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Phase and Layer Stability of Ni- and Ni(Pt)-Silicides on Narrow Poly-Si Lines

P. S. Lee,^a K. L. Pey,^{b,z} D. Mangelinck,^c J. Ding,^a D. Z. Chi,^d J. Y. Dai,^e
and L. Chan^e

^aDepartment of Materials Science, ^bDepartment of Electrical and Computing Engineering, ^dInstitute of Materials Research and Engineering, National University of Singapore, Singapore 119260

^cL2MP-CNRS, Faculté de saint Jérôme-case 151, 13397 Marseille Cedex 20, France

^eChartered Semiconductor Manufacturing Limited, Singapore 738406

The phase and morphology stability of NiSi and Ni(Pt)Si formed on the poly-Si lines and wide pads have been studied. Differences in the NiSi₂ nucleation temperature and the extent of layer inversion have been analyzed. The nucleation of NiSi₂ was hindered on the narrow poly-Si lines as compared to that on the large area poly-Si pads at 750°C. Stress is believed to play an important role in the delayed nucleation of NiSi₂. In addition, layer inversion was found to be less severe on the narrow poly-Si lines as compared to that on the poly-Si pads after being subjected to the same annealing condition. This is likely due to the limiting grain growth of the poly-Si in the narrow lines. Enhanced stability of Ni(Pt)Si was achieved up to 800°C on both poly-Si wide pads and narrow lines.

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Silicides are essential in the complementary metal oxide semiconductor technology as local interconnect and for contact applications. The once commonly used TiSi₂ has been replaced by CoSi₂ due to the sheet resistance of TiSi₂ which is a strong function of linewidth as a result of incomplete phase transformation of C54 phase on narrow lines. Nevertheless, CoSi₂ junctions may suffer high diode leakage because of nonuniform CoSi₂/Si interfaces or Co spiking. The high Si consumption of CoSi₂ may lead to problems in ultrashallow junction formation. Much effort has been channeled to develop a replacement silicide material that can be formed uniformly at low temperatures. NiSi is a promising candidate for future integrated circuit generations due to its linewidth independent low resistivity, low temperature one-step annealing and low silicon consumption.¹ However, NiSi is thermally stable only up to a temperature of 750°C. Thereafter, the high resistivity phase NiSi₂ starts to nucleate.² In addition, the stability of Ni silicides on poly-Si can be disrupted by the process of layer inversion, which may occur at temperature as low as 550°C,³ at which the layer reversal of the silicide and poly-Si bilayer occurs.

During the layer reversal, an abrupt increment in tensile stress in NiSi/poly-Si at 550°C was observed and grain growth from 25 to 300 nm was reported.⁴ This is due to the additional driving force for morphological changes arising from the grain boundary energy of poly-Si. The surface energy and interface energy of the poly-Si are also important in view of the changes in texture after grain growth of poly-Si from (110) to (111) which gives a lower surface energy than other orientations. The presence of silicide provides a fast diffusion path for the transport of material, and therefore enhances the grain growth of poly-Si. This causes severe roughening of the silicide/poly-Si interface and eventually leads to the inversion of the two layers. The driving force for poly-Si inversion is the enhanced poly-Si grain growth to reduce the grain boundary and interface energy in the poly-Si. It involves the growth of the existing grains (secondary grain growth) rather than nucleation of new grains (recrystallization). Layer inversion requires the deformation of the silicide, which also kinetically enhances the reaction by providing a fast diffusion path. The process starts with the growth of the poly-Si grains of many orientations into silicide, the energetically favored poly-Si grains (e.g., (111) orientation) will grow faster through the top silicide layer.⁵

This paper aims to study the silicidation on the narrow poly-Si lines and poly-Si pads using pure Ni and Ni(Pt). It is of technologi-

cal interest to explore the thermal windows for silicide, and identify the possible effects on shrinking the dimension of the poly-Si lines. Differences in the phase formation and tendency of layer inversion on the larger area pads and narrow lines were compared. The phase stability and morphology changes were studied using micro-Raman, micro-Rutherford back scattering (micro-RBS), and cross-sectional transmission electron microscopy (XTEM) analysis with diffraction analysis.

