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Micro-Raman Spectroscopy Investigation of Nickel Silicides and Nickel (Platinum) Silicides

P. S. Lee,[a,z] D. Mangelinck,[b] K. L. Pey,[c] Z. X. Shen,[d] J. Ding,[a] T. Osipowicz,[d] and A. See[e]

[a]*Department of Materials Science, National University of Singapore, Singapore 119260*
[b]*Institute of Materials Research and Engineering, Singapore 119260*
[c]*Department of Electrical Engineering, National University of Singapore, Singapore 119260*
[d]*Department of Physics, National University of Singapore, Singapore 119260*
[e]*Chartered Semiconductor Manufacturing Limited, Singapore 738406*

The formation of Ni silicides has been successfully monitored by Raman spectroscopy. Ni silicides formed at different annealing temperatures using rapid thermal annealing were analyzed using Rutherford backscattering spectroscopy and X-ray diffraction. Raman spectroscopy was further used to examine these samples. The results showed that Raman spectroscopy could accurately identify the phases of Ni silicides formed at various temperatures. These findings were used to demonstrate the increased thermal stability of NiSi by the addition of Pt. This study demonstrates the applicability of Raman spectroscopy for monitoring the formation of NiSi, which was suggested to be the future silicide for deep submicrometer integrated circuit processing. Raman spectroscopy offers a unique tool for phase identification at localized areas and mapping characterization of Ni silicides with micrometer spatial resolution.

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Silicides are used in complementary metal oxide semiconductor (CMOS) technology as local interconnect and contacts application. The present silicide materials, $TiSi_2$ and $CoSi_2$, have certain limitations that pertain to future implementation in high-performance CMOS applications. For example, the sheet resistance of $TiSi_2$ shows linewidth dependence due to insufficient nucleation density in narrow lines for complete phase transformation. $CoSi_2$ junctions can suffer high diode leakage because of nonuniform $CoSi_2$/Si interfaces or Co spiking. A replacement silicide material, which can be produced uniformly at lower process temperatures, is needed for shallow junction formation. NiSi is a suggested 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 750°C, above which the high resistivity phase $NiSi_2$ begins to nucleate. By alloying with a small amount of Pt, the thermal stability of NiSi was improved.[2] This should greatly favor the use of NiSi for deep subquarter micrometer CMOS technologies.

Raman spectroscopy provides information on the vibrational properties of a material. It serves as a material fingerprint and allows analysis of its vibrational modes and interatomic forces. It has been reported that Raman spectroscopy is a useful tool in the study of the formation mechanism of silicides.[3,4] In this paper, we have identified the Raman spectra from thin films of Ni_2Si, NiSi, and $NiSi_2$. From the phase identification obtained by Rutherford backscattering spectroscopy (RBS) and X-ray diffraction (XRD), Raman spectra of three different silicides have been established, and characteristic Raman peaks can be attributed to the thin films of Ni_2Si, NiSi, and $NiSi_2$. We further used Raman spectroscopy to demonstrate the increased thermal stability of NiSi by an addition of small amount of Pt. This study showed that Raman spectroscopy could be used to monitor the formation of Ni silicides.

The Ni and Ni(Pt) films were deposited by sputtering on p-type Si(100) wafers. The film thickness was determined to be ~300 Å by RBS. Prior to deposition, the wafers were subjected to RCA cleaning and an HF dip to avoid contamination and native oxides. These films were then annealed by rapid thermal processing between 300 and 900°C for 60 s in a nitrogen ambient. The films were analyzed by RBS of 2 MeV $^4He^+$ ions and XRD in Bragg Brentano geometry. The Raman spectra were recorded with two micro-Raman systems, with single-grating spectrographs, notch filters, and charge coupled device detectors. Three laser wavelengths of 488, 633, and 782 nm were employed in the investigation. No surface degradation of the sample was observed by visual inspection after the laser irradiation. All the spectra recorded using different laser wavelengths were in agreement with each other. In this paper, we report the Raman data obtained by the 633 nm laser excitation. These spectra were collected with 30 s integration time and 1.0 cm^{-1} spectral resolution.

