

Diffusion and redistribution of boron in nickel silicides

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Abstract. The diffusion and solubility of B implanted in δ -Ni₂Si and NiSi layers is studied by SIMS. It is observed that both diffusion and solubility are higher in δ -Ni₂Si than NiSi. The redistribution of B during Ni silicidation is also studied. The SIMS profiles show the presence of concentration step in the middle of the final NiSi layer. This profile shape is explained in light of the results obtained in preformed silicides. The proposed model is supported by redistribution simulations that can reproduce the main features of the profile.

Introduction

The silicide NiSi is used in microelectronics to reduce the contact resistance between the metallic interconnections and the doped silicon of the active devices [1]. It is formed by the reaction of a Ni film with the doped Si. The silicides δ -Ni₂Si and NiSi are formed sequentially during the silicidation process [2]. During their growth, both phases consume doped Si. The dopants present in the Si are redistributed in the silicides and in the Si [3]. It was observed that this dopant redistribution can improve the electrical properties of the final device by reducing the contact resistance [4]. Because of the constant downscaling of the devices and need for higher performances, understanding and controlling of this redistribution is critical. Redistribution of dopants is predicted to depend on their diffusivity and solubility in the different phases appearing during the phase sequence [5]. In this work, we first study B diffusivity and solubility in δ -Ni₂Si and NiSi by implanting it in pre-formed silicide layers and subjecting them to different heat treatments. The resulting concentration profiles are analyzed by secondary ion mass spectroscopy (SIMS). B redistribution during Ni Silicide formation is then studied by SIMS. A model is proposed to explain the features of the B profiles and it is supported by a simple redistribution simulation.

Experimentals

δ -Ni₂Si or NiSi layers were formed on a 30 nm SiO₂ layer on a Si substrate by reacting deposited Ni and Si layers of appropriate thicknesses. The δ -Ni₂Si and NiSi phases were obtained with 175 and 73 nm nominal thicknesses respectively. The samples were annealed at 700 °C for 2 h to ensure limited grain growth and grain size stability during the diffusion heat treatments. A 20 nm SiO₂ layer was deposited on the silicide to reduce implantation damages. B was implanted either in δ -Ni₂Si or NiSi through the 20 nm thick oxide layer, to a dose of 5×10^{15} atom cm⁻². Energies of 20 and 18 keV in δ -Ni₂Si and NiSi were used respectively. To study B redistribution during Ni silicidation, B was also implanted in a Si(001) substrate, at 10 kV to a dose of 1×10^{15} at.cm⁻² with an incidence angle of 7°. The sample was then subjected to an activation anneal at 1050 °C during 30 seconds and 70 nm Ni were deposited on the Si surface by magnetron sputtering. The different samples were annealed at 400, 450 and 550°C during 1h. The concentration profiles are measured by SIMS with a 3 kV Cs⁺ beam.

Results and discussion

The B concentration profiles measured in $\delta\text{-Ni}_2\text{Si}$ after heat treatment at 400 and 550°C are presented in Fig. 1.a. The profiles can be divided in two main parts. First, a bump can be observed from the surface to a depth of 100 nm. It is located at the depth of the initial Gaussian distribution and has a lower concentration. The maximum concentration of this bump decreases when the annealing temperature is increased. The second part of the profile, from 100 nm to the interface with the oxide layer at 280 nm, is almost flat. This profile shape could be explained using two different scenarios. First, it could be explained by diffusion in the B regime [6]. The bump would correspond to slow diffusion in the bulk of the grains, while the diffusion tail observed after 100 nm depth would correspond to fast diffusion along the grain boundaries. Second, the bump could correspond to precipitates. Indeed, the atoms forming precipitates do not diffuse and their contribution in the concentration profile is expected to have a constant shape. The lower gradient after 100 nm depth would correspond to atoms diffusing fast, both in the bulk and the grain boundaries and with a concentration below the solubility limit. The fact that the Gaussian part of the profile is decreasing in concentration with increasing the annealing temperature would then indicate precipitates dissolution. Both possible scenarios show that B diffusion is significant both in the bulk and the grain boundaries of in $\delta\text{-Ni}_2\text{Si}$. The solubility limit is given by the highest concentration of mobile B atoms. Thus, the solubility limit of B in $\delta\text{-Ni}_2\text{Si}$ is above 5×10^{20} and equal to 1×10^{20} according to the first and second scenarios respectively.

