Size-dependent change in interband absorption of Pb particles: Effects of surface atoms

Anno E,Tanimoto M

Size-dependent change in interband absorption of Pb particles: Effects of surface atoms

E. Anno and M. Tanimoto

Department of Physics, Asahikawa Medical College, Asahikawa, Hokkaido 078-8510, Japan

(Received 18 March 2002; revised manuscript received 8 July 2002; published 31 October 2002)

Interband absorption of Pb-island films, consisting of Pb particles larger than about 50 Å in diameter, has been measured in the photon energy range of 0.5–6.5 eV. The interband absorption located from 4.23 ± 0.07 to 4.44 ± 0.06 eV, the initial state for which is positioned at the bottom of the conduction bands, disappeared below about 300 Å in diameter. The interband absorption located from 3.68 ± 0.04 to 3.78 ± 0.04 eV was shifted to higher energies with decreasing particle size below about 300 Å in diameter, and became weaker with shift. The shift causes the initial state to be present in the lower portion of the conduction bands. The disappearance and the weakening are due to the decrease in the density of states (DOS) at the lower portion of the conduction bands. Such a decrease can be attributed to the effect of the reduced coordination number of surface atoms on the DOS of the conduction bands.

I. INTRODUCTION

Recently, there has been considerable interest in optical properties in the intermediate region between atomic and solid states. Clusters and small particles represent a special state of matter intermediate between atoms and solids. Interband absorption results from transitions between energy bands and closely depends on the density of states (DOS) of the energy bands. Thus, by studying the interband absorption of clusters and small particles, we can obtain information about the optical properties based on the energy bands and the DOS in the transition from the atomic to solid states.[1–4]

In bulk metals, the coordination number is lower for surface atoms than for bulk atoms; in the fcc lattice an atom has eight nearest neighbors at the (100) surface versus nine at the (111) and twelve in the bulk. As a result, the distribution of the DOS of the energy bands of the surface layer is narrower than that of the bulk.[5–8]

The reduced coordination number of surface atoms is of substantial interest in small particles because the ratio of surface to volume atoms increases with decreasing particle size. Due to such an increase, the reduced coordination number of surface atoms should affect depending on size the DOS for the small particles. The interband absorption, which reflects the DOS affected by the reduced coordination number of surface atoms, has not yet experimentally been reported for small metal particles.

In the present study, by referring to the DOS of $3d$ bands of the surface layer of bulk Cu,[6,7] we qualitatively show that the size-dependent change in the interband absorption of Pb particles originates from the effect of the reduced coordination number of surface atoms on the DOS of conduction bands.

II. EXPERIMENT

The samples were prepared by vacuum evaporation in conditions similar to those described in a previous study.[3] Pb (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 80 °C during deposition in order to obtain highly aggregated island films. In the case of the island film with a particle diameter of about 2500 Å, the temperature of the substrates and meshes was about 20 °C. 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 Pb particles was almost constant in the spectral range of interest here.

Optical and electron-microscopic investigations 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 an experimental accuracy of $\pm 0.1\%$ and $\pm(0.001–0.01)$ eV at room temperature with a double-beam spectrophotometer. The particle-size distribution and the electron-diffraction pattern were investigated with an electron microscope operating at 200 kV.

III. RESULTS

In the analysis of derivative spectra,[9] the locations of the maximum slopes in steps in the first derivative correspond to the locations of absorption. The derivatives in the present study are the first derivative. In the following figures, the arrows indicate the locations of the maximum slopes in the steps in the derivatives. Thus, the locations indicated by the arrows correspond to the locations of absorption. In the following, the location of the absorption is based on the location indicated by the arrow and is expressed by $E \pm \Delta E$. This expression shows that in the step in the derivative the slope is maximum in the range of $(E - \Delta E)$-$(E + \Delta E)$.

Figures 1(a), 1(b), 1(c), and 1(d) show transmittance spectra and their derivatives of Pb-island films with particle diameters of about 560, 440, 360, and 320 Å, respectively. In Fig. 1, as mentioned above, the locations of the absorption, labeled 1, 2, 3, and 4, in the transmittance spectra are based on the locations indicated by the arrows, labeled 1, 2, 3, and 4, respectively.

