PHYSICAL REVIEW B VOLUME 29, NUMBER 12 15 JUNE 1984

Dielectric function of monocrystalline $MoSi_2$ by spectroscopic ellipsometry

Ph. Ged*
Centre National d'Etudes des Télécommunications, Boîte Postale 98,
F-38243 Meylan Cédex, France

R. Madar and J. P. Senateur
Equipe de Recherche No. 155 associée au Centre National de la Recherche Scientifique,
Ecole Nationale Supérieure d'Ingénieurs Electriciens de Grenoble,
Boîte Postale 46, F-38402 Saint Martin d'Hères, France

(Received 22 November 1983)

The dielectric function of monocrystalline $MoSi_2$ has been investigated by spectroscopic ellipsometry in the (1–4.5)-eV range. The energy resolution of spectroscopic ellipsometry has been used for analyzing the mixing of metal *d* electrons and the silicon *p* electrons in the bulk monocrystalline disilicide, thus eliminating the contribution of intermediate phases. The dielectric tensor of $MoSi_2$ is seen to have the same tetragonal symmetry as the crystalline structure. Ellipsometric results are compared with published photoemission spectra.

INTRODUCTION

During the last few years metal silicides have been subjected to intensive analysis[1] both from a theoretical standpoint and for their potentialities in the silicon integrated-circuit technology. In order to understand the electronic structure of the silicides and their interface with silicon, electron spectroscopy techniques[2–4] have been used extensively, often with adjoining facilities of *in situ* metal deposition and reaction chambers.

The objective of this work is twofold. On one hand, we have investigated bulk monocrystalline $MoSi_2$. In contrast with the thin-layer approach, bulk properties can be assessed in this way without the possible interference of interfaces or other structural inhomogeneities. Furthermore, the use of single crystals eliminates the unwanted contribution of intergranular phases of polycrystalline samples. The Mo-Si system is of great interest because of refractory properties and the chemical stability of the silicon-rich metal disilicide. The respective metal and silicon contributions to the band structure of $MoSi_2$ have been looked into and compared both with measurements made on neighboring disilicides and with theoretical estimates from similar but somewhat simpler crystalline structures.[2]

This analysis as well as those carried out on other silicides shows a complex mixing of the metal *d* electrons and the Si *p* electrons in the (0–5)-eV energy range below the Fermi level. However, the energy resolution of electron spectroscopy techniques in this range is not as good as that of optical techniques.

The second objective of this work was then to obtain information on electronic density of states by spectroscopic ellipsometry. The main interest of ellipsometry, as compared with other optical reflectivity techniques, is that real and imaginary parts of the dielectric function of optically thick samples are directly available without the cumbersome Kramers-Kronig transform.[5]

The energy range investigated here goes from 1 to 4.5 eV. The dielectric tensor of crystalline $MoSi_2$ has been found anisotropic with the same symmetry as the tetragonal crystalline structure giving thus two different dielectric functions ($\epsilon_a=\epsilon_b\neq\epsilon_c$). These are compared with measurements made on high-purity polycrystalline molybdenum. The evolution from the metal response to the silicide one is discussed as well as the differences between ϵ_a and ϵ_c of $MoSi_2$. They are compared with published photoemission results.

Ellipsometry in this spectral range is thus seen to give detailed information on the electronic density of states in a silicon-metal system especially when an anisotropic response is expected.

CRYSTAL GROWTH AND PREPARATION

Large single crystals of $MoSi_2$ have been grown by a Czochralski technique. The crystals were pulled from an rf-levitated melt in a modified Hukin-type crucible.[6] The synthesis and the crystallization are carried out in the same crucible.

The synthesis is achieved by direct melting of molybdenum rods (99.9% purity) and silicon lumps (99.9% purity) and subsequent quenching.

Weight losses during the synthesis are less than 0.1% which, with the worst case assumption of a single-component volatilization, yields a maximum 0.05-at.% spread in composition. Oriented seeds were cut from a polycrystalline ingot obtained by pulling with a tungsten needle.

It is well known that, as the growing crystal becomes longer, the rate of heat transfer via the crystal is modified and as the level simultaneously falls in the crucible, the melt and liquid/solid interface temperatures are also modified. These changes must be accommodated by a temperature program if the growing crystal diameter is to remain constant.[7]

Another possibility that we have adopted to avoid the temperature decrease due to the molten volume decrease during the pulling operation, was to push a solid bar of alloy, with the same composition as the crystal one, into the melt at a speed which compensates for the crystallized mass pulled out of the melt. This technique allowed us to pull about 80% of the mass while in the classical Hukin-type crucible this ratio is not larger than 30% or 40%.