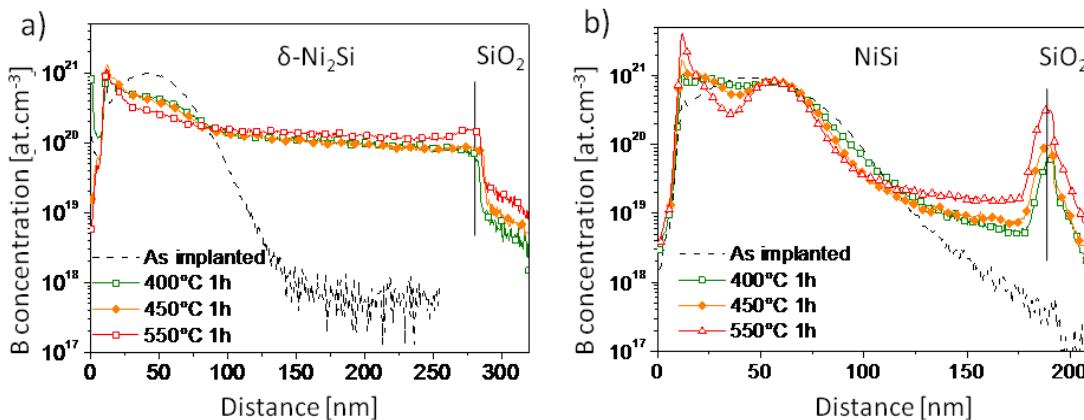


Figure 1 : B concentration profiles measured before annealing and after annealing at 400, 450 and 550°C for 1h in (a) $\delta\text{-Ni}_2\text{Si}$ and (b) NiSi.

The profiles measured before and after heat treatment at 400, 450 and 550°C in NiSi are shown in Fig 1.b. After heat treatment, the first part of the profile has a Gaussian shape. However, it is located deeper than the distribution measured before annealing. After annealing at 400°C, it is slightly narrower than the as-implanted distribution and becomes even narrower after annealing at 450°C and remains identical if the temperature is further increased to 550°C. Below 100 nm depth, the profile shows a negative concentration gradient. This gradient becomes smaller and the concentration increases when the annealing temperature is increased. The fact that the Gaussian part of the profile becomes narrower when the annealing temperature is increased cannot be explained using diffusion only. The fact that this distribution remains the same for an annealing temperature of 450 or 550°C indicates that the atoms contributing to this part of the profile are not diffusing, which indicates the presence of precipitates. The presence of B-rich precipitates in this Gaussian distribution was also evidenced using atom-probe tomography for the sample annealed at 550°C for 1h [7]. The fact that this Gaussian distribution is located slightly deeper than the original B distribution can be explained by heterogeneous nucleation on implantation defects. Thus, the narrow Gaussian distribution obtained after annealing would be related to the defect distribution and not the initial B distribution only. The second part of the profile, below 100 nm, exhibits a lower concentration that decreased when the temperature is increased, indicating B diffusion in NiSi. The solubility limit, given by the highest concentration of mobile species is 3×10^{19} at.cm⁻³.

The B profiles measured before and after Ni silicidation at 400, 450 and 550°C for 1h are shown in Fig. 2. The profile measured in Si before silicidation is calibrated in depth with respect to the Si substrate. The Ni and Si signals measured after heat treatment at 550°C for 1h are also given. After annealing, a broad B peak is observed close to the interface. However, it is difficult to define accurately the position of the interface using the Ni and Si signals because they are affected by the SIMS artifacts [8]. Thus, it is not possible to conclude if this B accumulation is located exactly at the interface or close to the interface in one of the two phases. Below the NiSi layer the B concentration decreases exponentially. This B signal is most probably due to the mixing effect of the well known SIMS collision cascades [9]. Indeed, B diffusion in Si is negligible at these temperatures [10] and B is not expected to diffuse deep in the Si substrate, whereas a signal is still measured in our case as far as 100 nm from the NiSi / Si interface. After silicidation at 450 and 550°C, the B profile forms a step in the middle of the NiSi layer, with a concentration that is lower in the top half than in the bottom half of the NiSi layer. After annealing at 550°C, the high concentration that was observed in the bottom half of the layer only is present throughout the whole layer. The fact that this step is identical after annealing at 400 and 450°C indicates that B does not diffuse in NiSi at this temperature. It diffuses only at 550°C, when the concentration becomes homogeneous in NiSi. Additional profiles (not shown here) show that the B concentration is already homogeneous after annealing the same sample at 500°C for only 1h [11]. This result is different from what was observed for the diffusion of B that was implanted in preformed NiSi, where diffusion was observed at a temperature as low as 400°C. This difference can be explained by the presence of an excess of point defects due to the implantation of B that would allow low temperature diffusion when B is implanted in NiSi.

