Optical absorption of continuous-network-structure Ag and Ir films: Presence of particlelike and conduction-electron-localized regions

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Optical absorption of continuous-network-structure (CNS) Ag and Ir films has been measured in the photon-energy range of 0.5–6.5 eV. As absorption due to conduction electrons, optical plasma-resonance absorption (OPRA), reported for Ag island films consisting of Ag particles, and weak Drude-type absorption (DTA) were found for the CNS Ag films, and only the weak DTA appeared in the CNS Ir films. The finding of the OPRA indicates that particlelike regions, where plasma oscillations of conduction electrons occur as in Ag particles, are present in the CNS Ag films. When the particlelike regions are formed, the region, where DTA occurs, is reduced. This reduction results in the weakening of the DTA. Thus the weak DTA supports the presence of the particlelike regions. If particlelike regions are present in the CNS Ir films also, conduction-electron localization as in Ir particles should occur in the particlelike regions. In this case, only the DTA, weak as in the CNS Ag films, must appear. This agrees with the above appearance. Thus conduction-electron-localized regions are present in the CNS Ir films. [S0163-1829(99)06831-9]

I. INTRODUCTION

In the growth of thin metal films formed by vacuum evaporation, continuous-network-structure (CNS) metal films, in which the deposit metal is separated by long, irregular, and narrow channels, are formed.[1] The CNS metal films are thin and their shapes are very irregular.

The structure of CNS metal films has mainly been investigated electron microscopically[1] and has not been studied in relation to optical properties. Sometimes optical properties reflect the structure of samples. Thus there is the possibility that new information on the structure of the CNS metal films is obtained from the investigation of the optical properties. It is thus interesting to study the structure of the CNS metal films from the viewpoint of the optical properties. With this study, optical properties due to conduction electrons are informative because the behavior of conduction electrons is very sensitive to the structure of samples.

CNS metal films are intermediates between continuous thin metal films and metal island films consisting of small metal particles.[1] In continuous thin metal films, a well-known example of optical properties due to conduction electrons is Drude-type absorption (DTA) appearing at low photon energies.[2] For continuous thin Au films,[3] it has been reported that the DTA is in close relation with the structure of the films, such as grains and surfaces. In metal island films, optical absorption due to conduction electrons is optical plasma-resonance absorption (OPRA) caused by plasma oscillations of conduction electrons in metal particles.[4] The OPRA is known to be closely related to the structure of the films, such as size and shape of metal particles and spacing between metal particles.[5,6]

OPRA does not appear in Cr and Fe (Ref. 7) and Ir (Ref. 8) island films because of conduction-electron localization in Cr, Fe, and Ir particles. The localization is based on the strong *d* character of conduction electrons.

For CNS metal films, there has been very little study of optical absorption due to conduction electrons. However, as in continuous thin metal films and metal island films, the optical absorption must be related to the structure of the CNS metal films, and the investigation of the optical absorption should give information on the structure.

In this work, optical absorption due to conduction electrons is studied for CNS Ag and Ir films. OPRA, reported for Ag island films,[9] and weak DTA are found for the CNS Ag films, and only the weak DTA appears in the CNS Ir films.

Based on the finding of the OPRA, the presence of particlelike regions, where plasma oscillations of conduction electrons occur as in Ag particles, in the CNS Ag films is discussed. Relating the presence to the reduction of the region, where DTA occurs (i.e., to the weakening of DTA), the weak DTA is shown to support the presence.

The appearance of only the weak DTA in the CNS Ir films is discussed in connection with conduction-electron localization in Ir particles.[8] That is, when conduction electrons in particlelike regions are localized as in Ir particles, OPRA does not occur and thus only DTA, weak as in the CNS Ag films, appears. This shows the presence of conduction-electron-localized regions in the CNS Ir films.

II. EXPERIMENT

In a vacuum chamber, electron-microscopic meshes covered with a carbon film and a fused-quartz substrate ($18\times 18\times 0.5\,mm^3$) were placed above an evaporation source. The meshes and substrate were adjacent, and the distance from the evaporation source was the same (30.3 cm) for the meshes and substrate.

