Optical properties of single-crystal titanium disilicide

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The near-normal reflectivity of single-crystal $TiSi_2$ from 0.01 to 8 eV and the dielectric functions obtained by Kramers-Kronig (KK) analysis are presented. The effect of an oxide overlayer on the optical properties is also considered. The low-energy response is discussed in terms of the Drude model; the higher-energy spectrum is interpreted on the basis of available information about the electronic structure. A comparison is made with the optical properties of pure Ti and other refractory-metal silicides.

INTRODUCTION

Refractory-metal silicides have been subjected to an extensive study due to their interest in the very-large-scale integration VLSI technology as Schottky barriers, Ohmic contacts, and low-resistivity interconnections.[1] They have attracted attention because of their excellent electrical properties and their high temperature stability. They have been examined under different physical aspects.[2] In this paper we focus on titanium disilicide, which is the only known stable phase of the Si-Ti reaction and which is one of the most conductive silicides.[3-5] The published results on $TiSi_2$ show that a variety of experimental techniques was used mainly to investigate chemical bonding and reactions at the Ti/Si interface and to characterize structural and transport properties in the polycrystalline phase. In particular, the Si-metal reaction was monitored by Rutherford backscattering spectroscopy,[6] medium-energy ion scattering,[7] and x-ray diffraction;[6,8] the chemical properties were studied using conventional and synchrotron photoemission[9,10] and Auger-electron spectroscopies.[9]

Detailed electronic structure calculations have been performed for refractory-metal silicides such as V, Cr, Mo, and W disilicides,[11-14] and the results, mainly in the form of densities of states (DOS), have been compared with the experimental data. Only recently the electronic properties of $TiSi_2$ have been considered within a wider study on 3d, 4d, and 5d transition-metal silicides in their real crystal structures,[15] in order to show the importance of including matrix elements to reproduce x-ray photoemission (XPS) and bremsstrahlung isochromat spectroscopy (BIS) spectra starting from the theoretical DOS.

Generally, optical properties of transition-metal silicides have not been investigated due to the lack of single crystals. We present here optical data on single-crystal $TiSi_2$, which have not been reported hitherto. It must be evidenced that the optical analysis of the single crystal eliminates all the problems arising in $TiSi_2$ polycrystalline films and which are connected to possible interferences with substrate interface and to structural inhomogeneities, such as intergranular phases and surface roughness, typical of thin-film growth.

Reflectivity (R) measurements were performed from the far infrared (FIR) to the vacuum ultraviolet, and the dielectric functions were derived using Kramers-Kronig transformations, checked through an ellipsometric measurement at one selected energy. The influence of an unavoidable oxide overlayer on the optical functions was also considered. The spectra were analyzed in terms of intraband and interband transitions by using the aforementioned information about electronic properties of refractory-metal silicides.

EXPERIMENTAL PROCEDURE AND RESULTS

$TiSi_2$ single crystal has been prepared from the commercially purchased powder compound of 95% purity (Ventron). Chemical transport reactions have been used in order to grow single crystals with iodine as a transport agent (alternatively, bromine or chlorine can also be used). The reaction transport was going on during four to eight weeks in silica glass crucibles, 20–40 mm in diameter and 200 cm in length. Tube furnaces with two

separately regulated zones were used to maintain a temperature gradient corresponding to the temperatures 1120 and 1080 °C at the ends of the crucible, respectively. Crystals with perfect growth faces arose in the cold zone. The material was not totally transported and it is expected that the process contributed to some purification of the end products with respect to the starting material. However, the quartz crucible was partially etched so that the oxygen contamination is possible.

The crystalline phase of the sample was identified by x-ray diffraction with a 4-circle Philips PV 1100 diffractometer: $TiSi_2$ has an orthorhombic structure, with lattice parameters $a = 8.295$ Å, $b = 4.796$ Å, and $c = 8.554$ Å. It was also established that the surface of our sample is a [00*l*]-type-oriented surface.

