Interband absorption of Ru studied by optical absorption of continuous thin films and small particles

E. Anno
Department of Physics, Asahikawa Medical College, Asahikawa 078, Japan

T. Yamaguchi
Research Institute of Electronics, Shizuoka University, Hamamatsu 432, Japan

(Received 11 July 1996; revised manuscript received 24 September 1996)

For continuous thin Ru films and Ru island films consisting of Ru particles smaller than about 320 Å in diameter, optical absorption has been measured in the photon energy range of 0.5–6.5 eV. Absorption, found below about 1 eV and at about 2, 3, 3.6, and 4.5–5 eV for the continuous thin films, shifted to higher energies and became weaker with decreasing particle size. This change is accompanied by lattice contraction and is similar to the lattice-contraction-induced change in interband absorption of hcp Co. Thus, the absorption is interband absorption as for hcp Co, and is due to transitions from *d* states into empty states above the Fermi level. The absorption at about 2, 3, and 3.6 eV shifted almost equally (0.2–0.3 eV) and disappeared at almost the same time below about 70 Å in diameter, indicating that *d* states are close to each other. The absorption at about 4.5–5 eV was still well defined at about 25 Å in diameter. Cu, Ni, and Pd particles have also shown such well-defined interband absorption. Thus, as for Cu, Ni, and Pd, *d* states are presumably in flat or parallel bands. [S0163-1829(97)00107-0]

I. INTRODUCTION

The electronic structure of small particles and clusters has been known to change with particle and cluster size.[1] With this change optical properties, such as interband absorption, of the small particles and the clusters also change. For example, in Cu particles,[2] *d* bands broaden with decreasing particle size because lattices contract with decreasing particle size, and with this broadening interband absorption due to transitions from lowest-lying *d* states into empty states above the Fermi level shifts to higher energies and becomes weaker. The shift is due to the lowest-lying *d* states shifting to lower energies relative to the Fermi level.[2] The weakening is caused by the joint density of states for the transitions decreasing due to the decrease in the density of states for the lowest-lying *d* states.[2]

As mentioned above, there is the example of the change in interband absorption with particle size. Thus if absorption, found for bulk, changes with particle size, there is the possibility that the absorption is interband absorption. When the absorption is interband absorption, we can obtain information on the interband absorption from the analysis of the change with particle size. Thus, the investigation of the change in absorption, found for bulk, with particle size is useful in the study of interband absorption.

There is very little data on interband absorption (and energy bands) of Ru. Continuous thin metal films have been accepted to have bulk optical properties.[3] In this study, comparing absorption of continuous thin Ru films with that of Ru island films consisting of Ru particles, the change in the absorption, found for the continuous thin films (i.e., for bulk), with particle size is investigated. Based on the similarity between this change, accompanied by lattice contraction, and the lattice-contraction-induced change in interband absorption of hcp Co,[4] interband absorption of Ru is identified. *d* states for transitions are discussed by analyzing the change in the absorption with particle size, and by referring to interband absorption of Cu (Ref. 2) and Ni and Pd (Ref. 5) particles.

II. EXPERIMENT

The samples were prepared by vacuum evaporation in conditions similar to those described in a previous paper.[5] Ru (purity 99.9%) was deposited both on a SiO_2-coated fused-quartz substrate and on SiO_2-coated carbon meshes, which were heated to about 600 °C during deposition. Then, the Ru island films were 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 and then cooled to room temperature at a rate of about 1–2 °C/m. Continuous thin Ru films have been produced by the above procedure, but the temperature of the substrate and the annealing was about 100 °C and the annealing time was 10 h. The weight thickness and the deposition rate were monitored with a quartz-crystal oscillator. In the spectral range of interest here, the transmittance of the evaporated SiO_2 film without Ru particles was almost constant.

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 were measured within experimental accuracies of $\pm 0.1\%$ and $\pm(0.001-0.01)$ eV at room temperature with a double-beam spectrophotometer. The derivative was measured at a wavelength difference of about 4 nm. The particle size and the electron diffraction pattern were investigated with an electron microscope operating at 200 kV. In the spectra in this paper, the scale of the derivative is the same and the inset shows the particle-size distribution in vol. %.

