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Interband absorption of vanadium studied by probing the size-dependent change in energy bands of vanadium particles

Eiji Anno[a)]
Department of Physics, Asahikawa Medical College, Asahikawa, Hokkaido 078-8510, Japan

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For interband absorption with peak at about 2.5–3.0 eV of vanadium, the contribution of the transition from the Fermi level in the region near state Σ_1 to state Σ_4 has been investigated experimentally. The contribution was proposed by Romaniello *et al.* [Phys. Rev. B **73**, 075115 (2006)]. When the size of vanadium particles was decreased, the interband absorption weakened remarkably. Considering the raising of the position of state Σ_1 with energy-band broadening due to lattice contraction, the remarkable weakening can qualitatively be ascribed to the ceasing of the transition mentioned above. This confirms the contribution. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2963710]

I. INTRODUCTION

Optical properties of metals are significantly influenced by interband absorption due to transitions between electronic states in energy bands. Studies of transitions are important because the feature of interband absorption, such as peak position, is determined from transitions.

Considerable effort has been devoted to identify transitions for interband absorption of vanadium,[1–5] which is a body-centered-cubic (bcc) transition metal, but the transitions have not been identified as yet. For example, although several transitions have been proposed for interband absorption with peak at about 2.5–3.0 eV,[1–5] transition for the interband absorption is still being discussed. Romaniello *et al.*[6] recently proposed transitions between the Fermi level (FL) of bands 3 and 5, including the transition from the FL in the region near state Σ_1 to state Σ_4 (the transition FL near $\Sigma_1 \rightarrow \Sigma_4$).

In the present study, it was observed for vanadium particles that interband absorption with peak at about 2.5–3.0 eV weakens remarkably with decreasing particle size.

As is well known, lattice constants of metal particles contract with decreasing particle size because of the hydrostatic pressure due to the particle surface stress,[7,8] and energy bands of the metal particles broaden with lattice contraction.[8] Based on this, energy bands of vanadium particles are considered to broaden with lattice contraction.

It is seen from a theoretical study[9] that when energy bands of vanadium are broadened by lattice contraction, the position of state Σ_1 is raised above the Fermi level. The raising causes state Σ_1 to be empty, and the transition FL near $\Sigma_1 \rightarrow \Sigma_4$ ceases. Thus, interband absorption originating mainly from this transition should weaken remarkably with energy-band broadening due to lattice contraction.

From this, it is shown that the remarkable weakening of interband absorption with peak at about 2.5–3.0 eV of vanadium particles can qualitatively be attributed to the ceasing of the transition FL near $\Sigma_1 \rightarrow \Sigma_4$, thereby confirming the contribution of this transition to the interband absorption.

II. EXPERIMENT

Samples in the present study are continuous-thin vanadium films and vanadium-island films. Island film is a system consisting of particles distributed on the substrate surface.

In a vacuum chamber, a fused-quartz substrate ($18 \times 18 \times 0.5$ mm^3) and electron-microscopic meshes covered with a carbon film were adjacently placed above an evaporation source. The distance from the evaporation source to the substrate and meshes was 30.3 cm. SiO_2 was first deposited both on the substrate and meshes by electron-beam heating in an oil-free vacuum of $\sim 10^{-8}$ Torr. Next, at pressures of $\sim 10^{-7}$ Torr, vanadium (purity 99.9%) was deposited to obtain continuous-thin films or island films. The films were then annealed for 1 h. During deposition and annealing, the substrate and meshes were maintained at a temperature of about 423 K for continuous-thin films and about 773 K for island films. After annealing, to prevent adsorption or chemical reactions on exposure to air, the films were coated with SiO_2 (thickness of 10–30 nm). The weight thickness, corresponds to an effective thickness for an ideal continuous film with bulk density, and the deposition rate were monitored with a quartz-crystal oscillator. Transmittance of the evaporated SiO_2 film was almost constant within the spectral range of interest here.

Optical and electron-microscopic investigations were carried out after exposing the samples to air. With a double-beam spectrophotometer (Shimadzu UV-365), transmittance spectra for normal incidence and their first derivatives were measured in the wavelength range of 190–2500 nm at room temperature within the experimental accuracy of $\pm 0.1\%$ and $\pm[0.3(190\text{ nm})-0.7(2500\text{ nm})]$nm. The first-derivative spectra were derived by computer applications based on the convolution method for a wavelength interval of about 4 nm. The image and electron-diffraction pattern of the films were investigated with an electron microscope operating at 200 kV (Hitachi H-800).