Reflectivity measurements with unpolarized light at near-normal incidence and at room temperature were performed in the 0.01–0.5 eV photon energy range using a Fourier-transform spectrometer Bruker IFS 113v, with a relative accuracy of ±1%, and with an Al mirror as reference, whose absolute R was carefully measured. In the photon energy range from 0.5 to 6 eV the reflectivity was obtained by a Perkin Elmer 330 automatic spectrophotometer, with a relative accuracy of ±5%. In the overlapping spectral region, R values obtained from the two instruments agree within the limits of experimental uncertainty. A dc hydrogen lamp and a Minuteman 302-VM monochromator were used for photon energies between 6 and 8 eV, and the relative accuracy was about ±10%. The reflectivity errors in all the energy regions are random and due mainly to the sample positioning, which limits the reproductibility of each measurement.

A problem arises from the high reactivity of Ti with oxygen, which leads to formation of a titanium oxide layer unless special handling techniques (ultrahigh vacuum or inert atmosphere) are used.[16,17] As it is well known, the Ti oxides may display a variety of structures and electrical properties which range from metallic behavior in TiO to insulating behavior in TiO_2. However, measurements combined of optical and Auger spectroscopy on titanium oxides grown on pure Ti under a variety of conditions[17] suggest that a layer some 80 Å thick of amorphous TiO_2 is formed in a few milliseconds from exposure to air. As regards the silicon-rich transition-metal silicides, most of them form SiO_2 in preference to metal oxide, while in the $TiSi_2$ case the Ti oxidation dominates.[18] Therefore, due to the decreased metal percentage with respect to the pure metal situation, it seems reasonable to assume on our $TiSi_2$ samples an amount of TiO_2 equivalent to a layer no more than 20÷30 Å thick. Repeated measurements of R on mechanical and chemical polished samples showed that the TiO_2 layer does not change appreciably over an interval of several hours. The effect of TiO_2 on the optical functions will be discussed below.

Reflectivity curve is shown in Fig. 1, together with that of pure Ti to make a comparison.[19] The latter corresponds to a Ti surface that, as in our experimental conditions, had not been particularly treated: its values are generally lower than surfaces cleaned in ultrahigh vacuum,[17] but no additional structures, due to the oxide, ap-
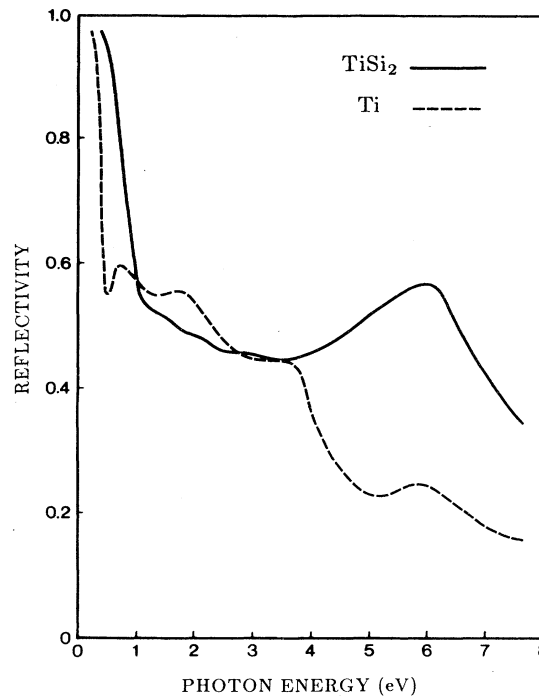

FIG. 1. Room-temperature reflectivity R of $TiSi_2$ and pure Ti (19).

pear in R up to 8 eV.

In the case of $TiSi_2$ we note a high reflectivity region in FIR, typical of a metal, a strong cutoff at about 1 eV, then two shoulders centered at 1.4 and 3 eV, and a great peak at 6 eV. Ti reflectivity spectrum from Ref. 19 shows a peak at 0.7 eV after the infrared cutoff and three structures at ≈1.6, 3.7, and 6 eV. The major differences between the two spectra are (i) the shift of the cutoff in R at higher energies in $TiSi_2$, and (ii) the region from 4 to 8 eV, where $TiSi_2$ is characterized by an abrupt rising in R, with the peak at 6 eV which is present in Ti as well, but with much less intensity.

