Dopant diffusivity and solubility in nickel silicides

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Boron and Arsenic diffusion in implanted Ni_2Si and NiSi layers has been studied using secondary ion mass spectrometry. These measurements show that As should not diffuse in the silicides at the temperatures used for silicidation. In contrast signifi- cant B diffusion is observed in both silicides at temperatures as low as 400°C. It is also observed that both dopants have higher solubilities in Ni_2Si than in NiSi. B and As solubilities below 1.10^{20} at.cm^{-3} are measured in NiSi.

1 Introduction

The silicide NiSi is currently used to form metallic contacts in microelectronics for 32 and 22 nm technology nodes. Ni silicides are formed by the reaction of a Ni layer with the Si substrate. The Ni_2Si phase forms during a first Rapid Thermal Anneal (RTA), while the low resistive silicide NiSi forms during a second RTA. During silicidation, dopants redistribute in the silicide /silicon structure. It is found that an accumulation at the silicide interface can enhance electrical properties of the silicide / silicon contacts [1] and can be used to modulate the gate work function [2, 3]. Dopant redistribution depends on their diffusivity and solubility in the different phases [4, 5]. A recent study using atom probe tomography evidenced the presence of B rich clusters in NiSi after silicidation on highly doped Si [6]. It shows that B cluster formation is possible in Ni silicides which should have an effect on redistribution and underlines the importance of dopant solubility. In addition, different authors have studied the possibility of implanting the dopants in preformed silicide and use the silicide as a diffusion source to form the junction in the silicon [7, 8]. In this case also, data about dopant diffusion and solubility in the silicide are important to predict dopant redistribution. In this case solubility could limit dopant out-diffusion from

the silicide [9]. However, few data about dopant diffusivity and solubility are available for Ni silicides [10] despite their importance in the present technologies.

In this work the diffusivity and solubility of B and As in Ni_2Si and NiSi are studied. Silicide layers are formed on oxidized substrates. Dopants are implanted into the silicides, and diffusion is observed by Secondary Ion Mass Spectrometry (SIMS) after different heat treatments.

2 Experiments

The silicide samples were produced through the reaction of a Ni layer deposited at room temperature by magnetron sputtering on a 150 nm Si layer grown by low pressure chemical vapor deposition at 550 °C on the 30 nm-thick oxide. The silicides were formed through a conventional RTA for 5 min at 350 °C or 500 °C to form Ni_2Si or NiSi respectively. Ni layers with different thicknesses were deposited in order to obtain the Ni_2Si or NiSi compositions. The Ni_2Si and NiSi compositions were obtained with 175 and 73 nm nominal thicknesses respectively. The samples were annealed at 700 °C for 2 h to ensure grain growth and grain size stability during the diffusion heat treatments. Transmission electron microscopy analyses (not shown here) were used to verify that the grains were columnar. B and As were implanted either in Ni_2Si or NiSi through the

20 nm thick oxide layer, to a dose of 5×10^{15} atom cm^{-2}. B was implanted at 20 and 18 keV in Ni$_2$Si and NiSi respectively and As was implanted at 120 and 100 keV in Ni$_2$Si and NiSi respectively. Doping conditions were targeted in order to confine the entire boron dose within the top half of the silicide layer.

Different diffusion anneals were performed. The 4 samples were annealed at 500 °C for 1h. In addition B implanted samples were also annealed at 400 °C for 1 h, and As implanted samples were also annealed at 650 °C for 4 h and 16 h.

3 Results and discussion

Figure 1 presents the B SIMS profiles measured in the Ni$_2$Si and NiSi layers after implantation and after following annealing at 400 and 500 °C for 1 h. The profiles measured in Ni$_2$Si (Fig. 1a) after annealing can be divided in two parts. A region close to the surface forms a hillock at the position of the original implantation peak. The hillock height decreases when the annealing temperature increases. In the second part, deeper than 100 nm, the concentration profile is almost flat. This profile shape can be explained using two different scenarios. First, it can be explained by the well known type B kinetic regime of diffusion [11, 12]. The top part would correspond to diffusion in the volume of the grains and the bottom part to the fast diffusion both in the bulk and in grains boundaries (GBs), with a lower gradient. In a second scenario, the top part of the profile could be due to the presence of dissolving precipitates. Precipitates are known to give an immobile contribution to the concentration profile [13] and, when they dissolve, act as a source of mobile species which diffuse below the solubility limit giving such profile shapes [14, 15]. Thus, the bottom part of the profile would be due to a type *A* diffusion in the volume and the GBs. For a type *B* diffusion, a break should be observed in the bottom profile due to the 4 orders of magnitude difference between lattice and grain boundary diffusion. The solubility limit is given by the maximum concentration of the mobile species which would be 1×10^{20} at cm^{-3} in this case and 5×10^{20} at.cm^{-3} according to the first scenario. Thus both possible scenarios show that B diffusion in the volume of Ni$_2$Si is fast at this temperature and that the solubility limit is at least 1×10^{20} at.cm^{-3}.

