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Optical properties of single-crystal TaSi₂ in the photon-energy range 0.6–20 eV

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Polarized reflectivity spectra of single-crystal TaSi₂ have been measured in the photon-energy range 0.6–20 eV to examine the electronic structure. An anisotropy has been definitely found below 12 eV. The complex dielectric functions and the optical conductivities are determined by Kramers-Kronig analysis. The spectral structures are discussed in terms of interband transitions among Ta 5*d* states and Si 3*s*-3*p* states, in comparison with published results on the density of states. The effective numbers of electrons contributing to optical transitions are also discussed.

INTRODUCTION

Refractory-metal (group-IVA, -VA, and -VIA) disilicides have good thermal and chemical stability, and high electrical conductivity. Their compatibility with conventional polysilicon processes has attracted attention in connection with application in very large-scale integration technology such as interconnects, gate materials, and Schottky barriers.¹ Most of the studies have concentrated on thin-film formation and characterization. The physical properties of single crystals have been less known so far.

In our previous paper, we presented the optical data of TiSi₂ single crystals up to vacuum ultraviolet (vuv) range.² Single crystals eliminate ambiguities common to polycrystalline samples arising from component fluctuation, structural inhomogeneity, and surface roughness. Moreover, surface treatment was performed to remove oxide layers on surfaces of as-grown crystals and restore the reflectivity. These optical data of single crystals provided valuable information concerning the electronic structure. In this paper, we apply this method to TaSi₂.

TaSi₂ has already received practical applications as a contact material in the last decade. The electronic structure of the valence and conduction bands of TaSi₂ has been studied by optical spectroscopy,^{3,4} electron spectroscopy,^{5–8} and band calculations.^{5–7,9} Specifically, x-ray

photoemission (XPS) and bremsstrahlung isochromat spectra (BIS) of systematically chosen transition-metal disilicides have been well described by the calculated spectra including matrix elements as well as the density of states (DOS).^{6,7} The overall band features originating mainly from Ta 5*d* states and Si 3*s*-3*p* states are now generally accepted. On the other hand, optical data of single-crystal TaSi₂ have not yet been reported. Only data for thin films prepared by sputtering are available in the range from 0.5–6.0 eV.^{3,4} An optical spectroscopic study up to the vuv range is therefore desirable for examining the electronic structure in detail.

Polarized-reflectivity (*R*) spectra of single-crystal TaSi₂ in the photon-energy range 0.6–20 eV are presented in this paper. The *R* data are transformed by Kramers-Kronig (KK) analysis into complex dielectric functions ($\bar{\epsilon}$) and optical conductivities (σ_{opt}). The spectral structures of σ_{opt} are interpreted as interband transitions corresponding to the DOS features of the published energy bands.^{6,9} The effective number of electrons contributing to optical transitions are also obtained from $\bar{\epsilon}$.

EXPERIMENTS

Single-crystalline samples were prepared in the vapor phase by chemical-transport reactions. Reacted tantalum

silicide (5–10 g) was degassed in the reaction quartz crucibles (35 mm in diameter and 200 mm in length). The transport agent I_2 was added from an enclosed soft glass ampoule in the already sealed crucible. The temperature of the charge was between 1100°C and 1150°C, whereas the growth temperature was between 1030°C and 1100°C. High temperatures and small temperature differences between the charge and growth zones improved the growth conditions and large crystals, platelike or needlelike, have been obtained after 3–4 weeks. A typical dimension of the sample surface used in the measurements was $1 \times 2 \text{ mm}^2$. The crystal structure of some samples has been checked by x-ray powder-diffraction analysis. It is the hexagonal C40-type structures [space group $D_6^4 (P6_222)$]. The lattice parameters are $a = 4.7821 \text{ \AA}$ and $c = 6.3693 \text{ \AA}$.¹⁰ The orientation of the sample was determined by x-ray-diffraction patterns.