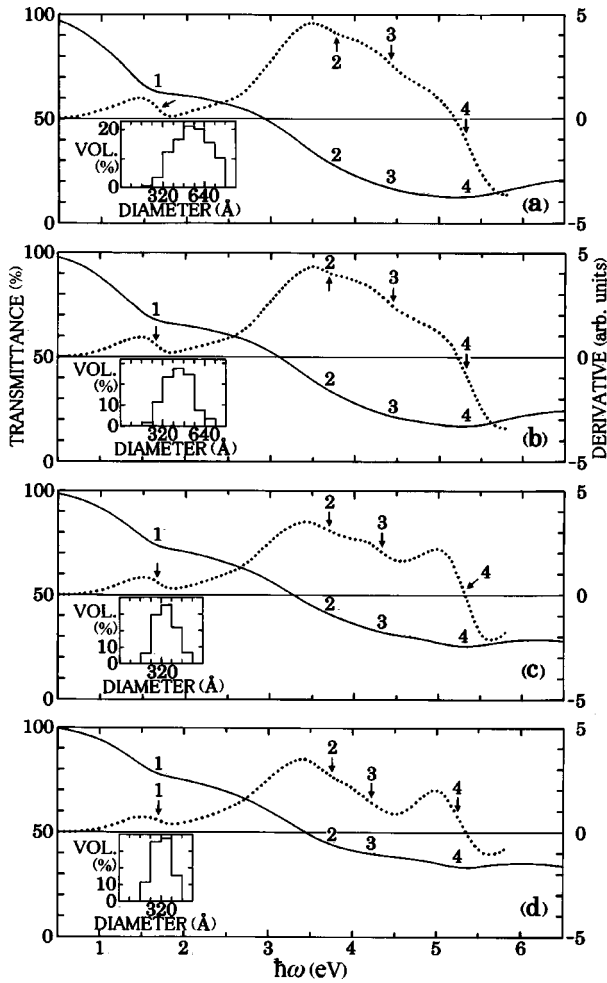Taking into account a previous study of continuous thin

FIG. 1. Transmittance spectra (solid curves) and their derivatives (dotted curves) for Pb-island films with particle diameters of about (a) 560, (b) 440, (c) 360, and (d) 320 Å. The weight thickness is (a) 142.0, (b) 120.7, (c) 99.4, and (d) 85.2 Å. The deposition rate was 0.12 Å/s. The substrate temperature was about 80 °C.
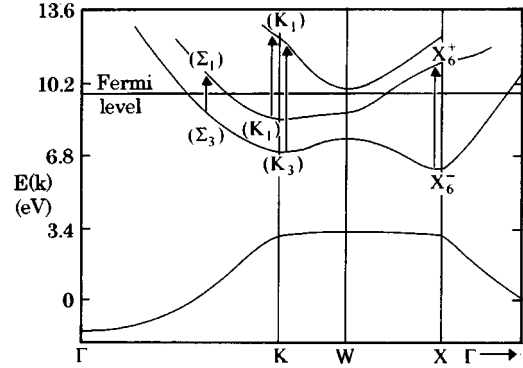

FIG. 2. Schematic figure of energy-band structure and interband transitions in bulk Pb reported in Ref. 10. The interband transitions are represented in the arrows. The bands (Σ_3) and (Σ_1) are parallel (Ref. 11). The energy-band structure in Ref. 10 is that by Loucks (Ref. 12).

Pb films,[10] the absorption labeled 1, 2, 3, and 4 in Fig. 1 is assigned to the interband absorption due to transitions between the initial and final bands (Σ_3)-(Σ_1),[11] (K_1)-(K_1), X_6^--X_6^+, and (K_3)-(K_1) in the Brillouin zone, respectively (Fig. 2). As shown in Fig. 2, the initial [(Σ_3), (K_1), X_6^-, and (K_3)] and final bands [(Σ_1), (K_1), X_6^+, and (K_1)] are present within conduction bands and are positioned below and above the Fermi level, respectively.[10,12] In the following, the absorption labeled 1, 2, 3, and 4 is referred to as the interband absorption 1, 2, 3, and 4, respectively.

In Fig. 1, the locations of the interband absorption 1 is (a) 1.67 ± 0.05 eV, (b) 1.66 ± 0.01 eV, (c) 1.67 ± 0.05 eV, and (d) 1.70 ± 0.02 eV, and the interband absorption 2 is located at (a) 3.78 ± 0.04 eV, (b) 3.68 ± 0.04 eV, (c) 3.70 ± 0.05 eV, and (d) 3.75 ± 0.05 eV.

The deep dips at about 4.5 and 5.6 eV in the derivatives in Figs. 1(c) and 1(d) show that the interband absorption 4 is sharper in Figs. 1(c) and 1(d) than in Figs. 1(a) and 1(b). In Fig. 1, the interband absorption 3 is located at (a) 4.43 ± 0.08 eV, (b) 4.44 ± 0.06 eV, (c) 4.32 ± 0.05 eV, and (d)

4.23 ± 0.07 eV, and the location of the interband absorption 4 is (a) and (b) 5.32 ± 0.07 eV, (c) 5.30 ± 0.05 eV, and (d) 5.25 ± 0.05 eV. From these, the interband absorption 3 and 4 slightly shifts with sharpening of the interband absorption 4. In the present study, it was difficult to clarify the reasons for the sharpening and the slight shift.

The interband absorption 1–4 is always found when the particle size is larger than about 300 Å in diameter, showing that the Pb particles larger than about 300 Å in diameter have optical properties the same as those of the bulk Pb.

