FORMATION OF TITANIUM SILICIDES AND THEIR REFRACTIVE INDEX MEASUREMENTS

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The refractive indices of Ti, Ti_5Si_4, and $TiSi_2$ films are measured by a polychromatic ellipsometer within the visible region. The wavelength dependence on the optical constants satisfactorily agree with the Drude model in the relaxation region. Transmission electron microscopy indicates that epitaxial C54-$TiSi_2$ is formed with annealing temperatures above 700°C.

Titanium silicides, with their distinct properties of high conductivity, strong adhesion with substrates, and high corrosion resistance to caustic gases, are prevalently applied in the very large-scale integration (VLSI) circuits as the gating material. The invention of charge coupled device (CCD) for optical sensing and storage extends their utility into the optical region. In this work, we first report the refrac-

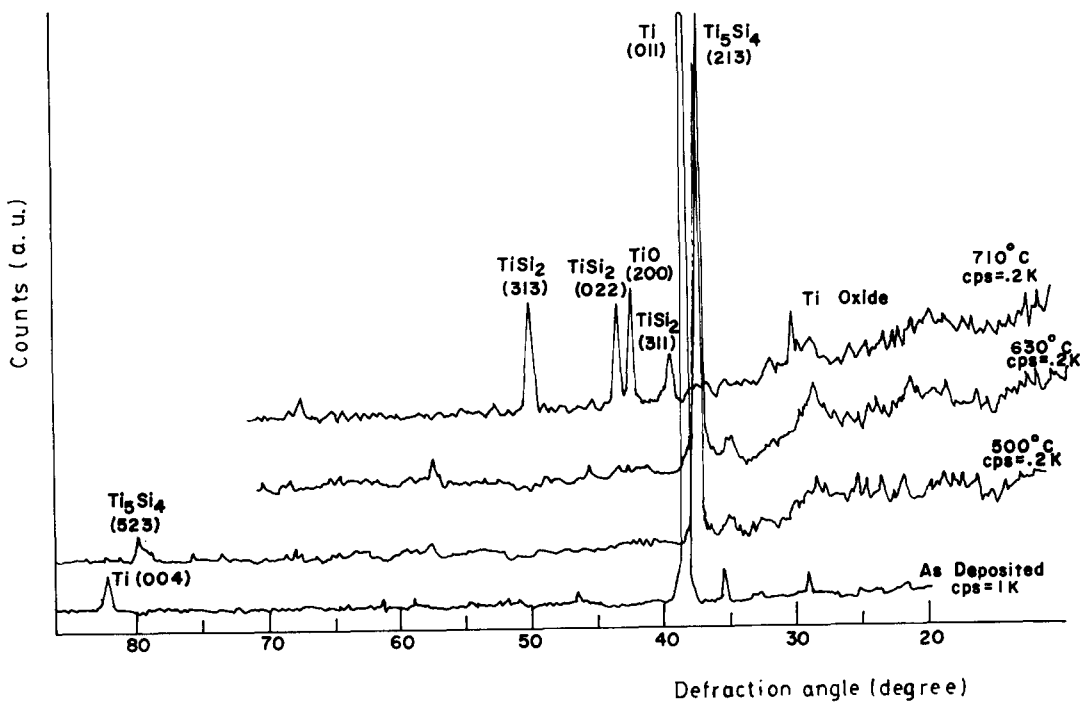

Fig. 1. XRD diagram of Ti/Si isothermally annealed for 55 minutes, the CPS is the counts per second.

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tive indices of titanium silicides measured by a polychromatic ellipsometer [1,2].

Titanium films were rf sputtered on the (111), ~1–10 Ω cm silicon substrates under a pressure of 3×10^{-3} Torr. The film thickness in this experiment is 610 Å as measured by an Inficon quartz thickness monitor during deposition. Before deposition, the silicon substrates are cleaned in sequences of ACE, TCE, deionized water and then boiled in $NH_4OH:H_2O_2:H_2O=3:3:7$ solution at 80°C for about 10 minutes. Finally, the wafers are etched in $HF:H_2O=1:50$ solution to remove the oxide layer. The X-ray diffraction (XRD) spectra as shown in fig. 1 indicate that the as-deposited Ti film has a characteristic peak near $d=2.24$ Å for the Ti (011) plane, which reveals the fact that polycrystalline Ti films are formed readily instead of amorphous state even without heat treatment.

