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Solid-Phase Reaction of Ni with Amorphous SiGe Thin Film on SiO_2

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A study on the reaction of Ni and amorphous $Si_{0.68}Ge_{0.32}$ film on SiO_2 is reported. The reaction was performed at 520°C in a conventional furnace. The resulting film was characterized using X-ray photoelectron spectroscopy (XPS) and Raman scattering spectroscopy. Ni induced crystallization of SiGe was confirmed by the Raman spectra. XPS results indicate Ni piled up at or near the interface of the crystallized SiGe and the SiO_2 substrate. The small amount of Ni inside the SiGe layer exists in more of a silicide- or germanide-like form. Ni enhanced oxidation of SiGe was found during the reaction and the oxidized layer was found to be a mixture of oxides of Si and Ge, with Ge piling up at the surface.

KEYWORDS: thin-film, silicon-germanium, amorphous, nickel, metal induced crystallization, oxidation

1. Introduction

Polycrystalline SiGe (poly-SiGe) is an attractive alternative to poly-Si in realizing thin film transistors (TFTs).[1] The main advantages of poly-SiGe over poly-Si are higher bulk carrier mobility and lower solid-phase crystallization temperature. When the Ge content in the film is raised, the mobility increases and the crystallization temperature decreases. Unfortunately, too high a Ge content is undesirable because of the increase in the leakage current resulting from a smaller energy bandgap and a more defective film. Therefore, lowering the crystallization temperature while maintaining a suitably low Ge content is one of the keys to optimizing the performance of SiGe TFTs.

Solid-phase reactions of metals with epitaxial SiGe on Si have been studied for various applications, including ohmic and Schottky contacts.[2,3] Recently, metal induced crystallization (MIC) of amorphous silicon (a-Si) and amorphous germanium (a-Ge) has been studied with great intensity.[4–6] MIC enables reduced-temperature solid-phase crystallization, which leads to the realization of TFTs at significantly reduced process temperature with improved characteristics.[7] Since MIC is a proven technique for lowering the crystallization temperature of a-Si, it is interesting to study the consequence of applying this technique to a-SiGe thin films.

While some possible mechanisms for MIC of a-Si and a-Ge have been proposed,[6,8,9] the reaction of metal with a-SiGe has not been reported. In this work, the reaction of Ni, a popular metal for MIC, with thin film a-SiGe on SiO_2 is studied.

2. Experimental

Thin 80 nm a-$Si_{0.68}Ge_{0.32}$ films were deposited at a rate of 1 nm/min at 450°C by low pressure chemical vapor deposition on oxidized Si wafers. SiH_4 and GeH_4 were used as the gas sources with flow rates of 150 sccm and 8 sccm, respectively. The deposition pressure was about 300 mTorr. The composition was obtained using Rutherford backscattering spectroscopy (RBS). One set of the wafers was then loaded into a vacuum chamber for the evaporation of Ni using tungsten filaments. The base pressure of the chamber was about 2×10^{-5} Torr. The distance between the tungsten filaments and the substrate is about 10 cm. The substrate was neither deliberately heated nor intentionally cooled during the evaporation. However, irradiation from the tungsten filaments heated up the substrate during the 15 minutes when the temperature of the Ni source was raised. 10 nm of Ni was deposited at a rate of about 0.1 nm/s. The deposition rate and the resulting thickness were monitored using a quartz resonator. The samples were left to cool down inside the chamber for 30 minutes before unloading. After the Ni deposition, the samples were annealed at 520°C for 1 hour in a conventional atmospheric pressure horizontal furnace. During the annealing, nitrogen was delivered at a flow rate of 5 L/min from a liquid nitrogen source at a purity of above 99.99%. However, since the tube was not completely sealed at the loading end, oxygen, together with the laboratory air, could diffuse into the tube to degrade the purity of the nitrogen in the tube. For comparison, a-SiGe samples without the Ni caps were simultaneously annealed.

Raman scattering spectroscopy and XPS were used to analyze the samples. For Raman spectroscopy, a Renishaw 3000 Micro-Raman system was used at room temperature with the 514.5 nm line from an Ar ion laser. The back-scattered light was collected and focused onto a single grating polychrometer. The dispersed light was detected by a Peltier cooled 576 × 384-pixel CCD. The overall resolution was better than 2 cm^{-1}. The XPS measurements were carried out using a monochromatic Al $K\alpha$ excitation radiation in an ultra high vacuum chamber with a base pressure of 2×10^{-9} Torr. The resolution was about 0.1 eV. Ar ions with energy of 4 keV were used for sputtering during the depth profile analyses. The sputter rate was calibrated to be 2 nm per minute for thermal silicon dioxide.