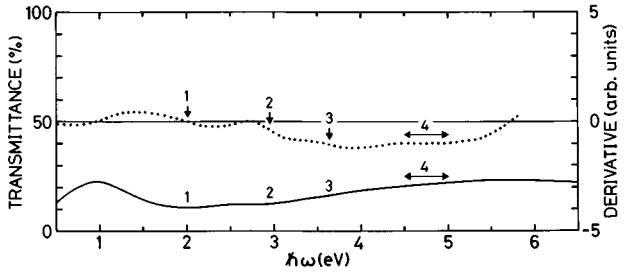

FIG. 1. Transmittance spectrum (solid curve) and its derivative (dotted curve) for a continuous thin Ru film. The weight thickness is 118.1 Å. The deposition rate was 0.12 Å/s.

III. RESULTS AND DISCUSSION

The contrast of polycrystalline particles is not uniform because of the diffraction contrast; i.e., polycrystalline particles show complex contrast structure.[6] The continuous thin Ru films and the Ru particles in this study showed such contrast. Thus they are polycrystalline.

In this study, only the hcp 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 the continuous thin Ru films and the Ru particles is not taken into account.

A. Spectra of continuous thin Ru films and Ru island films with large particle size

Figure 1 shows an example of the transmittance spectrum and its derivative of continuous thin Ru films. Below about 1 eV, transmittance decreases with decreasing energy. Four dips labeled 1, 2, 3, and 4 are found at about 2, 3, 3.6, and 4.5–5 eV in the transmittance spectrum, respectively. In the derivative the sloped part for the dip 4 is ill defined compared to the sloped parts for other dips. Thus the position of this dip is difficult to identify, so that the range of the presence is represented by the double-ended horizontal arrow.

Optical properties of continuous thin metal films have been accepted to be about the same as those of bulk metal.[3] Thus, based on the decrease in the transmittance and on the presence of the four dips, we see that in bulk Ru, absorption is present below about 1 eV and at about 2, 3, 3.6, and 4.5–5 eV in the range of about 0.5–5 eV.

Figure 2 shows the transmittance spectrum and its derivative of a Ru island film with particle diameter of about 320 Å. The decrease in the transmittance and the four dips in Fig. 1 are found in Fig. 2 also, and the general structures in the range of about 0.5–5 eV in the transmittance spectra in Fig. 2 almost agree with those in Fig. 1. This shows that in the range of about 0.5–5 eV, optical absorption of Ru particles with large particle sizes as in Fig. 2 is about the same as that of bulk.

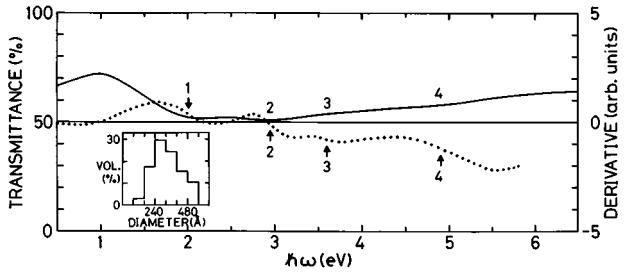

FIG. 2. Transmittance spectrum (solid curve) and its derivative (dotted curve) for a Ru island film with a particle diameter of about 320 Å. The weight thickness is 34.7 Å. The deposition rate was 0.06 Å/s.

When the weight thickness is thicker than that (34.7 Å) of the island film in Fig. 2, a continuous-network structure[7] due to agglomeration of large particles was formed on the substrate; i.e., island films were not formed. Thus island films with particle sizes smaller than that (about 320 Å in diameter) of the island film in Fig. 2 have been studied in this study.

In Fig. 1 the absorption for the dip 1 is slightly stronger than that for the dip 2 but in Fig. 2 the absorption is only slightly weaker for the dip 1 than for the dip 2. The reason for this difference is not clear. Above about 5.5 eV in Fig. 1, absorption increases with energy. This contrasts with the decrease in absorption above about 5.5 eV in Fig. 2. The cause of this contrast is not clear.