In an oil-free vacuum of $\sim 10^{-8}$ Torr, by electron beam heating, SiO_2 was first deposited both on the fused-quartz substrate and on the meshes. Next, at pressures of $\sim 10^{-7}$ Torr, metals (Ag and Ir, purity 99.999% and 99.9%, respectively) were deposited in order to obtain CNS Ag and Ir films and Ag island films. The films were then annealed for 1 h. During deposition and annealing, the substrate and meshes were held at about 80 °C for Ag and about 500 °C for Ir. After annealing, the films were coated with SiO_2 (thickness about 400 Å) to prevent adsorption or chemical reactions on exposure to air and then cooled to room temperature at a rate of about 1–2 °C/min. The transmittance of the evaporated SiO_2 film without the CNS and island films was almost constant in the spectral range of interest here.

Optical and electron-microscopic investigation were carried out after exposure of the samples to air. Transmittance spectra for normal incidence and their derivatives for a wavelength difference of about 4 nm were measured within experimental accuracy of ±0.1% and ±(0.001–0.01) eV at room temperature with a double-beam spectrophotometer in the photon-energy range of 0.5–6.5 eV. Micrographs of the samples were prepared with an electron microscope operating at 200 kV.

III. RESULTS AND DISCUSSION

In this study only the fcc structure could always be identified in electron-diffraction patterns. From this result, chemical reactions such as oxidation are considered to occur rarely. Thus the formation of a compound layer (such as oxide layer) on the surface of CNS Ag and Ir films and Ag particles is not taken into account.

A. Particlelike regions in CNS Ag films

In this section at first (Sec. III A 1) DTA and interband absorption of CNS Ag films are identified, and then (Sec. III A 2) the presence of particlelike regions in CNS Ag films is discussed based on the OPRA of CNS Ag films.

1. DTA and interband absorption of CNS Ag films

Figure 1(a) shows the electron micrograph of a CNS Ag film. Long, irregular, and narrow channels are shown. The contrast of this film is not uniform because of the diffraction contrast, showing the film to be polycrystalline.[10] The CNS films and particles in the following figures are also polycrystalline.

The transmittance spectrum and its derivative of the film of Fig. 1(a) are shown in Fig. 1(b). The scale of the derivative in this figure is the same as that in the following figures. There has been very little study of optical absorption of CNS Ag films. Here, absorption in the spectrum in Fig. 1(b) is identified from the comparison of the spectrum in Fig. 1(b) with the spectrum of continuous thin Ag films. However, there seems to be very little data on transmittance spectrum of continuous thin Ag films. In this study, the spectrum in Fig. 1(b) is compared with the simulated transmittance spectrum of continuous thin Ag films assumed to have bulk optical properties. The simulation was done as follows.

We consider here a continuous thin metal film of the complex index of refraction n_c, which is on the transparent substrate of the refractive index n_s. When the continuous thin metal film, the trasparent substrate, and the medium of the refractive index n_i, from which light is incident, are isotropic, the transmittance T for normal incidence of light is expressed by[11]

$$T/T_s = |A|^2,$$

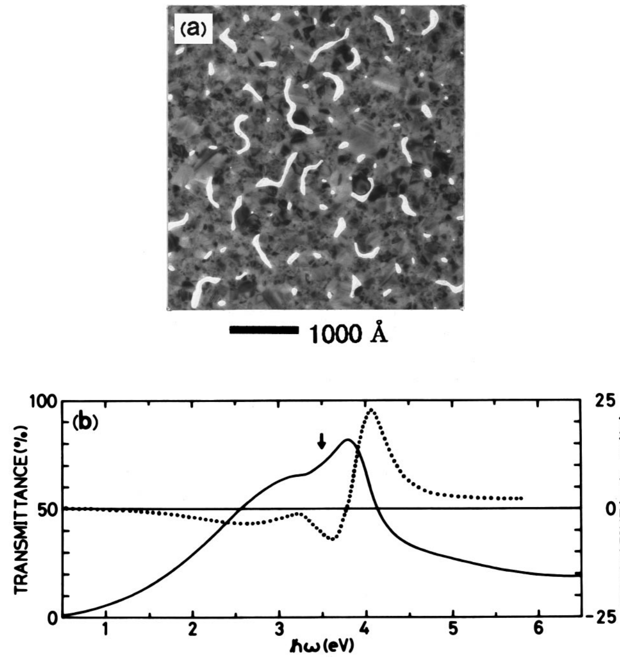

FIG. 1. (a) Electron micrograph of a CNS Ag film. The deposition rate was 0.91 Å/s and the weight thickness is 200.0 Å. (b) Transmittance spectrum (solid curve) and its derivative (dotted curve) of the same CNS Ag film. The arrow shows the small absorption.