[a)] Electronic mail: anno@asahikawa-med.ac.jp.

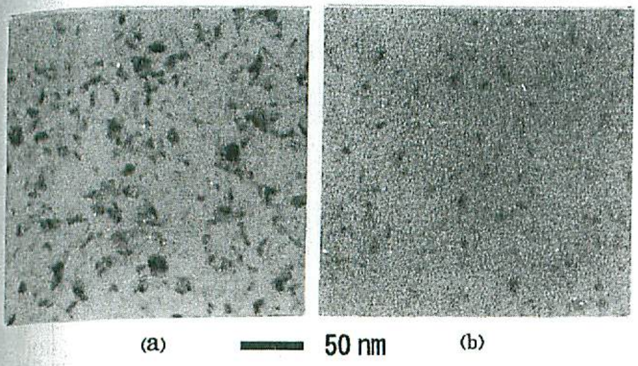

FIG. 1. Electron micrographs for the vanadium-island film with weight thickness of (a) 7.62 and (b) 3.81 nm. The optical spectra of the films (a) and (b) are shown in Figs. 3(a) and 3(b), respectively.

III. RESULTS

A. Electron-microscopic investigation

In metal-island films, metal particles grow through the agglomeration of smaller metal particles.[10] With this growth, the metal particles become large and their shapes become irregular. As a result of such growth, metal particles are larger and their shapes are more irregular for thick weight thickness than for thin weight thickness.[10]

It has been observed in the present study that the shape of vanadium particles tends to become irregular, and that outlines of the image of vanadium particles are not well defined because of the low contrast. The reasons for the tendency and the low contrast could not be made clear.

Electron micrographs of vanadium-island films with weight thicknesses of 7.62 and 3.81 nm are shown in Figs. 1(a) and 1(b), respectively. When particles were large, as shown in Fig. 1(a), particle shapes were irregular and outlines of the particles were not well defined. When particles were small, as shown in Fig. 1(b), outlines of the particles were ill defined. The particle size was thus difficult to estimate in the present study.

The diffraction contrast,[11] evidence for polycrystalline state, was difficult to investigate in the present study. It has been reported for metal-island films that when metal particles grow through the agglomeration of smaller metal particles, lattice defects are formed in the metal particles.[11] Therefore, vanadium particles in the present study are considered to be in a polycrystalline state.

In the present study, only the bcc structure could always be identified in electron-diffraction patterns of the films with weight thickness thicker than about 3.8 nm, implying that the formation of compound layers on the continuous-thin film surface and the particle surface or the change in continuous-thin films and particles into compound occurred rarely. When the weight thickness is thinner than about 3.8 nm, the image of vanadium particles and the electron-diffraction pattern of vanadium-island films were difficult to observe because of the low contrast. Thus, the crystal structure of the vanadium particles could not be identified. The A15-type structure has been found for particles of chromium (a bcc transition metal).[12] If vanadium particles have such a structure, optical absorption must be entirely different from that of the vanadium particles with a bcc structure. As shown below in Fig. 3 (Sec. III B), interband absorption in the range above about 5 eV, intrinsic absorption of vanadium, was observed down to the thinnest weight thickness [0.76 nm, Fig. 3(d)]. Based on this, vanadium particles for a weight thickness thinner than about 3.8 nm were regarded also to have a bcc structure.

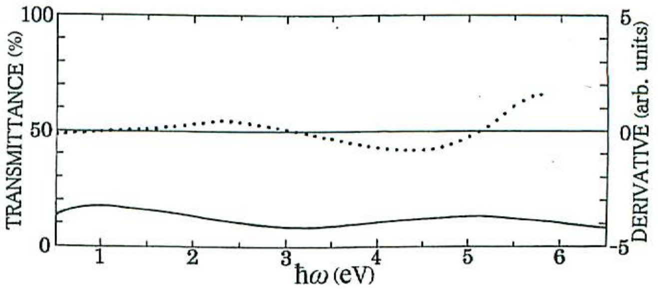

FIG. 2. Transmittance spectrum (solid curve) and the first derivative (dotted curve) of the continuous-thin vanadium film with weight thickness of 19.05 nm. The deposition rate was 0.03 nm/s.

