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Interplay Between Grain Boundary Grooving, Stress, and Dealloying in the Agglomeration of $NiSi_{1-x}Ge_x$ Films

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Germanosilicides, especially those formed on compressive substrates, are less stable than silicides against agglomeration. By studying the solid-state reaction of Ni thin film on strained $Si_{0.8}Ge_{0.2}(001)$, we show that nickel germanosilicide is different from nickel silicide and nickel germanide in several respects: the grains are smaller and faceted, the groove angle is sharper, and dealloying takes place. The germanium out-diffusion creates a stress in the film which favors grooving and agglomeration.
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$Si_{1-x}Ge_x$ alloys are under consideration for a wide variety of high-performance electronic and optoelectronic devices, including advanced metal-oxide-semiconductor field-effect transistors (MOSFETs), where the enhanced carrier mobility of Ge (channel) and the reduced contact resistance (source and drain) are particularly important. Reliable low-resistivity electrical contacts to the Ge-containing regions can be formed using the same process as for self-aligned silicides. $NiSi_{1-x}Ge_x$ is the contact of choice in such applications due to its low resistivity and the low processing temperature needed for its formation. Interfacial reactions of Ni with $Si_{1-x}Ge_x$ have been studied in the context of ohmic contacts and Schottky barriers for infrared detectors.[1-4] The downside of metal germanosilicides is their lower stability against agglomeration than the corresponding silicides.[5-8] Moreover, germanosilicide films formed on compressive substrates are less stable than those formed on relaxed substrates.[5-7] Because the formation energy of NiSi is lower than that of NiGe, the energy can be decreased by having more NiSi and less NiGe, i.e., by expelling Ge from $NiSi_{1-x}Ge_x$.[1] There is a tendency for increased Ge content of the $Si_{1-x}Ge_x$ alloy at the triple junction, i.e., the intersection of the semiconductor/germanosilicide interface and the grain boundary.[1,5,7-9] In this article, we examine the correlations between agglomeration, composition inhomogeneities, and interface morphology in $NiSi_{1-x}Ge_x$ films[e] formed on $Si_{0.8}Ge_{0.2}$. We demonstrate that germanosilicides exhibit a fundamentally different agglomeration mechanism than the corresponding silicide and germanide films.

Nickel films (15 nm thick) were dc magnetron sputtered (base pressure $<5 \times 10^{-7}$ Torr) onto a 73 nm thick strained $Si_{0.8}Ge_{0.2}(001)$. Rapid thermal annealing (RTA) in a N_2 ambient for 20 s between 300 and 800°C was employed to form the nickel germanosilicide. X-ray diffraction (not shown) indicates that only $NiSi_{1-x}Ge_x$ was formed during RTA at 400–800°C. At 300°C both $Ni_2Si_{1-x}Ge_x$ and $NiSi_{1-x}Ge_x$ were found.

Figure 1a is a high-resolution cross-sectional transmission electron micrograph (HRXTEM) of $NiSi_{1-x}Ge_x/Si_{0.8}Ge_{0.2}$ after RTA at 500°C. A well-defined groove forms at the (triple) junction of the $NiSi_{1-x}Ge_x$ grain boundary and the $NiSi_{1-x}Ge_x/Si_{1-x}Ge_x$ interface (the grain boundary groove at the free surface is very shallow). Similarly, grooves form at grain boundaries in NiSi on Si and NiGe on Ge, as shown in Fig. 1b and c. The grain boundary groove angle θ (defined in Fig. 1) in $NiSi_{1-x}Ge_x$ is considerably smaller than in NiSi and NiGe (the latter two are of similar magnitude).

