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In situ micro-Raman analysis and X-ray diffraction of nickel silicide thin films on silicon

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ABSTRACT

This article reports on the *in situ* analysis of nickel silicide (NiSi) thin films formed by thermal processing of nickel thin films deposited on silicon substrates. The *in situ* techniques employed for this study include micro-Raman spectroscopy (μRS) and X-ray diffraction (XRD); in both cases the variations for temperatures up to 350 °C has been studied. Nickel silicide thin films formed by vacuum annealing of nickel on silicon were used as a reference for these measurements. *In situ* analysis was carried out on nickel thin films on silicon, while the samples were heated from room temperature to 350 °C. Data was gathered at regular temperature intervals and other specific points of interest (such as 250 °C, where the reaction between nickel and silicon to form Ni_2Si is expected). The transformations from the metallic state, through the intermediate reaction states, until the desired metal–silicon reaction product is attained, are discussed. The evolution of nickel silicide from the nickel film can be observed from both the μRS and XRD *in situ* studies. Variations in the evolution of silicide from metal for different silicon substrates are discussed, and these include (1 0 0) n-type, (1 0 0) p-type, and (1 1 0) p-type silicon substrates.

1. Introduction

Nickel mono-silicide (NiSi) thin films are extensively used in CMOS ohmic contacts and interconnects. They have numerous advantages such as low formation temperature, low contact resistance, and low silicon consumption (Iwai et al., 2002). They also have other properties such as high etch rate selectivity, low stress, and good mechanical strength which make them suitable for the microsystems industry (Qin et al., 2000; Kang et al., 2007). Though (1 0 0) silicon is predominantly used in the CMOS industry, (1 1 0) silicon wafers are used extensively in the microsystems fabrication for their ability to generate vertical sidewalls during silicon bulk micromachining (Maluf and Williams, 2004). Studies in the past have indicated there are differences in nickel silicide formation on (1 0 0) and (1 1 1) silicon wafers (Yamauchi et al., 1993). This article compares nickel silicide formation on (1 0 0) and (1 1 0) silicon wafers. The transformation temperature from di-nickel silicide (Ni_2Si) to NiSi, stress levels in the NiSi thin films, and the crystallographic orientations of the same are studied using *in situ* techniques.

The *in situ* techniques employed for this study include micro-Raman spectroscopy and X-ray diffraction (XRD); in both cases the variations for temperatures up to 350 °C has been studied. The evolution of NiSi from Ni_2Si is discussed and there are variations in the transformation temperatures between (1 0 0) and (1 1 0) silicon. Raman studies have indicated that vacuum annealing of nickel thin films yields better NiSi thin films as opposed to annealing in ambient atmosphere. Raman spectroscopy and XRD have also been used to study variations in nickel silicide formation between n-type and p-type silicon.

2. Experimental

2.1. Deposition of nickel thin films on silicon substrates

Thin films of nickel were deposited on (1 0 0) n-type, (1 0 0) p-type, and (1 1 0) p-type substrates. Electron-beam evaporation of 50 nm of nickel was performed from 99.99% pure nickel sources, after pumping down to a base pressure of 2×10^{-7} Torr. All silicon samples were dipped in buffered hydrofluoric acid solution prior to

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nickel deposition in order to remove the native oxide which can inhibit the reaction of nickel and silicon to form nickel silicide.

2.2. Reference nickel silicide thin films

Nickel silicide (NiSi) thin films were analysed using Raman spectroscopy and X-ray diffraction; this was done to obtain reference data. These thin films were formed by vacuum annealing (9×10^{-6} Torr) nickel thin films on n-type (1 0 0) silicon samples at 350 °C for 30 min. These vacuum annealed nickel films were also 50 nm thick, as deposited on all samples prepared for *in situ* measurements. These films were characterised by Auger electron microscopy and secondary ion mass spectrometry to verify their composition and uniformity in composition, and the presence of a uniform mono-silicide (NiSi) thin film was verified (Bhaskaran et al., 2008).

