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Size-dependent change in parallel band absorption of Al particles

E. Anno and M. Tanimoto
Department of Physics, Asahikawa Medical College, Asahikawa, Hokkaido 078-8510, Japan

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Optical absorption of Al island films consisting of Al particles smaller than about 1200 Å in diameter has been measured in the energy range of 0.5–6.5 eV. Below about 200 Å in diameter, parallel band absorption, due to transitions between almost parallel bands, weakens and then disappears with decreasing particle size. Nguyen *et al.* [Phys. Rev. B **47**, 3947 (1993)] have reported that the parallel band absorption of Al particles is not visible when relaxation times for conduction electrons and the parallel band absorption are much smaller than those in the bulk. We investigate the relaxation times by simulating the optical plasma-resonance absorption of the Al island films with a Maxwell-Garnet-type effective medium theory. The very small relaxation times are pointed out to be a possible cause of the weakening and disappearance.

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I. INTRODUCTION

Optical properties in the transition from the atomic to the solid state are of fundamental interest. Clusters and small particles represent a special state of matter intermediate between atoms and solids. Interband absorption reflects optical properties based on transitions between bands.[1] Thus the interband absorption of clusters and small particles provides information about the optical properties based on the transitions between the bands in the transition from the atomic to the solid state.[2,3]

Metal clusters and particles smaller than the wavelength of incident light show, in addition to the interband absorption, optical plasma-resonance absorption due to plasma oscillations of conduction electrons in the clusters and particles.[4]

Recently, the absorption mentioned above has been studied not only for pure-metal clusters and particles, but also for bimetallic clusters such as $\mathrm{Au}_n\mathrm{Ag}_n$.[5]

Al is known as the ideal material for studying the optical properties of simple metals and has been extensively studied. It has been accepted both experimentally[6] and theoretically[7] that the optical spectrum of bulk Al is dominated by strong interband absorption at 1.55 eV and weaker interband absorption at 0.5 eV. The former of these has been identified as originating from transitions between almost parallel bands near the point W in the Brillouin zone.[6,7] This interband absorption is called parallel band absorption.

An optical study[8] of Al particles with diameters of 30–40 Å has reported that parallel band absorption is much less visible in the particles than in the bulk because of the overlap of the parallel band absorption and the optical plasma-resonance absorption broadened by the conduction-electron scattering at internal particle defects. This report implies that transitions between bands for parallel band absorption are unaffected by particle size down to particle diameters of 30–40 Å.

Nguyen *et al.*[9,10] have modeled experimental spectra of dielectric functions of Al island films consisting of Al particles with a Maxwell-Garnett-type effective medium theory, which is well known to be very useful for the study of the optical absorption of metal island films. These authors found as a result of their modeling that the mean free path of conduction electrons is much reduced from its bulk value (about 200 Å) owing to scattering at defects within particles. The reduced mean free path was found to be about 8 Å.

Considering the reduction in the mean free path, Nguyen *et al.*[9,10] regarded relaxation times for both the conduction electrons and the parallel band absorption to be much smaller than those in the bulk. Based on very small relaxation times, they showed that parallel band absorption in the Al particles is very broad and not visible.

In the present study, the influence of particle size on parallel band absorption of Al particles forming island films, in which the overlap of the parallel band absorption and the optical plasma-resonance absorption is small, is investigated. It is found that below about 200 Å in diameter, parallel band absorption weakens and then disappears with decreasing particle size. The reduced mean free path and the very small relaxation times, reported by Nguyen *et al.*,[9,10] are discussed, and these times are pointed out to be a possible cause of the weakening and disappearance.

II. TRANSMITTANCE OF METAL ISLAND FILMS

The present experimental study is based on transmittance spectra of Al island films consisting of Al particles. In this section, the method of analysis of the transmittance of metal island films is briefly discussed.

We consider here a continuous thin metal film on a transparent substrate. The thickness d of this film is smaller than the wavelength λ of light $(2\pi d \ll \lambda)$. When the film, substrate, and medium from which light is incident are isotropic, the transmittance T for normal incidence of light is expressed by[11]

$$T/T_s = \left[1 + \frac{2}{n_i + n_s}\frac{2\pi d}{\lambda}\mathrm{Im}(\varepsilon)\right]^{-1}, \tag{1}$$

where n_i is the refractive index of the medium from which light is incident, n_s the refractive index of the substrate, T_s $[=4n_in_s/(n_i+n_s)^2]$ the transmittance for the bare surface of the substrate, and $\mathrm{Im}(\varepsilon)$ the imaginary part of the dielectric constant ε of the film. As has been done in the present study, the ratio T/T_s can directly be measured by the double-beam spectrophotometer used with a bare substrate as reference sample.