Island films of fcc transition metals have shown the optical plasma-resonance absorption (OPRA),[5] which results from the plasma oscillation of conduction electrons and does not appear in the spectrum of bulk.[8] The above near agreement of the general structures of the transmittance spectra obviously shows that the OPRA is absent in the spectrum of the island film in Fig. 2. The reason may be that the OPRA is present in the energy range higher than that in this study, or that the OPRA does not occur because of the conduction-electron localization due to the strong *d* character as in Fe and Cr.[9]

B. Spectrum of Ru island films and interband absorption of Ru

Figures 3(a), 3(b), and 3(c) show the transmittance spectrum and its derivative of the island film with particle diameters of about 180, 120, and 70 Å, respectively. In Fig. 3(c), the positions, at which the dips seem to be present, are labeled in the transmittance spectrum, because in the derivative the sloped parts for the dips are not clear and thus the identification of the position of the dips is difficult.

The transmittance spectrum and its derivative at about 50 and 25 Å in diameters are shown in Figs. 4(a) and 4(b), respectively.

From Figs. 2–4, we see that the absorption below about 1 eV and for the dips shifts to higher energies and becomes weaker with decreasing particle size.

The lattice constant *a* has been investigated by measuring the diameter of the (110) diffraction ring. The diameter for the continuous thin film of Fig. 1 was about 1.4% smaller than that for the island film with particle diameter of about 25 Å [Fig. 4(b)]. This shows that the lattice constant *a* of the particles of about 25 Å in diameter is smaller than that for bulk by about 1.4%, and that as in noble- and transition-metal particles,[2,10,11] lattices of the Ru particles contract with decreasing particle size. The investigation of the lattice constant *c* was difficult because diffraction rings for this lattice constant were very weak.

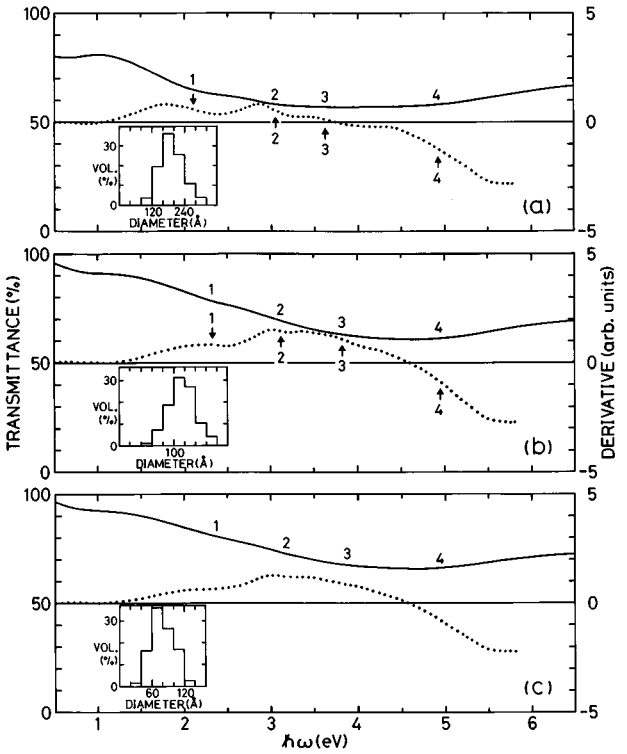

FIG. 3. Transmittance spectra (solid curves) and their derivatives (dotted curves) for Ru island films with particle diameters of about (a) 180, (b) 120, and (c) 70 Å. The weight thickness and the deposition rate are (a) 24.3 Å and 0.05 Å/s, (b) 17.4 Å and 0.05 Å/s, and (c) 13.9 Å and 0.08 Å/s.

The lattice contraction has been known to affect optical properties.[12] Thus the above shift and weakening found in Figs. 2–4 seem to result from the lattice contraction. This point is considered below by referring to the lattice-contraction effect on interband absorption of hcp Co,[4] of which the energy bands are presumably similar to those of Ru.