where

$$T_s = 4 n_i n_s / (n_i + n_s)^2$$

is the transmittance for the bare surface of the substrate and

$$A = \frac{2 n_c (n_i + n_s) \exp(-i\delta)}{(n_c + n_i)(n_c + n_s) - (n_c - n_i)(n_c - n_s)\exp(-i2\delta)}.$$

Here δ is given by

$$\delta = 2\pi n_c d/\lambda,$$

where d is the thickness of the continuous thin metal film and λ is the wavelength of light. The ratio T/T_s is measured directly when a double-beam spectrophotometer is used with a bare substrate as a reference sample.

The transmittance spectrum of the continuous thin Ag film (thickness 200 Å) assumed to have bulk optical properties was simulated from the above formula for T/T_s and the experimental complex index of refraction of continuous thin Ag films, accepted to have bulk optical properties.[2] In the simulation, n_i and n_s were regarded as the refractive index (1.46) of fused quartz[12] because the samples in this study are coated with SiO_2.

Closed circles in Fig. 2 show the simulated spectrum. Referring to the spectrum of the dielectric constant of the above continuous thin Ag films (Ref. 2) and to the spectrum of the optical conductivity of bulk Ag,[13] we see that absorption below and above about 3.8 eV in the simulated spectrum is DTA and interband absorption, respectively. The simulated spectrum is almost similar to the spectrum in Fig. 1(b). Thus absorption below and above ≃3.8 eV in the spectrum in Fig. 1(b) is, respectively, DTA and interband absorption. On the

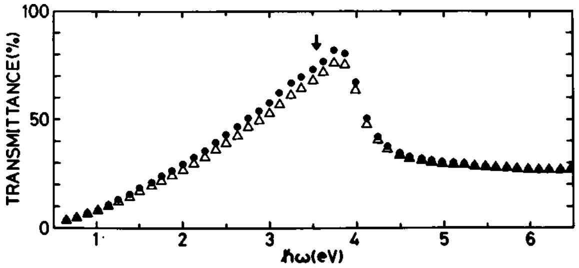

FIG. 2. Simulated transmittance spectra of continuous thin Ag films. Closed circles: simulation based on the complex index of refraction of bulk Ag; triangles: simulation based on the assumed small relaxation time (0.31×10^{-14} s) of conduction electrons. The weight thickness is 200.0 Å. The arrow shows the small absorption.

basis of the above similarity, it seems that in the CNS Ag film of Fig. 1(a), the channels have little effect on the DTA and the interband absorption.

Small absorption, indicated by the arrow, appears at $\simeq$3.5 eV in both the experimental [Fig. 1(b)] and simulated spectrum (Fig. 2). The cause of this small absorption is not clear.

The spectrum of the CNS Ag film [Fig. 1(b)] is similar to the experimental transmittance spectrum of a continuous thin Au film (thickness 480 Å),[6] which also shows DTA and interband absorption.

2. OPRA of CNS Ag films

In this section optical absorption of CNS Ag films with continuous-network structure, which is more pronounced than that in Fig. 1(a), is analyzed. When continuous-network structure becomes pronounced, channels also become pronounced. In this case, the contribution of the channels to conduction-electron scattering should significantly increase, and thus this scattering is considered to become strong. For CNS Ag films, there has been very little study of the change in optical absorption with strengthening of conduction-electron scattering. In this study this change was investigated based on the simulation as follows.