It has been known[13] that metal-island films consisting of small metal particles show optical plasma-resonance absorption, due to plasma oscillations of conduction electrons in the particles. Characteristic of this absorption is the pronounced shift to higher energies with decreasing weight thickness.[13] The decrease in the weight thickness from Fig. 1(a) to Fig. 1(d) is large (the decrease of about 40%), but the pronounced shift of the absorption to higher energies is not found in Fig. 1. Thus, the optical plasma-resonance absorption is not present in the spectra of Fig. 1. The optical plasma-resonance absorption seems to be present outside the spectral range of the present study (i.e., the energy range higher than about 6.5 eV).

Figure 3 shows transmittance spectra and their derivatives of Pb-island films with particle diameters smaller than about 300 Å. The particle diameters for Figs. 3(a), 3(b), 3(c), and 3(d) are, respectively, about 260, 140, 90, and 50 Å. The location of the interband absorption 1 is 1.72 ± 0.01 eV in Fig. 3(a). In Fig. 3(b), the step for this absorption is ill defined in the derivative, so that the location of the absorption was difficult to identify. Thus, the range of the presence of the interband absorption 1 (1.63–1.88 eV) is represented in the double-ended horizontal arrow.

The interband absorption 2 is located at 4.08 ± 0.04 eV in Fig. 3(a) and 4.10 ± 0.02 eV in Fig. 3(b), but this absorption was difficult to identify in Fig. 3(c) because in the derivative the step for the absorption is ill defined. In Fig. 3(c), thus, the range of the presence of the interband absorption 2 (4.00–4.25 eV) is represented in the double-ended horizontal arrow.

In the derivative in Fig. 3(d), the slope in the range of 4.30–4.58 eV is appreciably smaller than that in the range of
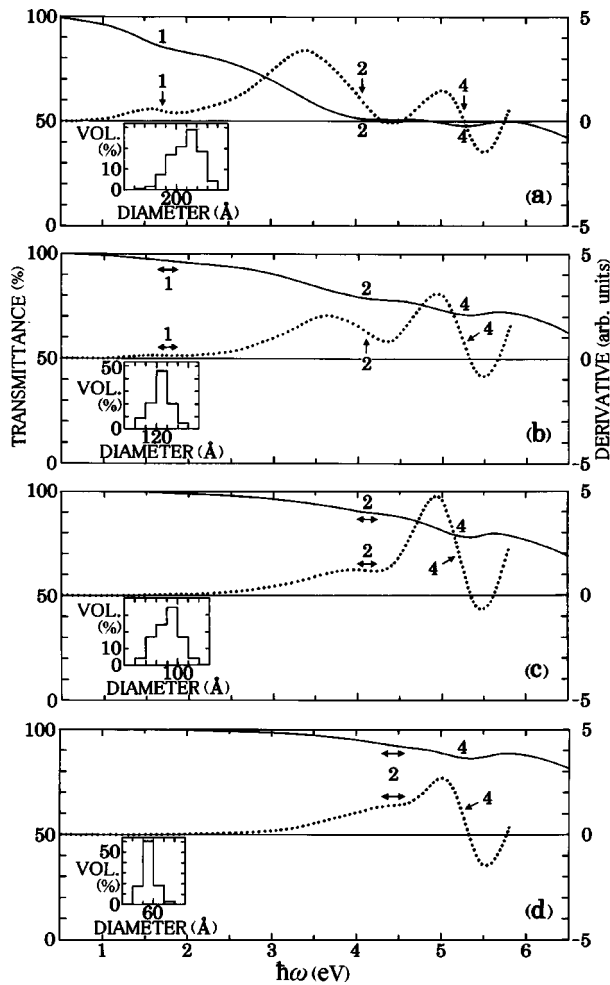
FIG. 3. Transmittance spectra (solid curves) and their derivatives (dotted curves) for Pb-island films with particle diameters of about (a) 260, (b) 140, (c) 90, and (d) 50 Å. The weight thickness is (a) 71.0, (b) 42.6, (c) 28.4, and (d) 14.2 Å. The deposition rate was (a) 0.12, (b) 0.11, (c) 0.12, and (d) 0.11 Å/s. The substrate temperature was about 80 °C.

about 3.1–4.3 eV. Based on the analysis of the derivative,[9] this small slope corresponds to the presence of the interband absorption 2. Thus, this absorption is present in the range of 4.30–4.58 eV, represented in the double-ended horizontal arrow. In Fig. 3, the interband absorption 4 is located at (a) 5.27±0.06 eV, (b) 5.25±0.05 eV, (c) 5.20±0.05 eV, and (d) 5.25±0.05 eV.

Figure 4 shows the transmittance spectrum and its derivative of a Pb-island film with a particle diameter of about 2500 Å. Above about 3.7 eV, the transmittance and the derivative were almost 0% and zero, respectively, so that these were not drawn in this figure.