Experimental

A layer of undoped polycrystalline-Si (poly-Si) was deposited by low pressure chemical vapor deposition (LPCVD) on a 400 nm thick oxide grown by furnace oxidation of the p-type Si(100). The poly-Si pads were doped with phosphorus (P) of dosage $5 \times 10^{15} \text{ cm}^{-2}$ at 40 keV and followed by an annealing at about 1000°C in N₂ ambient for 720 s. The poly-Si lines were patterned to 0.25 μm . $70 \times 70 \mu\text{m}$ poly-Si pads were defined in the vicinity of the poly-Si lines. After the poly-Si line patterning, nitride spacers were formed on the poly-Si sidewall. Following a dilute HF dip, Ni and Ni(Pt) films of about 30 nm were blanket sputter deposited. Rapid thermal annealing (RTA) was carried out in an N₂ ambient at temperatures ranging from 500 to 900°C for 60 s. The unreacted metal was subsequently removed by a selective etch using a H₂SO₄ and H₂O₂ mixture.

Micro-Raman measurements were done on the poly-Si pads. Mapping analysis along the n⁺ poly-Si lines was also performed. The Raman spectra were recorded with a confocal spectrometer in the backscattering configuration, fitted with single grating spectrographs, notch filters, and charge coupled device detector. A 513 nm argon laser was used and focused to a spot diameter of about 1 μm . The sample was mounted on a computer controlled x-y motorized stage which allows mapping analysis to be performed on narrow lines at micrometer intervals. An integration time of 300 s was used for these spectra with 1.0 cm^{-1} spectral resolution.

The micro-RBS measurements were carried out using 2 MeV He⁺ ions. The backscattered ions were detected with two detectors. The 300 mm² PIPS detector of 19 keV energy resolution at 145° scattering angle (Cornell Geometry) was used to generate the 2D RBS maps in order to identify the regions of interest. Once the regions were identified, the scan size was further reduced and the beam was raster scanned within the pad area only. On the identified pad areas, the backscattered particles were detected at a scattering angle of 160° (IBM geometry) using a 50 mm² PIPS detector with an energy resolution of 14 keV. The beam was focused to a beam spot of $\sim 5 \mu\text{m}$ and the beam current used was $\sim 100 \text{ pA}$. In order to

^z E-mail: elepeykl@nus.edu.sg

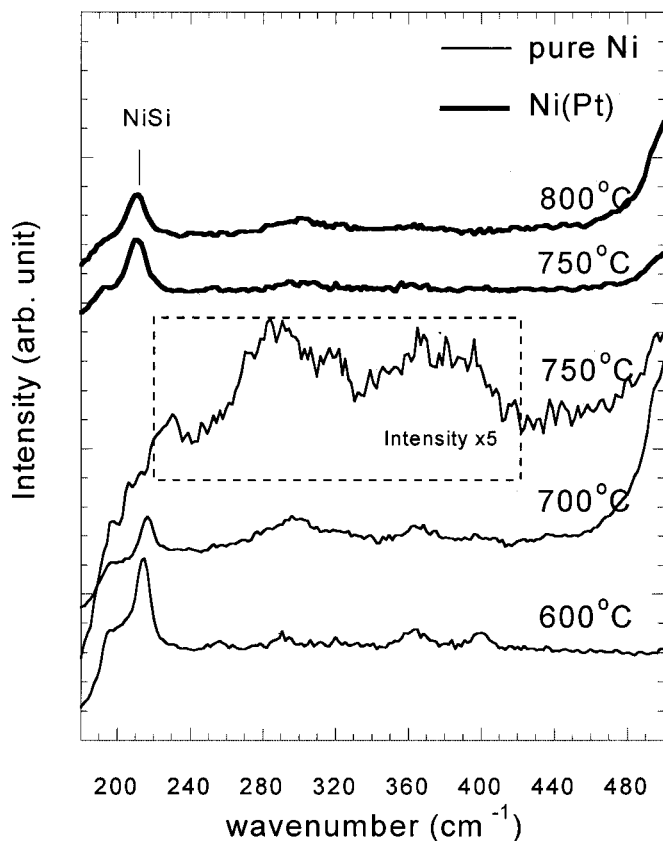


Figure 1. Micro-Raman analysis of Ni- and Ni(Pt)-silicided poly-Si pads at various silicidation temperatures.

obtain sufficient statistics, an average beam exposure of ~ 2 h was required. XTEM was performed along an isolated single poly-Si line.

