. Transmittance spectra for normal incidence and their derivatives were measured within an experimental accuracy of $\pm 0.1\%$ and $\pm(0.001-0.01)$ eV at room temperature and -193 °C with a double-beam spectrophotometer in the photon energy region from 0.5 to 6.5 eV. The derivative was measured at a wavelength difference of about 4 nm. The particle size and the electron-diffraction pattern were investigated with an electron microscope operating at 200 kV. In the spectra in this paper, the scale of the derivative is the same, and the inset shows the particle-size distribution in vol. %.

III. RESULTS AND DISCUSSION

In Co island films with particle diameters below about 300 Å, the fcc structure could always be identified in electron-diffraction patterns, and the general structures of transmittance spectra agreed well with those of Ni island films. Above this size, both hcp and fcc structures were found, which shows the presence of both hcp and fcc Co particles, and the general structures of transmittance spectra differed from those of Ni island films. Thus, in this study, Co island films with particle diameters below about 300 Å are thought to consist of fcc Co particles, and the OPRA of these films is investigated. The fcc Co particles in this study are considered to be ferromagnetic because the Curie temperature of fcc Co is known to be about 1127 °C.[10]

A. *d* character of conduction electrons

An example of the transmittance spectrum of fcc Co island films at room temperature is shown in Fig. 1 (about 275 Å in diameter). Taking into account the similarity between energy bands of fcc Co (Refs. 11 and 12) and Ni,[13–15] and referring to the transmittance spectra of the Ni island films,[6] we see that dip *C* is the interband-transition absorption due to transitions from the lowest-lying *d* states into empty *s*- and *p*-like states just above the Fermi level, and that the broad absorption (labeled

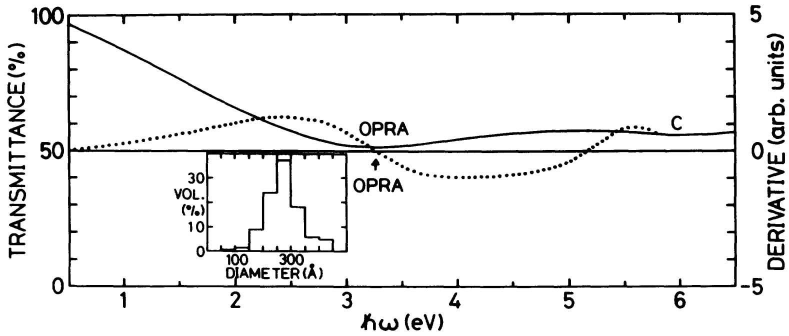

FIG. 1. Transmittance spectrum (solid curve) and its derivative (dotted curve) for a fcc Co island film with a particle diameter of about 275 Å. The weight thickness is 60.8 Å. The deposition rate was 0.14 Å/s. The half-width of the OPRA is 2.75 eV.

OPRA) appearing at the low-energy side is the OPRA. With decreasing weight thickness, the broad absorption is shifted to the higher-energy side. Such a shift is characteristic of the OPRA.[5,16,17]

In Ni, since *s* and *d* bands are hybridized (*s*-*d* hybridization) and the Fermi level intersects the *d* bands,[13-15] the *d* character of conduction electrons is strong. In the dynamical state due to the incidence of light, these electrons have a strong localizing tendency based on this *d* character.[6] The OPRA of Ni island films is damped by this tendency. Evidence of such damping is the fact that the OPRA is temperature independent, and that its half-width is almost constant (about 2.16 eV down to about 80 Å in diameter) irrespective of the particle-size distribution and the variety of particle shapes.[6]

The *d* character of conduction electrons of fcc Co must be strong because the energy bands are similar to those of Ni.[11-15] Thus the mechanism of the damping of the OPRA of fcc Co island films is predicted to be the same as that of Ni island films. This point was investigated by measuring the OPRA at room temperature and about −193 °C down to a particle size of about 30 Å in diameter.