The pulling rate was 10 mm/h under 1.5 bars of pure argon without any rotation. Single-crystal ingots of about 1 cm^3 were then cut into $10\times5\times1$ mm^3 slices. The slices were cut with the c crystalline axis parallel to the 10×5 mm^2 surface as determined by x-ray Laue orientation. Mechanical grinding and felt polishing were then used to obtain a mirrorlike surface. The electrical resistivity at room temperature was measured to be 10 ± 2 $\mu\Omega$ cm by a four-point probe technique.

ELLIPSOMETRIC MEASUREMENTS

Ellipsometry was carried out on a spectroscopic ellipsometer of the rotating polarizer type. Briefly, the sample is illuminated by linearly polarized white light. The elliptic polarization reflected by the sample is analyzed at each wavelength in order to obtain the complex reflectance ratio (ρ) of p-polarized to s-polarized waves. If the sample is optically semi-infinite and the interface with the ambient is abrupt, then its dielectric function is given by

$$\epsilon=\sin^2\phi+\sin^2\phi\tan^2\phi(1-\rho)^2/(1+\rho)^2\ , \tag{1}$$

where ϕ is the incidence angle. However, this equation is only valid for an isotropic medium and $\mathrm{MoSi_2}$ is expected to be uniaxial as it crystallizes in a body-centered tetragonal structure (Fig. 1) with $\epsilon_a=\epsilon_b\neq\epsilon_c$. If the c axis is parallel to the sample surface some separation of the two components can be achieved: when the plane of incidence is an a-c plane, we measure an effective ϵ_{ac} dielectric function while for the 90° rotated situation (plane of incidence along a-b) we obtain an effective ϵ_{ab}.

Following now a first-order expansion described by Aspnes[8] we define an averaged dielectric function ϵ, which in fact corresponds to the spherical part of the dielectric tensor, and some first-order correction terms $\Delta\epsilon_a=\Delta\epsilon_b$ and $\Delta\epsilon_c$:

$$\epsilon_a=\epsilon+\Delta\epsilon_a\ ,$$
$$\epsilon_c=\epsilon+\Delta\epsilon_c\ .$$

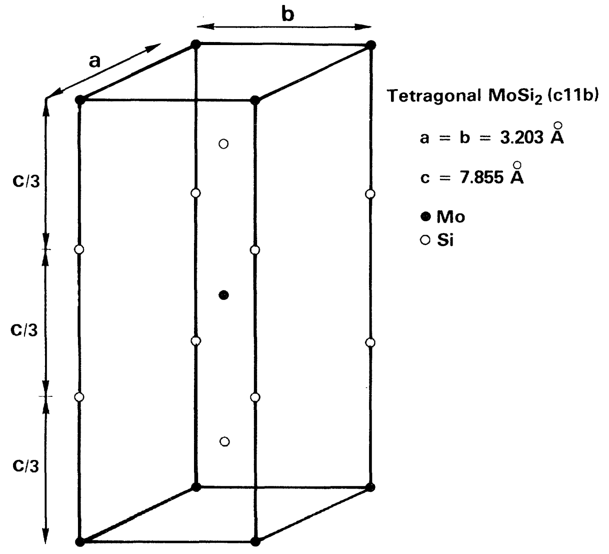

FIG. 1. Unit cell of tetragonal $\mathrm{MoSi_2}$.

Following Aspnes, we obtain for the uniaxial case

$$(\epsilon-2)\Delta\epsilon_a+\epsilon\Delta\epsilon_c=(\epsilon_{ab}+\epsilon_{ac}-2\epsilon)(\epsilon-1)\ , \tag{2a}$$

$$[\epsilon(1+\cos^2\phi)-2\sin^2\phi](\Delta\epsilon_c-\Delta\epsilon_a)=(\epsilon_{ac}-\epsilon_{ab})(\epsilon-1)\sin^2\phi\ . \tag{2b}$$

If we now take $\epsilon=(\epsilon_{ab}+\epsilon_{ac})/2$ instead on an effective medium average,[8] the above system is simplified with the possible gain that, as $|\epsilon|$ is usually far larger than 2, (2a) becomes $\Delta\epsilon_a+\Delta\epsilon_c=0$ which means that the corrections on ϵ, $\Delta\epsilon_a$, and $\Delta\epsilon_c$, are minimized.

