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 ^{4}He 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 $\lesssim 0.5\times 10^{16}$ N/cm^2, the reaction between Ni and Si is that observed for unimplanted samples both in the phase formed (Ni_2Si) and in rate of growth. For intermediate doses $\sim 0.9\times 10^{16}$ 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 Ni_2Si forms first and grows until all of the Ni film is consumed. Thereafter, the second phase NiSi begins to grow, converting the Ni_2Si to NiSi.[1,2] However, for samples annealed in a N_2 ambient rather than in vacuum, the formation of NiSi at the Ni_2Si-Si interface has been observed when unreacted Ni was still present on the sample surface.[3] It has been suggested that this effect is caused by impurities from the ambient diffusing through the Ni to the Ni-Ni_2Si interface so that the growth of the first phase ceases and that of the second phase starts.[3] Previous work has shown that when Ni films evaporated on Si substrates are implanted with a few atomic percent oxygen, a SiO_2 barrier to Ni diffusion will form during vacuum annealing and cause the simultaneous presence of NiSi, Ni_2Si, and unreacted Ni.[4] 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 $\sim 3\times 10^{-7}$ Torr during the evaporation. The Ni films were then implanted with N_2^+ at energies of 70 and 100 keV/atom. According to the range tables,[5] this places the N distribution well within the Ni layer ($R_p = 780$ and 1140 Å, and $\Delta R_p = 340$ and 430 Å, respectively). The samples were then annealed in vacuum ($\sim 1\times 10^{-6}$ Torr) at temperatures ranging from 290 to 450 °C for various times. Backscattering analysis with 2.0 MeV ^{4}He 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 Ni_2Si is formed. The growth rates are nearly the same and agree with published data.[2] The implanted sample behaves as would be the case without N implantation both in regard to the Ni_2Si 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.

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 Ni_2Si. 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 Ni_2Si, 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}

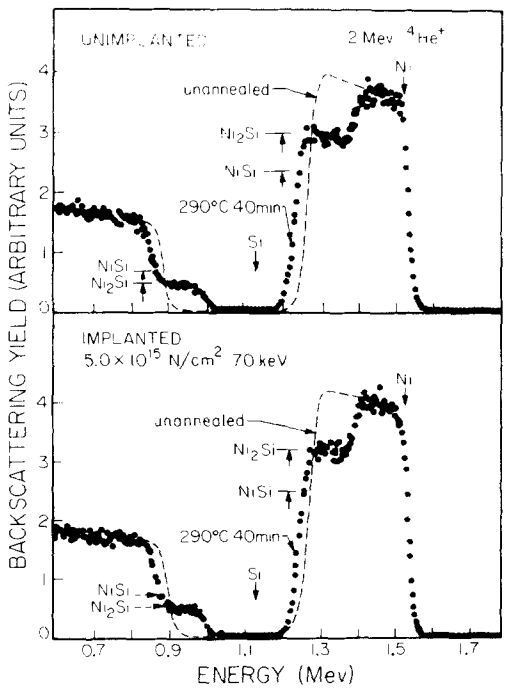

FIG. 1. MeV backscattering spectra of a 2000-Å Ni film on a Si ⟨100⟩ substrate, unimplanted and implanted with 5.0×10^{15} N/cm^2 and vacuum annealed at 290 °C for 40 min. Identical behavior is observed in regards to the Ni_2Si phase formed and the growth rate.

