Optical properties of tantalum disilicide thin films

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$TaSi_2$ polycrystalline films, grown by sputtering and subjected to a preliminary chemical and structural characterization, were studied by reflectance from 0.01 to 6 eV and thermoreflectance from 1 to 9 eV. The data were Kramers-Kronig transformed to obtain the dielectric functions. Low-energy response is discussed in terms of the Drude model; some indications concerning the interband structures are drawn on the basis of calculated density of states and of photoemission results. A comparison is made with the optical properties of isoelectronic pure refractory metals and their disilicides.

I. INTRODUCTION

In the last few years, extensive work on the physical properties of transition-metal–silicon compounds has been performed due to their technological interest. Experimental and theoretical studies aim to investigate structural and transport properties, identify the roles of the metal and silicon in the band structure, reveal the metal-silicon mixing or hybridization, and contribute to the understanding of chemical bonding. Particularly, refractory metal silicides have attracted attention because of their rather low resistivity and their high-temperature stability; in this context, tantalum disilicide has received much interest in microelectronics as a possible new metallization material for silicon integrated circuits.[1-3]

At present, several aspects of $TaSi_2$ have been examined. Electrical resistivity measurements[2,4] have been used in conjunction with Hall measurements[2] in order to determine transport parameters. Various techniques have been applied to investigate structural properties and crystallization kinetics: differential scanning calorimetry and electrical resistivity in nonisothermal conditions,[5] Rutherford backscattering, x-ray diffraction, Auger-electron spectroscopy, and scanning and transmission electron microscopies.[4] The electronic structure of different refractory disilicides, including $TaSi_2$, has been investigated by photoelectron spectroscopy with synchrotron radiation,[6] and the results have been interpreted[6,7] on the basis of calculated density of states. Detailed calculations of the $TaSi_2$ electronic band structure and of its correlated optical properties have not been published until now.

In this paper we present optical data on $TaSi_2$, which we believe to be heretofore unreported. Reflectance (R) measurements, from the far infrared to the ultraviolet, and thermoreflectance (TR) measurements from visible to vacuum ultraviolet were preformed. Dielectric functions were derived using Kramers-Kronig transformations and the spectrum was analyzed in terms of intraband and in-terband transitions. The disilicide's optical data were compared with the corresponding data for the pure Ta,[8] so that the role of Si in the compound formation could be investigated. Our analysis is supported by previous works[8,9] on electronic structure of isoelectronic refractory metals V, Nb, Ta, and of their silicides.[6,7,10]

II. EXPERIMENTAL PROCEDURE AND RESULTS

$TaSi_2$ films, with total thicknesses of 200 nm, have been prepared by sputtering from two targets of silicon and tantalum on thermally oxidized silicon wafers. These samples as deposited are amorphous; a thermal annealing at 900 °C in vacuum produces the formation of stoichiometric polycrystalline $TaSi_2$. We recall that $TaSi_2$, as V and Cr disilicides, crystallize in the hexagonal $C40$ structure (3 molecules per unit cell), with lattice constants $a = 4.783$ Å and $c = 6.565$ Å.[11]

Thickness and sample composition were controlled using 2-MeV ^{4}He Rutherford backscattering, while the material's purity was controlled by electron Auger spectroscopy. X-ray diffraction[4] was used to identify the phases and the extent of crystallization in order to determine the effect of annealing: sharpening and narrowing of diffraction peaks indicate grain growth upon annealing. In our samples the grain size approached the limit of the film thickness. Films with larger grains had lower electrical resistivity, about 50 $\mu\Omega$ cm at room temperature.

Absolute reflectivity measurements at near-normal incidence and at room temperature were performed in the 0.5–6 eV photon energy range using a reflectometer mounted on a Perkin-Elmer model 330 automatic spectrophotometer, producing R with an accuracy of 0.5%. In the photon energy range from 0.01 to 0.5 eV the reflectivity was obtained by a Fourier-transform spectrometer Bruker IFS 113v, using an Al mirror as reference. In the overlapping spectral range, the R values from two spectrophotometers agree within the limits of

experimental uncertainty. As in other metal disilicides,[12,13] both the R spectrum and consequently the effective dielectric function are expected to be influenced by surface roughness or native oxide surface layer, mostly in the uv range ($\omega > 3$–4 eV).

The resulting R spectrum is shown in Fig. 1, together with that of pure Ta.[8] The overall shapes of the two spectra are similar and are typical of metals: the high reflectivity in the infrared is followed by a sharp cutoff near the free-carrier plasma resonance. However, the Dingle plateau (for $\tau^{-1} < \omega < \omega_p$, where τ is the electron scattering time and ω_p the plasma frequency of free carriers), usually present in a good Drude metal, does not develop, because of the onset of strong interband transitions at relatively low energies. Reflectivity of $TaSi_2$ drops at about 1 eV, and presents two relevant structures at 1.4 and 2.4 eV, followed by two weak shoulders at 4 and 5.8 eV. We note that the major difference of the R spectrum of $TaSi_2$ with respect to Ta appears to be a shift to lower energies: in fact the strong cutoff at ≈ 1 eV and the first structure at ≈ 1.4 eV in $TaSi_2$ lie at ≈ 2 and ≈ 3 eV, respectively, in Ta.