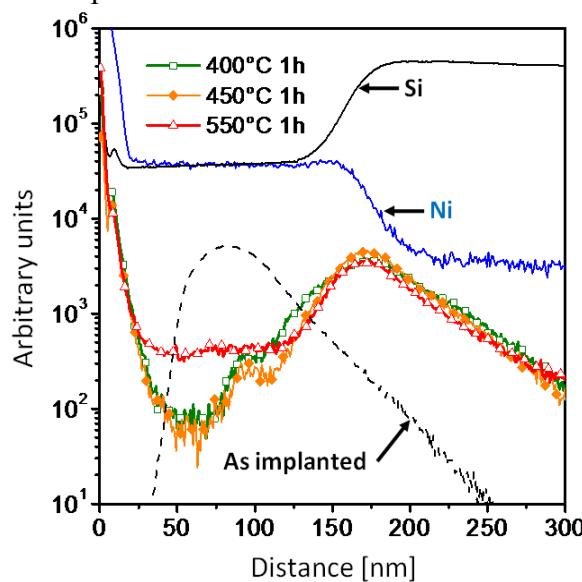


Figure 2 : B concentration profiles measured before and after silicidation at 400, 450 and 550°C for 1h. The Ni and Si profiles correspond to the sample heated at 550°C for 1h.

The presence of a step in the profile after annealing at 400 and 450°C can be explained by the redistribution of B during the growth of NiSi. After the complete formation of δ -Ni₂Si, NiSi forms at the δ -Ni₂Si / Si interface and grows at its two interfaces. Thus, the initial nucleation point of NiSi is eventually located at the middle of the NiSi layer. A different concentration in the two halves of the final NiSi layer can thus, be explained by a different redistribution at these two interfaces during the growth of NiSi. These two different redistributions can be understood using the information about the diffusivity of B observed in the two implanted silicides. Diffusion of B was observed to be fast in δ -Ni₂Si at least in the grain boundaries and negligible in NiSi at 400 and 450°C after redistribution. If B segregates at the surface of δ -Ni₂Si, then the B present at the top interface of NiSi will preferentially diffuse through δ -Ni₂Si to accumulate at the surface instead of being incorporated in the growing layer. At the bottom interface of NiSi, the B that is present in the

consumed Si cannot diffuse both in NiSi and Si and is incorporated in the growing NiSi layer. This redistribution mechanism involves only B diffusion and segregation at the different interfaces. It is a very simple mechanism if one considers all the other parameters that are believed to be able to affect dopant redistribution during silicidation [5]: the dopant solubility and partition in all the phases appearing during silicidation, the effect of the metal (and / or Si) chemical potential gradients on the ternary equilibria, the presence of strain and point defects generated by the reactions at the different interfaces and the possible presence of transient phases [12-13], in addition to the usual phase sequence. In order to verify that the proposed model can, alone, explain the measured redistribution profiles, it is compared to redistribution simulations. The objective of these simulations is to verify that the present mechanism can reproduce the measured profiles using realistic parameters. The B redistribution during the sequential growth of δ -Ni₂Si and NiSi was simulated using the finite difference method in one dimension by making different assumptions:

- In accordance with the results observed in this work for B diffusion in both silicides, the diffusion of B in δ -Ni₂Si was considered to be infinitely fast while the diffusion in NiSi was considered to be frozen out. In principle, the diffusion of B should also be negligible in Si at the temperatures used in this work [10]. However such an assumption is debatable. In principle, diffusion of As in Si is also negligible at the temperatures used for silicidation. Nevertheless, its rejection 10 to 30 nm deep in the Si was already reported by one author [14]. However, in the absence of such data in the case of B, it was decided to neglect its diffusion in Si.