Lattice constants of metal particles have been known to contract with decreasing particle size (Sec. I).[7,8] The diameters of the (110) and (200) diffraction rings were investigated. There was little difference in the diameters between the films with weight thickness thicker than about 3.8 nm, showing lattice contraction to be inconspicuous. Lattice contraction is presumably conspicuous for vanadium particles in the island films with weight thickness thinner than about 3.8 nm.

B. Spectra of vanadium-island films

To show experimental spectra compactly, the wavelength unit (nanometers) (Sec. II) is converted into the photon energy unit (eV) in the following figures. Due to the conversion, the slope sign of the derivative is reverse.

There are several differences between previously reported data.[1–6] Data on optical constants for evaporated continuous films (polycrystalline) in Ref. 2 almost agree with that for the bulk (polycrystalline) in Ref. 6. The spectral range is larger in Ref. 2 (0.5–6.5 eV) than in Ref. 6 (0.7–4.5 eV). From these, in the present study, the data in Ref. 2 is considered to be the reference data.

Figure 2 shows the transmittance spectrum and its derivative of the continuous-thin vanadium film with a weight thickness of 19.05 nm. Absorption appearing in this spectrum is almost in agreement with that in the spectrum of Ref. 2: absorption in the range below about 1 eV is the overlap of interband absorption and Drude-type absorption, and absorption with peak at about 3.0 eV and absorption in the range above about 5 eV are interband absorption. Such agreement supports that the continuous-thin vanadium film has a bcc structure. The increase in absorption with decreasing energy in the range below about 1 eV arises from Drude-type absorption, due to conduction electrons and increases with decreasing energy.[4,6]

When absorption increases, the transmittance for the absorption approaches 0%. The shape of the absorption tends to flatten with this approach. The shape of absorption in Fig. 2 was presumably affected by such a tendency, because the transmittance is close to 0%.

In derivative spectroscopy,[13] a step appearing in the first derivative shows the presence of absorption, and the position of the maximum slope in the step corresponds to that of the absorption. In Fig. 2, the shape of interband absorption with peak at about 3.0 eV was presumably influenced by the flattening tendency mentioned above. Thus, the position (3.64 ± 0.10 eV) of the maximum slope in the step may be different from that for no flattening tendency. For this reason, the position of the maximum slope was not indicated in Fig. 2.

By comparing the transmittance and derivative spectra of vanadium-island films with those of Fig. 2 (i.e., of the bulk), we can see the change in interband absorption with decreasing particle size.

In metal-island films consisting of metal particles smaller than the wavelength of incident light, absorption due to conduction electrons is optical plasma-resonance absorption caused by plasma oscillations of conduction electrons in the metal particles.[14] Drude-type absorption does not occur in the metal-island films.

The transmittance spectrum and its derivative of the vanadium-island film with a weight thickness of 7.62 nm are shown in Fig. 3(a) [the electron micrograph is Fig. 1(a)]. The increase in absorption with decreasing energy in the range below about 1 eV, found in Fig. 2, is not present, showing that Drude-type absorption does not occur as mentioned above. The derivative in the range above about 1 eV is similar to that in Fig. 2, so that interband absorption in the continuous film of Fig. 2 (i.e., of the bulk) occurs in the island film. Optical plasma-resonance absorption, not found in Fig. 3(a), is presumably present in the range above about 6.5 eV.

Absorption for almost constant transmittance in the range of about 0.5–1 eV in Fig. 3(a) is the first data on interband absorption of vanadium separated from Drude-type absorption.

In Fig. 3(a), because of the overlap between interband absorption, the slope in the lower-energy flank of interband absorption with peak at about 2.6 eV is gentle. Due to the gentle slope, the position (3.19 ± 0.15 eV) of the maximum slope in the step in the derivative may be higher than that for no overlap. For this reason, the position of the maximum slope was not indicated in Fig. 3(a). The overlap was difficult to separate in the present study.

Figure 3(b) shows the transmittance spectrum and its derivative of the vanadium-island film with a weight thickness of 3.81 nm [the electron micrograph is Fig. 1(b)]. The derivative is similar to that in Fig. 3(a), showing that interband absorption almost agrees with that of the bulk. The position (2.89 ± 0.18 eV) of the maximum slope in the step for interband absorption with peak at about 2.5 eV was not indicated as in Fig. 3(a).