When the weight thickness d_w, which is the total volume of particles per unit substrate surface area, of a metal island film is smaller than λ $(2\pi d_w \ll \lambda)$, Eq. (1) is applicable to the metal island film.[12–14] That is, such film can be regarded as a continuous film, the thickness of which is assumed here to be d_0. The second term on the right side of Eq. (1) gives the absorption spectrum. For metal island films composed of particles of the same shape and size, the second term is expressed by[14,15]

$$\frac{2}{n_i+n_s}\frac{2\pi d}{\lambda}q\varepsilon_a\frac{\Delta g}{(F+g)^2+(\Delta g)^2}, \tag{2}$$

where q $(=d_w/d_0)$ is the packing factor, ε_a the interparticle dielectric constant, and F the effective depolarization factor of the metal island films. Equation (2) is based on the Maxwell-Garnett-type effective medium theory, which takes into account dipole interactions among particles and their mirror images in the substrate. g and Δg are related to the dielectric constant ε_i of the particles by the relation[14,15]

$$g+i\Delta g=(\varepsilon_i/\varepsilon_\alpha-1)^{-1}. \tag{3}$$

When ε_i is represented by the Drude equation with a plasma frequency ω_p and a relaxation time τ of conduction electrons, ε_i is given by[15]

$$\varepsilon_i=1-\omega_p^2/(\omega^2+i\omega/\tau). \tag{4}$$

Optical plasma-resonance absorption for metal particles forming island films may be obtained using Eqs. (2)–(4). In this absorption, the peak value depends on d_w and τ, and the peak position and the broadening depend on F and τ, respectively.[14,15]

III. EXPERIMENT

In a vacuum chamber, electron-microscopic meshes covered with a carbon film and a fused-quartz substrate ($18\times18\times0.5\,\mathrm{mm}^3$) 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.

SiO_2 was first deposited both on the meshes and on the fused-quartz substrate by electron-beam heating in an oil-free vacuum of $\sim10^{-8}$ Torr. Next, at pressures of $\sim10^{-7}$ Torr, Al (purity 99.9999%) was deposited in order to obtain island films. The films were then annealed for 1 h. During deposition and annealing, the meshes and substrate were held at about 573 K. After annealing, the films were coated with SiO_2 (thickness 300–100 Å) to prevent adsorption or chemical reactions on exposure to air and then cooled to room temperature at a rate of about 1–2 K/min. The weight thickness and deposition rate were monitored with a quartz-crystal oscillator. The transmittance of the evaporated SiO_2 film without Al particles was almost constant within the spectral range of interest here.

Optical and electron-microscopic investigation were carried out after exposure of the samples to air. In the photon energy range of 0.5–6.5 eV, 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. The particle size and the electron-diffraction pattern were investigated with an electron microscope operating at 200 kV.

IV. RESULTS

Figures 1(a)–1(e) show the transmittance spectrum and its derivative of the Al island film with particle sizes of about 1200, 480, 320, 220, and 90 Å in diameter, respectively. Figure 1(f) shows the transmittance spectrum and its derivative of the Al island film with weight thickness of 9.0 Å. This film was difficult to investigate using electron microscopy because of the low contrast due to the SiO_2 coating. Particles become smaller with decreasing weight thickness.[14,16] Since the film of Fig. 1(f) has a thinner weight thickness than the film of Fig. 1(e), the particle size for the film of Fig. 1(f) is presumably smaller than that (90 Å in diameter) for the film of Fig. 1(e).

In Fig. 1(a), weak absorption and strong broad absorption are found at about 1.4 and 2.9 eV, respectively. The sloped part, indicated by the arrow, in the derivative corresponds to the presence of the weak absorption.[17] Referring to the optical spectrum of bulk Al,[6,7] we see that the weak absorption is parallel band absorption. The position (about 1.4 eV) of the parallel band absorption in Fig. 1(a) is lower than that (1.55 eV) in the bulk, because the strong broad absorption, which does not appear in the bulk, overlaps the parallel band absorption.

The parallel band absorption in Figs. 1(a)–1(c) is large enough to be measurable, showing that down to about 300 Å in diameter [Fig. 1(c)], there is little difference in the interband transitions between the bulk and particles. We see from Figs. 1(d)–1(f) that below about 200 Å in diameter, the parallel band absorption weakens and then disappears with decreasing particle size.

Optical plasma-resonance absorption occurring in metal island films is shifted to higher energies with decreasing weight thickness, because F in Eq. (2) increases due to the increase in the depolarization factor of the particles and to the weakening of dipole interactions among the particles and their mirror images in the substrate.[14,16] This weight-thickness-dependent shift is characteristic of the optical plasma-resonance absorption of the metal island films. The mirror-image effect does not occur in the present study, because the particles were coated with SiO_2.

As shown in Fig. 1, the strong broad absorption is shifted to higher energies with decreasing weight thickness. Such a shift agrees with the characteristic of the optical plasma-resonance absorption of the metal island films, proving the strong broad absorption to be the optical plasma-resonance absorption.