The B profiles in NiSi measured before and after similar heat treatments show more complex redistribution (Fig. 1b). After annealing at 400 °C for 1 h, the top of the implantation peak is modified. At a depth of ~40 nm the concentration decreases whereas accumulation is observed at the top interface with SiO$_2$. This phenomenon is more pronounced after the 500 °C anneal. It can be due to B segregation at this interface. A similar B accumulation at the Ni$_2$Si /SiO$_2$ interface is also observed in Fig. 1a. The 500 °C annealed sample exhibits a new Gaussian profile shape between 40 and 90 nm. This Gaussian has a smaller width than the initial Gaussian distribution and its center is

about 20 nm deeper in the NiSi layer than the initial distribution. The decay of the Gaussian is steeper after the 500 °C anneal than before annealing which can not be explained by diffusion only. It can be explained by the presence of non diffusing clusters having this Gaussian distribution. This was evidenced by several analyses after annealing of similar samples at different temperatures [16]. The fact that the B cluster distribution follows a Gaussian distribution suggests that B cluster formation may result from heterogeneous nucleation on implantation-induced defects. Below 100 nm, diffusion tails are observed for both temperatures and the concentration gradient is smaller after annealing at 500 °C indicating a faster diffusion at this temperature. B atoms are mobile for concentration lower than 3×10^{19} at cm^{-3} that corresponds to the B solubiliy limit in NiSi.
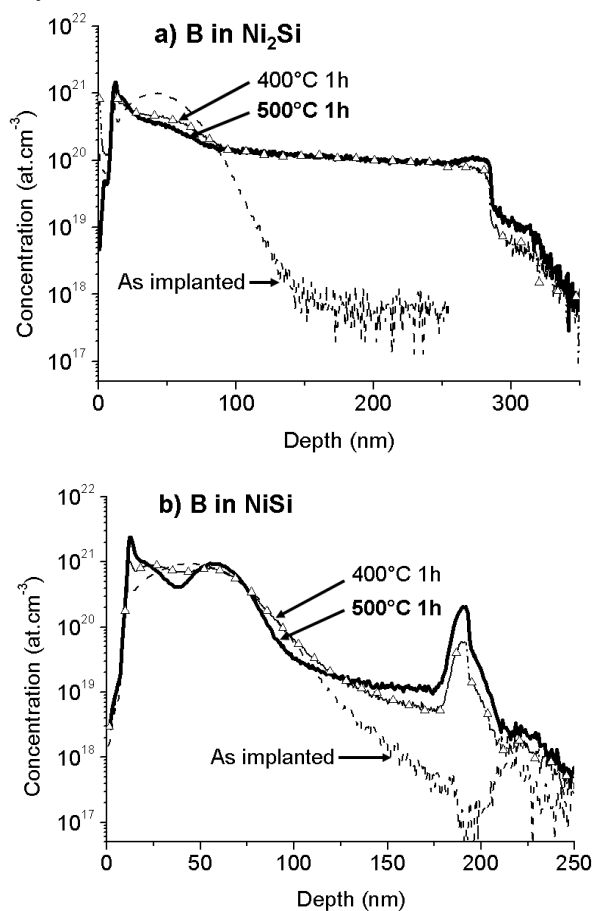

Figure 1 Concentration profiles of B implanted in a) Ni$_2$Si and b) NiSi and annealed at 400 and 500 °C for 1 h.

Arsenic concentration profiles in Ni$_2$Si and NiSi after annealing at 500 °C for 1 h and 650 °C for 4 h and 16 h are shown in Fig. 2. After annealing at 500 °C for 1 h, similar profiles are observed in Ni$_2$Si and NiSi. The Gaussian part of the implantation profile is unchanged but As accumulation is observed at the top and bottom interfaces with SiO$_2$.

This accumulation occurs at the bottom interface while no significant modifications of the profiles are observed in the middle of the layer. This can be explained by fast diffusion exclusively in GBs (C kinetic regime) [12, 17]. Indeed, it is common that high impurity concentration in GBs cannot be detected by SIMS due to the low GB density.

After annealing at 650 °C for 4 h the modifications of the profiles are more important. In the case of As implanted in Ni_2Si (Fig. 2a), flattening and broadening of the Gaussian part of the profile is observed. This phenomenon is stronger after annealing for 16 h. After 4 h annealing, below ~120 nm a diffusion tail is observed with a lower concentration gradient. This shape is typical of diffusion along the grain boundaries in the *B* kinetic regime. In a previous work, similar profile shapes could be explained in details by moderate diffusion in the volume and fast diffusion along interfaces and grain boundaries. 2D simulations based on Fick's equation could fit several similar profiles of As implanted in Ni_2Si and diffusion coefficients were measured [17, 18]. No indication of precipitation is observed, and the dopant is mobile at any observed concentration in the volume. Thus, As solubiliy limit is higher than 1×10^{21} at cm^{-3}. In the case of As implanted in NiSi, after annealing at 650 °C for 4 h, important As depletion is observed between 50 and 75 nm, after the maximum of the implantation peak. A lower concentration gradient is observed below 100 nm, indicating that diffusion has occurred. This is corroborated by the concentration profile measured after 16 h annealing that shows deeper As penetration in the layer. Similar to what was observed for B in NiSi (Fig. 1b) a Gaussian distribution narrower than the initial distribution is observed near the implantation peak (45 nm) after 4 h annealing. This distribution remains unchanged after 16 h annealing which indicates the presence of non diffusing clusters. Thus the solubility limit would be about 1×10^{20} at cm^{-3}, which is the highest concentration of mobile species. However, after annealing at 650 °C for 16 h, a shoulder appears in the profile at 130 nm that can not be explained by *Fickian* diffusion only. It might indicate precipitation at lower concentration than 1×10^{20} at cm^{-3}. Therefore 1×10^{20} at cm^{-3} can only be considered as a maximum value for the solubility limit of As in NiSi at 650 °C.