To provide a more complete description of the optical properties we calculated the complex dielectric function $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ and the complex refraction index $\tilde{n}(\omega) = n(\omega) + ik(\omega)$ employing the Kramers-Kronig relations: the results are plotted in Fig. 2. The R spectrum was extrapolated beyond the highest experimental energy ω_0 with a tail[14] $R(\omega) = R(\omega_0)(\omega_0/\omega)^s$. The s value was determined in order that the calculated n and k values agreed with the experimental values at $\omega = 1.96$ eV
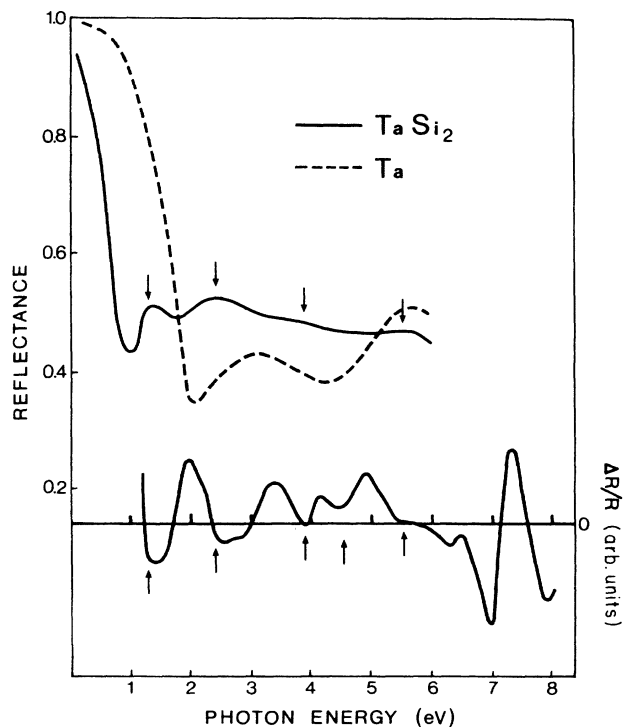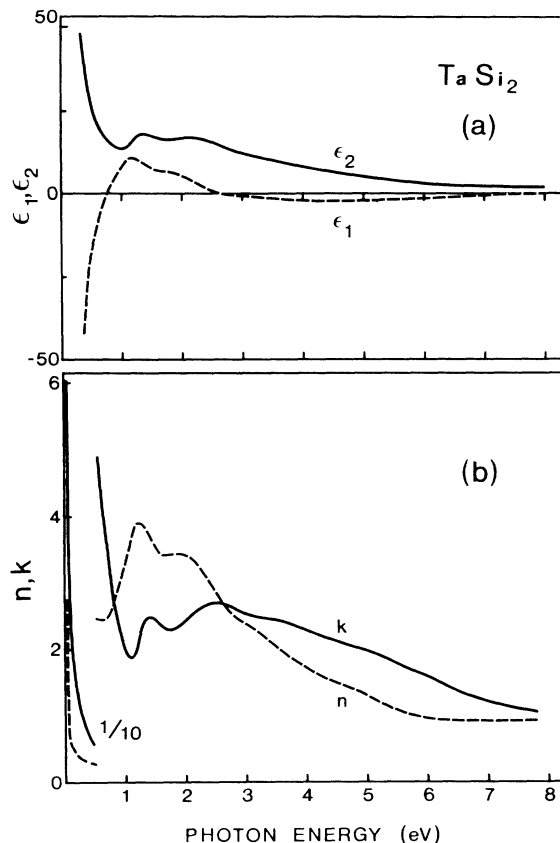

FIG. 2. (a) Real and imaginary parts of the dielectric function of $TaSi_2$. (b) Refraction index and extinction coefficient of $TaSi_2$.

FIG. 1. Room-temperature reflectivity R of $TaSi_2$ and pure Ta;[8] the thermomodulated reflectivity is also shown.

($\lambda = 632.8$ nm), carefully measured with a Gaertner ellipsometer L115B. The corresponding R values obtained using the ellipsometer and the spectrophotometer coincide within the limits of experimental uncertainty. We note that the resulting value of $s = 2.12$ does not correspond to the constraint $s = 4$ used, for example, in the case of Pt silicides:[15] this is not surprising, because it is well known[8] that an inverse fourth law does not work up to energies much higher than in our spectra even for pure transition metals.