Figures 3(c) and 3(d) show the transmittance spectra and their derivatives of the vanadium-island films with weight thicknesses of 1.40 and 0.76 nm, respectively. In contrast to Figs. 3(a) and 3(b), the transmittance is not constant in the range of about 0.5–1 eV, showing the change in interband absorption. For interband absorption with peak at about 2.6 eV in Fig. 3(c), the position of the maximum slope was difficult to distinguish in the step in the derivative because the slope is almost monotonous. The interband absorption is appreciably weaker than that in Figs. 3(a) and 3(b). In Fig. 3(d), the step, corresponding to the presence of absorption, was not detected by the derivative in the range of about 0.5–4 eV, showing interband absorption with peak at about 2.5–2.6 eV to be very weak.

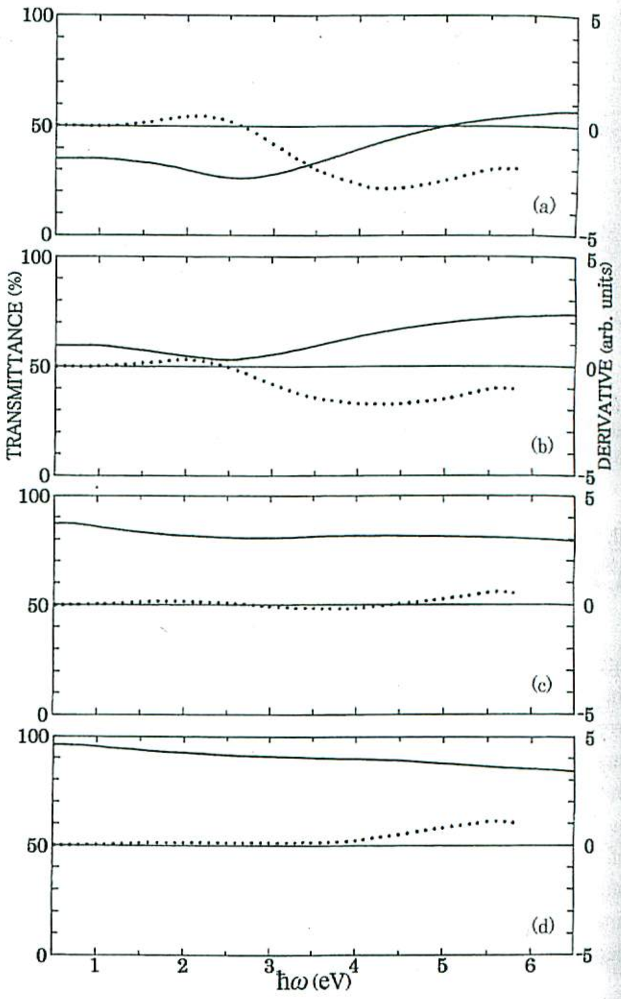

FIG. 3. Transmittance spectra (solid curves) and the derivatives (dotted curves) of the vanadium-island films with weight thicknesses of (a) 7.62, (b) 3.81, (c) 1.40, and (d) 0.76 nm. The deposition rate was 0.01 nm/s.

Weak interband absorption appearing at about 1.5 and 3.5 eV in the spectrum of Ref. 2 was not found for the spectra in the present study. The reason seems to be that the interband absorption is very weak and thus difficult to detect because of the overlap with interband absorption with peak at about 2.5–3.0 eV. The weak interband absorption is not found also for the experimental spectrum of Ref. 6.

IV. DISCUSSION

Considerable effort has been expended to identify the transition for interband absorption with peak at about 2.5–3.0 eV of vanadium. Transitions proposed so far are transition

$\Lambda_3 \to \Lambda_3$,[1,2] transition $G_1 \to G_1$,[3] transition in regions near the Σ axis,[4] transition $N_2 \to N_1'$,[5] and the transitions between the FL of bands 3 and 5 (Ref. 6, Sec. I).

The regions for the transitions between the FL of bands 3 and 5 are shown in cross sections of the Fermi surfaces in Ref. 6, i.e., the regions for Γ-N line, H-N line, and the ΓHP plane. When the energy bands in Refs. 4, 6, and 9 are referred to, the energy spacing between the FL of bands 3 and 5 can be estimated along the Γ-N line, H-N line, P-H line, and Γ-P line. The transition between the FL of bands 3 and 5 along the Γ-N line is the transition FL near $\Sigma_1 \to \Sigma_4$.[4,6,9] In Refs. 4, 6, and 9, the energy spacing $\Delta E_{F1,4}$ for the transition FL near $\Sigma_1 \to \Sigma_4$ is about 2.5–2.6 eV, almost in agreement with the peak position (about 2.5–2.6 eV) of the interband absorption in Figs. 3(a)–3(c). The energy spacing for other lines and for the transitions proposed in Refs. 1–3 and 5 does not agree with the peak position. In derivative spectra of Figs. 2 and 3, a step corresponds to interband absorption with peak at about 2.5–3.0 eV. This shows that the transition for the interband absorption is almost single. As such transition, based on the energy spacing mentioned above, the transition FL near $\Sigma_1 \to \Sigma_4$ is noted in the following.