Results

Figure 1 shows the formation of Ni- and Ni(Pt)-silicides on the $70 \times 70 \mu\text{m}$ poly-Si pads using micro-Raman after annealing at various temperatures. The fingerprint Raman spectra of various Ni-silicide phases has been identified previously with the silicide formation on Si(100).⁶ The formation of pure NiSi can be observed at 600 and 700°C on the poly-Si pads with the presence of the significant NiSi Raman peak at 215 cm^{-1} . At 750°C, the NiSi Raman peak disappears and this can be due to NiSi₂ nucleation or agglomeration or layer inversion. The spectrum is very close to that of pure NiSi₂, which has relatively weak intensity. The formation of NiSi₂ on the poly-Si pads at 750°C is expected since NiSi₂ was reported to nucleate at 750°C in an abrupt and almost instantaneous manner on Si(100).³ On the other hand, Ni(Pt)Si demonstrates an enhanced stability up to 800°C on the poly-Si pads as indicated by the presence of the strong NiSi Raman peak at 215 cm^{-1} .⁷

Figures 2a-d show the micro-RBS analysis on the Ni- and Ni(Pt)-silicided poly-Si pads after annealing at various temperatures. For the pure NiSi formed at 600°C (Fig. 2a), the composition ratio of Ni and Si correspond to NiSi. At 700°C (Fig. 2b), the reduced yield of Ni and the tailing at the Ni peak together with a relatively high ratio of Si are due to the start of layer inversion, at which the Si grains start to extend toward the free surface. This was affirmed by the increased Si intensity ratio from the Raman analysis even at 700°C. With Ni(Pt)-silicidation, the composition ratio of Ni to Si is close to Ni(Pt)Si at 700°C (Fig. 2c). At 750°C (Fig. 2d), there is a slightly higher Si yield due to the start of layer inversion. Therefore, RBS

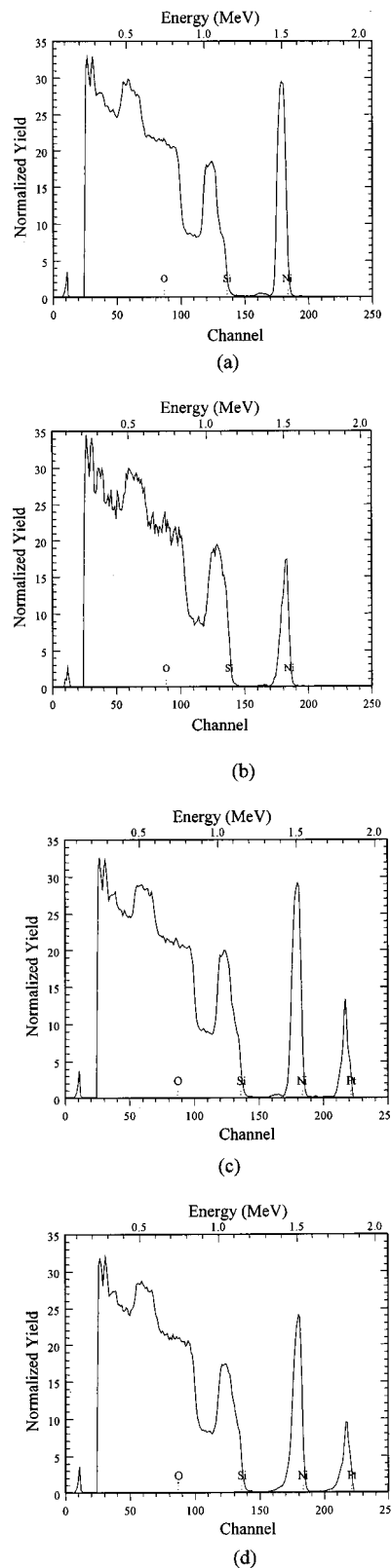


Figure 2. Micro-RBS analysis on poly-Si pads with Ni-silicidation at (a) 600°C (b) 700°C and Ni(Pt)-silicidation at (c) 700°C and (d) 750°C.

analysis shows that the Ni [or Ni(Pt)]-silicided P-doped wide poly-Si pads underwent layer inversion at temperatures about 700–750°C.