The electron micrographs and particle-size distributions in

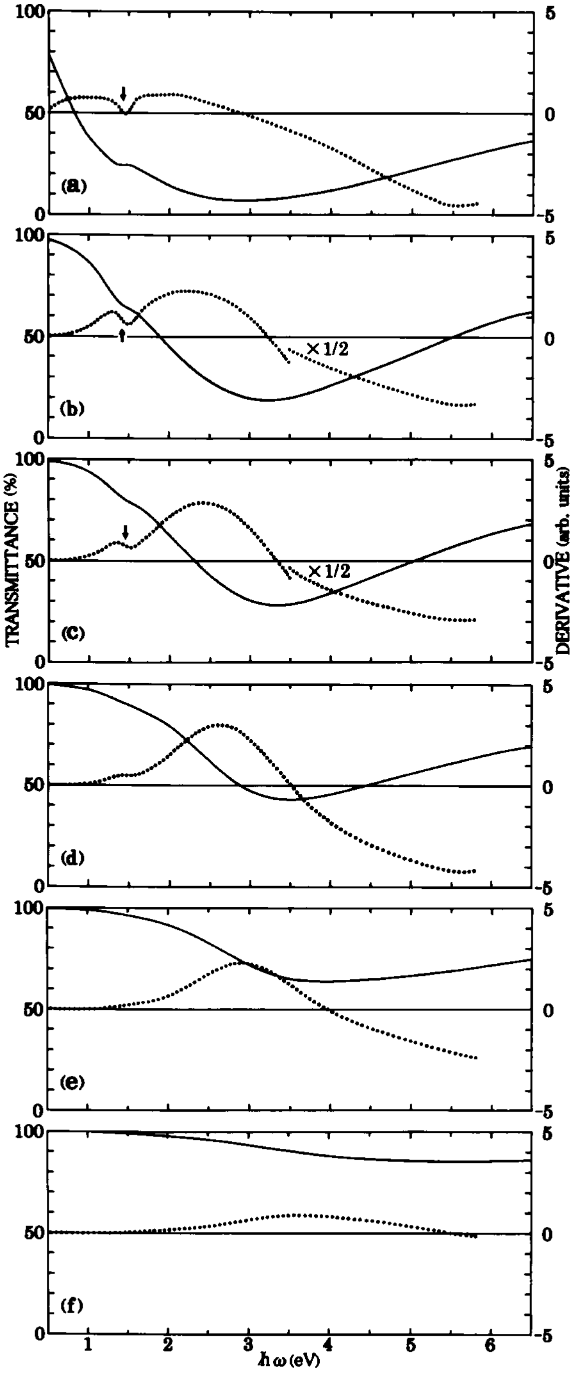

FIG. 1. Transmittance spectra (solid curves) and their derivatives (dotted curves) of six Al island films. The particle size is about (a) 1200, (b) 480, (c) 320, (d) 220, and (e) 90 Å in diameter. The particle size for the island film of (f) was difficult to measure. The full half width Γ is (a) 2.06, (b) 2.03, (c) 2.16, and (d) 2.83 eV. Γ was difficult to measure for the island films of (e) and (f). The half width $2\Gamma_{1/2}$, where $\Gamma_{1/2}$ is half of Γ at the low-energy flank, is (a) 1.66, (b) 1.72, (c) 1.74, (d) 1.92, (e) 2.44, and (f) 2.63 eV. The weight thickness is (a) 119.6, (b) 59.8, (c) 44.9, (d) 29.9, (e) 20.9, and (f) 9.0 Å. The deposition rate was (a) 0.35, (b) 0.43, (c) 0.51, (d) 0.37, (e) 0.48, and (f) 0.51 Å/s.

vol. % of the films of Figs. 1(a)–1(e) are shown in Figs. 2 and 3, respectively.

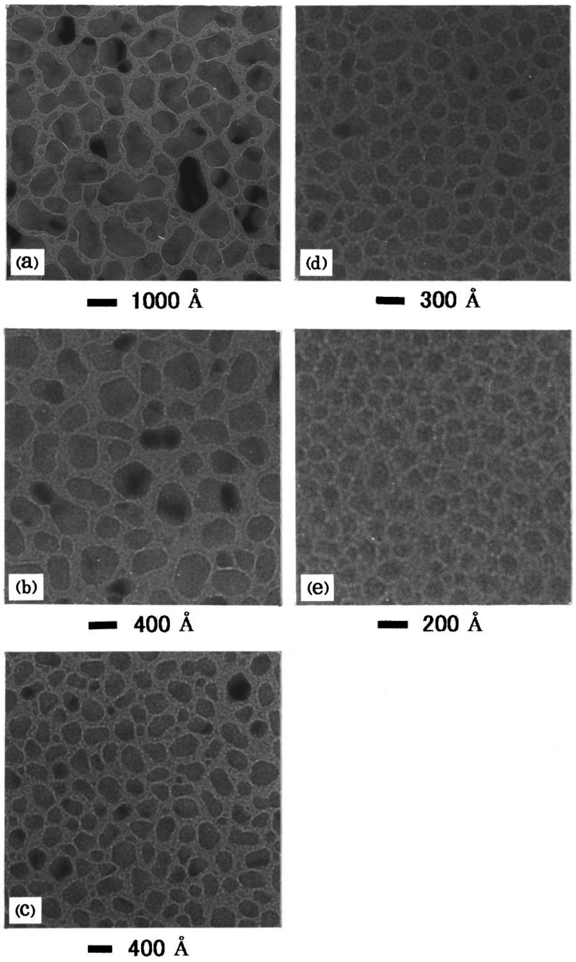

FIG. 2. (a)–(e) are electron micrographs for the island films of Figs. 1(a)–1(e), respectively.