To provide a more complete description of the optical properties, we have Kramers-Kronig analyzed our R data; the resulting complex dielectric function $\bar{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ and the complex refraction index $\bar{n}(\omega) = n(\omega) + ik(\omega)$ are plotted in Fig. 2. Although in general there is a direct correspondence among structures in ϵ_2 and R, we note that the peak at 6 eV, which is very strong in the R spectrum, is nearly absent in our ϵ_2. This occurs because the great oscillator strength of previous transitions exhausts the sum rule and forces ϵ_2 to decrease in this energy range.

To perform KK transformations we extrapolated the R spectrum beyond the last experimental energy ω_2 with a tail[20] $R(\omega) = R(\omega_2)(\omega_2/\omega)^s$; such extrapolation is expected to give quite good results if the parameter s can be adjusted to reproduce the value of some optical functions independently known at one or more selected energies. With that purpose we performed the measurement of n and k with a Gaertner L 125B ellipsometer, working at $\lambda = 632.8$ nm and at incidence of 70 deg; the R values ob-
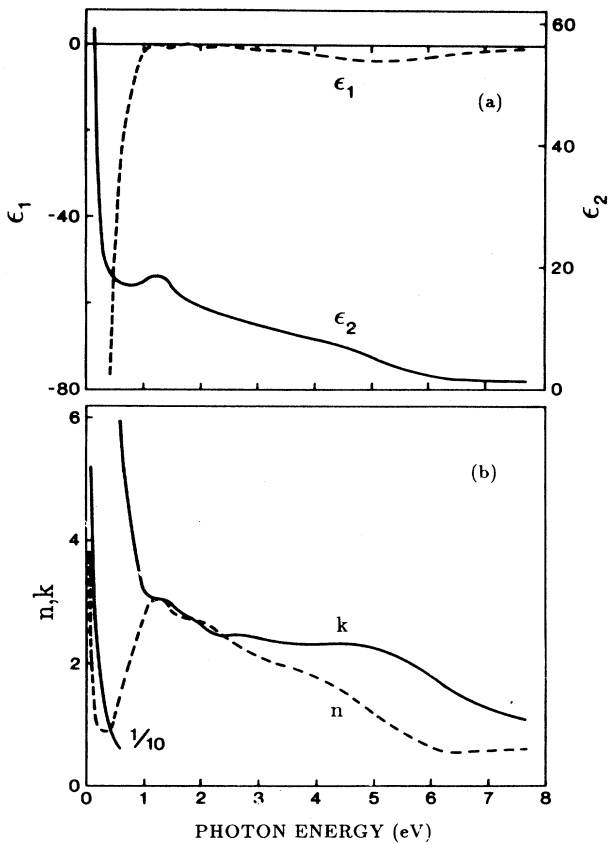
FIG. 2. (a) Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of $TiSi_2$. (b) Refraction index (n) and extinction coefficient (k) of $TiSi_2$.

tained using the ellipsometer and the spectrophotometer coincide within the limits of experimental uncertainty. The resulting value of s, determined so that the n and k values from KK transformations coincided at $\lambda = 632.8$ nm with ellipsometric values, was 2.85. We have to note that it does not correspond to the constraint $s = 4$ used, for example, in the case of Pt silicides.[21] This is not surprising, because it is well known[22] that an inverse fourth law does not work up to energies much higher than in our spectra, even for pure transition metals.

To evaluate the relative variation $\Delta \bar{n} / \bar{n}$ induced by errors in R, we have calculated $\bar{n}'$ from KK transformations using an R' spectrum shifted by ± 0.02 with respect to R. As expected, while in the infrared region $\bar{n}$ is very sensitive to small changes in R, for energies greater than 0.5 eV the maximum value of $\Delta \bar{n} / \bar{n}$ is about $\pm 7\%$.