In the investigation the strengthening of conduction-electron scattering was taken into account by the decreases in the relaxation time τ of conduction electrons. Very little is known about τ for CNS Ag films. Thus τ was assumed to decrease from the value $(3.1\times10^{-14}\,\mathrm{s})^2$ of bulk Ag to a small value $(0.31\times10^{-14}\,\mathrm{s})$. The formula for the absorption of CNS metal films has not been reported. As shown in Sec. III A 1, the simulated spectrum in Fig. 2 (closed circles) well reflects the optical absorption of the CNS Ag film of Fig. 1(a). For the absorption in the simulated spectrum in Fig. 2, the change due to the above decrease in τ was simulated in the following procedure.

Dielectric constant ε of bulk metals ($\varepsilon=n_m^2$, n_m is the complex index of refraction of bulk metals) consists of two terms,[14]

$$\varepsilon=\varepsilon_f+\delta\varepsilon_b,$$

where ε_f is the Drude term contributed by conduction electrons and $\delta\varepsilon_b$ is the bound-electron contribution arising from interband transitions. ε_f is expressed as[2,14]

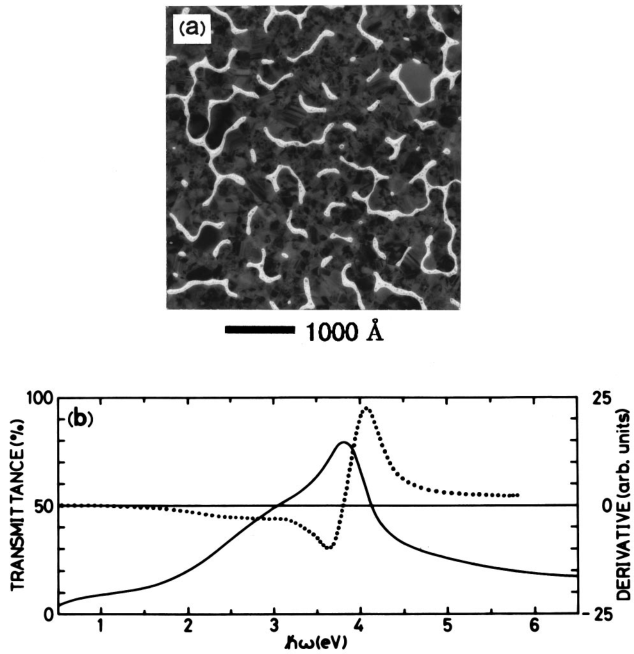

FIG. 3. (a) Electron micrograph of a CNS Ag film. The deposition rate was 0.53 Å/s and the weight thickness is 200.0 Å. (b) Transmittance spectrum (solid curve) and its derivative (dotted curve) of the same CNS Ag film.

$$\varepsilon_f=1-\omega_p^2/(\omega^2+i\omega/\tau),$$

where ω_p is the plasma frequency.

$\delta\varepsilon_b$ for bulk Ag was separated from bulk ε (Ref. 2) by subtracting ε_f, which has bulk ω_p $(1.4\times10^{16}/\mathrm{s})$ (Ref. 15) and bulk τ $(3.1\times10^{-14}\,\mathrm{s})$,[2] from the bulk ε. Adding the separated $\delta\varepsilon_b$ to ε_f having the bulk ω_p and the above small τ $(0.31\times10^{-14}\,\mathrm{s})$, ε for the small τ was obtained. The transmittance spectrum was simulated from the above formula for T/T_s and the complex index of refraction obtained from ε for the small τ.

Triangles in Fig. 2 show the simulated spectrum for the small τ. A comparison of the two simulated spectra in Fig. 2 shows that strengthening of the conduction-electron scattering increases DTA. The increase is conspicuous in the high-energy range (3.8–2.5 eV) of DTA.

For the CNS Ag films in this study, changing the deposition rate controlled the continuous-network structure. As shown in Fig. 3(a), the continuous-network structure is pronounced at a low deposition rate. Figure 3(b) shows the transmittance spectrum and its derivative of the film of Fig. 3(a). The transmittance in the range of about 3.8–1.3 eV in Fig. 3(b) is lower than that in Fig. 1(b), but the transmittance in the range below about 1.3 eV in Fig. 3(b) is higher than that in Fig. 1(b). Obviously, this difference in the spectrum between Figs. 1(b) and 3(b) does not agree with that between the two simulated spectra in Fig. 2. Thus the difference in the spectrum between Figs. 1(b) and 3(b) is not due to the strengthening of conduction-electron scattering.