Figure 2 shows the OPRA at room temperature for particle sizes of about 220 and 140 Å in diameter.

The OPRA of the fcc Co island films did not change as the temperature was decreased from room temperature to about −193 °C, and its half-width was almost constant [2.75 (Fig. 1)–2.84 eV (Fig. 2)] down to about 140 Å in diameter [Fig. 2(b)] irrespective of the particle-size distribution and the variety of particle shapes. This result agrees with the above evidence, and thus shows the above prediction to be valid.

When the *d* character becomes more strong, the localizing tendency is strengthened and the damping (i.e., the half-width) of the OPRA increases.[6] When the *d* character is very strong such as in Fe and Cr, conduction electrons are almost localized in the dynamical state due to the incidence of light, and the OPRA does not occur in island films.[18]

The almost constant half-width in the fcc Co island films is about 30% larger than that in the Ni island films. This difference shows that the *d* character is stronger in fcc Co than in Ni.

Important factors for the *d* character are the position of the Fermi level relative to the *d* bands and the *s*-*d* hybridization, which causes the mixing of *d*-wave functions into unfilled conduction bands.[19] The *d* character is

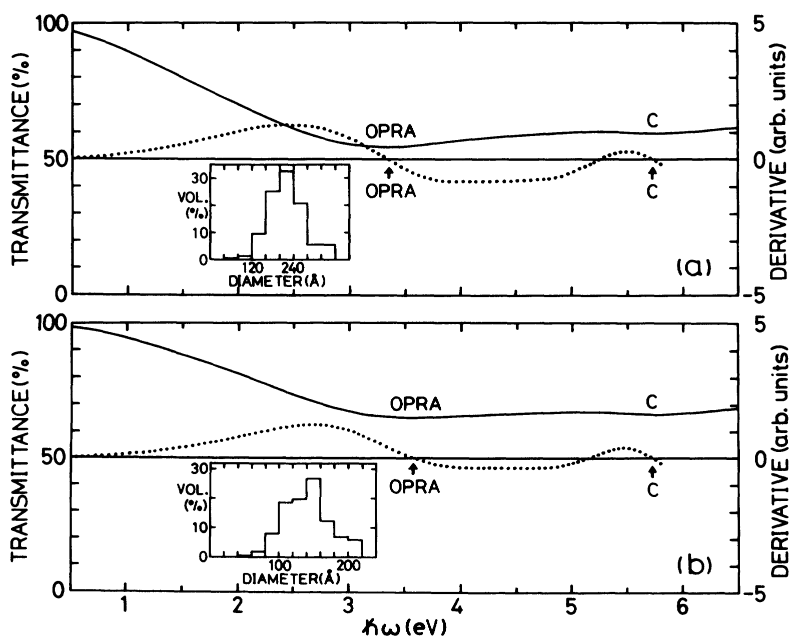

FIG. 2. Transmittance spectra (solid curves) and their derivatives (dotted curves) for fcc Co island films with particle diameters of about (a) 220 and (b) 140 Å. The weight thickness and the deposition rate are (a) 51.0 Å and 0.14 Å/s and (b) 38.2 Å and 0.10 Å/s. The half-width of the OPRA is (a) 2.76 and (b) 2.84 eV.

strong when the Fermi level intersects the d bands and/or when the hybridization is large.

In fcc Co and Ni, the Fermi level intersects the top or the upper part of the d bands.[12,14,15] Thus there seems to be little difference in the position of the Fermi level between fcc Co and Ni.

In paramagnetism the s-d hybridization in fcc Co is larger than that in Ni.[20] Data for the hybridization in ferromagnetism are scarce. As in paramagnetism, in ferromagnetism the d-band-width of fcc Co is large compared to that of Ni.[21] The hybridization is large as the d-band-width is large.[20,22] In ferromagnetism also, thus, the hybridization in fcc Co is presumably larger than that in Ni. The d character is thus considered to be stronger in fcc Co than in Ni because of the large s-d hybridization in fcc Co.