To estimate the effects of TiO_2 on the optical functions, we employed a three-phase model: $TiSi_2$-substrate–TiO_2-film–ambient. In the limit of a film thickness $d \ll \lambda$, the following expression for the pseudo-dielectric function $\langle \bar{\epsilon} \rangle$ is obtained:[23]

$$\langle \bar{\epsilon} \rangle \simeq \bar{\epsilon}_s + \frac{4\pi i d}{\lambda} \frac{\bar{\epsilon}_s (\bar{\epsilon}_s - \bar{\epsilon}_{ox})(\bar{\epsilon}_{ox} - \bar{\epsilon}_a)}{\bar{\epsilon}_{ox}(\bar{\epsilon}_s - \bar{\epsilon}_a)}$$

$$\times (\bar{\epsilon}_s - \bar{\epsilon}_a \sin^2\phi)^{1/2} .$$

Here, ϕ is the angle of incidence, and $\bar{\epsilon}_s$, $\bar{\epsilon}_{ox}$, and $\bar{\epsilon}_a$ are the effective complex dielectric functions of the substrate, of the oxide, and of the ambient, respectively. In our case $\langle \bar{\epsilon} \rangle$ is the complex dielectric function, as given by KK analysis; $\langle \bar{\epsilon} \rangle$ is represented in Fig. 2 together with the complex refraction index $\langle \bar{n} \rangle$. In the equation above we used the experimental values of $\bar{\epsilon}_{ox}$ determined from ellipsometric measurements.[24] In the 2–6-eV energy range, where amorphous TiO_2 presents a strong absorption band centered at about 4 eV, they are well fitted by an analytical form.[25] Our calculations for a TiO_2 layer 20 Å thick indicate that this layer appreciably affects R for energy $E > 3$ eV, and a maximum change of $\approx 10\%$ in the absolute R occurs for $E > 4$ eV. Near the absorption peak of TiO_2 the relative changes in $\langle \bar{\epsilon} \rangle$ and in $\langle \bar{n} \rangle$ are about 40 and 20%, respectively. They decrease progressively as the energy is lowered, and become negligible for $E < 1.5$ eV. We can rule out that the TiO_2 overlayer is thicker than ≈ 20 Å, because it would induce a spurious structure in $\bar{\epsilon}_s$ and $\bar{n}_s$ spectra near 4 eV (where $\bar{\epsilon}_{ox}$ has a strong resonance), while the experimental curves present a flat behavior.

DISCUSSION

All the theoretical results on the electronic properties of transition-metal silicides indicate that the interaction between silicon $3p$ and metal d levels is a general feature related to the formation of the compounds.[2] This interaction determines the formation of hybrid p-d bonding and antibonding states straddling a nonbonding (purely d) region. In the case of $3d$ metal disilicides (from $CaSi_2$ to $NiSi_2$), relative energy positions of these regions depend on the d-band occupation in the pure metal, so that the nonbonding states move from above E_f for the lightest silicide to well below E_f as the metal atomic number increases.[26] The calculations also show partial d character, due to the p-d hybridization, of the states with energies less than E_f even in the first silicides of the set, where the atomic metal configuration has zero or only a few d electrons.

The density of states of $TiSi_2$ in the energy range from ≈ 4 eV below E_f to E_f is dominated by bonding states; nonbonding d levels start from E_f, and antibonding states are completely empty.[10,15] The bonding region gives the greatest contribution to the photoemission response which shows a peak near $1 \div 1.2$ eV below E_f.[26]