Figures 5(a) and 5(b) show the electron micrographs of the Pb-island films with particle diameters of about 320 [Fig. 1(d)] and 90 Å [Fig. 3(c)], respectively. In the electron micrographs, the Pb particles show complex contrast structure due to the diffraction contrast.[14] The Pb particles in the present study are thus polycrystalline.

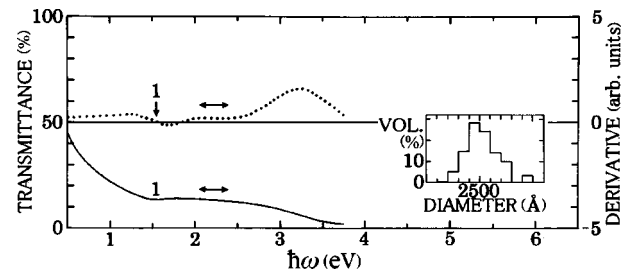Only the fcc structure could always be identified in

FIG. 4. Transmittance spectrum (solid curve) and its derivative (dotted curve) for a Pb-island films with a particle diameter of about 2500 Å. The weight thickness is 390.5 Å. The deposition rate was 1.03 Å/s. The substrate temperature was about 20 °C.

electron-diffraction patterns in the present study. This implies that the change of the Pb particles into compounds by chemical reactions occurred rarely.

IV. DISCUSSION

A. Absorption of continuous Pb films reported previously

Optical properties of continuous-thin-metal films, produced by vacuum evaporation, have generally been accepted to be the same as those of bulk metals. We compared previously reported optical spectra of continuous Pb films,[10,15] produced by vacuum evaporation, with the spectra of Fig. 1.

In the spectra of the continuous Pb films,[10,15] absorption is present at about 1 eV in addition to the absorption in Fig. 1. In the present study, continuous films were difficult to produce, and thus we could not confirm the absorption at about 1 eV for the continuous Pb films. The absorption at about 1 eV is present in the range of the Drude-type absorption, which does not occur in metal-island films.[13] Optical absorption, due to conduction electrons in lattice defects, has been reported to appear sometimes in the range of the Drude-type absorption of the continuous-thin-metal films produced by vacuum evaporation.[16] This absorption has not been reported for metal-island films.

For the continuous-thin-metal films produced by vacuum evaporation, it has been accepted that lattice-defect density becomes higher with increasing deposition rate and/or with lowering substrate temperature. The deposition rate for the continuous Pb films[15] is about 500Å/s. This value is very
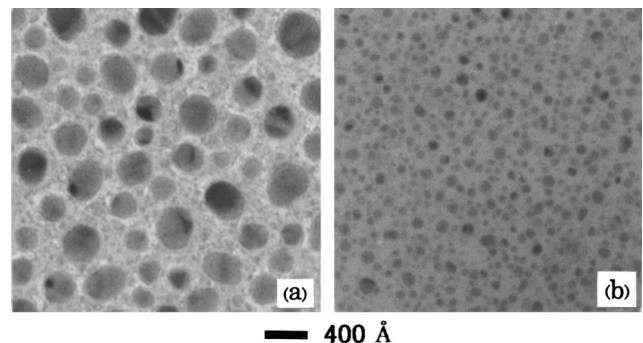

FIG. 5. Electron micrographs for the Pb island films with particle diameters of (a) about 320 Å [Fig. 1(d)] and (b) about 90 Å [Fig. 3(c)].

high, e.g., 500 Å/s is about 4100 times higher than 0.12 Å/s for the films of Fig. 1. Thus, the continuous Pb films should have a high lattice-defect density. From this, the absorption at about 1 eV in the spectra of the continuous Pb films[10,15] seems to be due to the conduction electrons in the lattice defects.

Absorption extending from about 1.5 to 3.5 eV is present in the spectra of the continuous Pb films.[10,15] The absorption has been regarded as the superposed absorption, mainly attributed to two interband transitions associated with energies of about 1.6–1.8 and 2.3 eV.[10] The presence of the absorption 1 in Fig. 1, the location of which is from 1.66 ±0.01 eV [Fig. 1(b)] to 1.70±0.02 eV [Fig. 1(d)], confirms the absorption due to the interband transition associated with the energy of about 1.6–1.8 eV. However, the absorption, which corresponds to the interband transition associated with the energy of about 2.3 eV, is not found in Fig. 1. This absorption is discussed in the following.

In Fig. 4 for the Pb-island film with particle diameter of about 2500 Å, we see from the analysis of the derivative[9] that weak absorption, not found in Fig. 1, is present in the transmittance spectrum in the range (2.05–2.40 eV) indicated by the double-ended horizontal arrow.

The deposition rate and the substrate temperature for the film of Fig. 4 are, respectively, about 9 times higher and 4 times lower than those for the films of Fig. 1. From this high deposition rate and low substrate temperature, the lattice-defect density should be higher in the particles in the film of Fig. 4 than in the particles in the films of Fig. 1. Thus, the appearance of the absorption in the range of 2.05–2.40 eV seems to be concerned with the lattice defects in the Pb particles.