3. Results and Discussions

Typical Raman spectra of the as-deposited samples and of the samples annealed without and with the Ni

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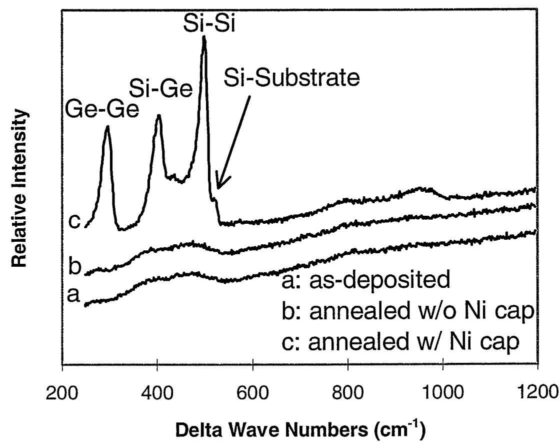
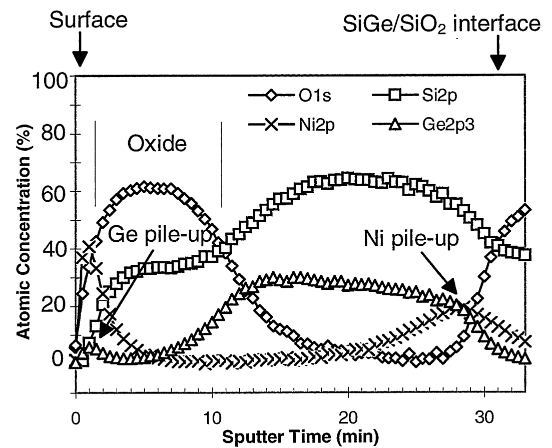


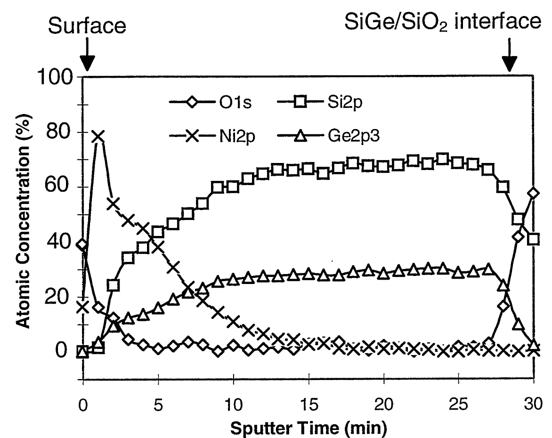
Fig. 1. Typical Raman spectra of the as-deposited Ni capped sample (line a) and of the samples anealed without (line b) and with (line c) the Ni caps.

caps are shown in Fig. 1. The Raman signal of the as-deposited sample (Line a) is composed of a broad structure from 250 to 500 cm^{-1}, which is located between those for pure a-Si and pure a-Ge. The broad structure is characteristic of an amorphous material. The spectrum for the sample without the Ni cap (Line b) is indistinguishable from that of the as-deposited sample, clearly indicating the sample remained amorphous. The spectrum taken from the Ni capped sample (Line c) shows three prominent peaks due to the optical phonon modes associated with the localized vibrations of Ge–Ge (295 cm^{-1}), Ge–Si (402 cm^{-1}) and Si–Si (499 cm^{-1}) pairs.[10] The minor peak at 520 cm^{-1} probably comes from the Si substrate underneath the oxide. The presence of these three peaks, which are characteristic of crystalline SiGe, shows that crystallization has occurred after 1 hour of annealing at 520°C. The amount of Ge in the film can be estimated by fitting the frequency of the Si–Si mode at 499 cm^{-1} to the curve given by Sui[10] relating the modal frequency to the Ge content in poly-SiGe. The estimated value of 0.31 is in good agreement with the value of 0.32 obtained from RBS. The agreement also indicates there is no significant stress in the film.

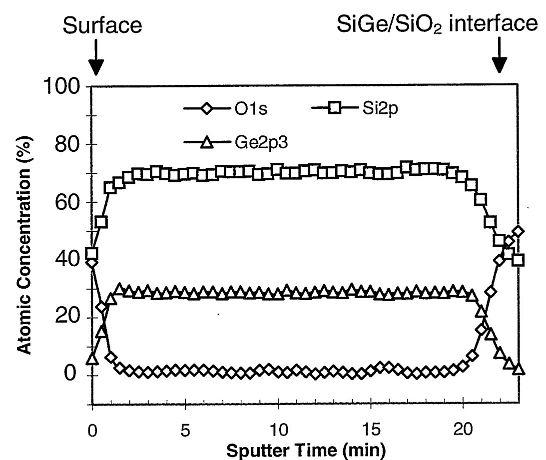
The XPS depth profiles for the annealed sample with the Ni cap, the as-deposited sample, and the annealed sample without the Ni cap are shown in Figs. 2(a)–2(c), respectively. From Fig. 2(a), the atomic concentration of oxygen near the surface of the Ni-capped sample is estimated to be about 60%, which indicates there is an oxide layer between the top Ni layer and the crystallized SiGe layer. If a sputter rate similar to thermal oxide were assumed, the thickness of this oxide layer would be about 20 nm. The profile in Fig. 2(b) shows that there is no detectable oxide layer between the Ni and the SiGe layers in the as-deposited sample, indicating the oxide was not formed during the Ni evaporation. Furthermore, the profile in Fig. 2(c) shows that the equivalent oxide thickness on the SiGe sample annealed without a Ni cap is less than 2 nm. These results indicate that Ni enhanced oxidation of SiGe occurred during the annealing.