When particles are polycrystalline, they show complex contrast structure (i.e., not uniform contrast structure) due to the diffraction contrast.[18,19] Such contrast is shown in Fig. 2. Thus the particles in the present study are polycrystalline.

V. DISCUSSION

A. Overlap with optical plasma-resonance absorption, chemical reactions, and interactions with SiO_2

The optical plasma-resonance absorption shifts considerably from about 2.9 eV [Figs. 1(a)] to about 5.5 eV [Fig. 1(f)]. Thus the overlap of the parallel band absorption and the optical plasma-resonance absorption decreases as the particles become smaller. This shows that the weakening and disappearance of the parallel band absorption are not caused by the overlap.

Only the fcc structure could always be identified in the electron-diffraction patterns of the films of Figs. 1(a)–1(e), which implies that the change into compounds (such as aluminum oxide) by chemical reactions occurs rarely. This is important because if such a change occurs, the optical plasma-resonance absorption would disappear. The identification of the fcc structure and the presence of the optical plasma-resonance absorption in Fig. 1 thus show that the

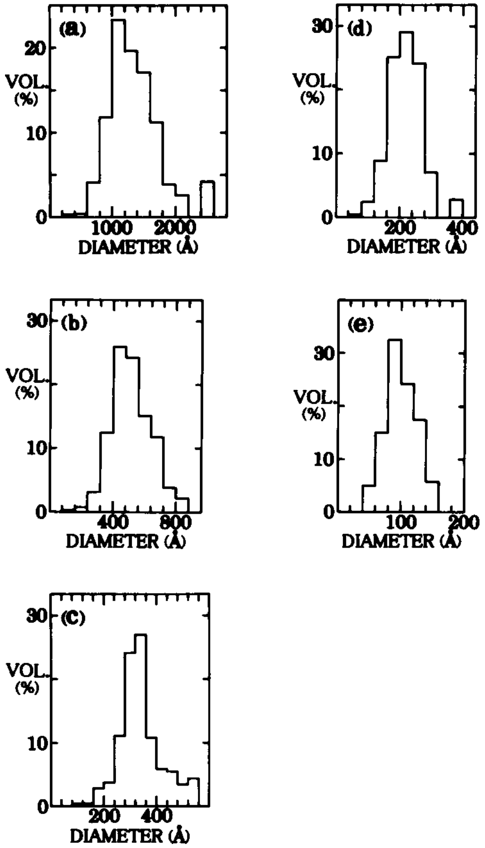

FIG. 3. (a)–(e) are particle-size distributions in vol. % for the island films of Figs. 1(a)–1(e), respectively.

disappearance of the parallel band absorption at smaller sizes is not due to a chemical change in the particles.

If electrons of the SiO_2 matrix occupy final states for the interband transitions of the Al particles, the transitions would not occur and thus the parallel band absorption would disappear. The valence band maximum of SiO_2 is about 6.3 eV lower than the Fermi energy of Ag.[20] The Fermi energy of Al is about 6.2 eV higher than that of Ag.[21] The difference between the valence band maximum of the SiO_2 and the Fermi energy of Al is thus large (about 12.5 eV), so that the valence band of the SiO_2 does not overlap the final states as these lie at higher than the Fermi energy.[7] Thus the electrons of the SiO_2 matrix can not occupy the final states, showing that the occupation of the final states is not the cause of the disappearance of the parallel band absorption.

B. Continuous Al films reported previously

In an optical study of continuous Al films evaporated on cold substrates ($T<200\,\mathrm{K}$),[22] it has been reported that the parallel band absorption is progressively reduced in intensity with lowering substrate temperature. This reduction has been explained as follows: disordered regions (e.g., grain boundaries), where the energy bands based on the concept of translational symmetry do not hold, increase when the substrate temperature is lowered.[22]

In another study of continuous Al films on cold substrates,[23] parallel band absorption was found to disappear completely at the substrate temperature of 25 K, which shows that the continuous films consist of the disordered regions only. In these films, however, residual interband absorption, which remarkably increases with decreasing photon energy, is present below about 3 eV.

In the present study, residual interband absorption is not found when parallel band absorption disappears [Figs. 1(e) and 1(f)]. If the Al particles consisted of disordered regions, we would not be able to identify the fcc structure in the electron-diffraction patterns of the Al particles. The fcc structure was identified in the electron-diffraction pattern of the film of Fig. 1(e). Thus the Al particles, in which the parallel band absorption disappears, do not consist of disordered regions.

We see from this discussion that the mechanism reported earlier for the change in parallel band absorption of continuous films is inapplicable to the weakening and disappearance in the present study.