The location of the absorption, attributed to the interband transition associated with the energy of about 2.3 eV,[10] almost agrees with the location of the absorption in the range of 2.05–2.40 eV in Fig. 4. As mentioned above, the lattice-defect density should be high in the continuous Pb films. Thus the absorption, attributed to the interband transition associated with the energy of about 2.3 eV,[10] also seems to be concerned with the lattice defects in the continuous Pb films. Further investigation of this absorption was difficult in the present study.

B. Effects of surface atoms

One of the conditions of occurrence of interband absorption, due to transitions between initial and final bands, is that the DOS for the initial bands is large. Knowledge of the DOS is thus important in the study of interband absorption. Very little has been known about the DOS of Pb particles and the surface layer of bulk Pb.

In bulk Pb, conduction bands are $6p$ bands because the Fermi level intersects the $6p$ bands.[12,17–19] The $6p$ bands do not hybridize with other bands such as the $6s$ and $5d$ bands, so that the conduction bands are narrow. For example, the width of the occupied conduction bands (i.e., the width from the bottom of the conduction bands to the Fermi level) is about 3.5–4.5 eV for bulk Pb (Refs. 12 and 17–19) and about 7–9.5 eV for bulk noble metals.[20]

d bands included in conduction bands of bulk noble and transition metals are also narrow. In bulk Cu, the width of $3d$ bands included in the conduction bands is about 4 eV.[6,7,20] The DOS of the $3d$ bands of the surface layer of the bulk Cu has been reported by a number of authors.[6,7] In the following, by referring to this DOS, we qualitatively consider the DOS of conduction bands of Pb particles and discuss the effect of the reduced coordination number of surface atoms on the interband absorption of the Pb particles.

In bulk Cu,[6,7] compared to the DOS of the $3d$ bands of the bulk, the DOS of the $3d$ bands of the surface layer is small at the lower portion and large at the upper portion, because the coordination number is lower for surface atoms than for bulk atoms. Due to such a distribution of the DOS, the surface layer has narrower $3d$ bands than the bulk. Surface atoms of the bulk Pb also have fewer neighbors. Thus, the distribution of the DOS of the conduction bands of the surface layer of the bulk Pb must be similar to that of the DOS of the $3d$ bands of the surface layer of the bulk Cu.

From the similarities, the DOS of the conduction bands of the surface layer of the bulk Pb is small at the lower portion and large at the upper portion. The DOS of the conduction bands of Pb particles should change from bulklike to surface-layer-like with decreasing particle size, because the ratio of surface to volume atoms increases with decreasing particle size. Based on these, we consider here the size-dependent change in the DOS of the conduction bands of the Pb particles as follows: the DOS of the conduction bands decreases at the lower portion and increases at the upper portion with decreasing particle size. As a result of such size-dependent decreases and increases in the DOS, the conduction bands of the Pb particles presumably become narrower with decreasing particle size.

There has been very little experimental data on effects of surface atoms on energy bands of metal particles and clusters. A theoretical study of metal clusters,[21] having a large ratio of surface to volume atoms, has reported that compared to the DOS of the $3d$ bands of bulk Ni, the DOS of the $3d$ bands of a Ni cluster consisting of 13 atoms is distributed mainly at the upper portion. For this distribution, the Ni cluster has narrower $3d$ bands than the bulk Ni. Such distribution qualitatively supports the size-dependent decrease and increase in the DOS of the conduction bands of the Pb particles, mentioned above.

The initial and final bands for the interband absorption 1–4 of the Pb particles are present within the conduction bands (Sec. III). If the initial band is positioned at the lower portion of the conduction bands and if the final band is hardly affected by particle size, the interband absorption is expected to weaken or to disappear with decreasing particle size because of the decrease in the DOS at the lower portion. With this weakening or disappearance, when the decrease in the DOS at the lower portion is small, the narrowing of the conduction bands is presumably inconspicuous.

C. Interband absorption of Pb particles

In the following, the interband absorption 1, 2, 3, and 4 is discussed in order 3, 4, 2, and 1. Very few data on the inter-

band absorption, related quantitatively to the DOS, have been reported for Pb particles and bulk Pb. The DOS was difficult to investigate quantitatively in the present study. Thus, in the following, we qualitatively discuss the change in the interband absorption in connection with the change in the DOS.

1. The interband absorption 3

In Fig. 1, the three steps in the range of 3–5.5 eV in the derivatives reflect the presence of the absorption of the triplet (i.e., the interband absorption 2, 3, and 4).[9] The middle step of the three steps corresponds to the presence of the interband absorption 3. Comparison of the derivatives in Fig. 1 with the derivative in Fig. 3(a) shows that the middle step disappears in Fig. 3(a). From this, we see that the interband absorption 3 first disappears when the particle size becomes smaller than about 300 Å in diameter [Fig. 3(a)].

