Nanoindentation Behaviour and Annealed Microstructural Evolution of Ni/Si Thin Film

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The nano-mechanical properties of as-deposited Ni/Si thin films indented to a maximum depth of 800 nm are measured using a nanoindentation technique. The microstructural evolutions of the indented as-deposited specimens and indented specimens annealed at 200 °C, 300 °C, 500 °C and 800 °C for 2 min, respectively, are examined via transmission electron microscopy (TEM) and micro-Raman scattering spectroscopy (RSS). The loading curve for the as-deposited Ni/Si thin film is found to be continuous. However, the unloading curve has a prominent pop-out feature. The hardness and Young’s modulus of the Ni/Si thin film are found to vary with the nanoindentation depth, and have values of 13 GPa and 177 GPa, respectively, at the maximum depth of 800 nm. The deformation induced in the nanoindentation process causes the microstructure of the indented zone in the as-deposited thin film to transform from a diamond cubic structure to a mixed structure comprising both amorphous phase and metastable Si III and Si XII phases. However, after annealing at temperatures of 200 °C–500 °C and 800 °C, the microstructure within the indented zone contains only Si III and Si XII phases and epitaxial NiSi2 phase, respectively. The annealing process prompts the formation of nickel silicides at the Ni/Si interface. The silicides have the form of Ni13Si in the samples annealed at 200 °C, but transform to low-resistivity NiSi at annealing temperatures of 300 °C or 500 °C. At the highest annealing temperature of 800 °C, the NiSi phases are replaced by high-resistivity NiSi2 phases. [doi:10.2320/matertrans.M2010323]

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1. Introduction

The mechanical properties and microstructural evolution of thin film materials have attracted significant attention in recent years due to their many applications in the MEMS and IC fields. The mechanical properties and microstructures of such materials not only govern the mechanical performance of the thin film system, but also determine the overall electrical and optical performance of the device itself. Moreover, the properties and microstructures of thin film materials generally differ from those of the corresponding bulk materials, and typically vary with the fabrication conditions, the film thickness, the substrate effect, the indentation maximum load, the loading rate, and so on. Various methods have been proposed for determining the mechanical properties of thin film systems and observing their microstructural evolution. Previous studies have reported that nanoindentation prompts a phase transformation within the indented zone, and therefore has a significant effect upon the load-displacement response of the film. Furthermore, for thin films deposited on a silicon substrate, various forms of silicide phase are formed at the film/substrate interface during substrate annealing. Therefore, in developing optimum thin film systems for MEMS and IC applications, it is essential that the nanoindentation behaviour and microstructural evolution of the thin film structure during nanoindentation and annealing are properly understood.

The formation of high-quality metallic silicides at low temperature is of significant benefit in developing miniaturised Si devices. For example, NiSi is a promising candidate for shallow junction formation due to its low formation energy, thermal stability and low Si consumption. High quality Ni silicides are formed at the Ni/Si interface of thin film systems by means of a solid-state reaction induced by isothermal furnace annealing or rapid thermal annealing (RTA) techniques. Nickel silicide has many phases, thereby compounding the complexity of its formation. However, previous research has shown that the predominant phases are Ni2Si, NiSi and NiSi2, respectively, where the formation of each phase is dependent upon the annealing temperature at which the reaction takes place. Although the formation and characteristics of Ni silicides for complementary metal-oxide-semiconductor (CMOS) applications have been extensively reported, the combined effects of nanoindentation deformation and annealing on the microstructural evolution and phase of Ni/Si thin films are not yet fully understood.

Accordingly, this study indents as-deposited Ni/Si thin films to a maximum depth of 800 nm, and then anneals the indented specimens at temperatures of 200 °C, 300 °C, 500 °C and 800 °C for 2 min, respectively. The hardness and Young’s modulus of the as-deposited Ni/Si film are determined from the loading–unloading curve, and the microstructural characteristics of the as-deposited and annealed specimens are observed using transmission electron microscopy (TEM). Finally, the effect of the annealing temperature on the composition of the Ni silicides formed at the Ni/Si interface is clarified via micro-Raman scattering spectroscopy (RSS).