With isothermal annealing at 500°C for 55 minutes in a vacuum of 10^{-6} Torr, the XRD peak shifts to $d=2.41$ Å corresponding to the Ti_5Si_4 (213) plane. The electron probe micro-analyzer (EPMA) indicates that the broad peaks near $d=3.05$ Å and $d=3.21$ Å are not due to oxides but rather due to the other complex compounds of Ti and Si. As the annealing temperature increases to 710°C, for 20 minutes epitaxial C54-$TiSi_2$ appears but with an additional peak near $d=2.14$ Å arising from the TiO (200). The surface depth-profile analysis by an Auger spectrometer (Perkin Elmer PH 590) indicates the presence of an oxide layer (fig. 2a) after the high temperature annealing. This oxide overlayer could be removed by polishing with 0.5 micron Al_2O_3 powder for about 5 minutes by hand and is clearly proved by fig. 2b. The Auger peak-to-peak signal indicates that the compound composition is $TiSi_2$. Inset is the

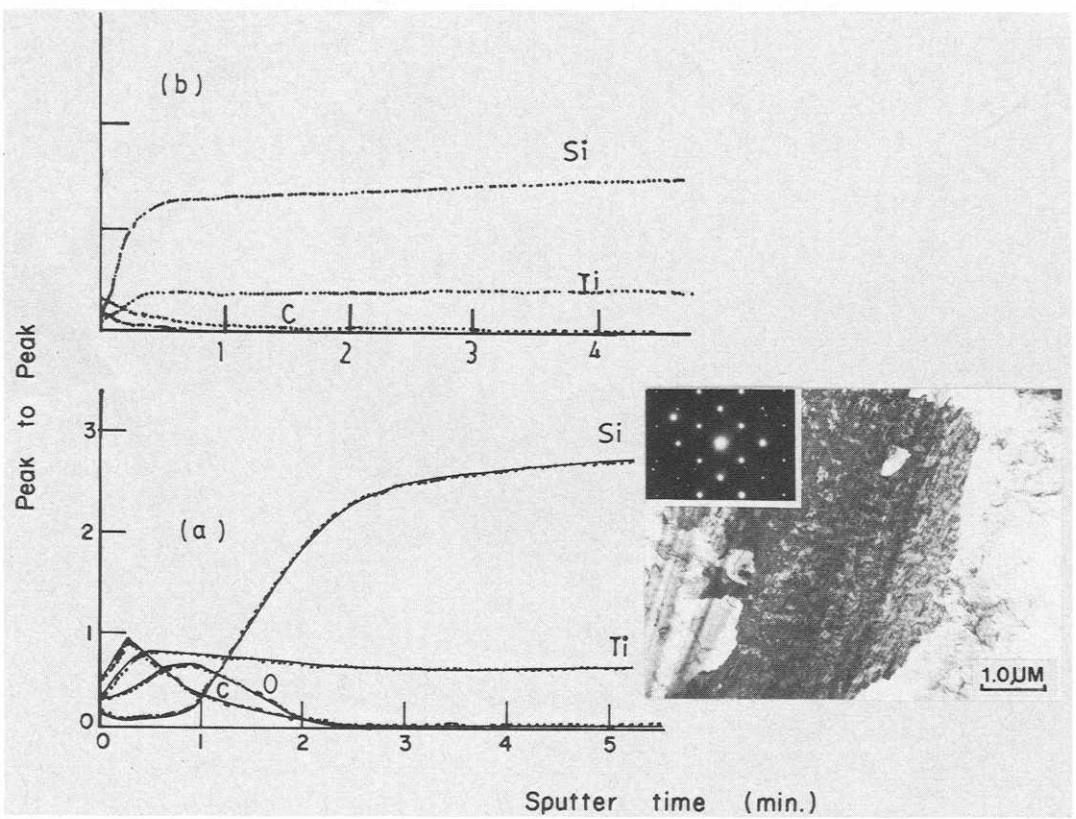

Fig. 2. (a) Auger peak-to-peak spectrum of $TiSi_2$ after 710°C, 20 min heat treatment. Inset is the TEM surface micrography and EDP. (b) Auger peak-to-peak spectrum of $TiSi_2$ after removal of surface layer by mechanical polishing treatment.