- The surface and interfaces were considered to be 0.5 nm thick, which corresponds to the assumption that is generally made for grain boundaries in polycrystals [6].

- A Henry type segregation law was assumed for the surface and interfacial segregation.

- Local equilibrium was assumed at every interface, and, at the beginning of the formation of a phase, its two interfaces are considered to be in equilibrium with each other.

- No information is available about the solubilities and partitioning coefficients in the literature for the Ni-Si-B system. Thus, the partitioning coefficients between the different phases were assumed to be independent of the concentration and equal to the ratios of the solubility limits measured in this work in the different phases. They are calculated based on solubilities equal to 1×10^{20} and 3×10^{19} at.cm⁻³ in δ -Ni₂Si and Ni respectively, and 2×10^{18} at.cm⁻³ for Si, which is the solubility measured in Si in equilibrium with SiB₃ [15] and extrapolated to a temperature of 500°C.

Solute segregation at a grain boundaries is generally quantified by the segregation factor, which is equal to the ratio of the concentration in the interface to the concentration in the bulk phase. However, when solute segregation occurs at an interface between two different phases where partitioning exists, the value of the segregation factor will depend on which phase is taken as a reference. Thus, to simplify the description of the parameters that were used in this simulation, the different segregation and partitioning coefficients are presented here as concentrations in equilibrium with Si when the concentration in Si is equal to 1 atom per unit volume (Table 1). A high value was chosen for the segregation at the surface of δ -Ni₂Si in order to simulate the accumulation of B at the surface of δ -Ni₂Si during NiSi growth. Arbitrary values of 1000 atoms per unit volume were chosen to simulate the segregation that was reported in the literature for the Ni / δ -Ni₂Si [16] and NiSi / Si [17] interfaces. In the absence of data in the literature about B segregation at the other interfaces, low values were selected for B segregation at the δ -Ni₂Si / Si and δ -Ni₂Si / NiSi interfaces.

The B concentration profile measured before annealing was used as initial condition for the simulation (Fig. 3.a). After complete formation of δ -Ni₂Si (Fig. 3.b.), the B present in the consumed Si is homogeneously distributed in the δ -Ni₂Si layer and, as expected, important segregation is observed at the surface of δ -Ni₂Si. At the beginning of the growth of NiSi, its two interfaces are in equilibrium. When NiSi grows (Fig. 3.c.), the B present in the consumed Si is accumulated in the bottom interface and more B is incorporated in NiSi while, as expected, the B preferentially accumulates at the surface of δ -Ni₂Si and the concentration remains low. After complete formation of NiSi, a step is observed in the profile and B accumulation is observed at the surface of NiSi and at the NiSi / Si interface.

Table 1: Segregation, partition and diffusion parameters used for the simulation of B redistribution during Ni silicides formation. The parameters are presented as concentrations in equilibrium with Si when the concentration in Si is equal to 1 atom per unit volume.

Phase	Surface	Bulk	Diffusion	Interface	Interfacial
	segregation	partition			segregation
Ni	0	0	None	Ni / δ-Ni ₂ Si	1 000
δ-Ni ₂ Si	50 000	50	∞	δ-Ni ₂ Si / Si	10
NiSi	—	15	None	δ-Ni ₂ Si / NiSi	10
Si	—	1	None	NiSi / Si	1 000