The thermomodulated reflectance technique with its derivative nature, was used in order to enhance weak structures that may be unseen in R. The TR spectrum, measured at 95 K from 1 to 9 eV using an apparatus described in detail in a previous paper,[16] is also reported in Fig. 1. We interpreted the TR spectrum as a local derivative of R with respect to the energy[17] so that zero crossings (from positive to negative) or positive minima correspond to peaks or shoulders in R, respectively. We can see that the structures are better resolved in TR than in R, particularly the ones at high energy, but their positions (indicated by arrows in Fig. 1) correspond very well in both spectra.

III. DISCUSSION

Theoretical studies on the optical and electronic properties of pure refractory metals V, Nb, and Ta (Refs. 8

and 9) indicate the following common features: (a) roughly 50% of the states below the Fermi level (E_F) are d-like, 25% are s-like and 25% are p-like; (b) the strong d-d bonding-antibonding interaction splits the d-bands into two groups of states which straddle E_F; (c) below 4 eV the majority of the strength in R spectra is due to transitions between sd- and p-bands; in fact these transitions shift the cutoff in R to lower energies, differing from the case of near-noble metals (Ni, Pd, Pt), where R decreases almost mononotonically up to ≈ 10 eV; (d) the plasma minimum in the reflectivities of these metals moves to higher energies by passing from V to Nb and Ta, because the smaller lattice constant in V forces greater overlapping between p states of neighboring atoms and therefore shifts the p-like bands to higher energies.

Generally the electronic properties of transition-metal silicides differ from those of respective pure metals, mainly in the d-band location and width;[10] moreover, new features occur, characteristic of the $Si(p)$-metal(d) bonding interaction. In the case of refractory metal silicides, the main features, derived by calculated electronic structure[6,7,18] and experimentally supported by photoemission results,[6] are (a) the occupied bands are dominated by metal d-derived states up to 3–4 eV from E_F; their density of states profile broadens and shifts to lower energies by going from V to Ta; (b) at greater distances from E_F silicon p-state character dominates the Si-metal bonding interaction; (c) nonbonding d states are found at E_F; (d) the bands are characterized by antibonding p-d interaction for energies greater than E_F.

On this basis the observed structures at low energies ($\omega < 4$ eV) in R can be attributed, as in Ta pure metal, to transitions from d to p bands. The lowering of these transitions with respect to Ta depends on d-d split reduction, due both to augmented Ta-Ta distance and coordination number lowering (from eight Ta atoms nearest neighbor at 2.86 Å in Ta metal, to six atoms at 3.24 Å in TaSi$_2$).

It is also interesting to note that, in contrast to pure metals, R spectra of refractory metal and near-noble metal silicides have similar shapes. This is also true in the latter because the center of gravity of d bands lowers below E_F with increasing Si content, allowing transitions from d to p bands to arise.

Although a definitive and detailed assignment of the structures requires the knowledge of joint density of states, our attribution is supported by our preliminary measurements of VSi$_2$ showing a similar spectrum, with the plasma cutoff and the interband structures shifted to lower energies with respect to both pure V and TaSi$_2$.

The infrared optical properties of TaSi$_2$ can be described by the aforementioned free-electron-gas model (Drude model) which has only two parameters, τ and ω_p, appearing in the complex dielectric function

$$\bar{\epsilon}(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \ .$$

A common test for the applicability of this model was used by plotting $\omega\epsilon_2(\omega)$ versus $\epsilon_1(\omega)$, which should yield a straight line. Indeed, the resulting plot is satisfactory over the limited range $0.06 \leq \omega \leq 0.25$ eV. The lower limit is due to the error in R, because it is well known[19] that even small ($\pm 0.1\%$) errors in far-infrared reflectance translate into a large uncertainty in the Drude parameters. The upper limit is due to the onset of interband transitions: in transition-metal silicides, they are present at still lower energies,[20] but their contribution to $\bar{\epsilon}(\omega)$ is relatively small compared to the Drude term. The values of Drude parameters obtained from a best fit on R or on $\bar{\epsilon}(\omega)$ are $\omega_p \approx 2.7$ eV and $\tau \approx 1.1 \times 10^{-14}$ sec, producing an optical conductivity, at zero frequency, $\sigma_{\text{opt}} = \omega_p^2 \tau / 4\pi \approx 1.64 \times 10^4 \ \Omega^{-1}\text{cm}^{-1}$. Although some caution is required as to their effective meaning (due to a test of the Drude model performed on a limited range,[21] and to errors in experimental far-infrared data and their effects on Kramers-Kronig analysis), these values tend to be in reasonable agreement with dc transport measurements which yield a σ_{dc} ranging from 1.6 to 2.3×10^4 $\Omega^{-1}\text{cm}^{-1}$ for sputtered TaSi$_2$ films.[2,5] Moreover, ω_p and τ values for TaSi$_2$ are typical of other silicides, for example, Pd$_2$Si where $\omega_p = 2.87$ eV and $\tau = 2.2 \times 10^{-14}$ sec were obtained by transport measurements.[22]

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