Based on the above lowering of the transmittance in the range of about 3.8–1.3 eV, new absorption, which overlaps the DTA and the small absorption, is considered to appear in the spectrum in Fig. 3(b). Henceforth this new absorption is referred to as the third absorption.

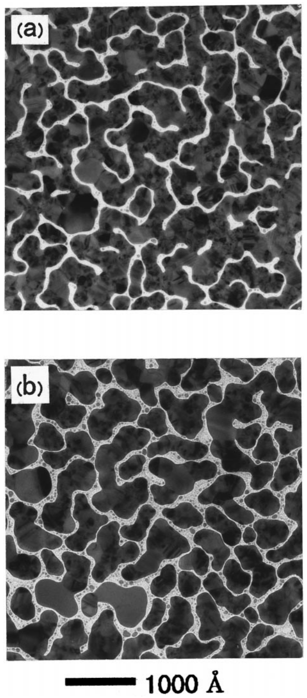

FIG. 4. Electron micrographs of (a) a CNS Ag film at a deposition rate of 0.41 Å/s and (b) a Ag island film at a deposition rate of 0.12 Å/s. The weight thickness is (a) 200.0 Å and (b) 200.0 Å.

In order to make the third absorption appreciable, the deposition rate was further lowered. As shown in Fig. 4(a), Ag particles appeared with lowering deposition rate. Figure 5(a) shows the transmittance spectrum and its derivative of the film of Fig. 4(a). The third absorption in Fig. 5(a) is appreciable compared to that in Fig. 3(b). At a very lowered deposition rate, Ag island films consisting of Ag particles were formed. Figure 4(b) shows the electron micrograph of an example of such Ag island films. The transmittance spectrum and its derivative of the island film of Fig. 4(b) are shown in Fig. 5(b), in which the third absorption is appreciable.

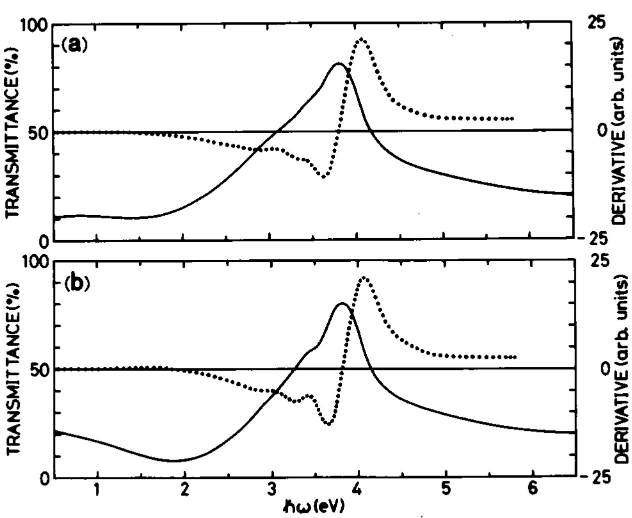

FIG. 5. Transmittance spectra (solid curves) and their derivatives (dotted curves) of the films of Fig. 4. (a) and (b) correspond to Figs. 4(a) and 4(b), respectively.

If the difference in the transmittance below about 3.8 eV between Figs. 1(b), 3(b), and 5 is due to the change in the reflectance, the transmittance above ≃3.8 eV also should be different (i.e., the reflectance should change above ≃3.8 eV also). However, the transmittance above ≃3.8 eV in those figures is almost the same. Thus the difference in the transmittance is caused by the change in the absorption.