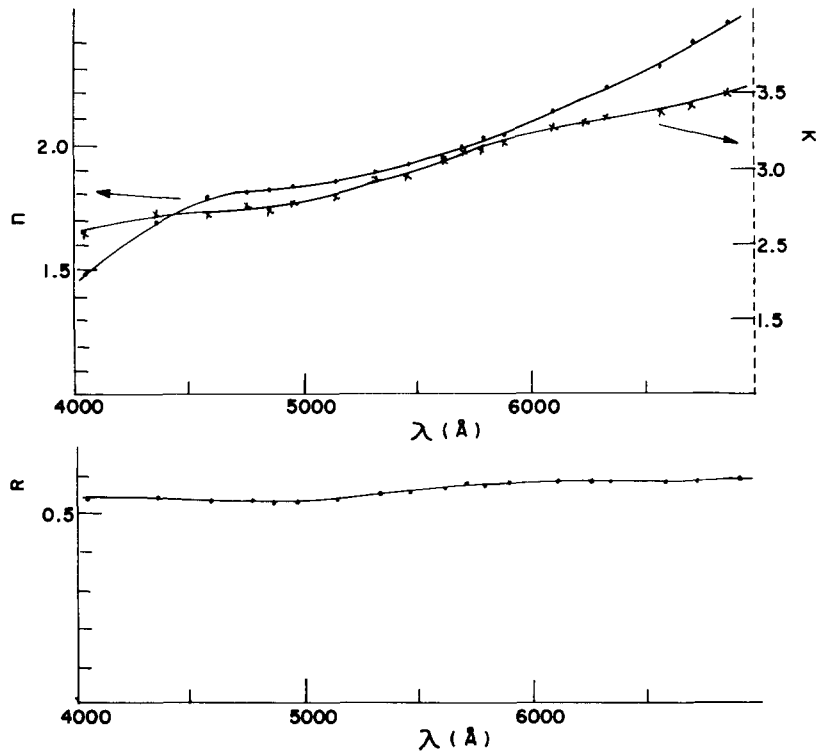

Fig. 3. n, k versus wavelength of as-deposited Ti film of 610 Å thickness.

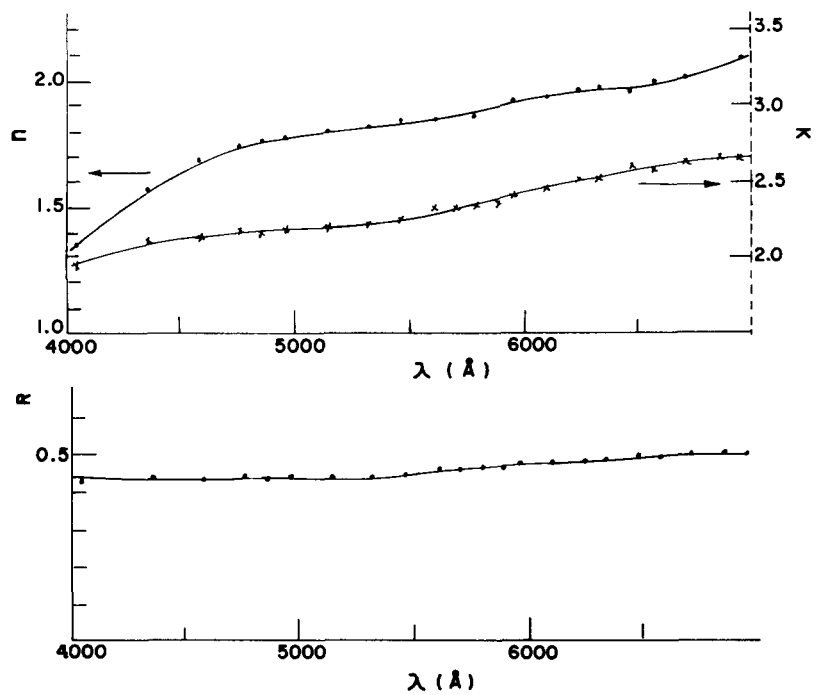

Fig. 4. n, k versus wavelength of Ti_5Si_4 of 809 Å.

TEM electron diffraction pattern which can be analyzed to show that the structure of $TiSi_2$ is face-centered orthorhombic C54 with $a_0=8.253$ Å, $b_0=4.783$ Å and $c_0=8.540$ Å. Two distinct modes of [102] and [101] $TiSi_2$ epitaxial films can be grown on (111) Si with structure of C54 [3]. The resistivities of the Ti/Si system measured by a four-point probe are 84.5, 79.3 and 21.05 μΩ cm for the as-deposited, 500°C and 710°C annealed samples, respectively. These values are close to the reported values for the Ti, Ti_5Si_3+TiSi and $TiSi_2$ films [4].

With the null ellipsometry, the Jones matrix [5] can readily solve the ratio of the reflectivities of the p and s waves, and is given by

$$\tilde{\rho}(n, k, d)=\tilde{R}_P/\tilde{R}_S$$

$$=-\tan A\,\frac{\tan C+\tilde{\rho}_c\tan(P-C)}{1-\tilde{\rho}_c\tan C\tan(P-C)}, \qquad (1)$$

where P, A and C are the orientation setting for the polarizer, analyzer and compensator, respectively. The Rutherford backscattering spectrometry indicates that the thickness of $TiSi_2$ swells by a factor of 1.7 from its original metal. The optical penetration depth $\delta_0=\lambda_0/2\pi k$ is about 477 Å for $\lambda_0\approx 6000$ Å with the imaginary part of the refractive index $k\approx 2$, while the silicide thickness can be estimated to be 610 Å × 1.7 = 1037 Å. Therefore, the ellipsometry equation for the single layer bulk material can be used to determine the complex refractive index $N=n-ik$, which gives