The OPRA is broadened with decreasing particle size below about 140 Å in diameter. The half-width at about 110 Å in diameter [Fig. 3(a)] is about 15% larger than that in Fig. 1. Figure 3(b) shows the OPRA at about 50 Å in diameter. Since this OPRA is very broad, the measurement of the half-width was difficult. As suggested by the Ni island films,[6] in which the broadening with decreasing particle size is found below about 80 Å in diameter, this broadening may be due to the fact that the d character is strengthened by the s-d hybridization enhancement due to lattice contractions.

As previously,[6] the half-width was obtained from the OPRA, not separated from the dip C, because the separation method is not yet established. Since the OPRA is asymmetric, its half-width was defined by $2\Gamma_{1/2}$, where $\Gamma_{1/2}$ is half of the half-width at the low-energy flank.

As can be seen from Figs. 1–3, the OPRA shifts with weight thickness. This shift may change the overlap of the OPRA and the dip C. On the basis of the almost constant half-width in Figs. 1 and 2, however, it is presumed that the overlap is small at the low-energy flank, and thus the change in the overlap has little effect on $\Gamma_{1/2}$.

B. Number of conduction electrons per atom

Comparing the locations of the OPRA of the fcc Co island films (Figs. 1–3) with those of the Ni island films,[6] we see that the locations (above about 3.3 eV) in the fcc Co island films are high relative to the locations (below about 3.2 eV) in the Ni island films.

The location $\hbar\omega_R$ of the peak of the OPRA is expressed by[7,8]

$$\hbar\omega_R = \hbar\omega_P F^{1/2}/[F(1-\varepsilon_0)+\varepsilon_0]^{1/2} ,$$

$$\omega_P^2 = 4\pi n e^2/m ,$$

where ω_P is the plasma frequency, F is the effective depolarization factor, ε_0 is the interparticle dielectric constant, n is the density of the conduction electrons, e is the electron charge, and m is the optical mass of the conduction electrons (i.e., the effective mass under the incidence of light).

In this study, ε_0 is the dielectric constant of the evaporated SiO_2 and is constant. Thus $\hbar\omega_R$ depends on m, F, and n.

Data for m of fcc Co seem to be very scarce. The effective mass m_s of s electrons of transition metals can be calculated from the d-state radius and the atomic sphere radius.[23] m_s of Co is almost comparable to that of Ni. Here this is applied to m, i.e., m of fcc Co is regarded to be almost comparable to that of Ni.

Factors contributing to F are the weight thickness d_W, the spacing between particles, and the particle shape.[16,17] When d_W and the spacing are large and when particles are flat, F is small.[16,17]

Figures 4(a) and 4(b) show electron micrographs of a Ni island film with a particle diameter of about 80 Å in