2.3. In situ Raman measurements

Raman measurements were carried out using a RENISHAW 1000 micro-Raman system equipped with a Peltier cooled CCD camera and a Leica microscope. The experiments were carried out at an excitation wavelength of 633 nm (He–Ne laser) with an accumulation time of 200 s. The laser spot was focused on the sample surface using a 50× objective with short-focus working distance at room temperature. For measurements at higher temperatures (20–350 °C in ambient atmosphere), a Linkam temperature stage and a 50× long-focus objective were used. With these objectives the lateral resolution on the sample was approximately 2 μm. Considering the volume of data gathered during the measurements, only temperature steps at which significant variations occurred have been plotted in the figures in this article.

2.4. In situ X-ray diffraction measurements

In situ Bragg–Brentano X-ray diffraction (XRD) measurements were carried out using a PANalytical X'Pert Pro Diffractometer. The desired temperatures and dwell times were programmed prior to the start of the analysis. The samples were placed on a platinum heating strip and they were heated to 350 °C with X-ray data collected at certain critical temperatures during the ramp-up. Samples were held at 350 °C for 30 min, to simulate nickel silicide formation conditions, before being cooled down. All measurements were done in vacuum (4×10^{-4} Torr). XRD data was collected over a 2θ range of 20° to 60°. Considering the volume of data gathered during the measurements, only the 2θ range and temperature steps at which significant variations occurred have been plotted in the figures in this article.

To determine the orientation of the reference nickel silicide thin films, glancing angle XRD (GA-XRD) was used. Glancing angle XRD analysis of these samples was done using a Scintag X-ray diffractometer operating with a cobalt X-ray source (at a wavelength of 0.179020 nm) at an X-ray incidence angle of 5°. The XRD results were shifted to correspond to the Cu Kα wavelength (λ = 0.154056 nm) to enable comparison to standard powder diffraction files (PDFs) from the International Centre for Diffraction Data (ICDD).

3. Results and discussion

3.1. Analysis of nickel silicide thin films

A Raman spectrum obtained for the reference nickel silicide thin film is shown in Fig. 1(a). NiSi belongs to the *MnP*-type

