# MICROSTRUCTURE AND ELLIPSOMETRY STUDIES OF VANADIUM, ZIRCONIUM AND COBALT SILICIDES

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(Received 6 April 1988; accepted 19 April 1988)

**Abstract**—The surface morphologies and structural phases of  $VSi_2$ ,  $ZrSi_2$  and  $CoSi_2$ , formed by rapid thermal annealing, were studied by transmission electron microscopy. Polycrystalline  $VSi_2$  and  $ZrSi_2$  and epitaxial  $CoSi_2$  were found to be the stable phases after annealing. The complex refractive indices were determined to be between 2 and 5 in the visible region.

Keywords: Microstructure, refractive index, silicides.

# 1. INTRODUCTION

Silicides grown from refractory metal films are widely used, because of their corrosion resistance and solderability, in electronic circuits for Schottky barrier and ohmic contacts. A study of surface morphologies, phase structures and optical properties of silicides, helps in understanding the electric transport phenomena and the modeling of the design of opto-electronic devices. In the past few years, we have reported the optical constants of thin films of Ni/Si [1], Pd/Si [2], Cr/Si, Mo/Si and Pt/Si [3], and Ti/Si [4] systems using a polychromatic ellipsometer within the visible region. In this work, the microstructures and the complex refractive indices of vanadium, zirconium and cobalt silicides were successfully measured.

After rapid thermal annealing, the final phases  $VSi_2$ ,  $ZrSi_2$  and  $CoSi_2$  are hexagonal C40, triclinic C49, and cubic  $C_1$  structures, respectively. CoSi<sub>2</sub> can be epitaxially grown on the (111) Si surface, whereas  $VSi_2$  and  $ZrSi_2$  are polycrystals. The ellipsometric measurement indicates that their real and imaginary parts of the refractive index are very close to each other and that they behave as low conductivity intermetallic compounds.

#### 2. SILICIDE FORMATION AND EXPERIMENTAL METHODS

The free energies of formation  $\Delta H$ , for Co, Zr and V silicides are shown in Table 1 [5]. The formation of the monosilicides of Co and Zr is favored because of their high formation energy and their simple crystal structure compared with that of the disilicides. For example, the unit cell of ZrSi has eight atoms, while that of ZrSi<sub>2</sub> (C49 structure) has 12 atoms. The low formation energy of CoSi<sub>2</sub> makes it kinetically easier for the nucleation and epitaxial growth on silicon substrates than other silicides.

Refractory metal films of about 300–400 Å were electron-gun deposited on [100] and [111] silicon substrates with a resistivity of  $1-10 \Omega$  cm. Before

deposition, the wafers were etched in buffered HF solution and then boiled in a sequence of acetone, trichloroethylene and de-ionized water and finally dried by a pressurized nitrogen-gun. The deposition rate was about  $1 \text{ A s}^{-1}$  under a vacuum of  $2 \times 10^{-6}$  torr and the thickness was determined by an Infincon quartz monitor. The metallization was performed by a rapid thermal annealing (RTA) method at the temperature of  $1100^{\circ}$ C in a Perkin Elmer HGA-300 furnace under a cooling rate of  $100-200^{\circ}$ C s<sup>-1</sup>. The annealing durations were 20, 20 and 100 s for Zr/Si, V/Si and Co/Si systems, respectively.

The surface morphologies and structures of the silicides were examined by transmission electron microscopy. The samples were cut into discs of 3 mm in diameter. The silicide surfaces were protected by resin while the back substrate sides were etched by a mixture of A (I<sub>2</sub>/0.25 g plus CH<sub>3</sub>COOH/1100 cc) and B (HF: HNO<sub>3</sub> = 1:3) solutions. For silicide compounds, phase identification was performed by indexing the selected area diffraction (SAD) patterns using the internal (Si: $d_{220}$ ) calibration data for obtaining the camera length, and the interplanar spacing  $d_{hkl}$  for the {hkl} planes was compared with the American Society for Testing and Materials (ASTM) X-ray diffraction cards.

The refractive indices of the samples were measured by a polychromatic ellipsometer as described in previous works. Samples showing a smooth mirror reflection, annealed by the face-to-face arrangement as implemented in this work, were free from oxidation as examined by Auger spectrometry. Since the measured k (imaginary part of the refractive index) is always greater than 3 within the visible region, the absorption depth  $\alpha^{-1} = \lambda/2\pi k$  should be smaller than 300 Å. Therefore, the thickness of the silicide is much greater than the absorption depth and the single-layer of air-material model can be used to analyze the data from the null ellipsometry measurements.

Table 1. The free energy of formation  $\Delta H$  for Co, Zr and V silicides

Silicides	Co <sub>2</sub> Si	CoSi	CoSi <sub>2</sub>	Zr <sub>2</sub> Si	ZrSi	ZrSi <sub>2</sub>	V <sub>3</sub> Si	V <sub>5</sub> Si <sub>3</sub>	VSi <sub>2</sub>
$\Delta H$ (Kcal g atom <sup>-1</sup> )	9.2	12	8.2	16.7	18.5	12.9	6.5	11.8	24.3



Fig. 1. The TEM bright field images of  $VSi_2$ . Inset is the SAD.