2. Experimental Procedure

The Ni/Si thin film specimens were prepared by depositing a Ni film with a thickness of approximately 100 nm on a silicon(100) substrate using a thermal evaporation technique in an inert nitrogen gas environment. The thickness of the Ni film was monitored continuously throughout the deposition
process using a quartz-crystal microbalance and was verified via X-ray reflectometry once the deposition process was complete. The nanoindentation tests were performed at room temperature using an MTS Nano Indenter-XP system with a Berkovich diamond pyramid tip. The specimens were indented to a maximum depth of 800 nm using the indenter system set in a depth-control mode. The indentation procedure involved the following steps: (1) loading to the position of maximum load (corresponding to the maximum indentation depth), (2) holding in this position for 10 s, and (3) smoothly unloading over a period of 30 s. The hardness and Young’s modulus of the Ni/Si thin film were then calculated from the load-displacement data using the Oliver and Pharr method.\(^{22}\)

Following the nanoindentation tests, the indented specimens were annealed for 2 min at temperatures of 200°C, 300°C, 500°C or 800°C using a Heatpulse 610i RTA system with a temperature accuracy of ±5°C. The annealing process was performed in a nitrogen environment (Ni purity: 99.999%, Ni flow rate: 3 L min\(^{-1}\)) with a heating rate of 200°C s\(^{-1}\) and a cooling rate of approximately 5°C s\(^{-1}\). Thin film specimens for TEM inspection were prepared from the as-deposited and annealed samples using an FEI Nova 200 focused ion beam (FIB) system with an operating voltage of 30 kV. During the preparation process, the FIB chamber was maintained at a constant pressure of 10\(^{-6}\)–10\(^{-7}\) torr using a hybrid pumping system comprising a mechanical pump and an oil diffusion pump. The TEM foils were milled from the thin film specimens using a Ga\(^+\) ion beam and were extracted in such a way that they included the centre of the indented zone. Note that before the foils were removed, a thin film (1 μm) of Pt was deposited on the specimen surface to protect the indentation region from accidental damage during the milling process. The cross-sectional microstructures of the as-deposited and annealed indented specimens were observed using a Philips Tecnai F30 Field Emission gun transmission microscope with a scanning voltage of 300 kV. In addition, the nickel silicides formed in the annealed indented specimens were analysed using TEM and micro-Raman scattering spectroscopy (RSS). The RSS procedure was performed at room temperature using a 513 nm Argon laser beam with a focused spot diameter of around 1 μm.

3. Results and Discussion

3.1 Loading–unloading curve

Figure 1 presents the loading–unloading curve of the as-deposited Ni/Si thin film indented to a maximum depth of 800 nm. For indentation depths of less than 80 nm, the indenter remains fully within the soft Ni layer, and thus the load acting on the indenter has a low and approximately constant value. However, as the indentation depth increases, the tip penetrates the underlying substrate, and thus the load increases rapidly. From inspection, the maximum load occurs at an indentation depth of 800 nm and has a value of 122 mN.

The loading curve is smooth and continuous. However, the unloading curve contains a prominent pop-out feature. The pop-out event occurs at a load of around 30 mN, i.e. a similar load to that reported by Yan et al.\(^{10}\) for nanoindentated single-crystal silicon. The pop-out feature observed in nanoindentation tests has been variously attributed to an undensification of Si,\(^{23}\) residual deformation of the thin film,\(^{24}\) phase transformation,\(^{25}\) and the indentation rate.\(^{26}\) Domnich et al.\(^{27}\) discussed the effects of phase transformation on the shape of the unloading curve of nanoindented silicon, and suggested that the pop-out feature was the result of the formation of Si III and Si XII phases. The TEM and micro-RSS results obtained in the present study suggest that the pop-out feature observed in the Ni/Si unloading curve shown in Fig. 1 is similarly the result of phase transformation within the indented zone.