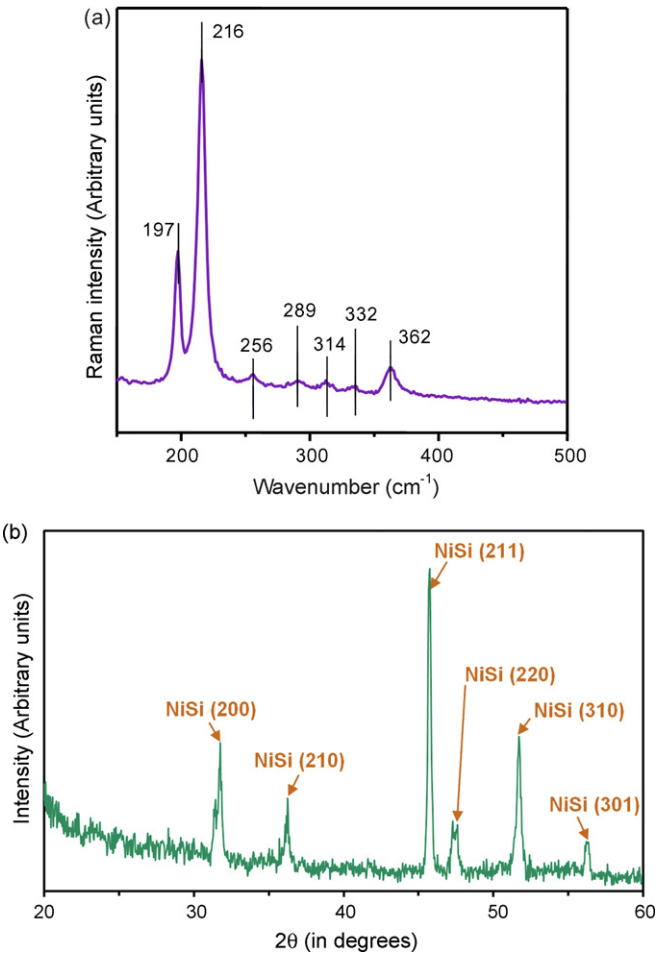

Fig. 1. (a) Micro-Raman spectrum and (b) X-ray diffractogram of nickel silicide film formed by vacuum annealing at 350 °C.

orthorhombic structure (space group *Pnma*, $D_{2h}{}^{16}$); therefore, the film is Raman active. In accordance with group theory (see, for example Hayes and Loudon, 1978; Donthu et al., 2004), 12 Raman active optical phonons exist for NiSi. Each of these 12 optical phonons can be observed in Raman spectra of NiSi single crystal collected in a specific measurement geometry. Raman spectra of NiSi films, NiSi powder, and polycrystalline NiSi will contain only some of these modes. Depending on the degree of texture, some Raman active modes may be more pronounced than others in thin film spectrum. Donthu et al. (2004) identified eight phonon peaks for nickel silicide powder at 197, 214, 255, 288, 314, 332, 360, and 397 cm^{-1}. The peaks at 197, 216, 256, 289, 314, 332, and 362 cm^{-1} were observed in the Raman spectra for the nickel silicide thin film shown in Fig. 1(a). According to factor group analysis, the peaks 197, 216, 332, and 362 cm^{-1} can be assigned to the A_g symmetry, while peaks at 256 and 314 cm^{-1} may belong to either B_{2g} or B_{3g} symmetry (Donthu et al., 2004). The five other phonon peaks, expected from group theory and, in particular, the peak at 397 cm^{-1} (Donthu et al., 2004), were not observed in this work.

Nickel silicide thin films were also analysed using glancing angle XRD. The peaks obtained in the diffractograms (Fig. 1(b)) were compared with the International Committee for Diffraction Data powder diffraction file (ICDD PDF) 85-0901 for indexing.[1]

[1] Powder Diffraction Pattern Files, International Centre for Diffraction Data (ICDD, formerly the Joint Committee for Powder Diffraction Studies), Newtown Square, PA 19073, Card 85-0901.