Figure 1 shows the Raman spectra for as-deposited Ni and samples annealed at temperatures ranging from 300 to 900°C. As shown in Fig. 1a, the as-deposited Ni film shows no Raman peaks. In contrast, the Raman spectrum of the samples annealed at 300°C has two strong peaks at ~100 and 140 cm^{-1}, with a weaker peak at 217 cm^{-1}. The Raman spectra obtained for samples after annealing at temperatures ranging from 500 to 700°C were similar, with a strong peak at 217 cm^{-1} and a lower intensity peak at 199 cm^{-1}. Other peaks, which were relatively weak, were found at around 258, 296, and 367 cm^{-1}. At 700°C, the peak intensity of NiSi varied with the location of the laser irradiation, and a silicon substrate peak at 520 cm^{-1} was observable in some areas. For samples annealed at 750 and 900°C (Fig. 1b), weak-intensity broad peaks in the range of 250 to 400 cm^{-1} were observed.

The films were analyzed using RBS and XRD. RBS analysis showed that after annealing at 300°C, about 400 Å of Ni_2Si was present together with 200 Å of NiSi. For annealing temperatures below 700°C, the film composition corresponded to NiSi (Fig. 2). Starting from 600°C, the RBS spectra show a tail in the Ni peak (Fig. 2), which indicates roughening of the silicide surface and/or of the silicide/silicon interface. $NiSi_2$ was found to be present at temperatures higher than 750°C. The XRD spectra (Fig. 3) confirm the presence of Ni_2Si and NiSi at 300°C, polycrystalline NiSi at temperatures between 500 to 700°C and epitaxial $NiSi^2$ at temperatures above 750°C.

From the XRD and RBS results, which allow us to determine the nature of the film, the Raman spectra obtained can be attributed to the different phases of Ni silicides formed at various annealing temperatures. From the results of RBS and XRD, the Raman spectra observed for Ni films annealed at 500 and 600°C (Fig. 1a) can be assigned to NiSi. The prominent peaks at ~217 and 199 cm^{-1} characterize the Raman spectra of NiSi thin film. For the samples annealed at 300°C, the Raman peaks at 100 and 140 cm^{-1} are characteristics of the presence of Ni_2Si. These two Raman peaks were also obtained by Nemanich *et al.* in their previous study of Ni_2Si

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[z] E-mail: leeps@charteredsemi.com

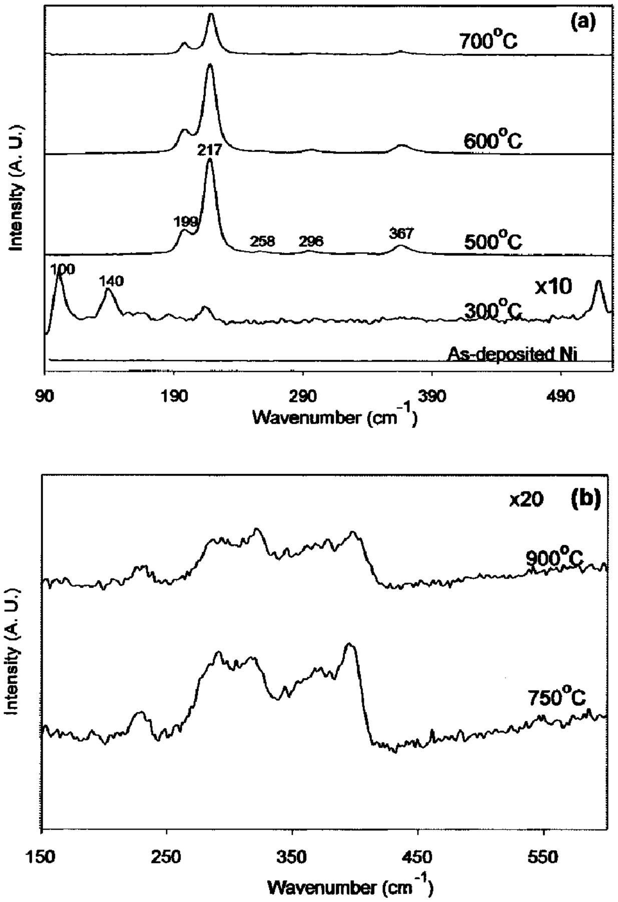

Figure 1. Raman spectra for Ni films on Si(100) (a) as deposited and after rapid thermal annealing at 300, 500, and 700°C and (b) after annealing at 750 and 900°C. The spectra in (b) were multiplied by 20 to take into account the difference in Raman peak intensity.