3.2 Young’s modulus and hardness of Ni/Si thin film

Figure 2(a) shows the variation of the Young’s modulus of the Ni/Si thin film with the nanoindentation depth. For indentation depths of less than 10 nm, the contact force is very low and the area between the indenter and the thin film is very small. As a result, the Young’s modulus has a relatively high value of 120 GPa since under low load conditions, the elastic modulus of a material varies inversely with the contact area. However, as the indenter penetrates more deeply into the Ni layer, the Young’s modulus reduces to a value of approximately 30 GPa at an indentation depth of approximately 25 nm, and then increases rapidly to a maximum value of around 188 GPa at a depth of 100 nm as a result of strain gradient hardening effects.\(^{28}\) At indentation depths of 100–200 nm, the indenter tip penetrates the Si substrate, and thus the Young’s modulus falls slightly to a value of approximately 180 GPa. For indentation depths of 200–800 nm (the maximum indentation depth), the indenter tip is embedded entirely within the Si substrate, and the Young’s modulus has a relatively constant value of 180 GPa, which is close to that of the Si(100) substrate (178 GPa).\(^{29}\)

Figure 2(b) shows the variation of the Ni/Si thin film hardness with the nanoindentation depth. At very low indentation depths (i.e. <10 nm), the thin film has a high hardness of around 8 GPa due to the small contact area between the film and the indenter. However, as the indentation depth increases, the hardness drops rapidly to a minimum value of approximately 3.5 GPa at an indentation...
depth of 15 nm. Thereafter, the hardness increases rapidly as the indentation depth approaches the thickness of the thin Ni film (i.e., 100 nm). For indentation depths of greater than 100 nm, the hardness has an approximately constant value of around 13 GPa, i.e., the same value as that of the Si(100) substrate (13 GPa).26)

3.3 Initial and indented microstructures of as-deposited Ni/Si thin films

Figure 3 presents a TEM micrograph of the as-deposited Ni/Si thin film system prior to the indentation process. It is observed that a well-defined boundary exists between the Ni film and the Si substrate. The insets in the upper-left and upper-right corners of Fig. 3 show the TEM diffraction patterns of the Ni thin film (label A) and Si substrate (label B), respectively, and confirm that the Ni film has a polycrystalline structure while the Si substrate has a single crystal structure.

Figure 4(a) presents a cross-sectional TEM micrograph of an as-deposited Ni/Si specimen indented to the maximum depth of 800 nm. The diffraction pattern in inset B shows that the microstructure of the indented zone comprises a mixture of amorphous phase and high pressure crystalline phases (Si III and Si XII). Si III phase is the body-centered cubic...
structure, with lattice parameter \( a = 0.664 \text{ nm} \)\(^{29}\) and Si XII phase is the trigonal structure, with lattice parameters \( a = 0.5609 \text{ nm} \), and \( \gamma = 11.007 \text{ nm} \)\(^{29}\). The micrograph also shows the presence of a crack extending from the indented zone into the silicon substrate. Table 1 lists the phases of indented zone and unindented interface for the specimens annealed at different temperatures. Figure 4(b) presents the micro-Raman spectra of the as-deposited indented specimen and the indented specimens annealed at temperatures of 200°C, 300°C, 500°C, and 800°C, respectively. The Raman spectrum of the as-deposited specimen (labeled as 25°C) has a narrow band peak at 169 cm\(^{-1}\) and a strong peak at 300 cm\(^{-1}\). The former peak confirms the presence of the Si III and Si XII phases within the microstructure,\(^{30}\) while the latter peak is attributed to the Si substrate.

### 3.4 Indented microstructure following annealing at different temperatures

Figure 5(a) presents a cross-sectional TEM micrograph of an indented specimen annealed at a temperature of 200°C. The diffraction patterns in the three insets show that the indented zone, the interface between the thin Ni film and the silicon substrate, and the silicon matrix are characterised by a mixture of Si III and Si XII phases (inset B), Ni\(_2\)Si phase (inset A), and a single crystal structure (inset C), respectively. The diffraction pattern in the upper-left corner of the high-magnification TEM micrograph in Fig. 5(b) confirms that the annealing temperature of 200°C is sufficient to enhance the diffusion of the Ni atoms to such an extent that Ni\(_2\)Si phase is formed at the Ni/Si interface. Ni\(_2\)Si phase has an orthorhombic structure, with lattice parameters \( a = 0.7068 \text{ nm} \), \( b = 0.5004 \text{ nm} \), and \( c = 0.3722 \text{ nm} \)\(^{31}\). Note that the presence of this Ni\(_2\)Si phase is confirmed by the peak in the corresponding Raman spectrum at 140 cm\(^{-1}\) (see Fig. 4(b)).

