Alteration of Ni silicide formation by N implantation

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The possibility of controlling the growth of nickel silicide by implanting N into thin Ni films evaporated on Si substrates has been studied using 4He backscattering spectrometry. The reaction between Ni and Si is completely halted below annealing temperatures of ~375 °C by implanted doses of 5 × 10^{16} N/cm^2. At higher annealing temperatures, localized intermixing takes place. For low doses ≤ 0.5 × 10^{16} N/cm^2, the reaction between Ni and Si is that observed for unimplanted samples both in the phase formed (NiSi) and in rate of growth. For intermediate doses ~0.9 × 10^{16} N/cm^2, the first phase formed corresponds to NiSi, and the growth rate is greatly reduced. These results are explained in terms of a silicon nitride barrier to Ni diffusion forming at the Ni/Si interface.

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It is known that the growth of Ni silicides can be greatly altered by the presence of impurities. For Ni films deposited on Si and annealed in vacuum, the metal-rich phase NiSi forms first and grows until all of the Ni film is consumed. Thereafter, the second phase NiSi begins to grow, converting the NiSi to NiSi. However, for samples annealed in a Ni ambient rather than in vacuum, the formation of NiSi at the NiSi/Si interface has been observed when unreacted Ni was still present on the sample surface. It has been suggested that this effect is caused by impurities from the ambient diffusing through the Ni to the Ni-NiSi interface so that the growth of the first phase ceases and that of the second phase starts. Previous work has shown that when Ni films evaporated on Si substrates are implanted with a few atomic percent oxygen, a SiO_x barrier to Ni diffusion will form during vacuum annealing and cause the simultaneous presence of NiSi, NiSi, and unreacted Ni. In the present work we investigated the effect on Ni silicide formation of a controlled introduction of N by ion implantation into Ni films.

Ni films, 2 kÅ thick, were evaporated onto Si (100) substrates in an oil-free, e-beam system at ~40 Å/sec with the vacuum kept at ~3 × 10^{-7} Torr during the evaporation. The Ni films were then implanted with N⁺ at energies of 70 and 100 keV/atom. According to the range tables, this places the N distribution well within the Ni layer (R_p = 780 and 1140 Å, and ΔR_p = 340 and 430 Å, respectively). The samples were then annealed in vacuum (~1 × 10^{-6} Torr) at temperatures ranging from 290 to 450 °C for various times. Backscattering analysis with 2.0 MeV 4He ions was used to measure composition profiles.

Figure 1 shows backscattering spectra for an unimplanted sample and a sample implanted with 0.5 × 10^{16} N/cm^2 annealed together at 290 °C for 40 min. In each case NiSi is formed. The growth rates are nearly the same and agree with published data. The implanted sample behaves as would be the case without N implantation both in regard to the NiSi phase formed and the growth rate.

The outcome of annealing at the same temperature of about 290 °C differs radically if the dose is approximately doubled.

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Figure 2 shows backscattering spectra for a sample implanted with 0.9 × 10^{16} N/cm^2 after annealing at 287 °C for 20 min and after additional 20-min annealings at 313, 350, and 368 °C. After 287 °C, 20 min, some slight reaction has occurred. After the whole series of annealings, the reaction has progressed and the amplitude of the signals indicate that the phase NiSi is formed instead of the usually observed first-phase NiSi. The growth rate is greatly suppressed, i.e., at 370 °C only ~9 min are required to completely transform the 2-kÅ Ni film to NiSi, whereas 600 Å of the implanted Ni film has been left unreacted after the 20-min isochronal annealing sequence up to 370 °C.

To determine the nature of the reaction of Ni containing high N doses with Si, we have implanted 5.0 × 10^{16}
oxide and is not mobile in Ni at these temperatures. This is consistent with the fact that Ni and N do not form a very stable
interface as a barrier forms quickly relative to the formation rate of N profile well within the Ni film. From this we conclude that Ni is mobile in Ni at the annealing temperature. This is because unreacted Ni is still present, indicates that a barrier to Ni diffusion has formed. In the case of oxygen as the impurity in Ni, oxygen atoms are not sufficient to allow Ni-Si to form, but may allow NiSi to form, thus altering the first phase formed. The formation of bubbles in implanted samples after high-temperature annealing may indicate that the implanted dose is greater than the solid solubility of O in Ni.

We model these results in the following way. Nickel is known to be the dominant diffusing species in Ni-Si formation and that Ni-Si will continue forming as long as a supply of Ni is present. The strong suppression of the Ni-Si formation for implanted doses \( \geq 0.9 \times 10^{16} \text{ N/cm}^2 \), which occurs while unreacted Ni is still present, indicates that a barrier to Ni diffusion has formed. In the case of oxygen as the impurity in Ni, this barrier is known to form at the silicide-Ni interface as SiO\(_2\). We propose that silicon nitride may play a similar role for N as the impurity in Ni. The results show that the barrier forms quickly relative to the formation rate of Ni-Si even though the calculated projected range would place the Ni profile well within the Ni film. From this we conclude that N is mobile in Ni at the annealing temperature. This is consistent with the fact that Ni and N do not form a very stable nitride. By comparison, oxygen does form a stable nickel oxide and is not mobile in Ni at these temperatures. This explains why substantial Ni\(_2\)Si growth occurs before the SiO\(_2\) barrier forms.

To summarize our model: upon annealing the implanted N, not being chemically bound to the Ni, quickly moves to the Ni-Si interface to form a barrier of silicon nitride to Ni diffusion before appreciable reaction takes place between the Ni and Si.

Below a certain critical dose (between 0.5 and \( 0.9 \times 10^{16} \text{ N/cm}^2 \)) not all diffusion paths are blocked, and the reaction of Ni with Si proceeds as in the unimplanted case. Above this critical dose (between 0.9 and \( 5.0 \times 10^{16} \text{ N/cm}^2 \)) all the diffusion paths are completely blocked and no reaction between Ni and Si takes place until very high temperatures when the barrier may fail locally. Near the critical dose the supply of Ni atoms is not sufficient to allow Ni\(_2\)Si to form, but may allow NiSi to form, thus altering the first phase formed. The formation of bubbles in implanted samples after high-temperature annealing may indicate that the implanted dose is greater than the solid solubility of N in Ni.

In summary, we have demonstrated that by implanting N doses of from 0.9 to \( 5.0 \times 10^{16} \text{ N/cm}^2 \) into Ni films on Si substrates, the reaction between Ni and Si can be strongly suppressed or stopped. We have explained this result in terms of a model similar to that proposed previously for oxygen impurities taking into account the differences in bonding to Ni between N and O.

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