Ellipsometry measurements of nickel silicides

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The real \((n)\) and imaginary \((k)\) parts of the refraction index of \(\text{Ni}_{2}\text{Si}\), \(\text{NiSi}\), and \(\text{NiSi}_2\) silicides are measured by an ellipsometer in the optical range of 4000–7000 Å. The \(n\) and \(k\) are within the values of 2.0–3.5 for the high-temperature annealed nickel silicides.

Silicides are essential parts of electronic devices such as solar energy converters\(^1\) and Schottky barrier image detectors.\(^2\) Therefore, a study of their optical properties is important to device modeling. Despite their widespread utility, only few such reports are in the literature.\(^3,4\) Silicides grown at high temperature are usually accompanied with a thin oxide layer on the surface which performs as an optical impedance-matching network. Direct determination of optical constants by conventional reflectivity methods usually introduces catastrophic errors. An ellipsometer which is capable of detecting the optical constants of multiple layers is implemented in this study. The refraction indexes of \(\text{Ni}_{2}\text{Si}\), \(\text{NiSi}\), and \(\text{NiSi}_2\) are measured by a homemade multiple wavelength ellipsometer which exploits a Babinet–Soleil compensator. The refraction indexes of high-temperature annealed nickel silicides are vastly different from the original metals.

In the silicides systems, multiple reflection occurs between interfacial layers of air to silicide (with subindices of 0 to 1), silicide to substrate (1 to 2), and silicide to air (1 to 0). Therefore, the total reflection is

\[
R = r_{01} + t_{01}f_{12}e^{-\alpha\theta} + t_{01}f_{12}^2 e^{-2\alpha\theta} + \ldots + t_{01}f_{12}^d e^{-d\alpha\theta} = (r_{01} + r_{12}e^{-\alpha\theta})/(1 + r_{01}r_{12}e^{-\alpha\theta}),
\]

where \(r_{mn}\) and \(t_{mn}\) are the reflectance and transmittance from mediums \(m\) to \(n\), respectively, and \(\beta\), which is the phase shift for light with incidence angle \(\phi\), through the silicide of thickness \(d\), and refraction index \(N_i\), is given by

\[
\beta = 2\pi\left(\frac{d}{\lambda}\right)N_i \cos \phi_i.
\]

If the reflectance \(R\) is decomposed into \(p\) and \(s\) polarized waves, the ellipsometry function becomes\(^5\)

\[
\rho = \tan \psi e^{i\Delta},
\]

\[
= \frac{R_p}{R_s} = \frac{(r_{01p} + r_{12p}e^{-\alpha\theta})}{(1 + r_{01p}r_{12p}e^{-\alpha\theta})} = \frac{(r_{01s} + r_{12s}e^{-\alpha\theta})}{(1 + r_{01s}r_{12s}e^{-\alpha\theta})},
\]

where \(\psi\) is the arc tangent of the ratio of the amplitude of \(p\) and \(s\) waves and \(\Delta\) is the difference between phase shift of the reflected \(p\) and \(s\) waves.

For absorption silicide films, \(N_i = n_i - ik_i\), we need data at more incident angles to solve for the parameters from sets of equations. Each incident angle \(\phi_i\) can give one pair of \(\Delta_i(B,\phi_i)\) and \(\psi_i(B,\phi_i)\). The parameter \(B\) specifying \(N_0\), \(N_1\), \(N_2\), \(d\), and \(\phi\) can be numerically solved from an elaborate least-mean-square-fit based on a modified Levenberg–Marquardt algorithm.\(^6\)

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FIG. 1. AES and TEM micrographics of \(\text{Ni}_2\text{Si}\). The relative Auger sensitivities for a primary electron-beam energy of \(E_p = 3\) keV are 0.27, 0.37, 0.52 and for the \(\text{Ni}\), \(\text{Si}\), and \(\text{O}\) atoms, respectively. The sputtering yield of silicides is uncalibrated.