Comparing the spectrum in Fig. 5(b) with the absorption spectrum of Ag island films,[9] we see that the third absorption is OPRA. In metal island films, the OPRA is due to plasma oscillations of conduction electrons in metal particles.[4]

Very few Ag particles are present in the CNS Ag film of Fig. 3(a), but the OPRA (i.e., the third absorption) appears in the spectrum [Fig. 3(b)]. This indicates that particlelike regions, where plasma oscillations of conduction electrons occur, are present in the CNS Ag film of Fig. 3(a). Considering the continuous-network structure of Fig. 3(a), the particlelike region is presumably the region, the most part of which is surrounded by channels. Such channels restrict the motion of conduction electrons within the region. This causes the behavior of the conduction electrons in the region to be similar to that in a Ag particle. In this study it was difficult to identify electron microscopically and optically the particlelike regions.

The fact that the continuous-network structure is more pronounced in Fig. 3(a) than in Fig. 1(a) shows that particlelike regions are formed when the continuous-network structure becomes pronounced. The formation of particlelike regions should be accompanied with the reduction of the region, where DTA occurs, i.e., the formation weakens the DTA.

The transmittance below about 1.3 eV in Fig. 3(b) is higher than that in Fig. 1(b), showing the DTA in Fig. 3(b) to be weaker than that in Fig. 1(b). This weakening of the DTA can be attributed to the above reduction of the region for DTA, which supports the presence of the particlelike regions in the CNS Ag film of Fig. 3(a).

More particlelike regions are formed when the continuous-network structure becomes more pronounced, i.e., the region, where the DTA occurs, is more reduced when the continuous-network structure becomes more pronounced.

The DTA below ≃1.3 eV in Fig. 5(a) is weaker than that in Fig. 3(b). This is due to the reduction of the region for the DTA because the continuous-network structure in Fig. 4(a) is more pronounced than that in Fig. 3(a). Note that the formation of Ag particles, shown in Fig. 4(a), also contributes to the reduction of the region for DTA. The Ag particles contribute to the OPRA in Fig. 5(a) also.

As mentioned above, the strengthening of conduction-electron scattering causes the increase in the DTA. Conduction-electron scattering must be stronger when continuous-network structure is more pronounced. Thus more increased DTA is expected when the continuous-network structure becomes more pronounced. This increasing tendency of the DTA competes with the above weakening tendency due to the reduction of the region for the DTA. As mentioned above for Figs. 1(b), 3(b), and 5(a), the DTA becomes weaker when the continuous-network structure becomes more pronounced. This shows that the weakening tendency is dominant in the competition.

In metal island films, the location of the OPRA is determined by the dipole interaction between metal particles and by the depolarization factor, depending on the metal particle shape.[5,6] In this study the investigation of factors contributing to the location of the OPRA of the CNS metal films was difficult because of the following reasons. The location of the OPRA could not be determined because the separation of the OPRA and the DTA was difficult, and it was difficult to distinguish between the particlelike regions and the region for the DTA.

For Ag particles embedded in the SiO_2 matrix, it has theoretically been reported that the interaction between Ag and SiO_2 causes resonance-type absorption, the peak of which is at about 3 eV.[16] The third absorption appears below about 2 eV [Figs. 3(b) and 5]. Thus the third absorption is not due to such interaction.

As shown in Figs. 1(b), 3(b), and 5, the structure of the derivative in the range of about 2.5–3.7 eV changes on going from Fig. 1(b) to 3(b) to 5(a) to 5(b). This change seems to correspond to the split of the small absorption. The cause of this split could not be made clear.

To further investigate the presence of particlelike regions, optical absorption of CNS Ir films is investigated in the following section.

B. Conduction-electron-localized regions in CNS Ir films

The electron micrograph of a CNS Ir film is shown in Fig. 6(a). The transmittance spectrum and its derivative of this film are shown in Fig. 7(a). The scales of this derivative and the derivatives in the following figures are five times the scales in Sec. III A. Absorption labeled 1, 2, and 3 is interband absorption.[8,17,18] This interband absorption is the same as that of continuous thin Ir films, accepted to have bulk optical properties.[8] Thus the interband absorption labeled 1, 2, and 3 is the same as that of bulk Ir. The sloped parts labeled 1, 2, and 3 in the derivative correspond to the presence of the interband absorption.[19] The DTA, which overlaps the interband absorption labeled 1, is present below $\simeq$1.2 eV.[8] Because of this presence, the absorption below $\simeq$1.2 eV increases appreciably with decreasing photon energy.