Figure 2a shows a cross-sectional TEM of $NiSi_{1-x}Ge_x$ formed on compressive $Si_{0.8}Ge_{0.2}$ at a lower magnification than that in Fig. 1a. The $NiSi_{1-x}Ge_x/Si_{1-x}Ge_x$ interface in this figure consists of a series of nearly flat sections, joined at relatively sharp corners. A large section of this interface appears to remain parallel to the initial flat

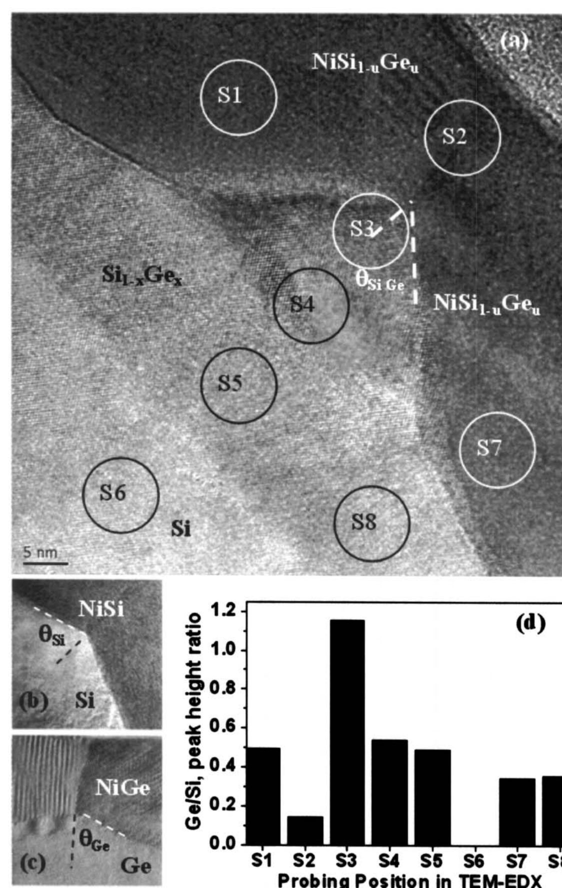

Figure 1. HRXTEM images of films annealed for 20 s: (a) $NiSi_{0.8}Ge_{0.2}$ at 500°C, (b) NiSi at 650°C, and (c) NiGe at 500°C. (d) TEM-EDX data obtained from the regions S1-S8 indicated in (a); the spectra were analyzed to estimate the Ge/Si peak height ratio.

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[e] We use the notation of $NiSi_{1-x}Ge_x$ and $Si_{1-x}Ge_x$ as labels for the nickel germanosilicide and solid solution silicon germanium alloy. The subscript x is not used to imply a specific composition of either phase or theat the two phases have the same germanium content.

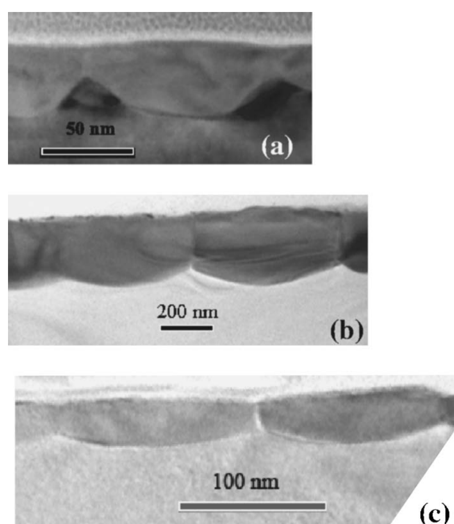

Figure 2. XTEM images of (a) a $NiSi_{1-x}Ge_x$ film formed on strained $Si_{0.8}Ge_{0.2}$ with RTA for 60 s at 550°C, (b) a NiSi film on Si with RTA for 60 s at 750°C, and (c) a NiGe film on Ge with RTA for 20 s at 500°C.

(001) surface of the $Si_{1-x}Ge_x$ substrate. Although the possible importance of this phenomenon has not previously been emphasized, polygonal $NiSi_{1-x}Ge_x$ interface morphologies can also be observed in earlier studies.[5,6,9,10] The NiSi/Si and NiGe/Ge interfaces appear to be much smoother curves (i.e., of nearly constant curvature), as shown by Fig. 2b and c. Constant curvature interfaces meeting at grain boundary grooves suggest that capillary equilibrium was established over the entire interface (assuming isotropic incoherent interface energies).