C. Mean free path and relaxation time of conduction electrons

1. Reduction in the mean free path and relaxation time

As mentioned in Sec. I, based on the reduced mean free path and the very small relaxation times, Nguyen *et al.*[9,10] showed parallel band absorption to be very broad and not visible. In the following, we investigate the mean free path and relaxation times by simulating the experimental spectra.

Nguyen *et al.*[9,10] have pointed out for Al island films that there is practically no influence of the particle shape distribution on the peak position and broadening of the optical plasma-resonance absorption and that the particle size and its distribution have practically no influence on the broadening of this absorption.

Equation (1), the second term of the right side of which gives the absorption spectrum, was applied to the spectra in the present study, and the full half width Γ of the optical plasma-resonance absorption was evaluated based on the photon energy ($\hbar\omega$) at which absorption is half of the peak value of the optical plasma-resonance absorption. If no influence mentioned above is valid, Γ should be almost constant irrespective of the particle size and the distributions of the particle shape and size. Γ was difficult to measure for the island films with particle sizes smaller than about 200 Å in diameter [Figs. 1(e) and 1(f)]. Although the spectrum for the island film with particle size of about 880 Å in diameter is not given in the present paper, Γ was evaluated also for this film. Figure 4 shows Γ.

In Fig. 4, Γ is almost constant above about 300 Å in diameter. This shows that no influence holds for the island films with particle sizes larger than about 300 Å in diameter [Figs. 1(a)–1(c)].

Our Al island films, for which no influence holds, can be regarded as consisting of Al particles having the same shape, size, and relaxation time of conduction electrons.[14–16] Thus Eqs. (2)–(4) are applicable to the Al island films with particle sizes larger than about 300 Å in diameter.

It is seen from Eqs. (2)–(4) that when the relaxation time τ of the conduction electrons satisfies the condition $\omega^2 \gg \tau^{-2}$ the full half width (here denoted by γ) of the optical

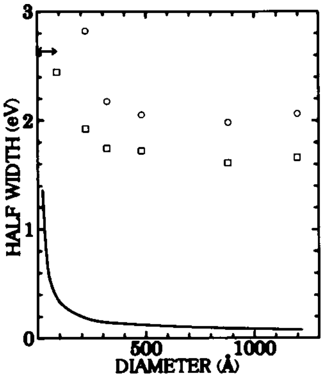

FIG. 4. Change in the half width of the optical plasma-resonance absorption with particle size. ○, full half width Γ; □, half width $2\Gamma_{1/2}$; ↔ the particle size range for $2\Gamma_{1/2}$ of the film of Fig. 1(f). Here Γ and $2\Gamma_{1/2}$ for the island film with particle size of about 880 Å in diameter are added, though the spectrum is not given in this paper. The solid curve is the full half width based on the Maxwell-Garnett-type effective medium theory and on the classical size-effect theory of conduction-electron scattering.

plasma-resonance absorption depends on τ through the relation $\gamma=\tau^{-1}$.[19] Referring to this relation, we estimated τ from Γ for the island films with particle sizes larger than about 300 Å in diameter. The estimated τ is shown in Table I.

We simulated the experimental optical plasma-resonance absorption of the island films with particle sizes larger than about 300 Å in diameter, by applying dielectric constant of Al, which takes into account τ in Table I, to ε_i [Eq. (3)] in the formula of Eq. (1). If τ in Table I is nearly the actual τ for the Al particles, the simulated absorption should fit the experimental absorption.

The dielectric constant of Al, which takes account of τ in Table I, was obtained as follows. In bulk Al, the dielectric constant $\varepsilon_{\mathrm{Al}}$ consists of two terms,[24]

$$\varepsilon_{\mathrm{Al}}=\varepsilon_f+\delta\varepsilon_b, \tag{5}$$

where ε_f is the Drude term contributed by conduction electrons and $\delta\varepsilon_b$ the bound-electron contribution arising from interband transitions. The expression for ε_f is the same as that for ε_i in Eq. (4),[24,25]

TABLE I. The particle diameter *D* for the island films of Figs. 1(a)–1(c), the full half width Γ of the optical plasma-resonance absorption of these island films, the relaxation time τ of the conduction electrons estimated from Γ, and the mean free path λ corresponding to τ. Bulk relaxation time and mean free path are also shown.

D (Å)	1200	480	320	Bulk
Γ (eV)	2.06	2.03	2.16	
$\tau(\times 10^{-16}\,\mathrm{s})$	3.20	3.25	3.05	102[a]
λ (Å)	6.67	6.77	6.35	206[b]

[a] Reference 22.
[b] Bulk τ (Ref. 22) $\times v_F$ (Fermi velocity, Ref. 21).

