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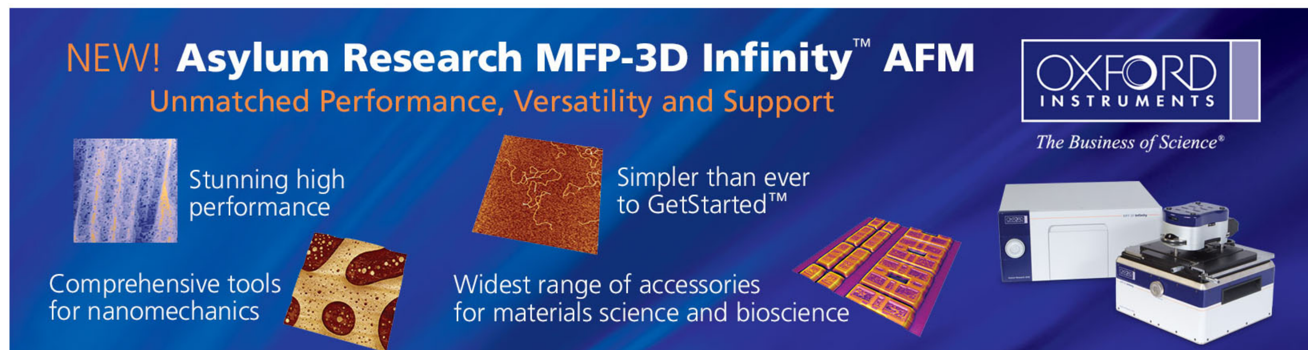

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APPLIED PHYSICS LETTERS **86**, 251906 (2005)

Study of thermal stability of nickel monogermanide on single- and polycrystalline germanium substrates

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We have investigated the thermal stability of nickel monogermanide (NiGe) films formed by rapid thermal annealing on both single- and polycrystalline Ge substrates. We found that the NiGe phase is the only one present after nickel germanidation in the temperature range 400–700 °C. A fairly uniform NiGe film formed on the single-crystalline Ge; it possessed excellent resistivity (15.6 $\mu\Omega$ cm) and was thermally stable up to 550 °C, but it degraded rapidly at higher temperatures as a result of agglomeration. In contrast, the NiGe film formed on the polycrystalline Ge exhibited much poorer thermal stability, possibly because of polycrystalline Ge grain growth, which resulted in columnar NiGe grains interlaced with Ge grains that had a dramatically increased sheet resistance. As a result, we observed that the sheet resistances of NiGe lines subjected to annealing at 500 °C depended strongly on the linewidth when this width was comparable with the grain size of the polycrystalline Ge. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1953880]

An extensive amount of renewed interest in Ge substrates has occurred recently because of their superior electrical properties, especially their higher mobility, when compared with their Si counterparts.[1,2] For instance, the selective deposition of Ge can result in a relatively low contact resistance for a self-aligned raised source and drain structure, as well as a suppression of the short channel effect.[3] To integrate Ge into current device processing, however, requires a thermally stable and uniform low-resistivity metal germanide film. Among the metal silicides, nickel monosilicide (NiSi) is the one of the most promising candidates for sub-100-nm technologies because of its low formation temperature, low resistivity (14–20 $\mu\Omega$ cm), low consumption of Si, resistance to bridging failure, and lack of resistivity degradation on narrow lines or gates.[4] These beneficial features of NiSi motivated us to investigate the mechanism of formation and thermal stability of NiGe formed on both single- and polycrystalline Ge substrates.