Figure 3, which shows sheet-resistance measurements, indicates that the resistivity of the $NiSi_{1-x}Ge_x$ increases with RTA temperature above 500°C. Because the X-ray diffraction data indicate that these films contained only one phase, the increasing sheet resistance must be associated with agglomeration (rather than the formation of a high resistivity phase). This interpretation is supported by the plan-view scanning electron micrographs (SEMs) of Fig. 4a and b, which show that little $NiSi_{1-x}Ge_x$ agglomeration has occurred at 500°C and substantial agglomeration has occurred at 650°C.

Comparison of the sheet resistance data for $NiSi_{1-x}Ge_x$ formed on strained $Si_{0.8}Ge_{0.2}$ with that of NiSi on Si suggests that agglomeration begins at temperatures below 500°C in the germanosilicide, whereas NiSi films (same thickness and annealing time, 20 s) show

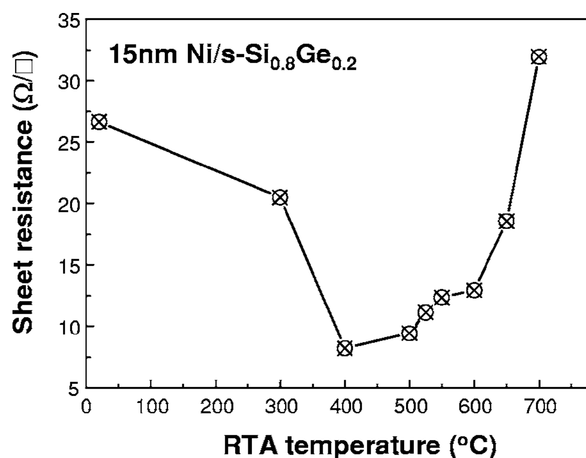

Figure 3. Sheet resistance measured from 15 nm Ni on strained $Si_{0.8}Ge_{0.2}$ after RTA for 20 s at various temperatures.

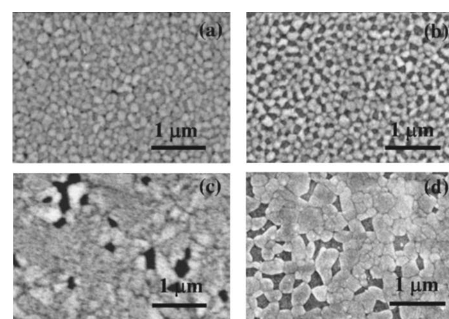

Figure 4. Plan-view SEM images (a) of a $NiSi_{0.8}Ge_{0.2}$ film annealed at (a) 500°C and (b) 650°C, (c) a NiSi film annealed at 600°C, and (d) a NiGe film annealed at 500°C. Light-colored areas correspond to the film and dark areas to the exposed substrate.

little agglomeration to temperatures 100°C higher. This is supported by the SEM micrographs of the $NiSi_{1-x}Ge_x$ and NiSi agglomeration morphologies in Fig. 4. These micrographs also show that the gaps in the $NiSi_{1-x}Ge_x$ are uniformly spaced with a separation comparable with the grain size, while in the NiSi, the hole spacing is nonuniform and several times larger than the grain size. NiGe films on Ge, Fig. 4d, exhibit a morphology very similar to that of NiSi on Si at a similar degree of agglomeration, Fig. 4c. This is surprising, because one would expect that the behavior of the $NiSi_{1-x}Ge_x$ should be intermediate between those of NiGe and NiSi.