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

$\varepsilon_{\mathrm{Al}}$ was modified based on τ in Table I; i.e., firstly, we separated $\delta\varepsilon_b$ from $\varepsilon_{\mathrm{Al}}$ (Refs. 26–28) by subtracting ε_f, which has the bulk ω_p (2.32×10^{16}/s, Ref. 29) and the bulk τ (10.2×10^{-15} s, Ref. 22), from $\varepsilon_{\mathrm{Al}}$, and then adding the separated $\delta\varepsilon_b$ to ε_f having the bulk ω_p and τ in Table I, we modified $\varepsilon_{\mathrm{Al}}$. The modified $\varepsilon_{\mathrm{Al}}$ was used as the above-mentioned dielectric constant of Al.

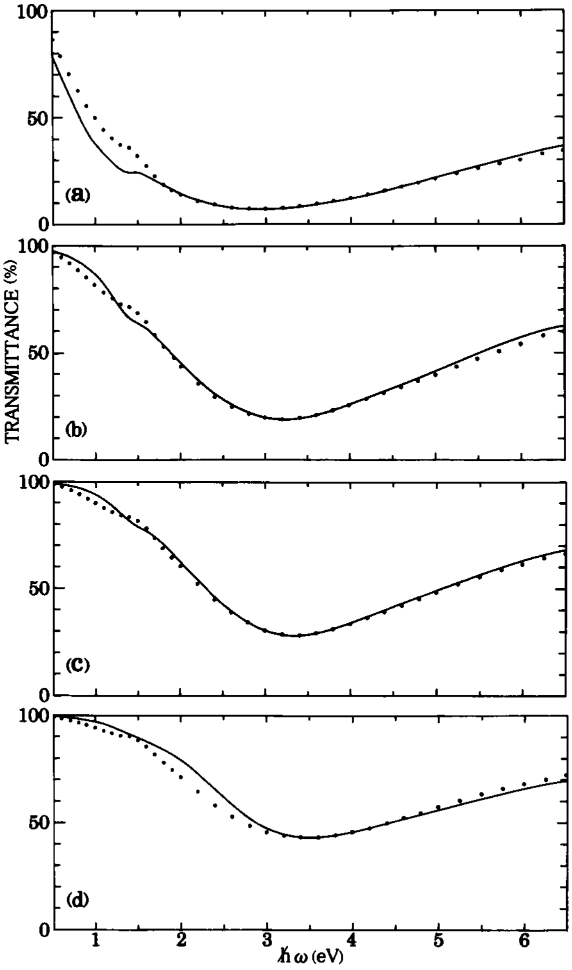

FIG. 5. (a)–(d) are experimental (solid curves) and simulated spectra (dotted curves) for the island films of Figs. 1(a)–1(d), respectively. In the simulation, the weight thickness is (a) 299.5, (b) 102.9, (c) 64.3, and (d) 4.21 Å, and the effective depolarization factor is (a) 0.056, (b) 0.074, (c) 0.082, and (d) 0.086.

In the simulation, the approximation based on the relation $\omega^2\gg\tau^{-2}$ was not done, because τ^{-1} is comparable to ω. Considering the fused-quartz substrate and the $\mathrm{SiO_2}$ coating in the present study, n_i and n_s in Eq. (1) were taken to be constant at 1.47 of $\mathrm{SiO_2}$ and ε_a in Eq. (2) was taken to be constant at 2.17 of $\mathrm{SiO_2}$. Here d_w and F in Eq. (2) were chosen to match the peak and its position of the experimental optical plasma-resonance absorption, respectively, as is often done in earlier studies.

The simulated spectra are shown in Figs. 5(a)–5(c), in which the experimental spectra are also shown. The simulated optical plasma-resonance absorption fits the experimental optical plasma-resonance absorption rather well. This shows that τ in Table I is correct.

From the good fit, the contribution of the overlap of the parallel band absorption and the optical plasma-resonance absorption to Γ is seen to be small. The parallel band absorption is stronger in the experimental spectra than in the simulated spectra. This is presumably because the parallel band absorption of our samples is stronger than that of the samples (Refs. 26–28), the optical constants of which were used in the simulation.

In a classical model of electron scattering,[30] τ is related to the mean free path λ as follows:

$$\tau^{-1}=\tau_{\text{bulk}}^{-1}+v_F/\lambda, \tag{6}$$

where τ_{bulk} is the bulk relaxation time[22] and v_F the Fermi velocity $(2.02\times 10^8\text{ cm/s})$.[21] Nguyen *et al.*[9,10] also used this equation in their studies. From τ in Table I and Eq. (6), λ was evaluated to be 6.35–6.77 Å (Table I). These values are comparable with λ (about 8 Å) reported by Nguyen *et al.*[9,10] From Eq. (6), this λ of about 8 Å corresponds to τ of 3.82×10^{-16} s which is comparable with τ in Table I.

The good fit of the simulated spectra to the experimental spectra and τ and λ comparable with those by Nguyen *et al.*[9,10] show that, as reported by Nguyen *et al.*,[9,10] the mean free path and the relaxation time of the conduction electrons of the Al particles larger than about 300 Å in diameter are much reduced by the scattering at internal particle defects. However, contrary to the case of Nguyen *et al.*[9,10] (Sec. I), the parallel band absorption is appreciably visible for these particles [Figs. 1(a)–1(c)]. This shows that the relaxation time for the parallel band absorption does not become very small when the mean free path is reduced to 6.35–6.77 Å.