The R spectra were measured at room temperature in two different systems, depending on the photon-energy range. They were measured with a 0.4-GeV electron-storage ring at Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo, in the photon-energy range 3–20 eV. The double-beam system was used in the photon-energy range 0.6–4.0 eV. Detailed procedures were described in Ref. 2. The absolute values of the reflectivity were determined at 2.41 eV using an Ar^+ laser and a photometer. Specimens were carefully etched by HF and HNO_3 solution just before every measurement to minimize the effect of surface oxidation. The relative accuracies of the obtained reflectivity were about $\pm 5\%$ in the range below 4 eV and about $\pm 10\%$ in the vuv range. These inaccuracies were mainly dominated by the imperfect reproducibility of the surface treatments.

RESULTS AND DISCUSSION

The R spectra are shown in Fig. 1. The solid and dashed curves correspond to spectra for lights polarized parallel and perpendicular to the c axis ([0001]), as indicated by $E_{\parallel c}$ and $E_{\perp c}$, respectively. In each spectrum, a sharp cutoff occurs at around 1 eV and is followed by

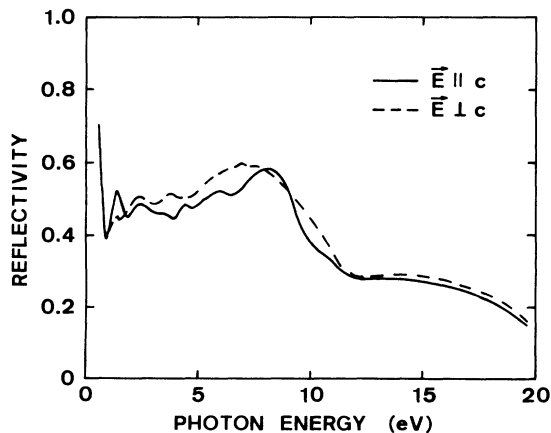


FIG. 1. Reflectivity spectra of $TaSi_2$ at room temperature. Solid and dashed curves correspond to the spectra for lights polarized parallel and perpendicular to the c axis, respectively.

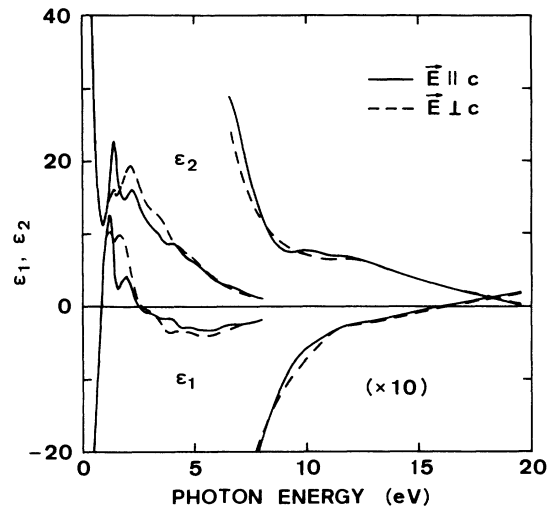


FIG. 2. Complex dielectric functions ($\bar{\epsilon}$) of $TaSi_2$. Upper and lower parts correspond to imaginary (ϵ_2) and real (ϵ_1) parts of $\bar{\epsilon}$, respectively. The spectra in the range above 6.5 eV are magnified by 10.

some structures in the visible range, a massive peak around 7–8 eV, and a broad hump around 15 eV. Definite anisotropy is seen in the range below 12 eV. The $E_{\parallel c}$ spectrum is more structured than the $E_{\perp c}$ spectrum: The $E_{\parallel c}$ spectrum has a sharp peak at 1.41 eV, three small structures at 2.40, 4.38, and 5.95 eV, and a large peak at 8.16 eV, whereas the $E_{\perp c}$ spectrum has only two small structures at 2.33 and 3.69 eV, and a great peak at 6.98 eV.