Finally we have

$$\epsilon_a=\epsilon_b=\epsilon-k\epsilon\ , \tag{3a}$$

$$\epsilon_c=\epsilon+k(\epsilon-2)\ , \tag{3b}$$

with

$$\epsilon=(\epsilon_{ab}+\epsilon_{ac})/2\ ,$$

$$k=(\epsilon_{ac}-\epsilon_{ab})(\sin^2\phi)/2[\epsilon(1+\cos^2\phi)-2\sin^2\phi]\ ,$$

which can be usually simplified into

$$\epsilon_a=\epsilon_b=\epsilon-k'\ , \tag{4a}$$

$$\epsilon_c=\epsilon+k'\ , \tag{4b}$$

with

$$k'=(\epsilon_{ac}-\epsilon_{ab})(\sin^2\phi)/[2(1+\cos^2\phi)]\ .$$

As pointed out in the original paper, this procedure yields only first-order approximations but is totally explicit without any singularity which can arise from the exact treatment.

Practically, the c axis of the crystal was found to be perpendicular to a cleavage plane of the sample by x-ray Laue imaging which gave us a good reference plane for the ellipsometric measurements.

The dielectric functions ϵ_a and ϵ_c of $\mathrm{MoSi_2}$ obtained by the above procedure between 1 and 4.5 eV are drawn on Fig. 2 along with the values obtained on high-purity polycrystalline molybdenum. The noise on the measured values is in the ±0.01 range, which is far better than the expected accuracy. The main source of inaccuracies is the assumption of an abrupt interface between sample and ambient which is certainly not the case, as the samples were only submitted to mechanical grinding and felt polishing. The

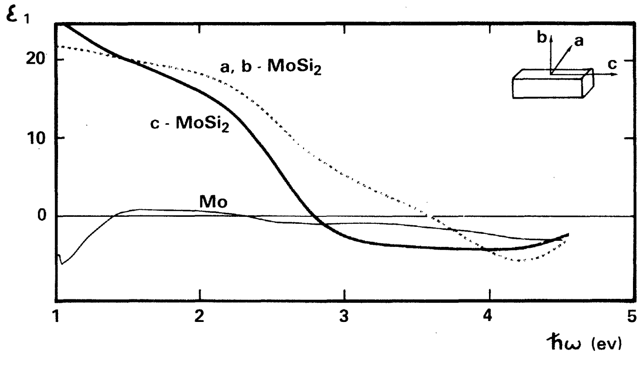

FIG. 2. Real part of the dielectric function of bulk polycrystalline Mo and of monocrystalline $\mathrm{MoSi_2}$ along different crystalline directions.

effective dielectric function measured here can be underestimated because of a rough superficial layer eventually mixed with a native oxide overlayer.[9]

This may explain the consistently larger values obtained by Nestell[10] with a combination of reflectance and transmittance measurements on thin layer evaporated Mo samples. However, our results and those of Ref. 10 do not differ more than those published on less reactive metallic surfaces.[9,11] Whatever the cause, our aim was not to get absolute values of dielectric functions but to compare the energy position of Mo and $MoSi_2$ structures and those are not displaced by an overlayer; furthermore, the relative positions of the two dielectric functions of $MoSi_2$ are not affected by the surface condition as the corresponding contribution can be reasonably assumed to be isotropic.

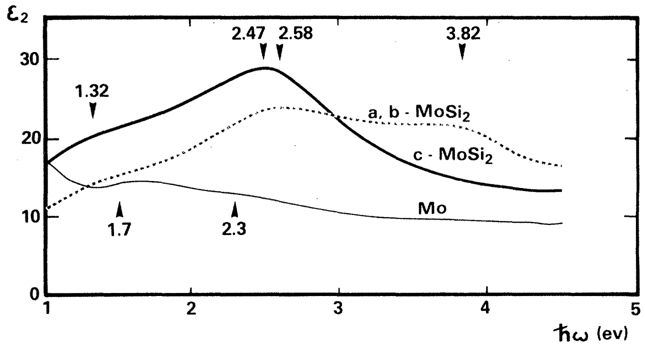

FIG. 3. Imaginary part of the same dielectric functions.

DISCUSSION

In contrast with photoemission results where the emitted-electron intensity describes the valence-band density with some contribution of a spectrally dependent absorption of the incident uv beam, the relation between the dielectric constant and valence-band density of states is more complex as conduction-band density of states and, in the case of crystalline structure, k-selection rules are involved.[12] However, some insight is obtained from the plasma sum rule which gives the effective number of electrons per atom n_{eff} contributing to the optical absorption up to a given photon energy:

$$n_{\text{eff}}(\omega_0) = (m/2\pi^2 N_a e^2) \int_0^{\omega_0} \omega \epsilon_2(\omega) d\omega \ ,$$

where m is the electron effective mass, N_a the density of atoms, and ϵ_2 the imaginary part of the dielectric function.