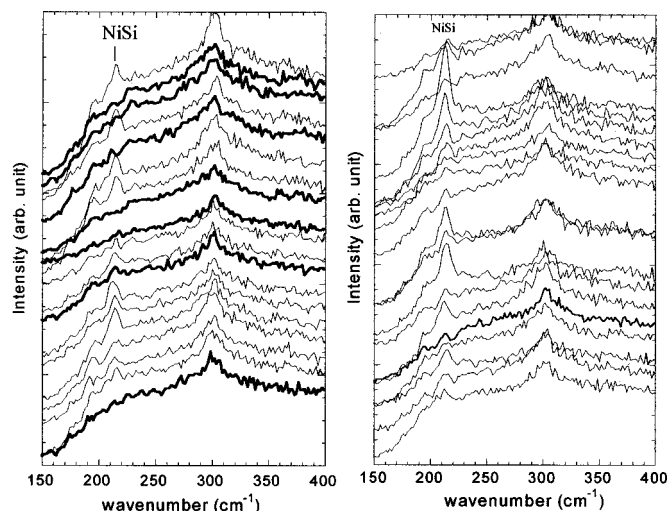


Figure 3. Micro-Raman analysis along a 0.25 μm poly-Si line of 100 μm length with (a, left) Ni-silicidation at 750°C and (b, right) Ni(Pt)-silicidation at 800°C. Bold lines indicate the absence of NiSi phase.

Figures 3a and b show the mapping analysis using micro-Raman on a single 0.25 \times 100 μm poly-Si line after Ni silicidation at 750°C and Ni(Pt) silicidation at 800°C, respectively. The formation of NiSi can be observed on many locations along the 100 μm long Ni-silicided poly-Si line at 750°C. The presence of NiSi on the narrow poly-Si lines at 750°C is indeed a little surprising in view of the detection of NiSi₂ and the absence of NiSi on the poly-Si pads at 750°C. There are certain locations at which the NiSi Raman signal is absent and this can be attributed to the NiSi₂ nucleation or layer inversion in which the poly-Si extended to the surface, both leading to the disappearance of the NiSi Raman signal. In contrary, Ni(Pt)Si was detected from almost all the analyzed locations along the narrow poly-Si line after silicidation at 800°C. This is in agreement to the analysis on the wide poly-Si pad regions which show the formation of Ni(Pt)Si even at 800°C.

Figure 4 shows the XTEM analysis of a 0.25 μm Ni-silicided poly-Si line that was annealed at 750°C and the corresponding diffraction pattern. From the diffraction analysis, it was confirmed that NiSi is still present on the narrow lines after annealing at 750°C.

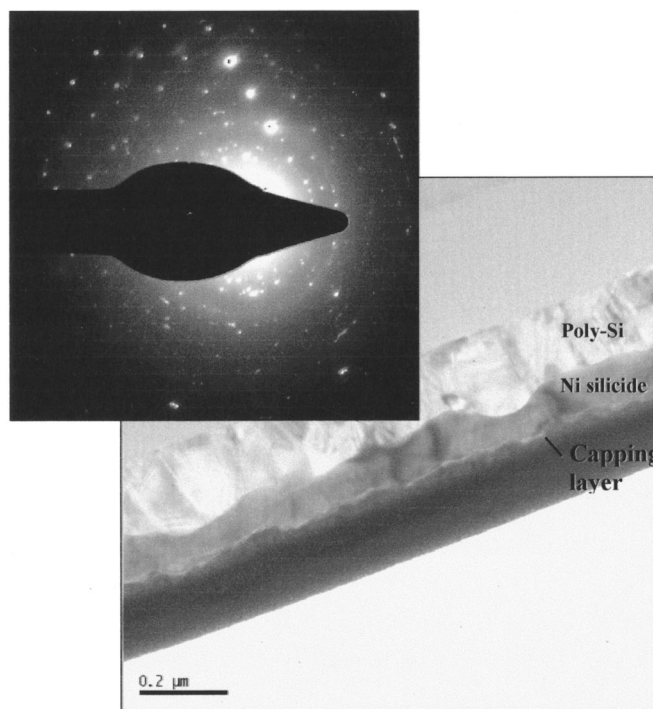


Figure 4. XTEM analysis along a 0.25 μm poly-Si line with Ni-silicidation at 750°C. The inset shows the diffraction pattern of the Ni-silicided film.

The silicide formed is rather uniform with no protrusions or layer inversion being observed. In other words, the absence of NiSi Raman signal at certain locations along the pure Ni-silicided 0.25 μm poly-Si lines of 100 μm length as shown by the Raman mapping analysis in Fig. 3a is unlikely due to severe layer inversion. Consequently, the presence of NiSi₂ is most probably responsible for the absence of the NiSi Raman signal at those locations along the poly-Si lines.