The complex dielectric function

$$\bar{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$$

is obtained by the KK analysis of the R spectra to interpret the optical properties from a microscopic point of view. The $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ spectra are shown in Fig. 2. The R spectra are extrapolated into the unmeasured range in this analysis. In the lower photon-energy range, intraband transition due to free carriers is dominant. The published R data of thin films are then well described by the Drude model with two parameters; the plasma frequency ($\omega_p \approx 2.7 \text{ eV}$) and the mean free time between scattering events ($\tau \approx 1.1 \times 10^{-14} \text{ sec}$).³ These parameters are also estimated from the dc conductivity $\sigma = \omega_p^2 \tau / 4\pi$. The anisotropy of the dc conductivity is known to be small:^{11,12}

$$\sigma([0001]) = 5.0 \times 10^4 \Omega^{-1} \text{ cm}^{-1}$$

and

$$\sigma([1010]) = 2.5 \times 10^4 \Omega^{-1} \text{ cm}^{-1}$$

at 293 K. Accordingly, one may extrapolate the $E_{\parallel c}$ and $E_{\perp c}$ spectra by the same unpolarized spectrum described by the ω_p and τ of the thin films. In the higher photon-energy range, the R spectra are extrapolated by the conventional method;

$$R(E) = R(20 \text{ eV})(20 \text{ eV}/E)^s.$$

The parameter s is adjusted so as to minimize the deviation between the calculated optical constants and the

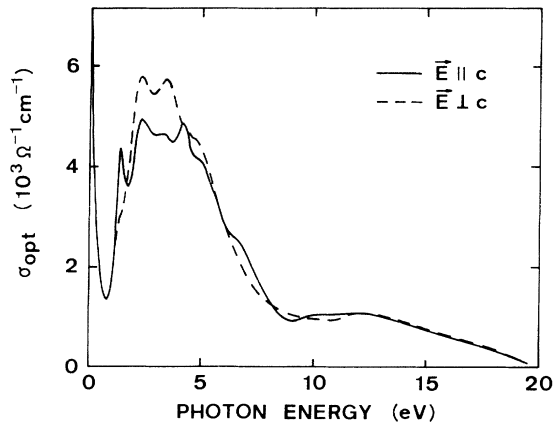


FIG. 3. Optical conductivities of TaSi₂.

published data determined by ellipsometry at 1.960 eV: $(n, k) = (3.44, 2.38)$ for thin films.³ The average of our data for $E_{||c}$ and $E_{\perp c}$ was compared with their data. The optimum s value was 6.8.

The solid and dashed curves in Fig. 2 correspond to the $E_{||c}$ and $E_{\perp c}$ spectra, respectively. The right half of the spectra were magnified by 10 for improved visibility. In the ϵ_2 spectra, the peaks of the reflectivity around 7–8 eV almost disappear, and new humps at 10 and 12 eV appear instead of the hump around 15 eV in the R spectra. Other features are similar to those of the R spectra. The present result improves the earlier published data in some points. First, the data of single crystals eliminate all the problems of polycrystalline films and samples, and provide definite anisotropy. Second, the ϵ_2 data in the vuv range are determined and the accuracy of the KK analysis is increased by the R data over the wider range.

The ϵ_2 value decreases by a factor of $1/\omega$ even if the oscillator strength and the joint density of states remain constant, and overall features of interband transitions are not easily seen in the $\bar{\epsilon}$ spectra. Accordingly, the optical conductivity $\sigma_{\text{opt}} = \omega\epsilon_2/4\pi$ is shown in Fig. 3 to interpret the spectral structures in terms of interband transitions. Each spectrum is dominated by a great peak extending in the range 0.5–8 eV followed by a small hump located at about 12 eV. An anisotropy is definitely seen in the lower range: The $E_{||c}$ spectrum has a peak at 1.43 eV, whereas the $E_{\perp c}$ spectrum has only a shoulder there. On the other hand, the peaks around 2.3 and 3.4 eV and the shoulder around 5 eV for the $E_{||c}$ are smaller than those for the $E_{\perp c}$. Moreover, the peak at 4.11 eV and the shoulder at 6.9 eV for $E_{||c}$ are not seen in the $E_{\perp c}$ spectrum.