Starting from this simple expression two pieces of information can be obtained. At a given photon energy, effective densities of states can be compared through ϵ_2 values. Secondly, the structures observed in the variations of ϵ_2 versus photon energy can be correlated and occasionaly identified with photoelectron spectra and computed band structures.

Below 3 eV, the ϵ_2 spectra of molybdenum shows two slight maxima at 1.7 and 2.3 eV (see Fig. 3). These are consistent with the optical conductivity results of Nestell[10] and are due to transitions from the d band to the Fermi level. In the silicide the 1.7-eV maximum is shifted to 1.32 eV for both a and c directions but the 2.3-eV maximum goes to 2.47 eV for ϵ_a and 2.58 eV for ϵ_c. It appears, thus, that in the silicide the maximum of the effective electron density is shifted to about 2.5 eV below the Fermi level. These features can be compared with the 2.2-eV peak observed by photoemission[2] on bulk polycrystalline samples which is attributed to metal d electrons. The energy differences of the maximum can be due to the experimental techniques, but they more probably arise from differences in sample preparation, as the photoemission results were obtained on polycrystalline $MoSi_2$ with small amounts of an intergranular second phase. Such sample dependent shifts were observed on bulk and thin film Pd_2Si (Ref. 3) which in the latter case was suspected to contain excess silicon.

If below 3 eV the electron effective density is smaller along the a and b directions than along c, the situation is inverted above 3 eV where the a and b density shows a well marked maximum at 3.82 eV. This feature is totally absent from the ϵ_c curve. If we assume that the corresponding transition ends at the Fermi level, hybridized Si p and Mo d electrons would be very good candidates as theoretical calculations show a strong interaction between Si p and Mo d electrons around 4 eV. However, the corresponding expected photoelectron feature is not always present in published results: it is seen on thin Mo layers reacted with silicon[4] but not on polycrystalline samples[2] where it may be masked by the more proeminent 2-eV peak.

In the (1–4.5)-eV energy range explored here, the total effective number of electrons participating in the optical absorption process is very similar for the two different crystalline directions a and c. Thus, if we assume that the differences in the ϵ_2 spectra are, for the main part, due to valence-band density of state differences, the above discussion points to Mo d electrons more strongly coupled with Si p ones along a and b directions than along c, giving rise to an enhanced contribution at 3.8-eV and a smaller one at 2.5 eV. However, this point needs to be confirmed by other spectroscopic techniques.

CONCLUSION

In conclusion, we have shown that spectroscopic ellipsometry in the (1–4.5)-eV range on metal silicide can provide information complementary to electron spectroscopy techniques, in particular, with the possibility of crystalline orientation dependent analysis.

For monocrystalline $MoSi_2$ we have determined its dielectric tensor, which shows the same symmetry as the crystalline structure.

Another point that emerges from this work is the large difference between the dielectric functions of silicide, metal, and silicon in the transparency domain of Si. This demonstrates the possibility of *in situ* ellipsometry, for instance, around 1.3 eV, for monitoring diffusion and silicide formation through a silicon layer.

[*] Present address: Télématique S.A.-Zirst, F-38240 Meylan, France.

[1] An extensive review is given by L. J. Brillson, Surf. Sci. Rep. (to be published).

[2] J. H. Weaver, V. L. Moruzzi, and F. A. Schmidt, Phys. Rev. B 23, 2916 (1981).

[3] A. Franciosi and J. H. Weaver, Phys. Rev. B 27, 3554 (1983), and references therein.

[4] G. Rossi, I. Abbati, L. Braicovich, I. Lindau, W. E. Spicer, V. del Pennino, and S. Nannarone, Physica 117&118B, 795 (1983).

[5] See, for instance, D. E. Aspnes, in *Optical Properties of Solids: New Developments,* edited by B. O. Seraphin (North-Holland, Amsterdam, 1976), pp. 800–846.

[6] D. Hukin British Patent No. 1 269 762 (1972).

[7] D. W. Jones, in *Refractory Metal Crystal Growth Techniques in Crystal Growth,* edited by C. H. L. Goodman (Plenum, London, 1974).

[8] D. E. Aspnes, J. Opt. Soc. Am. 70, 1275 (1980).

[9] D. E. Aspnes and A. A. Studna, Phys. Rev. B 27, 985 (1983).

[10] J. E. Nestell, Jr., R. W. Christy, Mitchell H. Cohen, and G. C. Ruben, J. Appl. Phys. 51, 655 (1980); J. E. Nestell, Jr. and R. W. Christy, Phys. Rev. B 21, 3173 (1980).

[11] D. E. Aspnes, E. Kinsbron, and D. D. Bacon, Phys. Rev. B 21, 3290 (1980).

[12] F. Wooten, *Optical Properties of Solids* (Academic, New York, 1972).