The relaxation time for the parallel band absorption was difficult to investigate directly in the present study. There is thus the possibility that the weakening and disappearance of the parallel band absorption are because the relaxation time for this absorption becomes very small below about 200 Å in diameter. Thus the very small relaxation times are pointed out here to be a possible cause of the weakening and disappearance of the parallel band absorption.

2. Size-dependent increase in conduction-electron scattering

Similar to the case of Γ, the half width $2\Gamma_{1/2}$, where $\Gamma_{1/2}$ is half of Γ at the low-energy flank, was evaluated. $2\Gamma_{1/2}$ is shown in Fig. 4. The double-ended horizontal arrow in Fig. 4 indicates the particle size range for $2\Gamma_{1/2}$ of the island film of Fig. 1(f). The particle size for this film is smaller than about 90 Å in diameter as mentioned in Sec. IV.

In Fig. 4, $2\Gamma_{1/2}$ increases with decreasing particle size below about 200 Å in diameter and Γ for the film with diameter of about 220 Å is appreciably larger than that for the films with diameters larger than 300 Å. Thus, similar to $2\Gamma_{1/2}$, Γ presumably increases with decreasing particle size below about 200 Å in diameter.

For the optical plasma-resonance absorption of island films assumed to consist of spherical Al particles without size distribution, the full half width, defined as in Sec. V C 1, was evaluated from a classical size-effect theory[31] of conduction-electron scattering and Eqs. (1)–(4). In this case, the full half width is given by

$$\tau_{\text{bulk}}^{-1}+v_F/R, \tag{7}$$

where R is the particle radius. The term v_F/R originates from conduction-electron scattering at the particle surface.

The solid curve in Fig. 4 shows the full half width by Eq. (7). The full half width appreciably increases below about 200 Å in diameter. This shows that the scattering at the particle surface becomes more effective below about 200 Å in diameter. Such more effective scattering may be a factor contributing to the size-dependent increases in $2\Gamma_{1/2}$ and Γ below about 200 Å in diameter.

From the size-dependent increase in $2\Gamma_{1/2}$ and Γ, it is evident that $2\Gamma_{1/2}$ and Γ below about 200 Å in diameter include the contribution from the particle size distribution. Figure 5(d) shows the experimental spectrum for the island film with particle size of about 220 Å in diameter [Fig. 1(d)] and the simulated spectrum obtained by the same procedure as that for Figs. 5(a)–5(c). Here τ estimated from Γ(2.83 eV) is 2.33×10^{-16} s. The fit of the simulated spectrum to the experimental spectrum is not good. We speculate this to be due to the contribution of the particle size distribution to Γ.

VI. SUMMARY

Optical absorption of Al island films consisting of Al particles has been measured. It was found that below about 200 Å in diameter parallel band absorption weakens and then disappears with decreasing particle size.

Nguyen *et al.*[9,10] have reported that the mean free path of conduction electrons of Al particles is much reduced owing to scattering at defects within the particles. Based on this reduction, they have regarded relaxation times for both the conduction electrons and the parallel band absorption to be much smaller than those in bulk, and shown that the parallel band absorption is very broad and not visible because of the very small relaxation times.

We investigated the mean free path and the relaxation time of the conduction electrons by simulating the optical plasma-resonance absorption with a Maxwell-Garnett-type effective medium theory.

From the good fit of the simulated absorption to the experimental absorption, the mean free paths for particles larger than about 300 Å in diameter were found to be 6.35–6.77 Å, which correspond to the relaxation times of $3.05-3.25\times 10^{-16}$ s, respectively. These values are comparable with the values (about 8 Å and 3.82×10^{-16} s) obtained by Nguyen *et al.*[9,10] Thus the reduced mean free path and the very small relaxation time of the conduction electrons were confirmed for the particles larger than about 300 Å in diameter. However, the parallel band absorption of these particles was appreciably visible contrary to the result by Nguyen *et al.*[9,10] This shows that the relaxation time for the parallel band absorption does not become very small even when the conduction-electron mean free path becomes as small as to 6.35–6.77 Å.

Nguyen *et al.*[9,10] have shown that the disappearance of parallel band absorption can be attributed to very small relaxation times. In the present study, it was difficult to investigate directly the relaxation time for the parallel band absorption. It is thus possible that the weakening and disappearance of the parallel band absorption are because the relaxation time for this absorption becomes very small below about 200 Å in diameter. However, this issue still needs to be settled by detailed investigation of the relaxation time involved in parallel band absorption in Al particles.

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[1] B. R. Cooper, H. Ehrenreich, and H. R. Philipp, Phys. Rev. **138**, A494 (1965); J. H. Weaver, Phys. Rev. B **11**, 1416 (1975); R. Lässer, N. V. Smith, and B. L. Benbow, *ibid.* **24**, 1895 (1981); G. Fuster, J. M. Tyler, N. E. Brener, and J. Callaway, *ibid.* **42**, 7322 (1990).