It is seen from the derivatives in Fig. 3 that when the weight thickness is thinner than about 3.8 nm [Fig. 3(b)] the step for interband absorption with peak at about 2.5–2.6 eV becomes less and less defined with decreasing weight thickness. The particle size is decreased with decreasing weight thickness, as reported by Ref. 10 (Sec. III A) and as shown in Fig. 1. Therefore, when the weight thickness is thinner than about 3.8 nm, interband absorption with peak at about 2.5–2.6 eV weakens remarkably with decreasing particle size.

The change in the interband absorption, mentioned above, shows that energy bands of vanadium particles are changed with decreasing particle size. As the factors, affect depending on particle size the energy bands of metal particles, the lattice contraction, and the coordination-number reduction originating from low coordination number of surface atoms has been accepted so far.[15] To my knowledge other factors have not yet been accepted. Thus, these two factors are considered in the following.

In bulk metals, surface layers have narrower energy bands than the bulk,[16] because the coordination number is lower for surface atoms than for bulk atoms. In metal particles, with decreasing particle size, the low coordination-number of surface atoms becomes dominant because the ratio of surface to volume atoms increases. Thus, we predict for metal particles that when particle size is decreased, the coordination number is reduced and energy bands narrow with coordination-number reduction. Such reduction was difficult to investigate in the present study. Very little data on the coordination-number reduction has been reported for vanadium particles. As far as I know, the coordination-number reduction has been reported only for tin particles.[17]

Energy-band narrowing with coordination-number reduction, mentioned above, is attended with the change in the distribution of the density of states (DOS) of the energy bands: the DOS of the occupied conduction bands (the conduction bands from the bottom to the Fermi level) usually increases at the upper portion and decreases at the lower portion.[18] If the DOS at the FL in the region near the state Σ_1 is increased in such a change, the transition FL near $\Sigma_1 \to \Sigma_4$ should be strengthened. This point was difficult to investigate in the present study. For vanadium particles, there has been very little data on the influence of the energy-band narrowing on the DOS at the Fermi level.

It is well established that lattice constants of metal particles contract with decreasing particle size (Sec. I).[7,8] It has been reported for bcc transition metals (iron and chromium)[19] that the nearest-neighbor interatomic distances contract (about 25%–30% contraction) in the transition from bulk state to clusters consisting of a few atoms. From these, lattice constants of vanadium particles in the present study should contract with decreasing particle size. It has been accepted that energy bands broaden with lattice contraction.[20] Energy-band broadening with lattice contraction has been found for metal particles (copper, gold, and ruthenium) in previous studies[8] where the samples were prepared by the same method as that of the present study. Lattice contraction is presumably conspicuous for weight thickness thinner than about 3.8 nm (Sec. III A). It is thus reasonable to consider that when weight thickness is thinner than about 3.8 nm, energy bands of vanadium particles broaden with lattice contraction.

Using the augmented-plane-wave method, Papaconstantopoulos *et al.*[9] have calculated the energy band of vanadium self-consistently for normal and 5%-reduced lattice constants. As far as I know, the energy bands of vanadium at different lattice constants have been reported only by them.

Based on the calculated energy bands in Ref. 9, interband absorption due mainly to the transition FL near $\Sigma_1 \to \Sigma_4$ is changed by lattice contraction as follows. At the normal lattice constant, the Fermi level intersects state Σ_1 (Ref. 9), the bottom of which is positioned in the immediate vicinity of the Fermi level. In this case, the transition from the FL in the region near state Σ_1 to state Σ_4 is possible.[6] The energy bands of vanadium are broadened by lattice contraction.[9] With the energy-band broadening, the position of state Σ_1 is raised relative to the Fermi level, and then this state becomes empty.[9] As a result, the transition FL near $\Sigma_1 \to \Sigma_4$ ceases because state Σ_1 is empty. Thus, interband absorption due mainly to the transition FL near $\Sigma_1 \to \Sigma_4$ should weaken remarkably with energy-band broadening due to lattice contraction.