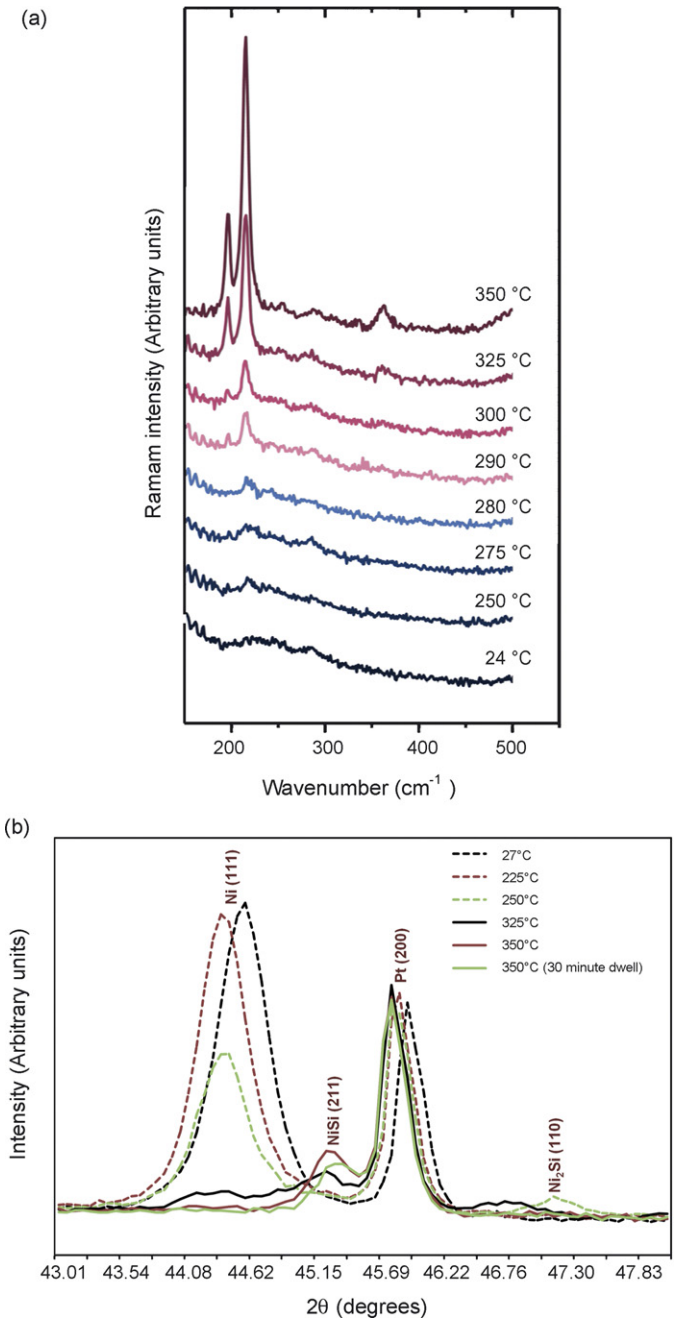

Fig. 2. (a) Micro-Raman spectra and (b) X-ray diffractograms registered at different temperatures for nickel thin film deposited on n-type (1 0 0) silicon substrate.