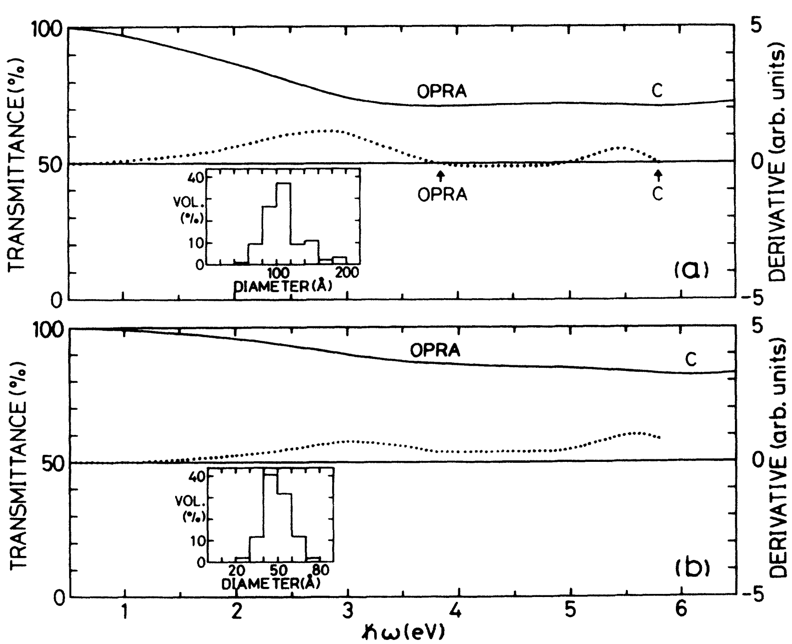

FIG. 3. Transmittance spectra (solid curves) and their derivatives (dotted curves) for fcc Co island films with particle diameters of about (a) 110 and (b) 50 Å. The weight thickness and the deposition rate are (a) 29.4 Å and 0.09 Å/s and (b) 14.7 Å and 0.09 Å/s. The half-width of the OPRA is (a) 3.16 eV.

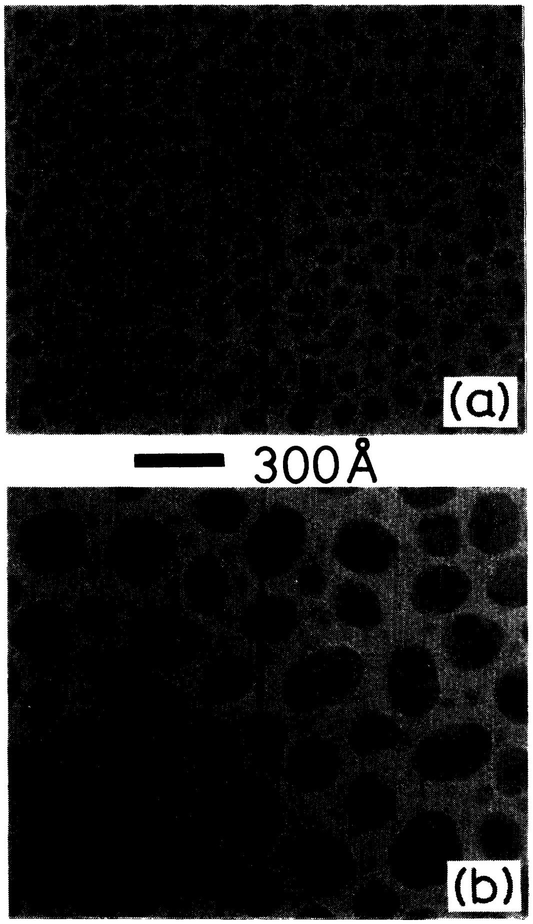

FIG. 4. Electron micrographs for (a) a Ni island film with a particle diameter of about 80 Å (Ref. 6), where the weight thickness and the deposition rate are 19.6 Å and 0.14 Å/s, and (b) the fcc Co island film of Fig. 2(a).

the previous study[6] and the fcc Co island film in Fig. 2(a), respectively. d_W and the spacing in Fig. 4(b) are appreciably larger in comparison with those in Fig. 4(a). Since the particles in Fig. 4(b) are much larger than those in Fig. 4(a), presumably the particles in Fig. 4(b) are flat compared to those in Fig. 4(a).[16,17] Thus the fcc Co island film in Fig. 4(b) has a smaller F than the Ni island film in Fig. 4(a).

From the above values of m and F, if n of fcc Co is comparable to or lower than that of Ni, $\hbar\omega_R$ for the fcc Co island film in Fig. 2(a) must be lower than that (about 2.9 eV) for the Ni island film in Fig. 4(a). However, $\hbar\omega_R$ (about 3.3 eV) in Fig. 2(a) is conspicuously higher than 2.9 eV. This shows that n of fcc Co is high compared to that of Ni.