Discussion

The enhanced stability of Ni(Pt)Si was previously demonstrated on Si(100) and Si(111) wafers and was attributed to the change in

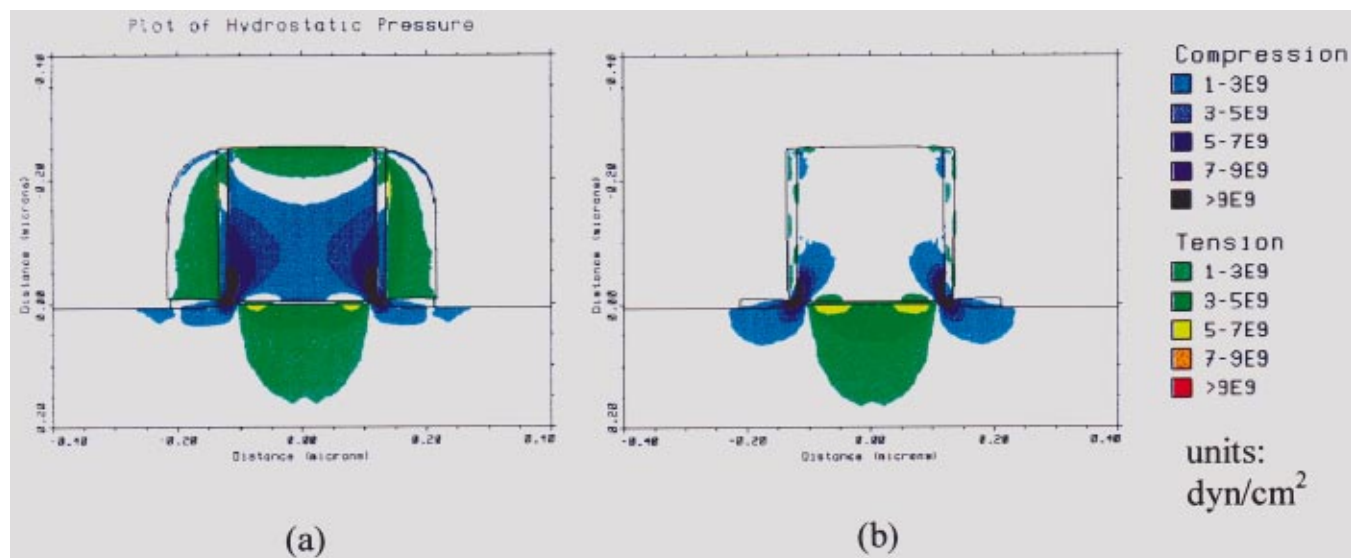


Figure 5. T-SUPRE 4 stress analysis of a 0.25 μm poly-Si gate electrode (a) with and (b) without sidewall nitride spacer.

the Gibbs free energy (G) and the formation of texture in Ni(Pt)Si which changes the interfacial energy (σ).⁸ Both factors could affect the nucleation-controlled reaction of NiSi₂ formation according to the classical nucleation concept where the nucleation rate, $N \propto \exp(-\sigma^3/\Delta G^2)$. The Ni(Pt)Si formed on the poly-Si pads and lines are polycrystalline films, and therefore the interfacial energy should not contribute too much changes in the interfacial energy term compared to pure NiSi case. Therefore, the Gibbs free energy seems to play a preponderant role in the Ni(Pt)Si stability.

The electron diffraction analysis confirms the presence of NiSi on the pure Ni silicided 0.25 μm narrow lines at 750°C. This further corroborates the results of micro-Raman that show the presence of NiSi on narrow poly-Si lines at 750°C. This set of result is different from that on the poly-Si pads where the formation of NiSi₂ was found at 750°C [same as those on blanket Si(100)]. The stress/strain might affect the difficult nucleation of NiSi₂ on poly-Si lines at 750°C. From the simulations using T-SUPREME 4 as shown in Fig. 5 (no implantation or annealing was introduced during the simulation), a large amount of compressive stress is generated in the poly-Si gate by the presence of sidewall nitride spacers which exert tensile stress. Similar results were obtained using Raman shift experiments, which obtain a compressive stress near the edges of the poly-Si gates.⁹ It has also been reported that the tensile stress exerting on the nitride/poly-Si interfaces increased with decreasing poly-Si linewidths.¹⁰ This stress state may be a hindrance to the nucleation of NiSi₂, and therefore slightly delayed the nucleation of NiSi₂ on poly-Si lines. In fact, it has been shown that NiSi₂ formation is more favorable inside smaller contact holes in which compressive stress is more relaxed and the presence of compressive stress was ascribed to inhibit nucleation of NiSi₂ on the narrow poly-Si lines.¹¹

On the other hand, the nucleation and propagation of NiSi₂ on large areas of poly-Si or Si(100) may be easier compared to narrow poly-Si lines due to a larger availability of nucleation sites. Similar linewidth dependence of the nucleation sites density has been observed for the TiSi₂ formation in submicrometer lines, due to nucleation controlled transformation of C49 to C54 phase.¹² In addition, the absence of the NiSi Raman signal at certain locations along the poly-Si line seems to suggest the possibility of the coexistence of NiSi and NiSi₂ at 750°C along the line. This suggestion is not eliminated because NiSi₂ usually nucleates at 750°C.