In this study, we used Ga-doped *p*-type single-crystalline 2 in. Ge (100) wafers having a resistivity of 0.05 Ω cm and undoped 125 nm thick polycrystalline Ge thin films having a sheet resistance larger than 1 kΩ/sq deposited on oxidized 6 in. Si (100) wafers through ultrahigh-vacuum chemical vapor deposition.[5] After dipping them in dilute HF solution, we loaded the wafers immediately into an electron-beam evaporation system operating at a base pressure of 1.0×10^{-6} Torr. A 20 nm thick Ni film was then deposited onto the single- and polycrystalline Ge surfaces at room temperature with a rate of 1 Å/s. Nickel germanidation reactions on the blank and patterned wafers were performed through rapid thermal annealing (RTA) at various temperatures for 30 s under a flowing N_2 atmosphere. We measured the sheet resistance of nickel germanide by using a four-point probe method and used bridge resistor structures to investigate the effect of the linewidth on the sheet resistance of NiGe. Phase identification was performed using x-ray diffraction (XRD) measurements in the conventional θ–2θ geometry. We analyzed the microstructures and compositions of the nickel germanide samples using cross-sectional transmission electron microscopy (XTEM) and energy-dispersive spectrometry (EDS).

Figures 1(a) and 1(b) present the XRD spectra of the nickel germanide formed on single- and polycrystalline Ge substrates, respectively, at different RTA temperatures. For the nickel germanide formed on the single-crystalline Ge, all of the peaks observed in the temperature range of 400–700 °C identify the orthorhombic NiGe phase. At lower temperatures, the peak profiles of NiGe remained virtually unchanged, but the relative intensity of the NiGe peak in the (111) orientation increased and the full width at half maximum narrowed upon increasing the temperature. These tendencies indicate that the (111) orientation is preferred for NiGe grains during high-temperature annealing, possibly because of the fact that the surface energy of NiGe in the (111) orientation is the smallest among all of the possible orientations. We found, however, that the intensities of the peaks decreased significantly after annealing at 700 °C; this phenomenon may arise from a structural change of the NiGe grains, but the mechanism needs further investigation. For the nickel germanide formed on the polycrystalline Ge, we observed that NiGe was also the only phase after annealing. None of the peaks underwent any observable change upon increasing the annealing temperature, except for that of the polycrystalline Ge (111) orientation. This result suggests that the (111)-oriented polycrystalline Ge grains can undergo further growth during nickel germanidation. Using Scherrer's formula, we estimated the average grain sizes of polycrystalline Ge for the (111) orientation to be 26, 28, 32, 38, and 52 nm after annealing at 400, 500, 550, 600, and 700 °C,

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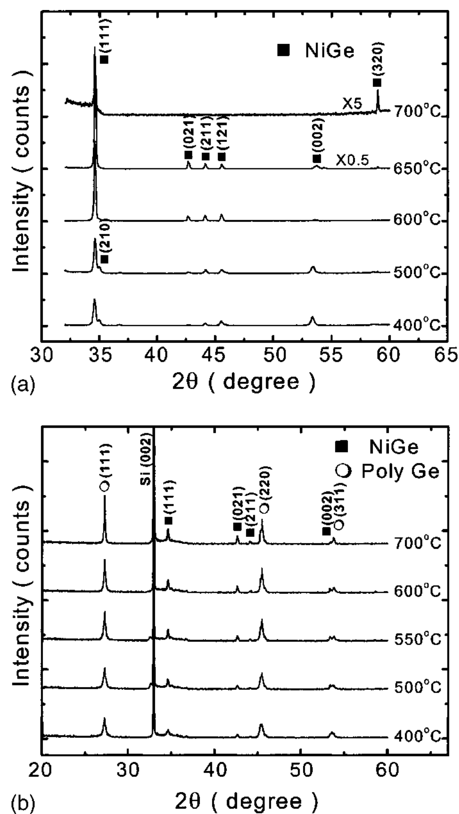

FIG. 1. XRD spectra of nickel germanide formed on (a) single- and (b) polycrystalline Ge substrates at different RTA temperatures.

respectively. Clearly, steep increases in the polycrystalline Ge grain size occur at temperatures above 500 °C.