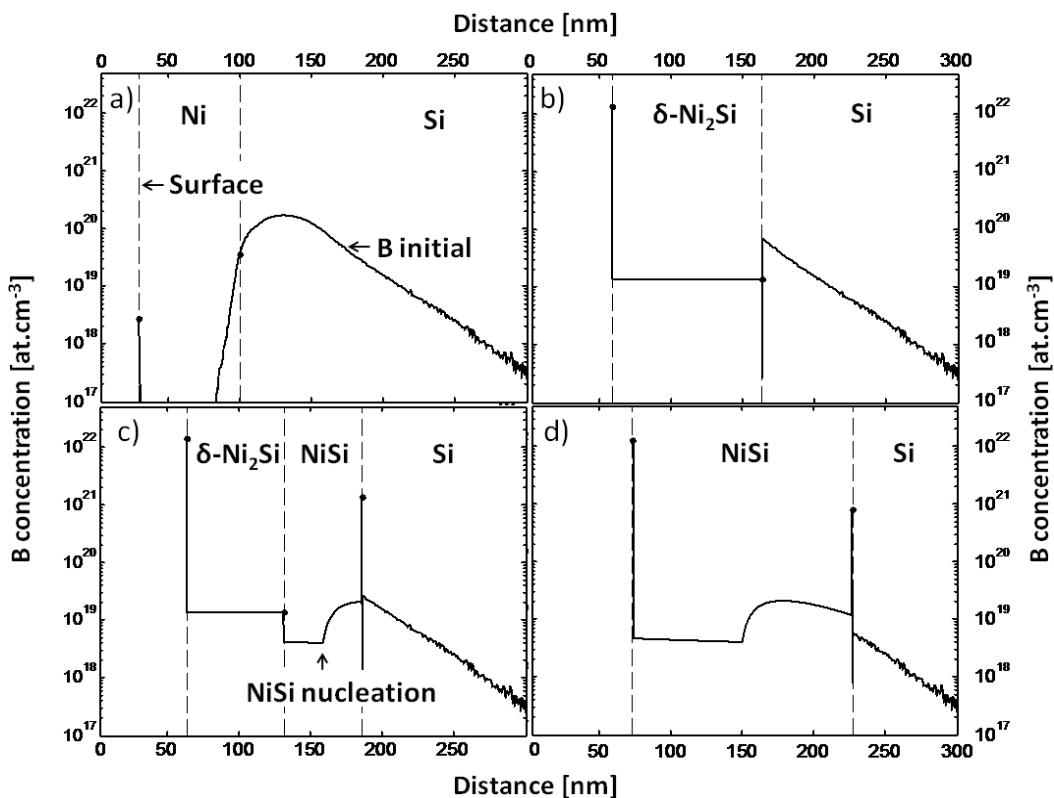


Figure 3: Simulation of the B redistribution during the sequential growth of Ni silicides. The different plots show (a) the B distribution before silicidation, (b) after complete formation of δ-Ni₂Si, (c) during the growth of NiSi, and (d) after complete formation of NiSi. The B concentration at the different interfaces is represented by the black dots.

Similar results were obtained when diffusion was neglected in the bulk of δ-Ni₂Si but was considered to be fast at δ-Ni₂Si grain boundaries only (both interfaces of δ-Ni₂Si in equilibrium). It was also observed that the bulk partitioning coefficients had little impact on the qualitative result of the simulation. The value chosen for the equilibrium concentration in Si (i.e. partitioning coefficient between Si and both silicides) has also no importance because diffusion is neglected in Si and the silicides are never in equilibrium with the bulk of Si. Because diffusion is also neglected in NiSi, only the B segregated at the NiSi / Si interface is transported by the bottom interface of NiSi during its growth in the simulation. It is, however, debatable whether some of the B is actually also transported in front of the moving interface through the snowplow phenomenon in the real system. The most important parameters that control the final profile shape are the segregation coefficient at

the surface of $\delta\text{-Ni}_2\text{Si}$ and the segregation at the NiSi / Si interface. It should be noted that despite the high segregation coefficient used for B segregation at the surface of $\delta\text{-Ni}_2\text{Si}$, the value of the surface concentration remains realistic. This simulation shows that it is possible to explain B redistribution during Ni silicidation using only B diffusion in $\delta\text{-Ni}_2\text{Si}$ and segregation at the different interfaces.

Conclusion

Diffusion and solubility of B implanted in $\delta\text{-Ni}_2\text{Si}$ and NiSi were studied by SIMS. B solubility is higher in $\delta\text{-Ni}_2\text{Si}$ than in NiSi. B diffusion is fast in $\delta\text{-Ni}_2\text{Si}$ at 400°C which is the lowest temperature used in this study, while B diffusion is negligible in NiSi during an annealing at 450°C for 1h. After Ni silicidation of a B implanted substrate, the B concentration profile exhibits a step in the middle of the NiSi layer. This profile can be explained mainly by the fast diffusion of B in $\delta\text{-Ni}_2\text{Si}$ and its segregation at the surface of the $\delta\text{-Ni}_2\text{Si}$ layer. This model is supported by a redistribution simulation. The simulation can reproduce the features observed in the measured profiles, showing that B diffusion and segregation at the surface and interfaces can, alone, explain the measured profile shapes.

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