## 3. EXPERIMENTAL RESULTS

#### A. Vanadium/silicon system

Vanadium, a grayish malleable ductile polyvalent metal, was electron-gun deposited on *n*-type [001] silicon substrates. The metallization was performed by RTA at a temperature setting of  $1100^{\circ}$ C for 20 s. The bright field image examined by TEM as shown in Fig. 1, indicates a polycrystalline structure with a grain size of 0.35–0.4  $\mu$ m. The four intense spots as shown in the inset SAD are identified to be due to the diffraction of the [100] silicon substrate. The spacing between the ring patterns clearly indicates that the polycrystalline phase is VSi<sub>2</sub>. The crystal structure of VSi<sub>2</sub> as shown in Fig. 2 is hexagonal C40 similar to the CrSi<sub>2</sub> structure.

The real part of the refractive index n of the as-deposited vanadium film, shown in Fig. 3, is

monotonically increased from 2.5 to 4.0 as the wavelength increases from 400 to 700 nm, whereas k is rather flat and pinned around 2.5, resulting in a normal reflectance around 50%. After annealing, the n and k of VSi<sub>2</sub> (Fig. 4), lying between 2.0 and 3.0 within the visible region, are close together and smaller than the values of their original metals.

#### B. Zirconium/silicon system

Zirconium, a steel-gray strong ductile, chiefly tetravalent metal with a high melting point, is highly resistant to corrosion. Zirconium films of 300 Å





Fig. 2. The hexagonal C40 structure of VSi<sub>2</sub>.



Fig. 3. The n and k of the as-deposited vanadium film.



Fig. 4. The n and k of the VSi<sub>2</sub> film.





Fig. 6. The n and k of the ZrSi<sub>2</sub> film.



Fig. 7. The TEM bright field of ZrSi<sub>2</sub>. Inset is the SAD.

thickness were deposited on [111] *n*-type Si substrates. The change of *n* and *k* of the virgin film as shown in Fig. 5 is not large, and the reflectivity lies between 60 and 70%. After annealing, the values of *n* and *k* of  $ZrSi_2$  (Fig. 6) approach each other and

ZrSi2

intersect near 500 nm, which usually corresponds to the plasma oscillation frequency. The TEM of  $ZrSi_2$ , depicted in Fig. 7, also shows a polycrystalline structure with a grain size of almost 0.15 nm. The diffraction patterns indicate that the structure is the triclinic C49 phase. The relative positions of the atoms and the lattice constants of the three main axes are sketched in Fig. 8.

#### C. Cobalt/silicon system

Cobalt is a lustrous silver-white magnetic metal. Metal films of 400 Å thickness were electron-gun deposited on [111] Si substrates. The refractive indices n and k increased from 2.0 to 3.0 and from 3.0 to 5.0 respectively, as the wavelength changed from 400 nm to 700 nm, as shown in Fig. 9. After rapid annealing at 1100°C for 100 s, we obtained the final stable CoSi<sub>2</sub> phase. n and k are considerably different near 580 nm, as shown in Fig. 10. The kvalues are reduced to within a value of 1 and 2, invoking a trend towards a non-metallic compound.



Fig. 8. The triclinic C49 structure of ZrSi<sub>2</sub>.



Fig. 9. The n and k of the as-deposited cobalt film.



Fig. 10. The *n* and *k* of the  $CoSi_2$  film.



Fig. 11. The TEM bright field of CoSi2. Inset is the SAD.

The TEM micrograph as shown in Fig. 11 indicates that the  $CoSi_2$  film can be epitaxially grown on the [111] Si substrates, and that the structure is the cubic  $C_1$  phase. The lattice positions for a unit cell are sketched in Fig. 12.

#### 4. DISCUSSION

From the classical Drude model, the refractive index n increases and k decreases upon the transformation from metals to semimetals as a result of the decrease of the conduction electron density. The Drude model implies [6]

$$n^{2} - k^{2} = 1 - \frac{\omega_{p}^{2}\tau^{2}}{1 + \omega^{2}\tau^{2}},$$
  
$$2nk = \frac{\omega_{p}^{2}\tau}{\omega(1 + \omega^{2}\tau^{2})},$$
 (1)

where

$$\omega_p = \left(\frac{4\pi Ne^2}{m}\right)^{1/2}$$

is the plasma frequency, N is the free-electron density, m the electron mass and  $\tau$  the carrier relaxation time. The d.c. resistivity  $\rho_0$  is correlated to  $\tau$  as given by

$$\rho_0 = \frac{m}{Ne^2\tau}.$$
 (2)