Figure 6(a) presents a TEM micrograph of an indented Ni/Si specimen annealed at a temperature of 300°C for 2 min. The selected area diffraction patterns corresponding to the Ni layer (inset A), the indented zone (inset B), and the Si substrate (inset C) confirm that the Ni layer has a polycrystalline structure, the indented zone comprises a mixture of Si III and Si XII phases, and the Si substrate has a diamond cubic single crystal structure. The presence of the Si III and Si XII phases in the indented zone is confirmed by the peak at 169 cm\(^{-1}\) in the corresponding Raman spectrum (see Fig. 4(b)). In addition, the peaks at 198 cm\(^{-1}\) and 219 cm\(^{-1}\) show that the interfacial region near the indented zone contains NiSi phase.\(^{3,33}\) Similar results are reported by Oyama et al.\(^{34}\) and Kittl et al.;\(^{35}\) Oyama et al.\(^{34}\) develop a silicidation process for fabricating nickel silicide gate capacitors using a unique cl plasma process of metal chloride reduction chemical vapor deposition (MCR-CVD) at low temperatures below 300°C. Kittl et al.\(^{35}\) use an optimized 2-step rapid thermal process (RTP) to form NiSi gates at temperature of 300°C. Both two processes show that the NiSi phase can be obtained by simple solid phase diffusion method at low temperatures of approximately 300°C. Note that NiSi phase belongs to the orthorhombic structure, with lattice parameters \( a = 0.523 \text{ nm} \), \( b = 0.326 \text{ nm} \), and \( c = 0.566 \text{ nm} \).\(^{36}\) Interestingly, the Ni\(_2\)Si peak at 140 cm\(^{-1}\) is no longer observed, which suggests that the Ni\(_2\)Si phase changes to NiSi as the annealing temperature is increased. The presence of the NiSi phase in the interfacial region is confirmed by the diffraction pattern presented in Fig. 6(b).
Figure 7(a) presents a TEM micrograph of the indented Ni/Si specimen annealed at 500°C for 2 min (diffraction patterns of zones A, B and C shown in insets). The diffraction pattern presented in inset A shows that the elevated annealing temperature results in the formation of a NiSi layer in the upper part of the indented zone. In addition, a mixture of Si III and Si XII phase is formed in the central and lower regions of the indented zone (see inset B). The presence of the NiSi layer and the Si III and Si XII phases is confirmed by the prominent peaks in the corresponding Raman spectrum at 198 cm\(^{-1}\), 219 cm\(^{-1}\), and 169 cm\(^{-1}\), respectively (see Fig. 4(b)). Figure 7(b) presents a high-magnification view of the morphology of the indented zone in Fig. 7(a). The diffraction patterns in insets A and B, corresponding to regions A and B, respectively, confirm the existence of NiSi phase in the upper region of the indented zone. The morphology and structures of the NiSi phases are similar to those observed by Julies et al. in a Ni/Si binary system.\(^{15}\)

Fig. 6 (a) Bright field TEM micrograph of indented Ni/Si specimen annealed at 300°C for 2 min (diffraction patterns of zones A, B and C shown in insets); (b) Bright field TEM micrograph of Ni/Si thin film interface showing formation of NiSi phase.

Fig. 7 (a) Bright field TEM micrograph of indented Ni/Si specimen annealed at 500°C for 2 min (diffraction patterns of zones A and B shown in insets); (b) High-magnification view of morphology of indented zone in Fig. 7(a); (c) Bright field TEM micrograph of Ni/Si thin film interface showing formation of NiSi phase.
The diffraction pattern presented in inset C confirms the existence of Si III and Si II phases in the indented zone, and therefore supports the findings of Zarudi et al.\textsuperscript{37} for indented silicon structures. Figure 7(c) presents a cross-sectional TEM image of the interface microstructure of the specimen annealed at temperature of 500°C. It is found that the elevated temperature during the annealing process has a significant effect on the formation of NiSi phase at the Ni/Si interface.