For the Pb particles, there have been very few data on the initial and final bands for the interband absorption 3, due to the transition X_6^--X_6^+. Here we regard the final band X_6^+ to be unaffected by particle size.

The initial band X_6^- is positioned at the bottom of the conduction bands at the point X,[10,12,17–19] so that the disappearance of the interband absorption 3 results from the decrease in the DOS at the lower portion of the conduction bands. Thus, the disappearance of the interband absorption 3 agrees with the disappearance expected above (Sec. IV B), showing that the DOS of the conduction bands of the Pb particles decreases at the lower portion below about 300 Å in diameter because of the effect of the reduced coordination number of surface atoms.

The final band X_6^+ must be unaffected by particle size as regarded above. Thus, for example, the energy position of this band should not be shifted when the particle size decreases. Before the disappearance at about 260 Å in diameter [Fig. 3(a)], the location of the interband absorption 3 in Fig. 1 is the lowest in Fig. 1(d) (4.23±0.07 eV) and the highest in Fig. 1(b) (4.44±0.06 eV). Thus, the difference in the location of the interband absorption 3 in Fig. 1 is slight (0.08–0.34 eV). Based on this, the disappearance can be regarded to occur separately from the shift of the energy positions of the initial and final bands, i.e., the energy positions are not shifted down to about 260 Å in diameter.

Because there is no shift of the energy positions, the narrowing of the conduction bands is inconspicuous at point X down to a particle diameter of about 260 Å. This is presumably because the decrease in the DOS at the lower portion of the conduction bands is small.

In the present study, we could not clarify why the reduced coordination number of surface atoms affects the DOS of the conduction bands below about 300 Å in diameter. It should be noted that the size of about 300 Å in diameter is significant also in the size-dependent melting temperature of Pb particles. That is, in the data of a previous study,[22] the melting temperature of the Pb particles is found to decrease conspicuously with decreasing particle size below about 300 Å in diameter. This decrease in the melting temperature is based on the size-dependent increase in the ratio of surface to volume atoms. The present and previous studies[22] seem to

show that, in Pb particles, effects of surface atoms become dominant in physical properties below about several hundred ångstroms.

2. The interband absorption 4

Similar to the case of the interband absorption 3, the initial band (K_3) for the interband absorption 4, due to the transition (K_3)-(K_1), is positioned at the bottom of the conduction bands at point K.[10,12,17–19] We thus expect that the interband absorption 4 also disappears with decreasing particle size. However, this interband absorption is well defined down to a particle size of about 50 Å in diameter [Fig. 3(d)]. Therefore, the influence of the decrease in the DOS at the lower portion is small for the DOS for the initial band (K_3). The reason is presumably because the DOS for the initial band (K_3) is originally large. For example, based on the data in Ref. 19, the DOS at (K_3) is 4.2 times larger than that at the initial band X_6^- and 3.6 times larger than that at the initial band (K_1).

In Figs. 1 and 3, the interband absorption 4 is located in the narrow range of 5.20±0.05 eV [Fig. 3(c)]–5.32 ±0.07 eV [Figs. 1(a) and 1(b)], implying that the location is almost constant when the particle size decreases. From this, down to a particle diameter of about 50 Å [Fig. 3(d)] the energy positions of the initial and final bands for the interband absorption 4 are not shifted.

Because there is no shift of the energy positions, the narrowing of the conduction bands is inconspicuous at point K down to a particle diameter of about 50 Å. The reason is that as mentioned above, the influence of the decrease in the DOS at the lower portion is small for the DOS for the initial band (K_3).

As mentioned above, irrespective of particle size, the interband absorption 4 is well defined, and the energy position of the final band (K_1) is almost constant. This implies that the final band (K_1) is to operate constantly when the particle size decreases. It is thus reasonable to consider that down to a particle size of about 50 Å in diameter, the final band (K_1) is unaffected by particle size.

3. The interband absorption 2

The interband absorption 2 is located from 3.68 ±0.04 eV [Fig. 1(b)] to 3.78±0.04 eV [Fig. 1(a)] for particles larger than about 300 Å in diameter (Fig. 1) and is shifted to higher energies with decreasing particle size below about 300 Å in diameter (Fig. 3). At about 50 Å in diameter [Fig. 3(d)], the location is in the range of 4.30–4.58 eV. Based on these locations, the shift of the interband absorption 2 is 0.48–0.94 eV. Furthermore, the interband absorption 2 becomes weaker when the particle size becomes smaller than about 100 Å in diameter [Figs. 3(c) and 3(d)].

The final band (K_1) for the interband absorption 2, due to the transition (K_1)-(K_1), is the same as that for the interband absorption 4.[10,12,17–19] This band is considered to be unaffected by particle size, as mentioned above. Thus, the shift and the weakening of the interband absorption 2 should correspond to the shift of the initial band and to the decrease in the DOS for the initial band, respectively.