As  $\tau$  increases,  $\rho_0$  decreases and k increases inclining towards a metallic behavior. Table 2 indicates that the resistivities change from the virgin metals to silicides. The correlations between the resistivity and refractive index as formulated in eqns (1) and (2) are not congruent. For example, CoSi<sub>2</sub> has a much higher resistivity than the Co, but *n* always stays larger than k. However, the values of *n* and k for the V and Zr silicides are reversed. Therefore, the Drude model is



Table 2. The resistivities and relative values of n and k for the Co, Zr and V silicides

Metals/silicides	v	VSi <sub>2</sub>	Zr	ZrSi <sub>2</sub>	Co	CoSi <sub>2</sub>
Resistivity $(\mu \Omega \text{ cm})$	25	13.3	$ \begin{array}{c} 40 \\ k > n \end{array} $	75	7	66
Relative values of <i>n</i> , <i>k</i>	n > k	k > n		n > k	n > k	n > k



Fig. 13. The theoretical calculations of *n* and *k* by the classical Drude model ( $\triangle$ ) and the quantum screened charge theory ( $\bigcirc$ ). The conduction electron density and relaxation time are assumed to be  $3.8 \times 10^{23} \,\mathrm{cm^{-3}}$  and  $1.0 \times 10^{-16} \,\mathrm{s}$ , respectively.

invalid for the interpretation of the optical constants of these polyvalent metals and silicides.

The optical constants were then derived from the static Hartree dielectric function  $\epsilon(\hat{q}, \omega)$ , where  $\hat{q}$  is the incident photon wavenumber, defined as the ratio of the applied field over the total field (including the applied and induced fields). The charge redistribution due to the screening effect is the origin of the induced field. The quantum screened charge density may arise from the scattering of the electron wavenumber from  $\hat{k}$  to  $\hat{k} + \hat{q}$  within the filled Fermi states or due to the hybridization of valence d states to the conduction  $\hat{k}$  states; these are called the pseudopotential screened charge and the hybridization screened charge, respectively. Including these effects we can obtain [7, 8]

$$\epsilon(\hat{q},\omega) = 1 - \frac{4\pi e^2}{q^2} \left\{ \sum_{k < k_F} \frac{f(E_{k+\hat{q}}) - f(E_k)}{E_{k+\hat{q}} - E_k - \hbar\omega + i\hbar\eta} \right.$$
$$\times \frac{2\langle \hat{k} + \hat{q} | W | \hat{k} \rangle}{E_k - E_{k+\hat{q}}} n_q^{scr} + \sum_{d,k > k_F} \frac{f(E_{k+\hat{q}}) - f(E_k)}{E_{k+\hat{q}} - E_k - \hbar\omega + i\hbar\eta} \\\times \left[ \frac{2\langle \hat{k} + \hat{q} | \Delta | d \rangle \langle d | \Delta | \hat{k} \rangle}{(E_d - E_k)(E_k - E_{k+\hat{q}})} \right]$$

$$-\frac{\langle \hat{k} | \Delta | d \rangle \langle d | \Delta | \hat{k} \rangle}{(E_d - E_k)^2} \bigg] n_q^{scr} \bigg\}, \tag{3}$$

where  $f(E_k)$  is the Fermi-Dirac distribution,  $\eta = 1/\tau$ ,  $\Delta$  is the variation of the pseudopotential excluding the *d* state value. The  $n_q^{sr}$  is the charge redistribution due to the pseudopotential *W*, and is given by

$$n_{q}^{scr} \simeq 2 \sum_{k>k_{F}} \frac{\langle \hat{k} + \hat{q} | W | \hat{k} \rangle}{E_{\hat{k}} - E_{\hat{k} + \hat{q}}} + \sum_{d,k>k_{F}} \left[ \frac{2\langle \hat{k} + \hat{q} | \Delta | d \rangle \langle d | \Delta | \hat{k} \rangle}{(E_{d} - E_{\hat{k}})(E_{\hat{k}} - E_{\hat{k} + \hat{q}})} - \frac{\langle \hat{k} | \Delta | d \rangle \langle \hat{k} | \Delta | \hat{k} \rangle}{(E_{d} - E_{\hat{k}})^{2}} \right].$$
(4)

We assume a spherical Fermi surface and a small value of q, so that the scattering of the electrons by the incident photon is within the same Fermi surface. Inserting the proper pseudowavefunctions of valence and core electrons, we can evaluate n and k by the quantum screened charge theory. Taking the values of the parameters as  $\tau = 1.0 \times 10^{-16}$  s, and  $q = 2.3 \times 10^{-4} k_F$ , we can plot the calculated refractive indices as shown in Fig. 13 which are very close to the experimental values as measured in this experiment. A more refined calculation implies the fact that k increases as the relaxation time decreases, and n and k decrease as q increases and are rarely affected by the binding energies of the d states.

Acknowledgement—The work was supported by the National Science Council of the Republic of China.

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