The weight thickness (40.7 Å) of the film of Fig. 6(a) is thinner than that (51.0 Å) of the continuous thin Ir film studied previously.[8] Thus the transmittance of the film of Fig. 6(a) is expected to be high compared to that of the continuous thin Ir film. However, the transmittance below about 1.2 eV in Fig. 7(a) is comparable to that in the spectrum of the continuous thin Ir film.[8] This shows that the DTA is increased in the film of Fig. 6(a). As mentioned in Sec. III A 2, the increase in the DTA is possible when conduction-electron scattering becomes strong. Presumably, in the case of the film of Fig. 6(a), channels, not present in the continuous thin Ir film, contribute to conduction-electron scattering. The strong conduction-electron scattering due to this contribution is considered to be responsible for the increased DTA of the film of Fig. 6(a).

It has been reported for Ir that interband absorption does not exist at about 1.1 eV in the region of the DTA.[8] There has been very little data on the complex index of refraction, which is corrected for this nonexistence. Thus, for CNS Ir films, simulation of transmittance spectrum, such as in the CNS Ag films (Fig. 2), was difficult.

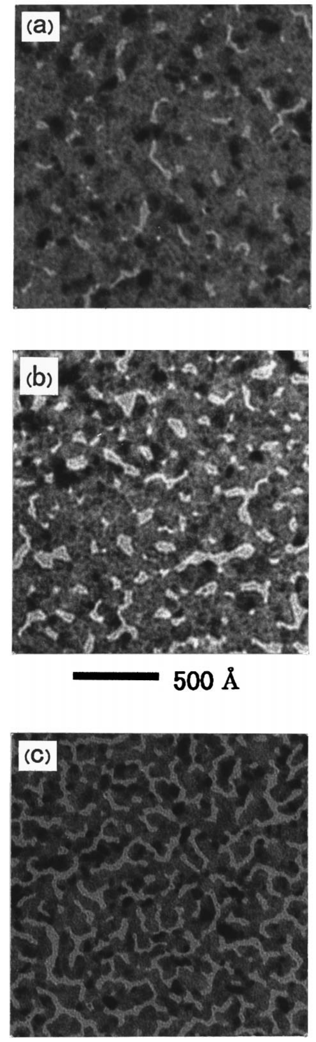

FIG. 6. Electron micrographs of CNS Ir films with weight thickness (a) 40.7, (b) 33.3, and (c) 27.2 Å. The deposition rate was (a) 0.05, (b) 0.05, and (c) 0.04 Å/s.

For the CNS Ir films in this study, changing the weight thickness could control the continuous-network structure. As shown in Figs. 6(b) and 6(c), the continuous-network structure becomes pronounced with decreasing weight thickness. There are very few Ir particles in the films of Fig. 6.

The transmittance spectra and their derivatives of the films of Figs. 6(b) and 6(c) are shown in Figs. 7(b) and 7(c), respectively. As in the case of the interband absorption in Fig. 7(a), the interband absorption in Figs. 7(b) and 7(c) is the same as that of bulk Ir.

In Fig. 7 only the DTA appears as absorption due to conduction electrons. When the continuous-network structure becomes pronounced in Fig. 6, in Fig. 7 the DTA becomes less and less defined though the interband absorption remains well defined. This shows that only the DTA weakens when the continuous-network structure becomes pronounced.

Conduction electrons of Ir have strong *d* character based on large hybridization of *s* and *d* bands, and thus the conduction electrons have a strong localizing tendency.[8,20] Because of this localizing tendency, conduction-electron localization occurs in Ir particles in the dynamical state due to the incidence of light.[7,8] Plasma oscillations of conduction electrons