From this discussion, when the particle size decreases down to about 50 Å in diameter, the energy position of the initial band (K_1) is lowered by 0.48–0.94 eV towards the bottom of the conduction bands [i.e., towards the initial band (K_3) for the interband absorption 4]. In the present study, we could not clarify the cause of this lowering.

The energy spacing between the initial band (K_1) and the bottom of the conduction bands [i.e., the initial band (K_3)] equals the difference in the location between the interband absorption 2 and 4. The energy spacing is reduced from 1.33–1.75 to 0.57–1.09 eV in the lowering mentioned above, showing that the lowering causes the initial band (K_1) to be close to the bottom of the conduction bands. Based on this, here the initial band (K_1) after the lowering is regarded to be present in the lower portion of the conduction bands, i.e., the initial band (K_1) is regarded to be shifted to the lower portion of the conduction bands.

From the weakening of the interband absorption 2, we see that the DOS for the initial band (K_1) decreases when this band is shifted to the lower portion of the conduction bands. That is, the weakening shows a decrease in the DOS at the lower portion of the conduction bands. Thus, the weakening of the interband absorption 2 agrees with the weakening expected in Sec. IV B and shows that the DOS of the conduction bands decreases at the lower portion because of the effect of the reduced coordination number of surface atoms. The interband absorption 2 differs from the interband absorption 3 in that the DOS for the initial band (K_1) decreases when this band is shifted to the lower portion of the conduction bands.

4. The interband absorption 1

It is seen in Fig. 3 that the interband absorption 1, due to the transition (Σ_3)-(Σ_1), becomes weaker and then disappears with decreasing particle size below about 140 Å in diameter [Fig. 3(b)]. The origin of this interband absorption is different from that of the interband absorption 2–4; i.e., the interband absorption 1 occurs under the condition that the initial (Σ_3) and final bands (Σ_1) are quite parallel.[10,11] Thus, the weakening and the disappearance are presumably because these bands become nonparallel with decreasing particle size. The mechanism of the change from parallel to nonparallel was difficult to make clear in the present study.

D. Spectral simulation, contraction of lattice constants, and interactions with SiO$_2$

In the study of the size-dependent change in interband absorption of metal particles, it is useful to compare experimental spectrum with simulated spectrum based on bulk optical constants.[3] For bulk Pb, there seem to be very few data on optical constants, which are corrected for the absence of the absorption at about 1 and 2.3 eV mentioned in Sec. IV A. For this reason, the transmittance spectrum of the Pb-island film with bulk optical constants was difficult to simulate in the present study.

The contraction of lattice constants changes energy-band structure and thus affects interband absorption.[23] It is well established[24–26] that lattice constants of metal particles con-

tract with decreasing particle size, and it has been reported[3,4] that interband absorption of metal particles becomes weaker and then disappears with contraction of lattice constants.

In the present study, although lattice constants were investigated based on electron diffraction rings, the contraction was not found. For bulk Pb, it has theoretically been reported[19] that the contraction of lattice constants increases the energy spacing between the initial and final bands for the interband absorption 2–4. Thus, we can predict the interband absorption 2-4 to shift to higher energies with contraction of lattice constants. As mentioned in Secs. IV C 1–IV C 3, except for the interband absorption 2, the interband absorption is not shifted to higher energies when the particle size decreases. These results show that the size-dependent disappearance and weakening of the interband absorption of the Pb particles do not arise from the contraction of lattice constants.

In the following discussion, we assume the Pb particles to have the Fermi energy the same as that of the bulk Pb, because there has been very little data on the Fermi energy of the Pb particles. If electrons of the SiO$_2$ matrix occupy the final bands for the interband absorption of the Pb particles, the transitions between the initial and final bands would be restricted and thus the interband absorption would weaken or disappear.

The valence-band maximum of SiO$_2$ is about 6.3 eV lower than the Fermi energy of bulk Ag,[27] and the Fermi energy of the Pb particles is about 3.9 eV higher than that of the bulk Ag.[28] The difference between the valence-band maximum of the SiO$_2$ and the Fermi energy of the Pb particles is thus large (about 10.2 eV), so that the valence band of the SiO$_2$ does not overlap the final bands, which lie at values higher than the Fermi energy. The electrons of the SiO$_2$ matrix thus cannot occupy the final bands. This shows that the occupation of the final bands is not the cause of the size-dependent disappearance and weakening of the interband absorption of the Pb particles.

V. SUMMARY

We have experimentally investigated the size-dependent change in the interband absorption of the Pb particles forming island films. The interband absorption located from 4.23±0.07 to 4.44±0.06 eV, the initial band for which is positioned at the bottom of the conduction bands, first disappeared when the particle size becomes smaller than about 300 Å in diameter. The disappearance shows a decrease in the DOS at the lower portion of the conduction bands.