Comparison between the concentration profiles for As and B in both silicides after similar heat treatments (500 °C 1h) shows unambiguously that diffusion of B is greater than that of As both in Ni_2Si and NiSi. The same is observed in other silicides as $CoSi_2$ and WSi_2 [10]. More generally, smaller dopants are faster diffusers in silicides [10, 19].

Another important information is that As diffusion is very limited at 500 °C after 1h. Typical annealing temperatures used to form Ni_2Si and NiSi are 300 °C and 450 °C for about 90 s or less, respectively. Thus, As intrinsic

Table 1 As and B solubility measured in Ni_2Si and NiSi.

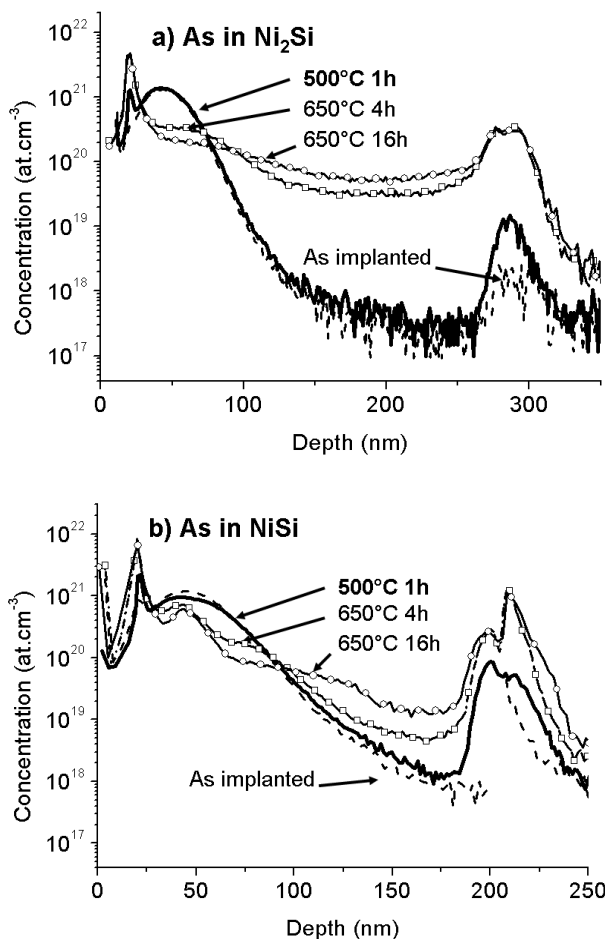| Silicide	Dopant	Temperature (°C)	Solubility (at cm^{-3})
Ni_2Si	B	400 - 500	$\geq 1 \times 10^{20}$
	As	650	$> 1 \times 10^{21}$
NiSi	B	500	$= 3 \times 10^{19}$
	As	650	$\leq 1 \times 10^{20}$

Figure 2 Concentration profiles of As implanted in a) Ni_2Si and b) NiSi and annealed at 650 °C for 4h and 500 °C for 1 h.

diffusion is not expected to occur in Ni_2Si or NiSi for such heat treatments.

The different conclusions about B and As solubilities in Ni_2Si and NiSi are summarized in Table 1. Although no solubility limit could be evidenced in Ni_2Si, the results indicate that dopant solubility is higher in Ni_2Si than NiSi. In NiSi, dopant solubility is limited to concentrations close to the dopant concentrations used to dope the Si source and drain regions, indicating that dopant precipitation is possible in devices. Precipitation is even more probable considering the fact that high local concentrations can arise at in-

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terface during redistribution, due to interfacial segregation and the snowplow phenomenon [20, 21].

4 Conclusion

NiSi and Ni$_2$Si samples were fabricated and implanted with B and As to study dopant diffusion and solubility in silicides. SIMS profiles measured before and after annealing were used to study dopant profile evolutions. The results show that As diffusion is very low at 500 °C after 1 h annealing. Little diffusion is observed at the grain boundaries, while no diffusion occurs in the volume of the grains, which shows that As should not diffuse during a typical silicidation rapid thermal anneal. In contrast to As, B diffusion is significant both in the volume and GBs in the same conditions. Information about solubilities in both silicides indicate that solubilities are higher in Ni$_2$Si than NiSi for both dopants. The low solubilities observed in NiSi show that compound formation is possible at the concentrations used in production devices. This information will be critical for understanding of dopant redistribution during Ni silicides formation.

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