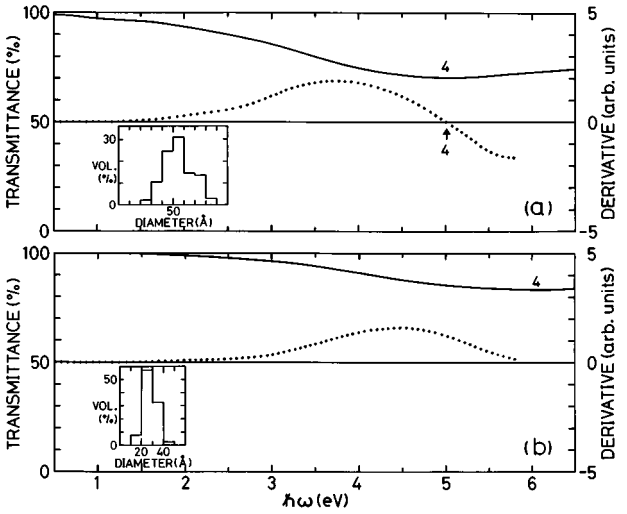

FIG. 4. Transmittance spectra (solid curves) and their derivatives (dotted curves) for Ru island films with particle diameters of about (a) 50 and (b) 25 Å. The weight thickness and the deposition rate are (a) 10.4 Å and 0.09 Å/s and (b) 7.0 Å and 0.10 Å/s.

For ferromagnetic hcp Co, the effect of the lattice contraction of 6% in a and c on interband absorption due to transitions from d states into empty states above the Fermi level has theoretically been studied in the range of 0–6.8 eV by neglecting the effect of the anisotropy relative to the c axis on the transitions.[4] The study showed that the interband absorption shifts to higher energies and becomes weak. The shift and weakening are, respectively, in qualitative agreement with the above shift and weakening found in Figs. 2–4. This agreement shows that the shift and the weakening found in Figs. 2–4 result from the lattice contraction, and thus that the absorption below about 1 eV and for the dips is interband absorption due to transitions from d states into empty states above the Fermi level.

In Ref. 4, it has also been shown that the lattice contraction broadens d bands of hcp Co. From this broadening and the above size-dependent lattice contraction of the Ru particles, d bands of the Ru particles are considered to broaden with decreasing particle size.

Mechanisms of the shift and the weakening of the absorption below about 1 eV and for the dips are presumably the same as those for the Cu particles in Sec. I: When d bands broaden with decreasing particle size, the shift and the weakening are, respectively, due to the shift of d states and due to the decrease in the density of states (DOS) for d states.

d and empty states for the absorption below about 1 eV must be present near the Fermi level because the absorption appears in the low-energy range.

The shift of the absorption for the dips 1–3 is appreciable in the comparison of Fig. 2 with Fig. 3(b) and is almost equal, i.e., the shift for the dips 1, 2, and 3 is, respectively, about 0.3, 0.2, and 0.2 eV. We see from Figs. 3 and 4 that below about 70 Å in diameter [Fig. 3(c)], the absorption for the dips 1–3 disappears at almost the same time. The nearly equal shift and disappearance show d states for the absorption for the dips 1–3 to be close to each other, because as mentioned above, the change in d states (i.e., the shift of d states and the DOS decrease for d states) is responsible for the shift and weakening.

The absorption for the dip 4 is different from the absorption for other dips in that it is still well defined at a particle size of about 25 Å in diameter [Fig. 4(b)]. Cu (Ref. 2) and Ni and Pd (Ref. 5) particles have also shown such well-defined interband absorption, as mentioned below.

In the Cu particles,[2] the interband absorption mentioned in Sec. I (due to transitions, occurring primarily along the L direction, from lowest-lying d states into empty states above the Fermi level)[13] is still well defined at about 35 Å in diameter. The reason is that the joint density of states (JDOS) is originally large because the band for the lowest-lying d states is flat near L.[14] In the Ni and Pd particles,[5] interband absorption that is mainly due to transitions between d states and empty states above the Fermi level in the Σ direction,[15,16] where the bands for the d and empty states are quite parallel over an extended region, is still well defined at about 30–15 Å in diameter. This is due to the fact that the JDOS is originally large because of the quite parallel bands.