Figure 2 displays the sheet resistance of the NiGe film as a function of the RTA temperature. For comparison, the sheet resistance of the NiSi film formed on the single-crystalline Si is also presented. It is clear that the sheet resistance of the NiSi film, which is well known to be the stable phase at temperatures above 450 °C, remains in a low-resistivity state at temperatures up to 700 °C. NiGe exhibits poorer thermal stability than NiSi, however, and its sheet resistance increased drastically at relatively low temperatures. In the case of the single-crystalline Ge, we attribute the cause of the dramatic increase in the resistance observed at temperatures above 550 °C to the agglomeration of the NiGe film, because the formation of a high-resistivity phase is ruled out by the XRD results. On the other hand, in the case of the polycrystalline Ge, the rapid degradation in sheet resistance that occurred at temperatures above 500 °C can be associated with the grain growth, which is supported by the previous results. Indeed, similar behavior has been observed in studies of silicides formed on polycrystalline Si,[6–8] and it has been ascribed to the formation of discontinuous silicide films induced by polycrystalline Si grain growth beneath the surface. The driving force for this grain growth is believed to be the reduction of the grain boundary and interface energies.[6–8] It is also noteworthy that the lowest value of sheet resistance of the NiGe film formed on the polycrystalline Ge is slightly higher than that of the others (see the discussion below).

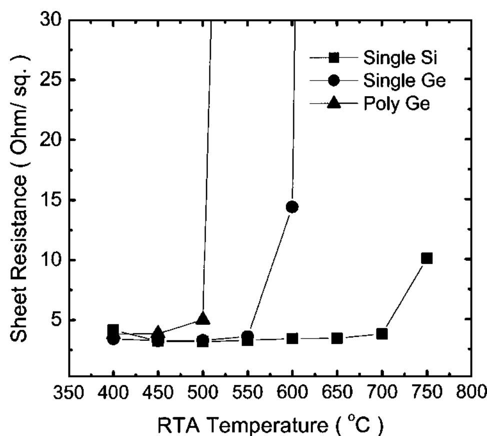

FIG. 2. The sheet resistances of the NiGe film plotted as a function of the RTA temperature. For comparison, the sheet resistances of the NiSi film formed on single-crystalline Si are also included.

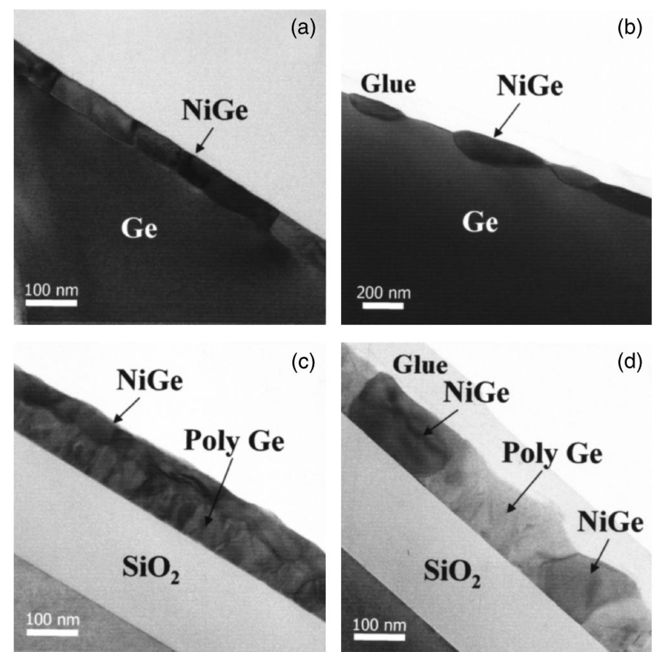

FIG. 3. XTEM micrographs of NiGe formed on the single-crystalline Ge annealed at (a) 450 and (b) 600 °C, and on the polycrystalline Ge annealed at (c) 450 and (d) 550 °C.