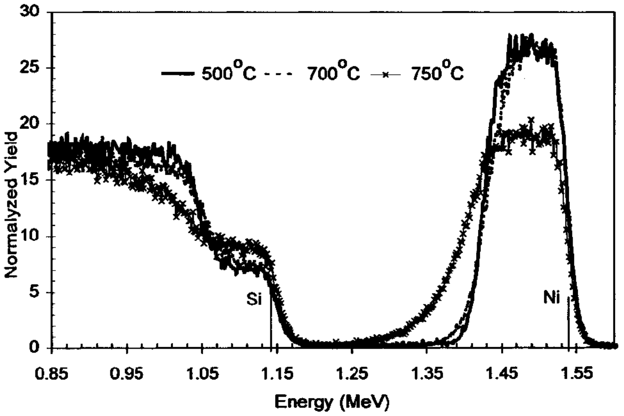

Figure 2. RBS spectra of 2MeV $^4He^+$ for Ni films on Si(100) after annealing at 500, 700, and 750°C.

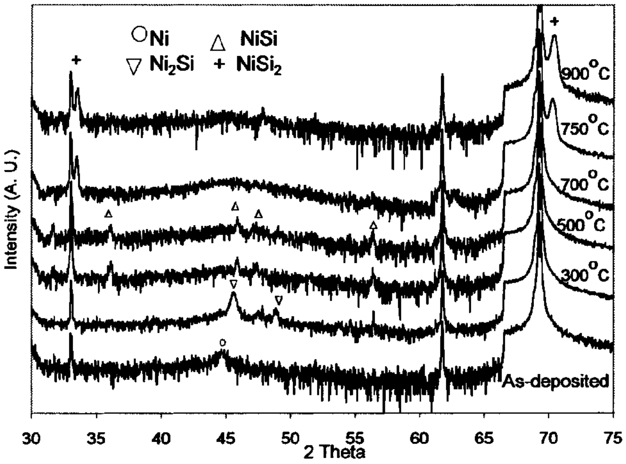

Figure 3. XRD spectra (Cu Kα) of as deposited Ni films on Si(100) and after rapid thermal annealing at 300, 500, 700, 750, and 900°C. (Intensity scale is expressed in a logarithmic manner.)

formed by annealing of an Ni film on hydrogenated amorphous Si and Ni on Si(111).[4] The small peak at 217 cm^{-1} is certainly due to the thin layer of NiSi observed by RBS. Upon a further increase, the annealing temperature to 750°C and above, the presence of $NiSi_2$ gave rise to the broad peaks between 250 and 400 cm^{-1}. Thus, the observed Raman spectra changes with respect to phase transformation allow monitoring of Ni silicide formation by reacting with the Ni thin film on the Si substrate.

The Raman activity and polarization properties are determined by the crystal symmetries. Hence, the dramatic change in the Raman spectra can be attributed to the phase change of Ni silicides. The Raman spectrum is related to the crystallographic structure of the compounds. For the as-deposited Ni film, the absence of signals is typical for metallic films that crystallize in a high-symmetry structure with an equivalent atom site (monatomic) that has no optic lattice vibration. In NiSi (space group *Pnma*, D_{2h}^{16}), which has an orthorhombic structure (MnP type), the film is Raman active. There exist previous Raman studies of silicide films belonging to the orthorhombic structures, *e.g.*, $TiSi_2$ and PtSi, which have produced identifiable and distinctive Raman spectra for phase characterization. As shown in this work, significant Raman peaks can also be detected from Ni_2Si, which has an orthorhombic structure. On the other hand, $NiSi_2$ (space group $Fm\bar{3}m$, O_h^5) has a cubic structure (CaF_2 type) which is the same for $CoSi_2$. Distinct Raman peaks are difficult to obtain for both compounds as shown for $NiSi_2$ in this study and for a $CoSi_2$ film.[5] This result complies with the selection rule that the more symmetrical the unit cell, the fewer the number of modes that have Raman activity.