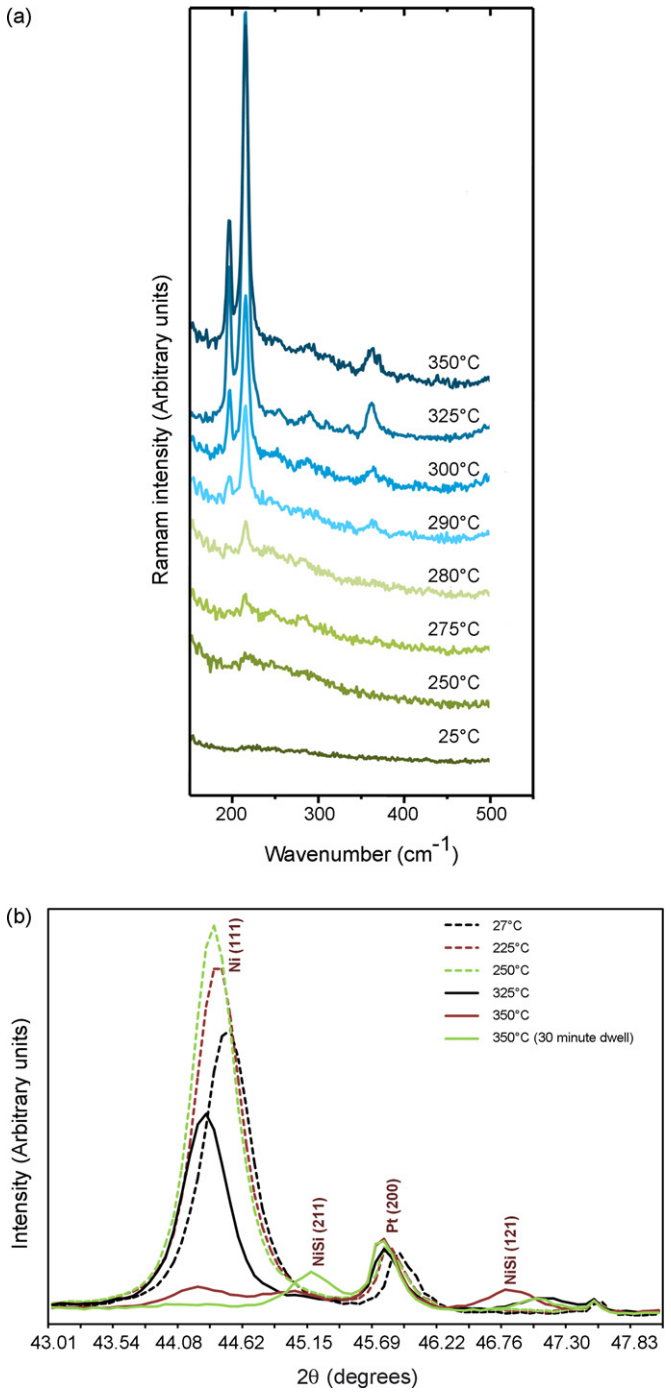

Fig. 3. (a) Micro-Raman spectra and (b) X-ray diffractograms registered at different temperatures for nickel thin film deposited on p-type (1 0 0) silicon substrate.

These results indicate the presence of a preferentially oriented polycrystalline thin film.

3.2. *In situ* measurement results for nickel on n-type (1 0 0) silicon

Raman spectra obtained while heating nickel thin films on n-type (1 0 0) silicon are shown in Fig. 2(a). The absence of peaks for the as-deposited Ni film (see spectrum at 24 °C, for example) is typical for metallic films that have no optic lattice vibrations. Ni_2Si peaks are expected at 100 and 140 cm^{-1}, but due to the presence of strong background in this region of the spectra and relatively large noise, the appearance and disappearance of the Ni_2Si phase cannot be conclusively determined. However, these two peaks are typically accompanied by a small peak at ~217 cm^{-1} and a very weak peak at ~190 cm^{-1} (Lee et al., 2000; Nemanich et al., 1984) related to a small presence of NiSi. Therefore, in this work we draw our conclusion about the presence of Ni_2Si phase based on the appearance of a small single peak at ~215 cm^{-1}, while the conclusion on the formation of NiSi phase was made from the appearance of double peak at ~196 and 215 cm^{-1}. Based on this it seems that the Ni_2Si and NiSi phases start to form at 250 and 290 °C, respectively.

The diffractograms in Fig. 2(b) show the XRD peaks obtained while the sample was heated to 350 °C. Nickel and silicide peaks are concentrated in the 2θ range of 40–50°; the peaks at 44.54° and

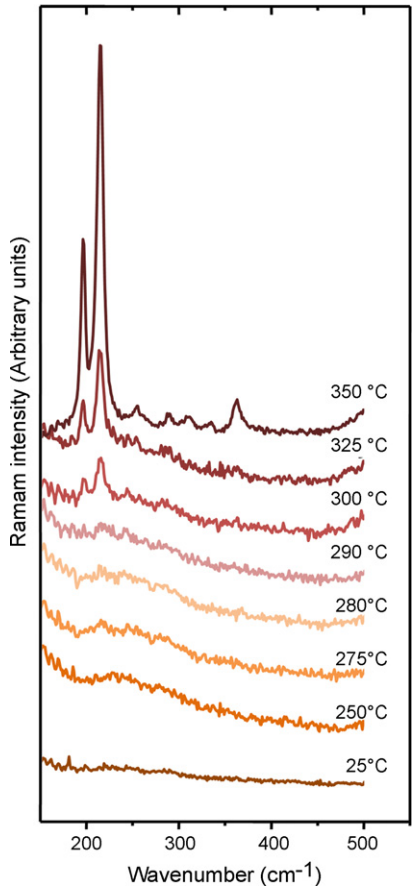

Fig. 4. . Micro-Raman spectra registered at different temperatures for nickel thin film deposited on p-type (1 1 0) silicon substrate.