Figures 3(a) and 3(b) present XTEM micrographs of NiGe formed on the single-crystalline Ge at 450 and 600 °C, respectively. We observed clearly that the NiGe annealed at 450 °C, which is the sample having the lowest resistance, exhibits a fairly uniform film having a thickness of 48 nm and resistivity of 15.6 $\mu\Omega$ cm, which is comparable with that of NiSi (14–20 $\mu\Omega$ cm). After annealing at 600 °C, however, severe agglomeration and separation of NiGe occurred, which is consistent with our observed sheet resistance behavior. It is apparent, therefore, that the NiGe film is less thermally stable morphologically than is the NiSi film. We attribute this result to the lower surface energy of Ge and the lower melting point of NiGe, with respect to its counterpart, because both the lower surface energy of Ge and the higher migration of NiGe can accelerate the rate of agglomeration.[9–11] Figures 3(c) and 3(d) display XTEM micrographs of NiGe formed on the polycrystalline Ge at 450 and 550 °C, respectively. After annealing at 450 °C, the NiGe film (thickness: ~48 nm) is also uniform, but it has a relatively rough surface and interface between the NiGe film and the polycrystalline Ge; this situation may arise from the initial roughness of the polycrystalline Ge film, which, therefore, results in the slightly higher resistivity (18.4 $\mu\Omega$ cm).

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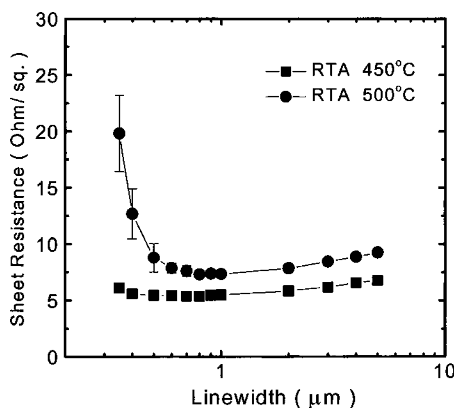

FIG. 4. The sheet resistances, plotted as a function of the annealing temperature, of NiGe films of different linewidths formed on the polycrystalline Ge.

After annealing at 550 °C, however, the uniform NiGe film disappeared and we observed only columnar NiGe and Ge grains, which we identified through EDS analysis. We believe that this phenomenon arose from polycrystalline Ge grain growth induced by the NiGe during annealing. These gradually enlarged polycrystalline Ge grains penetrated into the upper NiGe film and then triggered the downward diffusion of Ni to form the columnar NiGe grains. Eventually, the columnar NiGe and Ge grains interlaced. Obviously, this broken NiGe film accounts for the drastic increase in the resistance that we observe in Fig. 2. The XRD results also provide evidence for grain growth and suggest that the Ge grains grew at temperatures above 500 °C.

Figure 4 presents the sheet resistances, as a function of the annealing temperature, of the NiGe films of different linewidths that were formed on the polycrystalline Ge. After annealing at 450 °C, the sheet resistance remained nearly constant as the linewidth decreased, suggesting that the formation of NiGe is independent of the linewidth. After annealing at 500 °C, however, the sheet resistance increased, especially when the linewidth shrank to below 0.5 μm. The higher resistance is due to the rougher interface between the NiGe film and the polycrystalline Ge that is caused by grain growth; as the linewidth is scaled down to a level comparable with the grain size, the upwardly growing polycrystalline Ge grains may break the continuity of the NiGe lines and result in the rapid increase observed in the sheet resistance.

We have investigated the thermal stability of NiGe formed on both single- and polycrystalline Ge substrates through RTA processing. On single-crystalline Ge, the uniform NiGe film that formed was thermally stable up to 550 °C. When the annealing temperature increased, agglomeration of the NiGe resulted in a dramatic increase in its sheet resistance. For the NiGe formed on the polycrystalline Ge, the rougher surface and interface led to a slight increase in the sheet resistance of the NiGe film and the thermal stability was severely degraded by NiGe-induced polycrystalline Ge grain growth. When the linewidth of the polycrystalline Ge was comparable with the grain size, we observed a tremendous increase in the degradation in the sheet resistance of the NiGe lines after annealing at 500 °C.

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