From this discussion, the remarkable weakening of interband absorption with peak at about 2.5–2.6 eV of vanadium particles (Fig. 3) can qualitatively be ascribed to the ceasing of the transition FL near $\Sigma_1 \to \Sigma_4$ caused by energy-band broadening due to lattice contraction. This confirms the contribution of this transition to the interband absorption. Presumably, the transitions between the FL of bands 3 and 5 (Ref. 6), with the exception of the transition FL near $\Sigma_1 \to \Sigma_4$, also weakly contribute to the interband absorption.

Laurent *et al.*[4] proposed the transition in regions near the Σ axis, but they did not specify the initial and final states.

Estimation of particle size and lattice contraction was difficult as mentioned in Sec. III A. In the present study, thus, the relation between particle size, lattice contraction, and weakening of the interband absorption was difficult to estimate quantitatively.

In Ref. 9, with the exception of state Σ_1, band 3 remains partly occupied under lattice contraction (e.g., along Γ-P line). From this, very weak interband absorption with peak at about 2.5–2.6 eV for the weight thickness of 0.76 nm [Fig. 3(d), Sec. III B] seems to show that under lattice contraction the transitions between the FL of band 3, remains partly occupied, and band 5 weakly contribute to the interband absorption. This point was difficult to study in detail in the present study.

In Ref. 9, the energy spacing $\Delta E_{1,4}$ between the bottom of state Σ_1 and state Σ_4 increases with energy-band broadening due to lattice contraction. The increase is about 14% (about 0.35 eV) for the 5% lattice contraction,[9] at which state Σ_1 is positioned above the Fermi level. At the normal lattice constant, $\Delta E_{1,4}$ almost equals $\Delta E_{F1,4}$, because the bottom of state Σ_1 is positioned immediately next to the Fermi level.[4,6,9] The peak position of the interband absorption, which corresponds to $\Delta E_{F1,4}$, is almost constant (about 2.5–2.6 eV) in Figs. 3(a)–3(c); that is, an increase in $\Delta E_{F1,4}$ (i.e., in $\Delta E_{1,4}$) was not found. This shows that the position of the bottom of state Σ_1 is raised above the Fermi level in a small increase in $\Delta E_{1,4}$. Such a rise seems to be because the bottom is positioned immediately next to the Fermi level.

Energy-band broadening due to lattice contraction in vanadium particles, mentioned above, may be the result of competition with energy-band narrowing due to coordination-number reduction. In the present study, it was difficult to investigate this competition. There has been very little study of the mechanism of the competition between energy-band broadening due to lattice contraction and energy-band narrowing due to coordination-number reduction.

If electrons of the SiO_2 matrix occupy state Σ_4 in the energy bands of vanadium particles, the transition FL near $\Sigma_1 \rightarrow \Sigma_4$ would be restricted and thus interband absorption due mainly to this transition would weaken remarkably as in Fig. 3. There is very little data on the Fermi energy E_F of vanadium particles. This E_F is assumed to be the same as that of the bulk. As in the case by Ashcroft and Mermin,[21] E_F of bulk vanadium was calculated from the lowest valence (2) (Ref. 22) and the lattice constant (0.303 nm).[23] E_F of vanadium particles is about 4.5 eV higher than that of bulk silver, and E_F of bulk silver is about 6.3 eV higher than the valence-band maximum of SiO_2.[24] From these values, E_F of vanadium particles is much higher (about 10.8 eV) than the valence-band maximum of SiO_2. Thus, the valence band of SiO_2 does not overlap state Σ_4 lying at values higher than E_F, i.e., the electrons of the SiO_2 matrix cannot occupy state Σ_4. Therefore, the remarkable weakening of the interband absorption is not caused by the occupation of state Σ_4.

V. SUMMARY

Transition for interband absorption with peak at about 2.5–3.0 eV of vanadium was studied experimentally. It was found that when the size of vanadium particles is decreased, the interband absorption weakens remarkably. This change can qualitatively be attributed to the ceasing of the transition FL near $\Sigma_1 \rightarrow \Sigma_4$, based on the shift of the position of state Σ_1 with energy-band broadening due to lattice contraction. Therefore, the contribution of this transition to the interband absorption, proposed by Romaniello *et al.*,[6] was confirmed.

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