45.88° are those of nickel (from the sample) and platinum (from the heating stage), respectively.[2,3] Due to thermal expansion, peaks shift left; the shifts are more prominent in nickel than in platinum. This could be due to platinum and nickel being located at different heights with respect to the detector and the different thermal expansion co-efficients of the two metals. When the sample reaches a temperature of 250 °C, there is a drop in intensity of the nickel peak and a small peak appears at 47.09° which correspond to Ni_2Si.[4] At 325 °C, the nickel silicide (NiSi) peak at 45.21° becomes prominent. The diffractogram labelled '350 °C (30 min dwell)' in Fig. 2(b) corresponds to the XRD data collected after the sample was held at 350 °C for 30 min and this indicates a nickel silicide thin film with a preferential (2 1 1) orientation.

3.3. In situ measurement results for nickel on p-type (1 0 0) silicon

Raman measurements were carried out for these samples under similar conditions to those on n-type (1 0 0) silicon substrates. The spectra obtained at various temperatures are shown in Fig. 3(a). The weak single peak at ~215 cm^{-1} (Ni_2Si) again appears at 250 °C and double peaks at 215.6 and 196.5 cm^{-1} (NiSi) start to appear at 290 °C.

[2] Powder Diffraction Pattern Files, International Centre for Diffraction Data (ICDD, formerly the Joint Committee for Powder Diffraction Studies), Newtown Square, PA 19073, Card 87-0712.

[3] Powder Diffraction Pattern Files, International Centre for Diffraction Data (ICDD, formerly the Joint Committee for Powder Diffraction Studies), Newtown Square, PA 19073, Card 04-0802.

[4] Powder Diffraction Pattern Files, International Centre for Diffraction Data (ICDD, formerly the Joint Committee for Powder Diffraction Studies), Newtown Square, PA 19073, Card 80-2283.

The diffractograms in Fig. 3(b) show the XRD peaks obtained while the sample was heated to 350 °C. The peaks at 44.54° and 45.88° are those of nickel (from the sample) and platinum (from the heating stage), respectively.[2,3] In this case, the drop in intensity of the nickel peak occurs at 325 °C. After dwelling at 350 °C for 30 min, the nickel silicide (NiSi) peaks at 45.21° which corresponds to an orientation of (2 1 1) becomes prominent. There is a small peak at 46.75° which corresponds to nickel silicide (1 2 1), and appears only during the initial 350 °C measurements. The peak for Ni_2Si at 47.09° is not prominent during this measurement cycle.

3.4. In situ measurement results for nickel on p-type (1 1 0) silicon

Raman spectra obtained while heating nickel thin films on p-type (1 1 0) silicon are shown in Fig. 4. The formation of Ni_2Si and the transformation from Ni_2Si to NiSi seem to occur at slightly higher temperatures on these samples when compared to the nickel deposited on (1 0 0) silicon substrates. The spectrum at 350 °C indicates a polycrystalline film with strong NiSi peaks at 215.6 and 196.5 cm^{-1} and weak NiSi peaks at 255, 289, 310, 332, and 362 cm^{-1}.

4. Conclusions

This article reports on the *in situ* characterisation of nickel thin films on silicon substrates, while the samples were heated to 350 °C. The transformations from the metallic state, through the intermediate reaction states, until the desired metal–silicon reaction product (NiSi) is attained are discussed. The evolution of nickel silicide (NiSi) from the nickel film can be observed from both the Raman and XRD in situ studies. Raman studies of nickel silicide formation on both n-type and p-type (1 0 0) silicon substrates suggest that the transformation temperature for both are similar (around 290 °C); though XRD studies indicate the transformation temperature to be around 325 °C for p-type (1 0 0) silicon. This discrepancy could be due to the fact that the laser used for Raman measurements analyses a much smaller area (few μm^2) while XRD probes a much larger area (few mm^2). Raman spectra also indicate that the transformation from Ni_2Si to NiSi occurs only at around 300 °C for (1 1 0) silicon as opposed to 290 °C for (1 0 0) silicon.

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