FIG. 2. AES and TEM micrographics of \(\text{NiSi}\).
Nickel films of about 400 Å thickness were electron-gun evaporated on [100] silicide substrates at a pressure of $5 \times 10^{-7}$ Torr. The metallization of Ni$_2$Si is performed at a temperature of 300 °C under a vacuum of $1 \times 10^{-6}$ Torr for 20 min. Longer annealing time will cause Ni$_2$Si to become NiSi. The NiSi silicide usually forms at an annealing temperature of 400 °C. The depth profiles of the Ni$_2$Si and NiSi phase have been identified by Auger electron spectroscopy (AES) as shown in Figs. 1 and 2, respectively. A thin oxide layer is present on the surfaces of both silicides. The insets of the transmission electron micrographs (TEM) as shown in Figs. 1 and 2 indicate that the silicides Ni$_2$Si and NiSi are both orthorhombic polycrystalline structure with grain size being 30–70 and 30–100 nm, respectively. With the annealing temperatures increased to 700 °C for a duration of 45 min, the end phase NiSi$_2$ is produced. The NiSi$_2$ is epitaxially grown on silicon substrate as shown in Fig. 3(a) which has a distinct intersection with the silicon substrate as revealed in Fig. 3(b). The surface of nickel silicide can be considered as isotropic since the grain size is much smaller than the light spot size (~2 nm). The resistivities of Ni$_2$Si, NiSi, and NiSi$_2$ measured by a four-point probe are 28.75 $\mu\Omega$ cm, 35.7 $\mu\Omega$ cm, and 48.5 $\mu\Omega$ cm, respectively. These are much greater than for pure Ni metal (6.844 $\mu\Omega$ cm).

The real and imaginary parts of the refraction index of the as deposited; 300 °C, 20 min; 400 °C, 30 min; and 800 °C, 45 min annealed samples are shown in Figs. 4, 5, 6, and 7, respectively. The reflectivity at 6000 Å, for the as-deposited Ni films as calculated from Fig. 4 is 0.69 which is close to the reported value of 0.64. These curves indicate that the imaginary part of the refraction index is always greater than 2.0 in the visible region indicating their visible opacity. For an EM wave, in which the phase velocity is greater than the Fermi velocity of the electron, and assuming the silicide has cubic symmetry, the Drude theory indicates

$$n^2 - k^2 = 1 - \frac{4\pi\sigma(0)\omega\tau}{\omega(1 + \omega^2\tau^2)} = 1 - \frac{\omega_p^2\tau^2}{1 + \omega^2\tau^2},$$

$$2nk = \frac{\omega_p^2\tau}{1 + \omega^2\tau^2},$$

where $\tau$ is the electron relaxation time, $\omega_p$ is the plasma frequency, and $\sigma(0)$ is the dc conductivity. In the visible range,

$$\sigma(0) \approx \frac{\omega_p^2\tau}{1 + \omega^2\tau^2}.$$
region, we have $1/\tau \ll \omega \ll \omega_p$, the imaginary part of the refraction index falls proportional to $1/\omega^2$ and remains larger than the real part. This is what we have observed for Ni$_2$Si and NiSi$_2$ and NiSi$_2$ silicides but not for the high-temperature annealed NiSi$_2$.

In ellipsometry measurement, the incident angle should be accurately determined. As an example, for a thin (60 Å) oxide layer on silicon, an error of 0.05° in the determination of the incident angle will cause more than 30% of error in the determination of the film index. For thicker films, the allowable uncertainty of $\phi_i$ can be larger. This is the most difficult task in this multiple-layer ellipsometry measurement. The refraction indexes of silicides change greatly from phase to phase. The optical constants are mainly controlled by conduction-electron, and by valence and core-electron absorptions through interband and intraband transitions for pure transition metals and metal-rich silicides, and for the higher temperature annealed (silicon-rich) silicides, respectively.

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5. S. Chao, Ph.D. dissertation, The University of Texas at Austin, 1981.