$$N=n_0\tan\phi_0\{1-[4\rho/(1+\rho)^2]\sin^2\phi_0\}^{1/2}, \qquad (2)$$

where n_0 is the refractive index of air, and ϕ_0 is the incident angle. Fig. 3 is the ellipsometry measurement of the as-deposited Ti film on Si substrate, showing that the real and imaginary parts of the refractive index both increase as the wavelength increases. For the heat treated Ti_5Si_4 silicide, the values of the refractive index as shown in fig. 4 decrease and those of the reflectance decrease by about 12%.

As the annealing temperature increases further, the final phase $TiSi_2$ is formed. The measured refractive indices for the polished surface are shown in fig. 5. The n and k intersect near $\lambda\approx 6200$ Å, which usually occurs at the plasma oscillation frequency for high mobility metals. The plasma frequency decreases as the conduction electron density decreases due to the

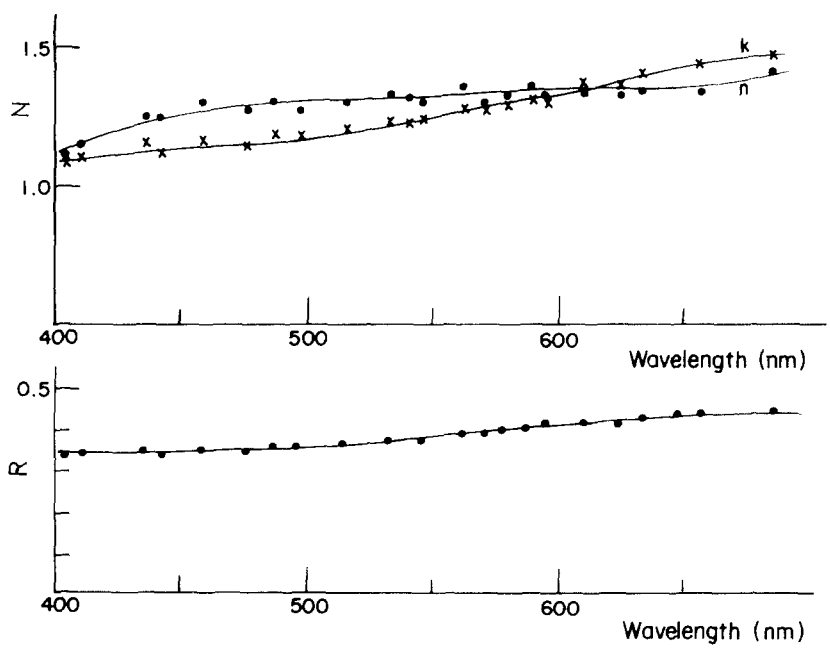

Fig. 5. n, k versus wavelength of $TiSi_2$ for polished surface.

charge transfer from the titanium to silicon during silicide formation.

The Drude model of free electron gas implies a relation of [6]

$$n^2-k^2=1-\omega_p^2\tau^2/(1+\omega^2\tau^2)\,,$$

$$2nk=\omega_p^2\tau/(1+\omega^2\tau^2)\omega\,, \qquad (3)$$

where τ is the electron relaxation time, and ω_p is the plasma frequency. In the infrared region, where $\omega \ll 1/\tau$, then $2nk \gg n^2-k^2$, and

$$N^2=(n+ik)^2 \approx 2ink \approx \omega_p^2\tau i/\omega\,,$$

which implies $n \approx k \approx \omega_p(\tau/\omega)^{1/2} \gg 1$. Therefore the reflectivity

$$R=[(n-1)^2+k^2]/[(n+1)^2+k^2]$$

is very high and falls into the classical skin-effect region. Within the visible light, $1/\tau \ll \omega \ll \omega_p$, we have $n^2-k^2 \approx 1-\omega_p^2/\omega^2$, and $2nk \approx \omega_p^2\tau/\omega$, then n^2-k^2 is very negative, or $k \gg n$, therefore $R \approx 1$. This is the relaxation region. As the annealing temperature increases, the real part of the refractive index remains almost unchanged, but the imaginary part will drastically decrease. Since silicides are metallic compounds, the number of conduction electrons decreases due to the hybridization of the 4d electrons of Ti with the valence 3p electrons of Si and empty 3d orbitals of Si. The decrease of conduction electrons presumably decreases the plasma frequency, and k is likely to approach n, and the silicides have a lower reflectivity than pure Ti metal within the visible region. This is what we have observed for titanium silicides.

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