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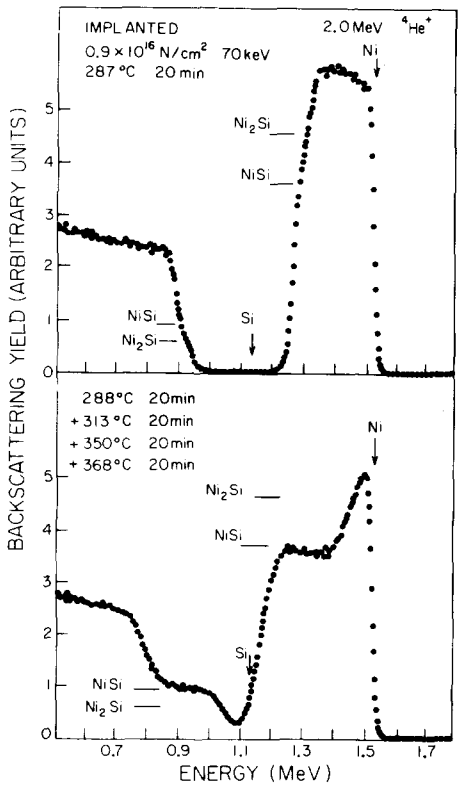

FIG. 2. MeV backscattering spectra of a 2000-Å Ni film on a Si ⟨100⟩ substrate, implanted with 0.9×10^{16} N/cm^2 and annealed at 287 °C for 20 min (top) and after additional 20-min annealings at 313, 350, and 368 °C (bottom). Only a slight reaction is seen after the first annealing, indicating the presence of a barrier to Ni diffusion. After the complete annealing sequence (bottom) NiSi rather than the usual Ni_2Si is the first phase formed.

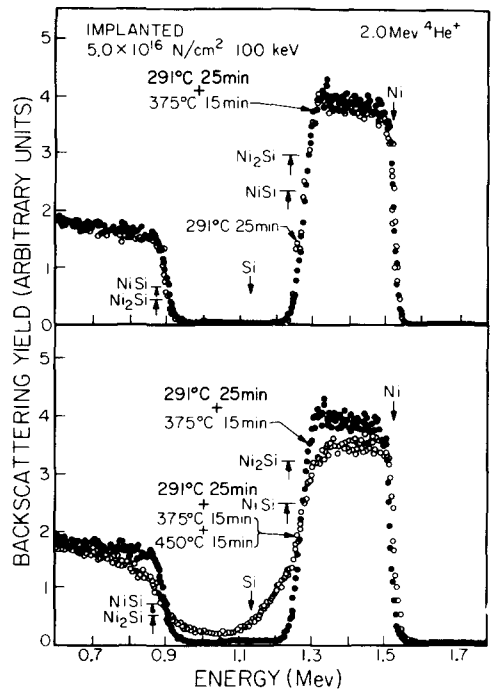

FIG. 3. MeV backscattering spectra of a 2000-Å Ni film on a Si ⟨100⟩ substrate, implanted with 5.0×10^{16} N/cm^2 and annealed at 291 °C, 25 min, 375 °C, 15 min, and 450 °C, 15 min. No reaction occurs after the first two annealing steps (top). After the complete sequence (bottom) only localized interdiffusion of the Ni and Si has taken place.

N/cm^2 at 100 keV/atom and sequentially increased the annealing temperatures from 290 to 450 °C. Backscattering spectra taken after each annealing step are shown in Fig. 3. No detectable reaction has taken place after 290 °C, 25 min, or after 290 °C, 25 min, and 375 °C, 15 min annealings (Fig. 3, top). After annealing the sample further at higher temperature (450 °C, 15 min), there is substantial localized interdiffusion between the Ni and Si. Microscopic inspection of the sample shows the Ni surface to be laterally nonuniform. There are large numbers of small outward bulges suggestive of blisters or submerged bubbles.

We model these results in the following way. Nickel is known to be the dominant diffusing species in Ni_2Si formation[1] and that Ni_2Si will continue forming as long as a supply of Ni is present.[3] The strong suppression of the Ni_2Si formation for implanted doses $\gtrsim 0.9\times10^{16}$ N/cm^2, which occurs while unreacted Ni is still present, indicates that a barrier to Ni duffusion 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_2Si even though the calculated projected range would place the N 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_2Si 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 0.9×10^{16} 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 5.0×10^{16} 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_2Si 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 5.0×10^{16} 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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