According to the ultraviolet-photoemission-spectroscopy, XPS, and bremsstrahlung-isochromat-spectroscopy (BIS) studies of transition-metal disilicides,^{6,7,13} the overall features of their valence and conduction bands are dominated by Si s and p states, and metal d states. Most of the Si s states are concentrated at 8–10 eV below the Fermi level E_F and partially contribute to the conduction bands. Due to a hybridization between the Si p and the metal d states, they contribute the large peaks in DOS below and above E_F . The metal d states are distributed in a narrower range, about 6 eV below and above E_F , than the Si p states. The states orig-

inating mostly from the metal d states are situated in between the bonding and antibonding states of the p - d -hybridized states. They are called as "quasigap" states. The center of the quasigap states moves across E_F from above to below as the number of metal d electrons increases from Ti to Ni. As for TaSi₂, the DOS has been presented in Fig. 8 of Ref. 9. The XPS and BIS spectra in Fig. 4 of Ref. 6 are also beneficial, although d states contribute to XPS and BIS more strongly than p states do. These two results of the band distribution are comparable in overall features: The bonding and antibonding states of Si $3p$ -Ta $5d$ hybridized states dominate the overall feature including two peaks located 2.0 eV below and 4.0 eV above E_F , and the quasigap states consisting largely of Ta $5d$ states are located in between the bonding and antibonding states. However, minor structures of the quasigap states in the two band distributions are different because the XPS and BIS spectra include broadening due to the experimental resolution of 0.7 eV. Specifically, the DOS of Ref. 9 exhibits a small peak at E_F and a small band gap in the conduction band at about 1.5 eV above E_F , with two peaks at both band edges.

The joint density of states and transition probability are needed to interpret the anisotropic structures of the σ_{opt} spectra in detail, but they have not yet been reported. Accordingly, these spectral structures are roughly ascribed to interband transitions among the DOS features, by comparing their energies. The structures around 6–8 eV probably correspond to the transitions between the bonding and antibonding states. The structures from 1 to 6 eV are related to the quasigap states. The sharp structures in this range may be explained by the structured DOS of Ref. 9. In particular, the sharp structure at 1.43 eV agrees well with the energy separation between the E_F and the lower edge of the band gap in the conduction band. On the other hand, the spectral structures above 8 eV cannot be sufficiently interpreted because of overlap of many transitions. However, it is probable that they are partially related to the Si s states concentrated at about 10 eV below E_F as well as Ta d and Si p states.

The effective number of electrons per molecule contributing to the optical properties over a finite frequency range, $n_{\text{eff}}(\omega)$, is obtained from the finite-energy oscillator-strength (f) sum rules.¹⁴ Contribution at zero frequency is estimated from $\sigma_{\text{opt}}(0) = 3.75 \times 10^4 \Omega^{-1} \text{cm}^{-1}$.¹¹ The spectral structures from 1 to 8 eV dominate the f sum rule. The $n_{\text{eff}}(\omega)$ gently increases above 8 eV, and reaches about 5.7 electrons per molecule at 20 eV. Since $E = 20$ eV almost exhausts the valence-electron oscillator strength and is lower than the lowest core transitions from Ta $4f$ states (23 eV),⁵ $n_{\text{eff}}(20 \text{ eV})$ roughly corresponds to the number of valence electrons. The number of valence electrons per molecule is evaluated as 13 for the $5d^3 6s^2$ configuration of Ta and the $3s^2 3p^2$ configuration of Si. Consequently, about two-fifths of the valence electrons contributes to the optical transition below 20 eV.

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