Figure 8(a) presents a TEM micrograph of the specimen annealed at 800°C. The selected area diffraction patterns presented in insets A and B contain regular diffraction spots in addition to the Si spots. Thus, it is inferred that the microstructure of the indented zone contains only epitaxial NiSi\textsubscript{2}. The presence of the NiSi\textsubscript{2} phase is confirmed by the prominent peak at 371 cm\textsuperscript{-1} in the corresponding Raman spectrum in Fig. 4(b). Observing the spectrum, it is noted that the NiSi peak evident at lower annealing temperatures is absent at an annealing temperature of 800°C, which suggests that NiSi\textsubscript{2} nucleation (or agglomeration) or layer inversion occurs as the annealing temperature is increased. Indeed, as shown in Fig. 8(b), the annealing process also induces the formation of NiSi\textsubscript{2} phase between the Ni layer and the Si substrate. Note that the formation of NiSi\textsubscript{2} silicide phase is to be expected here since NiSi\textsubscript{2} is known to nucleate abruptly and instantaneously at a temperature of 750°C on Si(100) substrates.\textsuperscript{38}

Overall, the microstructural observations presented above show that metal-rich Ni\textsubscript{2}Si, which is an unstable phase with high resistivity, forms at the Ni/Si interface of the thin film system at an annealing temperature of 200°C. At higher annealing temperatures, the Ni\textsubscript{2}Si phase presented at the Ni/Si interface is replaced by either monosilicide NiSi (300°C and 500°C) or disilicide NiSi\textsubscript{2} (800°C). These nickel silicide phases at the Ni/Si interface of the thin film system is formed by solid phase diffusion reaction during annealing process. The results presented in this study also reveal that the microstructure of the indented zone depends on the annealing temperature and nanoindentation deformation. For as-deposited Ni/Si specimen, the microstructure of the indented zone is characterized by a mixture of amorphous phase and the Si III and Si XII phases. During the subsequent annealing process at 200°C and 300°C, the indented zone contains a mixture of Si III and and Si XII phase. However, the silicidation behaviour is more pronounced at the higher annealing temperatures of 500°C and 800°C. The microstructure of the indented zone for the specimens annealed at 500°C and 800°C comprises NiSi phase and NiSi\textsubscript{2} phase, respectively. The increased presence of nickel silicide within the indented zone shows that the combined effects of the deformation induced during the indentation process and the heating effect induced during the annealing process have a significant effect on the nanosilicidation behavior and corresponding mechanism. It is clear that nanoindentation causes a significant distortion of the lattice structure within the indented zone. During annealing, the distortion of crystalline structure in the indented zone results in an increased number of diffusion paths between the Si substrate and the Ni layer, leading to the enhancement of the diffusivity of Ni atoms and crystallization of NiSi.

4. Conclusion

This study has investigated the nano-mechanical properties of as-deposited Ni/Si thin films indented to a maximum depth of 800 nm. The indented microstructures of the as-deposited specimens and specimens annealed at temperatures of 200°C, 300°C, 500°C and 800°C, respectively, for 2 min have been examined using TEM and micro-RSS methods. The indentation test results have shown that the load-displacement curve of the as-deposited Ni/Si thin film has a distinct pop-out feature in the unloading portion of the curve. In addition, the TEM and RSS results have revealed that the microstructural characteristics of the indented zone and the Ni/Si interface are significantly dependent on the annealing temperature. For the as-deposited specimens, the indentation deformation prompts a phase transformation from a pure diamond cubic phase to a mixture of amorphous phase and Si
III and Si XII phases. For the indented specimens annealed at 200°C, the microstructure of the indented zone comprises a mixture of Si III and Si XII phases. Furthermore, the annealing temperature results in the formation of Ni5Si3 phase at the Ni/Si interface as the result of a diffusion of the Ni atoms. In the specimens annealed at 300°C and 500°C, the microstructure within the indented zone is characterised by a mixture of Si III and Si XII metastable phases and Ni5Si3 phases at the Ni/Si interface. Finally, at the highest temperature of 800°C, the Si III and Si XII phases disappear and the microstructure of both the indented zone and at the Ni/Si interface contains Ni5Si3 phase only.

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REFERENCES