It was shown that layer inversion started to occur after annealing at 700°C on the P-doped poly-Si pads while virtually no inversion was present at 600°C. Full layer inversion has been observed at silicidation temperature of 600°C with pure NiSi on the undoped poly-Si.¹³ Thus, the onset temperature for layer inversion is higher on the P-doped poly-Si compared to the undoped poly-Si due to a larger grain size of the P-doped poly-Si. The microstructure of the poly-Si prior to silicidation plays an important role in controlling the extent of layer inversion since the driving force for inversion is to reduce grain boundary and surface energies of the poly-Si grains. It is well known that the poly-Si grain is in needle-like columnar form in the as-deposited state using the conventional LPCVD process.¹⁴ No or little grain growth will occur with these intrinsic undoped poly-Si grains even after annealing up to 1000°C.¹⁴ The silicide enhanced grain growth in poly-Si occurs mainly by the growth of the existing grains via secondary grain growth. This can be driven solely by the reduction of the total energy associated with the normal grain boundaries. With the highly disorder poly-Si, recrystallization occurs which is the process in which new grains nucleate and grow within a pre-existing crystalline matrix. The primary recrystallization is usually a defect energy driven recrystallization. Subsequent secondary recrystallization involves secondary grain growth, which refers to the phenomenon in which a few grains grow very fast while other grains shrink and eventually disappear.

With P doping, significant grain growth has been observed for P-implanted samples.¹⁵ Wada and Nishimatsu¹⁶ observed that the grain growth rate increased with P-doping. Mei *et al.*¹⁷ later confirmed this effect.

The group V element can cause higher grain boundary motion and grain growth rate due to an increase in the point defect concentration.¹⁸ With an enlarged and stabilized starting poly-Si grain, the tendency for layer inversion will be reduced.

In addition, the addition of Pt into the Ni silicide film seems to have little effect on the extent or onset temperature of layer inversion. Similar results have been obtained with the use of the Ni/Pt bilayer on poly-Si.¹³ This may be due to the relatively small changes in the grain boundary diffusion and/or the mechanical properties of the silicides such as plastic deformation temperature or film stress of both NiSi and Ni(Pt)Si. These factors are important in the process of layer inversion as evident by the findings that the effects of impurity strengthening using C implant into silicide¹⁹ or changing film thickness can modify the layer inversion behavior.

At 700°C, the RBS spectrum of pure Ni-silicided poly-Si pad has already exhibited obvious layer inversion. However on the poly-Si lines at the same silicidation temperatures, there seems to be no tendency of layer inversion on the narrow poly-Si lines. This suggests that layer inversion is more extensive on large areas compared to narrow areas (lines). This may be due to the linewidth effect whereby on the narrower lines, grain growth of the poly-Si lines can be pinned by the edges of the lines. The corollary of that is the restricted extent of layer inversion on the poly-Si lines. Supporting this is the higher activation energy of grain growth for metal films on narrow lines than that on blanket films; which was attributed to the geometry constraints on grain growth.²⁰

In conjunction, the stress factor could not be neglected in view of the large compressive stress generated in the poly-Si lines by the sidewall spacer. The stress increases as the poly-Si linewidth shrinks. With the formation of silicide on top (usually in compression), the stress generated in the smaller poly-Si lines could be less tensile (compensated by the initial compressive state), and therefore reduces the grain boundary diffusion and restricts the grain boundary migration or grain growth of the poly-Si, which is the basic process of layer inversion.

Conclusion

We have confirmed the presence of NiSi at 750°C on narrow poly-Si lines while NiSi₂ was detected at this temperature on a large area pads. The difference has been attributed to the presence of compressive stress on the narrow poly-Si lines exerted by the spacers on both sides. The extent of layer inversion was found to be more severe on the poly-Si pads compared to that on the narrow lines, suggesting that the grain growth of the poly-Si in the lines may be pinned by the edges of the lines. The formation of Ni(Pt)Si was demonstrated to be stable up to even 800°C on both narrow poly-Si lines and pads.

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