The results presented above, taken in toto, suggest that the grooving, interface morphology, and agglomeration properties of $NiSi_{1-x}Ge_x$ are quite different from those of NiSi and NiGe. Clearly, a major difference between them is that the germanosilicide is a solid-solution alloy. As such, the thermodynamics of the system are strongly influenced by alloy thermodynamics rather than just interface energies (the normal basis for discussions of agglomeration). In fact, it may be that the variation of composition and its influence on the thermodynamics and kinetics of the system is responsible for the differences between the $NiSi_{1-x}Ge_x$ and its terminal phases NiSi and NiGe. To this end, we employed energy-dispersive X-ray spectroscopy (TEM-EDX) to determine the relative concentrations of Si and Ge at different locations in the microstructure (labeled S1-S8 in Fig. 1a).

Each EDX measurement averages over a cylinder of material of approximate diameter 5 nm. The results, shown in Fig. 1d, suggest that the Ge content of the $Si_{1-x}Ge_x$ alloy and the $NiSi_{1-x}Ge_x$ film are indistinguishable at all locations in these two materials that are not near the grain boundary (spots S1, S4, S5, S7, and S8). Interestingly, the Ge concentration is reduced by approximately a factor of three near the grain boundary in the $NiSi_{1-x}Ge_x$ (spot S2), consistent with results in Ref. 5. The Ge concentration in the $Si_{1-x}Ge_x$ alloy immediately below the triple junction (spot S3) is increased by more than a factor of two. Similar observations were made in the Ti-$Si_{1-x}Ge_x$ system.[11] This suggests that the $NiSi_{1-x}Ge_x$ film was formed sufficiently rapidly that there was little time for Si/Ge redistribution and that the Ge depleted from the $NiSi_{1-x}Ge_x$ flowed down the grain boundary toward the triple junction with $Si_{1-x}Ge_x$. The triple junction moves up, trapping the high concentration of Ge along its track.

In the Ni-Si-Ge phase diagram,[8] the tie-lines connect regions with composition near $NiSi_{0.8}Ge_{0.2}$ with regions with compositions near $Si_{0.3}Ge_{0.7}$ at 600°C. Therefore, as the film/substrate systems evolves, the germanosilicide expels germanium into the silicon–germanium. Because Ge diffusion is faster along the $NiSi_{1-x}Ge_x$ grain boundary than within a $NiSi_{1-x}Ge_x$ grain, the grain boundary is the fastest path for Ge egress. This explains why the region near the grain boundary in the germanosilicide is Ge-poor compared with the rest of the germanosilicide film (see Fig. 1). Because the expelled

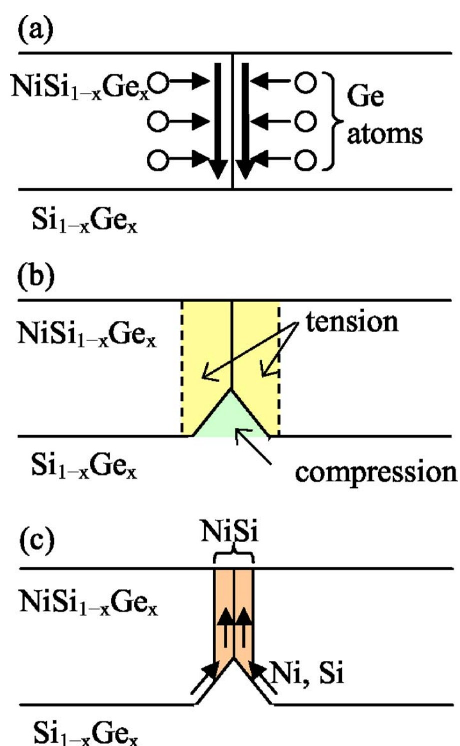

Figure 5. (Color online) Schematic of the grooving mechanism in nickel germanosilicide: (a) Ge out-diffusion, (b) stress state in the system, and (c) in-diffusion of Ni and Si.

Ge enters the $Si_{1-x}Ge_x$ directly under the germanosilicide grain boundary, this region should be richer in Ge than the rest of the substrate, as also seen in Fig. 1.