Factors which determine n are the lattice constant and the number n_c of conduction electrons per atom. As mentioned above, the lattice may contract in Ni and the fcc Co island films, of which particle diameters are smaller than about 80 and 140 Å, respectively. Thus, for films with particle diameters larger than these sizes, the lattice constant was investigated by measuring the diameters of the (111), (220), and (113) diffraction rings.

The diameters of the rings for the fcc Co island films were about 0.5–0.7 % smaller than those for the Ni island films. This shows the lattice constant of fcc Co to be larger than that of Ni by about 0.5–0.7 %, which is comparable to the case of the bulk lattice constants (fcc Co: 3.54 Å, Ni: 3.52 Å).[24] Thus n_c of fcc Co must be larger than that of Ni.

Theoretically, n_c of Ni is between 1 and 2.[19] Comparison of n_c of fcc Co and Ni is difficult because data for n_c of fcc Co are very scarce.

The s-d hybridization, as mentioned above, mixes d-wave functions into unfilled conduction bands. By this mixing, compared to the numbers at the unhybridization, the number of d electrons per atom is reduced, while n_c is increased.[19] A large n_c is expected when the hybridization is large. As mentioned above, the hybridization is larger in fcc Co than in Ni. If, at the unhybridization, n_c of fcc Co is comparable to that of Ni, the large hybridization in fcc Co may cause n_c of fcc Co to be larger than that of Ni. However, at present, further investigation of this point seems to be difficult because data for n_c at the unhybridization are very scarce.

IV. SUMMARY

The OPRA of fcc Co island films has been measured. The half-width of the OPRA of the fcc Co island films was larger than that of the Ni island films. From this, the d character of conduction electrons of fcc Co was found to be stronger than that of Ni. Such a difference in the character could qualitatively be explained by the difference in the s-d hybridization. The OPRA of the fcc Co island films was located at photon energies higher than those for the Ni island films. By considering the factors for the location, the number of conduction electrons per atom was shown to be larger in fcc Co than in Ni. It was indicated that this difference in the number may be caused by the difference in the s-d hybridization.

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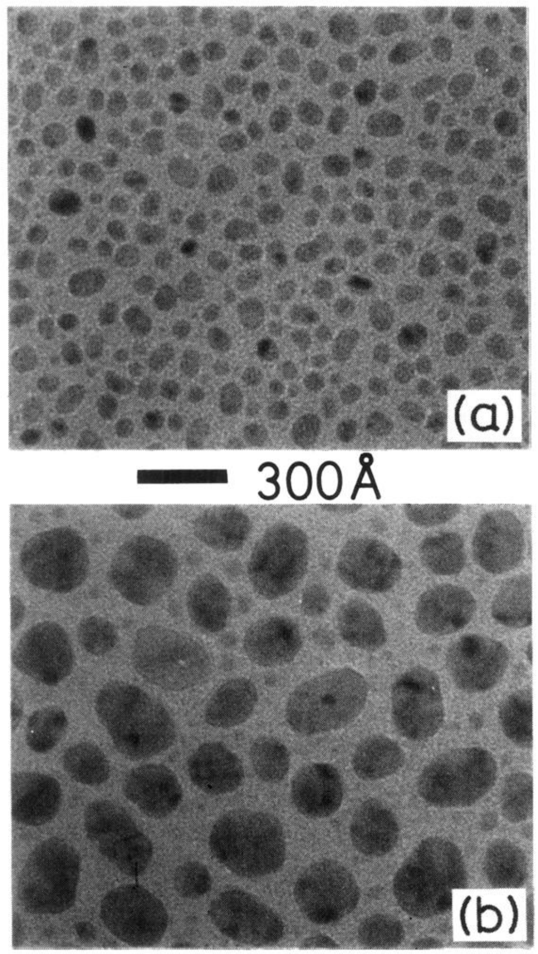

FIG. 4. Electron micrographs for (a) a Ni island film with a particle diameter of about 80 Å (Ref. 6), where the weight thickness and the deposition rate are 19.6 Å and 0.14 Å/s, and (b) the fcc Co island film of Fig. 2(a).