Based on the above cases of the Cu, Ni, and Pd particles, d states for the absorption for the dip 4 are presumably present in flat or parallel bands.

For metal island films, it has theoretically been reported that the dipole interaction between particles has an effect on the OPRA.[17] However, very little has been reported on the effect of interactions between particles on interband absorption. Thus the effect of interactions between the Ru particles was not considered in this study.

For Ag particles embedded in a SiO_2 matrix, the influence of the interaction between the particles and the matrix on the OPRA has theoretically been reported.[18] However, for metal particles embedded in matrices, very little has been reported on influences of interactions between the particles and the matrices on interband absorption. Thus, in this study, the influence of the interactions between the Ru particles and the SiO_2 matrix was not taken into account.

IV. SUMMARY

Optical absorption of continuous thin Ru films and Ru island films has been measured. For the continuous thin film, absorption was found below about 1 eV and at about 2, 3, 3.6, and 4.5–5 eV in the range of about 0.5–5 eV. This absorption was found for the island films also, and it shifted to higher energies and became weaker with lattice contraction, which occurs with decreasing particle size. Based on the similarity between this change and the lattice-contraction-induced change in interband absorption of hcp Co, the absorption could be shown to be interband absorption due to transitions from *d* states into empty states above the Fermi level.

The shift of the absorption at about 2, 3, and 3.6 eV was almost equal, and this absorption disappeared at almost the same time below about 70 Å in diameter. This shows *d* states for the absorption to be close to each other. The absorption at about 4.5–5 eV was still well defined at about 25 Å in diameter. Such well-defined interband absorption has been found for Cu, Ni, and Pd particles also, in which the well definition is due to the presence of *d* states in flat or parallel bands. Thus *d* states for the absorption are presumably present in flat or parallel bands.

ACKNOWLEDGMENT

One of us (E.A.) is grateful to Professor M. Ido (Hokkaido University) for useful discussions and encouragements throughout this work.

[1] See, for example, P. M. Messmer, S. K. Knudson, K. H. Johnson, J. B. Diamond, and C. Y. Yang, Phys. Rev. B **13**, 1396 (1976); R. Arratia-Perez, A. F. Ramos, and G. L. Malli, *ibid*. **39**, 3005 (1989); K. Lee and J. Callaway, *ibid*. **48**, 15 358 (1993), and references therein.

[2] E. Anno, Surf. Sci. **260**, 245 (1992).

[3] See, for example, P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972); **9**, 5056 (1974).

[4] N. I. Kulikov and E. T. Kulatov, J. Phys. F **12**, 2267 (1982).

[5] E. Anno and T. Yamaguchi, Surf. Sci. **286**, 168 (1993).

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

[7] D. W. Pashley, M. J. Stowell, M. H. Jacobs, and T. J. Law, Philos. Mag. **10**, 127 (1964).

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

[9] E. Anno, Surf. Sci. **311**, 224 (1994).

[10] G. Apai, J. F. Hamilton, J. Stoher, and A. Thompson, Phys. Rev. Lett. **43**, 165 (1979).

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

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

[13] R. Lässer, N. V. Smith, and R. L. Benbow, Phys. Rev. B **24**, 1895 (1981).

[14] B. R. Cooper, H. Ehrenreich, and H. R. Philipp, Phys. Rev. **138**, A494 (1965).

[15] C. S. Wang and J. Callaway, Phys. Rev. B **9**, 4897 (1974); D. G. Laurent, J. Callaway, and C. S. Wang, *ibid*. **20**, 1134 (1979).

[16] N. V. Smith, R. Lässer, and S. Chiang, Phys. Rev. B **25**, 793 (1982); R. Lässer and N. V. Smith, *ibid*. **25**, 806 (1982).

[17] B. N. J. Persson and A. Liebsh, Phys. Rev. B **28**, 4247 (1983).

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