The interband absorption located from 3.68±0.04 to 3.78±0.04 eV was shifted to higher energies with decreasing particle size below about 300 Å in diameter, and it was located in the range of 4.30–4.58 eV when the particle size decreased to about 50 Å in diameter. The shift causes the initial band to be present in the lower portion of the conduction bands. The interband absorption became weaker with such a shift. Thus, the weakening also shows a decrease in the DOS at the lower portion of the conduction bands.

The effect of the reduced coordination number of surface atoms on the DOS of the conduction bands of the Pb par-

ticles was qualitatively considered based on the DOS of the $3d$ bands of the surface layer of the bulk Cu. Owing to this effect, the DOS decreases at the lower portion of the conduction bands when the particle size decreases. This decrease in the DOS qualitatively agrees with the decrease in the DOS for the interband absorption. Thus, the size-dependent disappearance and weakening of the interband absorption of the Pb particles can be attributed to the effect of the reduced coordination number of surface atoms on the DOS of the conduction bands. It is not clear why the reduced coordina-

tion number of surface atoms becomes effective for the DOS of the conduction bands below about 300 Å in diameter.

[1] U. Kreibig, in *Growth and Properties of Metal Clusters*, edited by J. Bourdon (Elsevier, Amsterdam, 1980), p. 371.

[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).

[4] E. Anno and T. Yamaguchi, Phys. Rev. B **55**, 4783 (1997).

[5] P. H. Citrin, G. K. Wertheim, and Y. Baer, Phys. Rev. Lett. **41**, 1425 (1978).

[6] J. A. Appelbaum and D. R. Hamann, Solid State Commun. **27**, 881 (1978).

[7] J. G. Gay, J. R. Smith, and F. J. Arlinghaus, Phys. Rev. Lett. **42**, 332 (1979); J. R. Smith, J. G. Gay, and F. J. Arlinghaus, Phys. Rev. B **21**, 2201 (1980).

[8] J. Tersoff and L. M. Falicov, Phys. Rev. B **26**, 6186 (1982).

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

[10] H. G. Liljenvall, A. G. Mathewson, and H. P. Myers, Philos. Mag. **22**, 243 (1970), and references therein.

[11] The transition between the bands (Σ_3) and (Σ_1) is because these bands are parallel. As a study of interband absorption between parallel bands, see, for example, N. W. Ashcroft and K. Sturm, Phys. Rev. B **3**, 1898 (1971).

[12] T. L. Loucks, Phys. Rev. Lett. **14**, 1072 (1965).

[13] See, for example, S. Norrman, T. Andersson, C. G. Granqvist, and O. Hunderi, Phys. Rev. B **18**, 674 (1978), and references therein.

[14] U. Kreibig, Z. Phys. B **31**, 39 (1978); E. Anno and R. Hoshino, J. Phys. Soc. Jpn. **50**, 1209 (1981).

[15] A. I. Golovashkin and G. P. Motulevich, Zh. Eksp. Teor. Fiz. **53**, 1526 (1967) [Sov. Phys. JETP **26**, 881 (1968)].

[16] O. Hunderi and H. P. Myers, J. Phys. F: Met. Phys. **3**, 683 (1973); O. Hunderi, Phys. Rev. B **7**, 3419 (1973).

[17] F. R. McFeely, L. Ley, S. P. Kowalczyk, and D. A. Shirley, Solid State Commun. **17**, 1415 (1975).

[18] A. D. Zdetsis, D. A. Papaconstantopoulos, and E. N. Economou, J. Phys. F: Met. Phys. **10**, 1149 (1980).

[19] K. Kubo and J. Yamashita, J. Phys. F: Met. Phys. **16**, 2017 (1986).

[20] R. Lässer, N. V. Smith, and B. L. Benbow, Phys. Rev. B **24**, 1895 (1981); G. Fuster, J. M. Tyler, N. E. Brener, J. Callaway, and D. Bagayoko, *ibid.* **42**, 7322 (1990).

[21] R. P. Messmer, S. K. Knudson, K. H. Johnson, J. B. Diamond, and C. Y. Young, Phys. Rev. B **13**, 1396 (1976).

[22] T. B. David, Y. Lereah, G. Deutscher, R. Kofman, and P. Cheyssac, Philos. Mag. A **71**, 1135 (1995).

[23] See, for example, H. Tups, A. Otto, and K. Syassen, Phys. Rev. B **29**, 5458 (1984).

[24] P. A. Montano, W. Schulze, B. Tesche, G. K. Shenoy, and T. I. Morrison, Phys. Rev. B **30**, 672 (1984).

[25] A. Balerna, E. Bernieri, P. Picozzi, A. Reale, S. Santucci, E. Burattini, and S. Mobilio, Phys. Rev. B **31**, 5058 (1985).

[26] R. Lamber, S. Wetjen, and N. I. Jaeger, Phys. Rev. B **51**, 10 968 (1995).

[27] B. N. J. Persson, Surf. Sci. **281**, 153 (1993), and references therein.

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