The morphology of the grain-boundary groove in $NiSi_{1-x}Ge_x$ is quite different from those in NiGe and NiSi. In the latter cases, the film/substrate interfaces are uniformly curved while the groove has more abrupt features in $NiSi_{1-x}Ge_x$ (see Fig. 2). This is consistent with the much faster grooving seen in $NiSi_{1-x}Ge_x$, i.e., when grooving is fast there is not sufficient time available to diffusionally smooth the interfaces. We also note that the apparent groove angle θ is significantly smaller in $NiSi_{1-x}Ge_x$ than in NiSi or NiGe (see Fig. 1). Because $NiSi_{1-x}Ge_x$ ($Si_{1-x}Ge_x$) are continuous solid solutions between NiSi and NiGe (Si and Ge), we expect that the grain boundary and interface energies are also smooth interpolations between these limits. Therefore, it is doubtful that this large angle change is associated with differences in the interface/grain boundary energies. Rather, we suggest that the morphology observed during the grain-boundary grooving in $NiSi_{1-x}Ge_x$ is kinetically determined (i.e., the triple junction angle observed at this scale is not the equilibrium angle). While Ge diffusion can change the compositions of the two phases, it is only transport of the Ni that controls morphology change (we note that the solubilities of Ni in $Si_{1-x}Ge_x$ and $NiSi_{1-x}Ge_x$ are negligible).

The difference in groove morphology between the NiSi, NiGe, and $NiSi_{1-x}Ge_x$ is likely associated with the fact that of these three, only in $NiSi_{1-x}Ge_x$ does the composition vary. Germanium diffuses down the $NiSi_{1-x}Ge_x$ grain boundary, as shown in Fig. 5a, at the same time as the film grooves. This leads to a depletion of Ge and a tensile stress in the film (the atomic volume of nickel silicide is 10% lower than that of nickel germanide) as shown in Fig. 5b. Due to the difference of formation enthalpies, it is favorable to replace NiGe with NiSi. The tensile stress can be relieved if the NiGe unit cells are replaced with more NiSi unit cells. This is similar to heteroepitaxy, where misfit dislocations (i.e., extra unit cells in the film) can relieve stress. This requires extra Ni at the grain boundary, where the Ge depletion takes place.

While the film is under tension, the substrate is under compression just below the triple junction because the lattice parameter of $Si_{1-x}Ge_x$ increases with Ge content. Formation of new $NiSi_{1-x}Ge_x$ at the grain boundary in the film would relieve the tensile stress in the film. This requires short-range Ni diffusion along the grain boundary, Fig. 5c. (Note, there is also diffusion of Ni along the interface to remove gradients in interface curvature.) This should occur readily given the fast out-diffusion of Ge and in-diffusion of Si along the grain boundary. Hence, the fast grooving can ultimately be traced to the grain-boundary diffusion of Ge out of the $NiSi_{1-x}Ge_x$ film. This mechanism does not replace the "usual" grooving mechanism observed in NiSi and NiGe.[12] The two effects combine and lead to faster agglomeration in nickel germanosilicide than in the silicide or germanide. If the grain boundary and interface energies were small the usual grooving mechanism would be very slow but the mechanism presented would still work as it does not depend on these energies.

In summary, we demonstrated that the agglomeration of nickel germanosilicide is fundamentally different from that in NiSi and NiGe in that it occurs more quickly and leads to very different grooving morphologies and composition changes. Of particular importance is the coupling between the change in alloy composition that occurs through fast grain-boundary diffusion and the acceleration of grooving associated with inhomogeneous compositional stress effects. The fast grooving in $NiSi_{1-x}Ge_x$ leads to groove morphologies that are much farther from equilibrium than in NiSi or NiGe (nonuniform interface curvature). The composition changes that occur in $NiSi_{1-x}Ge_x$ are the cause of the widely observed acceleration of agglomeration in this system.

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