[2] P. Picozzi, S. Santucci, M. De Crescenzi, F. Antonangeli, and M. Piacentini, Phys. Rev. B **31**, 4023 (1985).

[3] E. Anno, Surf. Sci. **260**, 245 (1992); Phys. Rev. B **55**, 4783 (1997).

[4] See, for example, A. Kawabata and R. Kubo, J. Phys. Soc. Jpn. **21**, 1765 (1966); U. Kreibig and L. Genzel, Surf. Sci. **156**, 678 (1985), and references therein.

[5] See, for example, E. Cottancin, J. Lermé, M. Gaudry, M. Pellarin, J.-L. Vialle, M. Broyer, B. Prével, M. Treilleux, and P. Mélinon, Phys. Rev. B **62**, 5179 (2000).

[6] See, for example, L. G. Schulz, J. Opt. Soc. Am. **44**, 357 (1954); L. G. Schulz and F. R. Tangherlini, *ibid.* **44**, 362 (1954); H. E. Bennett, M. Silver, and E. J. Ashley, *ibid.* **53**, 1089 (1963); H. G. Liljenvall, A. G. Mathewson, and H. P. Myers, Solid State Commun. **9**, 169 (1971); O. Hunderi and P. O. Nilsson, *ibid.* **19**, 921 (1976), and references therein.

[7] See, for example, H. Ehrenreich, H. R. Philipp, and B. Segall, Phys. Rev. **132**, 1918 (1963); W. A. Harrison, *ibid.* **147**, 467 (1966); D. Brust, Phys. Rev. B **2**, 818 (1970); N. W. Ashcroft and K. Sturm, *ibid.* **3**, 1898 (1971), and references therein.

[8] C. G. Granqvist and O. Hunderi, Phys. Lett. A **73**, 213 (1979); J. Appl. Phys. **51**, 1751 (1980).

[9] H. V. Nguyen, I. An, and R. W. Collins, Phys. Rev. B **47**, 3947 (1993).

[10] H. V. Nguyen and R. W. Collins, J. Opt. Soc. Am. A **10**, 515 (1993).

[11] M. Born and E. Wolf, *Principles of Optics*, 5th ed. (Pergamon, New York, 1975), p. 61; T. Yamaguchi, H. Takahashi, and A. Sudoh, J. Opt. Soc. Am. **68**, 1039 (1978), and references therein.

[12] S. Yamaguchi, J. Phys. Soc. Jpn. **15**, 1577 (1960).

[13] R. H. Doremus, J. Appl. Phys. **37**, 2775 (1966).

[14] S. Yoshida, T. Yamaguchi, and A. Kinbara, J. Opt. Soc. Am. **62**, 1415 (1972); T. Yamaguchi, S. Yoshida, and A. Kinbara, Thin Solid Films **21**, 173 (1974).

[15] T. Yamaguchi, S. Yoshida, and A. Kinbara, Thin Solid Films **18**, 63 (1973).

[16] V. V. Truong and G. D. Scott, J. Opt. Soc. Am. **66**, 124 (1976); **67**, 502 (1977).

[17] M. Cardona, *Modulation Spectroscopy* (Academic, New York, 1969), pp. 105–115.

[18] U. Kreibig, Z. Phys. B **31**, 39 (1978).

[19] E. Anno and R. Hoshino, J. Phys. Soc. Jpn. **50**, 1209 (1981).

[20] B. N. J. Persson, Surf. Sci. **281**, 153 (1993).

[21] C. Kittel, *Introduction to Solid State Physics*, 6th ed. (Wiley, New York, 1986), p. 134.

[22] A. G. Mathewson and H. P. Myers, J. Phys. F: Met. Phys. **2**, 403 (1972).

[23] L. G. Bernland, O. Hunderi, and H. P. Myers, Phys. Rev. Lett. **31**, 363 (1973).

[24] H. Ehrenreich and H. R. Philipp, Phys. Rev. **128**, 1622 (1962).

[25] P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).

[26] *CRC Handbook of Chemistry and Physics*, 66th ed. (CRC, Boca Raton, 1985), p. E-375. $\varepsilon_{\mathrm{Al}}$ was obtained from optical constants in this reference. The optical constants are based on the data in Ref. 27.

[27] E. Shiles, T. Sasaki, M. Inokuti, and D. Y. Smith, Phys. Rev. B **22**, 1612 (1980).

[28] D. Y. Smith, E. Shiles, and M. Inokuti, in *Handbook of Optical Constants of Solids*, edited by E. D. Palik, (Academic, Orlando, FL, 1985), p. 369. $\varepsilon_{\mathrm{Al}}$ was obtained from optical constants in this reference.

[29] C. Kittel, *Introduction to Solid State Physics* (Ref. 21), p. 262.

[30] S. Norrman, T. Andersson, C. G. Granqvist, and O. Hunderi, Phys. Rev. B **18**, 674 (1978).

[31] See, for example, U. Kreibig and C. V. Fragstein, Z. Phys. **224**, 307 (1969), and references therein.