Having identified the Raman spectrum for pure Ni silicide films at different temperatures, the reaction of Ni(Pt) films on Si(100) was monitored. The concentration of Pt added was determined by RBS to be 5 atom %. After rapid thermal processing in an N_2 atmosphere at temperatures ranging from 500 to 900°C, NiSi was found to be the stable phase up to 900°C as reported by Mangelinck *et al.*[2] Raman spectroscopy was used to examine these films and demonstrated that the NiSi Raman peaks were identifiable up to 900°C as shown in Fig. 4. The Raman results are in good agreement with XRD and RBS characterization of the samples.[2] The Raman spectrum for Ni(Pt)Si is relatively similar to that for pure NiSi films. The high-intensity peak at 217 cm^{-1} is still present for identification of NiSi even with the presence of small amount of alloying element. The ability of Raman spectroscopy in monitoring the improved thermal stability of NiSi by the addition of Pt serves as a further proof that the Raman spectroscopy can be used to characterize accurately the different phases of Ni silicides.

The appearance of a silicon Raman peak at 520 cm^{-1} in Ni(Pt)Si samples, starting from 800°C annealing, can be attributed to agglomeration as observed by scanning electron microscopy (SEM).[2] For pure NiSi samples formed at 700°C, agglomeration was also observed and can account for the difference in the Raman peak

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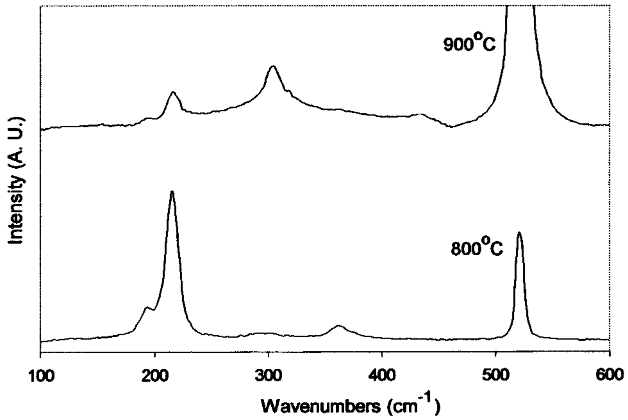

Figure 4. Raman spectra for annealed Ni(Pt) films on (100)Si at 800 and 900°C.

intensity at different areas and the presence of an Si peak in some cases. At higher annealing temperatures, no Si peaks were detected in accordance to better substrate coverage of disilicide films as observed by SEM. This demonstrates that Raman spectroscopy can be used to study agglomeration.

Raman spectroscopy is complementary with RBS and Auger measurements that yield chemical compositions. The ability of micro-Raman spectroscopy for in-line process monitoring and local phase identification has created much interest for silicide characterization.[6,7] Based on the Raman spectra for Ni silicides obtained in this study, this nondestructive technique offers a way to perform local mapping of Ni silicide phases with micrometer precision at the device level. This development is important for understanding process integration issues as device dimensions shrink with technology advancement.

Beside phase identification, characterization of silicide films have received increasing attention in recent years. Investigations have been conducted for stress and strain measurements by the shift of the Si substrate peak.[8-10] The strong intensity and narrow peak at 217 cm^{-1} for NiSi offers another possible avenue to explore the stress of silicide films, which is a critical issue in device fabrication. Recently, silicide film uniformity,[5] determination of nucleation sites,[11] and grain size and shape[12] were also made possible by the Raman microprobe. As a result of this study, these potential applications can be tapped by Raman spectroscopy on Ni silicide characterization.

This technique, while useful for identifying various crystalline phases produced by thin film reactions, still suffers from a lack of standards in some cases. Although the sharp line spectra can be associated with appropriate crystalline structures, we should be cautioned that there might be some Raman-active modes that are not detected because of the thin films and weak signals. Orientation effects in the film could also be responsible for not detecting some of the Raman-active modes.

This study characterizes the Raman spectra of nickel silicides after rapid thermal processing at different temperatures. We further demonstrate the improved thermal stability of NiSi achieved by the addition of Pt, using Raman spectroscopy as a phase-characterization tool. This nondestructive technique has the potential for exploring additional aspects such as stress or film properties. A baseline for analyzing Ni silicides on a microscopic scale was created for process monitoring in very large scale integrated device fabrication.

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