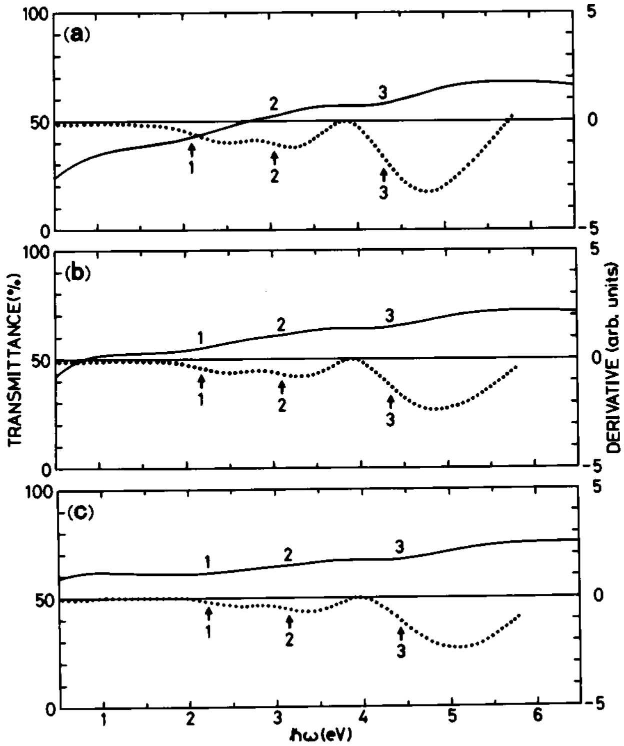

FIG. 7. Transmittance spectra (solid curves) and their derivatives (dotted curves) of the CNS Ir films of Fig. 6. (a), (b), and (c) correspond to Figs. 6(a), 6(b), and 6(c), respectively.

do not occur in Ir particles because of the conduction-electron localization, so that the OPRA does not occur in Ir island films.[8]

For the CNS Ag films (Sec. III A 2), it is pointed out that the behavior of conduction electrons in particlelike regions is similar to that in Ag particles. Thus if particlelike regions are present in CNS Ir films, the conduction-electron localization as in Ir particles should occur in those regions, and thus plasma oscillations of conduction electrons cannot occur in those regions. In this case, only the DTA appears as absorption due to conduction electrons, and as in the CNS Ag films, the DTA weakens when the continuous-network structure becomes pronounced.

The above appearance and weakening of the DTA, based on the conduction-electron localization, agree with those found experimentally in Fig. 7. This agreement shows that particlelike regions, where conduction electrons are localized, are present in the CNS Ir films, i.e., shows that conduction-electron-localized regions are present in the CNS Ir films.

As in the DTA for the CNS Ag films (Sec. III A 2), the competition between the increasing tendency due to the strengthening of conduction-electron scattering and the weakening tendency due to the reduction of the region for the DTA should occur in the CNS Ir films. The weakening found in Fig. 7 shows that the weakening tendency is dominant in the CNS Ir films also.

Interband absorption different from that of bulk Ir has been reported for Ir particles smaller than about 80 Å in diameter.[8] The interband absorption of the CNS Ir films in this study is the same as that of bulk Ir. Thus the particlelike regions in the CNS Ir films in this study are presumably larger than about 80 Å in diameter.

In this study the CNS Ir films are embedded in the SiO_2 matrix. There seems to be very little information on the interaction between Ir and SiO_2. Thus the interaction was not considered in this study.

IV. SUMMARY

Optical absorption of CNS Ag and Ir films has been measured. As absorption due to conduction electrons, the OPRA, reported for Ag island films, and weak DTA were found for the CNS Ag films in which there are very few Ag particles. The finding of the OPRA indicates that particlelike regions, where plasma oscillations of conduction electrons occur as in Ag particles, are present in the CNS Ag films. This presence is supported by the weak DTA because the formation of the particlelike regions reduces the region, where the DTA occurs, and thus weakens the DTA.

In the CNS Ir films, only the weak DTA appeared as absorption due to conduction electrons. If particlelike regions are present in the CNS Ir films, conduction-electron localization as in Ir particles should occur in those regions. In this case only DTA, weak as in the CNS Ag films, must appear as absorption due to conduction electrons. This appearance based on the conduction-electron localization agrees with the above appearance. This agreement shows that conduction-electron-localized regions (i.e., particlelike regions, where conduction electrons are localized) are present in the CNS Ir films.

Particlelike regions and conduction-electron-localized regions are structurally characteristic appearing only in the response of CNS metal films to light.

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