With this preliminary information, which essentially concerns the occupied valence states, we analyze our optical data by considering two different spectral regions typical of a metallic response: the intraband (or free-electron) and the interband regions. Starting from the latter, we recall that in pure Ti the interband absorption begins below 0.2 eV,[19] although it is small and without relevant structures; it arises by optical transitions from filled to empty states of the d bands (these transitions are partially allowed because the bands are strongly hybridized with s or p character). Interband transitions become stronger from 0.5 eV and induce the slope change in R which indicates the regime of direct optical transitions. The same situation happens in $TiSi_2$, where the

plateaulike region in R, developing for $0 < \omega < \omega_p$ in an ideal metal (Drude model, where ω_p is the free-carrier plasma frequency), does not appear. Interband absorption is superimposed on a free-electron background so that even at rather low energy it is impossible to clearly distinguish between the two contributes: low-energy interband transitions involve occupied hybrid p-d bonding levels near E_f and empty d levels above E_f. Transitions starting in the region where bonding states show a peak in the DOS spectrum have the most important results, because they determine both the slope change of R near 1 eV and the following shoulders. From the reflectivity data it appears that the mixed region where intraband and interband transitions coexist with comparable weights is more extended in the silicide, and that the contribution of interband transitions becomes dominant at higher energy than in pure Ti. The reason is probably due to the p-d interaction which in $TiSi_2$ creates a zone, just near E_f, where the DOS is lower than in Ti. Relatively few bands cut E_f, so that the possibility of interband transitions becomes strong only when the DOS reaches the peak at $1 \div 1.2$ eV below E_f.

It is clear that a complete attribution of the structures in R depends on the knowledge of the joint density of states (JDOS), because the dielectric function is related both to valence-band states (which are the states involved in photoemission spectra) and conduction-band states, with the intermediate of selection rules. However, we can say that the shape of the optical functions confirms the energy distribution of states theoretically foreseen, and provides information complementary to electron spectroscopy techniques.

Because of the lack of optical data on the isoelectronics silicides (Zr and Hf silicides), we compare $TiSi_2$ with those few refractory-metal silicides which have been optically studied up to now.[27−29] The optical properties seem quite similar; however, we have to remark that the cutoff region in R is less pronounced than, for example, in $TaSi_2$,[27] $MoSi_2$,[28] and WSi_2,[29] where R reaches a sharp minimum and then rises noticeably. We can argue that the quasigap observed in these disilicides, which induces strong transitions onsets beyond 1 eV, is greater than in $TiSi_2$, where the displacement of bonding states to higher binding energies is only a little noticeable in comparison with heavier silicides.[26] It follows that we have a more broadened interband region and a less structured reflectivity spectrum beyond the cutoff.

As to the free-carrier-related optical properties, we studied the low-energy response with the aim of extracting the parameters ω_p and τ, the plasma frequency and the electronic scattering time, respectively, which enter in the Drude dielectric function

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

and which can be compared with the analogous quantities obtained by transport measurements; here ϵ_∞ is the high-frequency dielectric constant. The applicability of the Drude model may be tested by plotting $\omega\epsilon_2(\omega)$ versus ϵ_1, which should give a straight line. This happens within the limited range $0.06 < \omega < 0.12$ eV. As pointed out above, the upper limit is due to the onset of the interband transitions, while the lower limit is due to the error in R, because even small ($\pm 1\%$) errors in FIR reflectivity translate into a large uncertainty in the Drude parameters.[30] The values of ω_p and τ obtained by analyzing the Drude region of $\bar{\epsilon}(\omega)$ are $\omega_p = 4.2$ eV and $\tau = 4.5 \times 10^{-14}$ s. The optical conductivity at zero frequency results $\sigma_{opt} = \omega_p^2 \tau / 4\pi \approx 1.6 \times 10^5$ Ω^{-1} cm^{-1}, so that the resistivity is $\rho \approx 6.4$ $\mu\Omega$ cm; this is in quite good agreement with four-points-probe electrical measurements, which give us $\rho \approx 10$ $\mu\Omega$ cm. dc resistivity has been measured in $TiSi_2$ polycrystalline samples,[3−5] and at room temperature it oscillates between 14 and 25 $\mu\Omega$ cm, depending on the silicide's growth procedure; therefore, electrical conductivity is higher in single crystals than in films, as expected and as appeared from previous results on other disilicides such as $CoSi_2$ and $MoSi_2$.[31,32] A more complete comparison between single crystals and polycrystalline $TiSi_2$ films, by means of optical and transport measurements, is in progress.

ACKNOWLEDGMENTS

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