(a)



(b)



(c)

Fig. 2. XPS depth profiles of Ni, Si, O, and Ge in (a) an annealed sample with a Ni cap, (b) an as-deposited sample, and (c) an annealed sample without a Ni cap.

Since the reaction was not carried out in a completely sealed system to eliminate oxygen contamination, oxidation could not be avoided. The XPS results in Fig. 2(a) show that the oxidized layer is a mixture of (SiGe)O with the Ge content much less than the value of 0.32 in the original SiGe film. The presence of a Ni peak near the surface in Fig. 2(a) indicates some Ni remained on the

surface of the oxide. Previous studies on the thermal oxidation of SiGe reported that, when the Ge content was less than 0.5,[11] the oxidized layer was pure SiO_2 and that no Ge pile-up could be detected on the surface. Therefore, it is somewhat unexpected that a small but visible pile up of Ge should be observed on the surface of the oxide layer, given that the Ge content was only 0.32 in the film. We believe that Ge migrated from SiGe through the oxide to the surface during the oxidation. However, the presence of the top Ni layer capped the evaporation of Ge, which otherwise would have been lost in the form of GeO.[12]

The depth profile in Fig. 2(b) for the as-deposited sample shows that some Ni penetrated into the SiGe layer before the annealing. This may be due to heating of the sample by the tungsten filament heater before and during the evaporation. But the redistribution of Ni shown in Fig. 2(a) is much more significant after the crystallization. Starting from the top surface, the Ni content initially decreases with Ar sputtering, bottoms out in the bulk of the crystallized SiGe, before rises to a maximum near the interface between the SiGe layer and the SiO_2 substrate. No significant change of Ge to Si ratio was detected in the bulk of the crystallized SiGe layer. This is consistent with earlier reports on the reaction between Ni and crystalline SiGe.[13]

The variations of the XPS spectra of Ge3d, $Ni2p_{3/2}$ and Si2p with sputter time, taken from an annealed Ni capped sample, are summarized in Figs. 3(a)–3(c), respectively. The two peaks near 32 eV and 29.5 eV in the Ge3d spectra (Fig. 3(a): 1 min- and 6 min-lines) indicate Ge is only partially oxidized inside the oxide layer. Ni on the surface seems to be unreacted, as indicated by the peak at around 852.7 eV for the 1 min-line in Fig. 3(b). The equivalent $Ni2p_{3/2}$ peaks in the bulk of SiGe (Fig. 3(b): 16 min- and 25 min-lines) occur at a binding energy of 853.6 eV, which is shifted by about 0.9 eV from its elemental value of 852.7 eV. This indicates that the Ni in the bulk probably exists in a silicide- or germanide-like form. On the contrary, the Ge3d and the Si2p (Fig. 3(c): 16 min- and 25 min-lines) peaks in the bulk show no detectable chemical shifts from their elemental values of 29.4 eV and 99.5 eV, respectively. This is because the concentration of Ni is rather too small to react with a significant fraction of Si and Ge.

The pile-up of Ni at the bottom $SiGe/SiO_2$ interface could not have resulted from that interface acting as a trap of Ni, since no detectable Ni pile-up was found at the top SiO_2/SiGe interface. Hayzelden[8] found that $NiSi_2$ moved with the Si crystallization front during Ni induced crystallization of a-Si. It is probably also true that in our samples, nodules of Ni(SiGe) alloy moved with the crystallization front before being stopped by the SiO_2 interface, thus resulting in a Ni concentration peak at or near the bottom interface of $SiGe/SiO_2$.

4. Conclusion

Without causing changes to the Si to Ge ratio, Ni can induce the crystallization of SiGe thin films on SiO_2 at low temperature. During the crystallization, Ni migrates through the SiGe film and piles up at the interface of the SiGe film and the SiO_2 substrate. Ni inside the SiGe is in a silicide- or germanide-like form. Ni on the surface enhanced the oxidation of SiGe during the annealing and the oxidized layer was found to be a mixture of oxides of Si and Ge, with Ge piling up at the surface. This pile-up

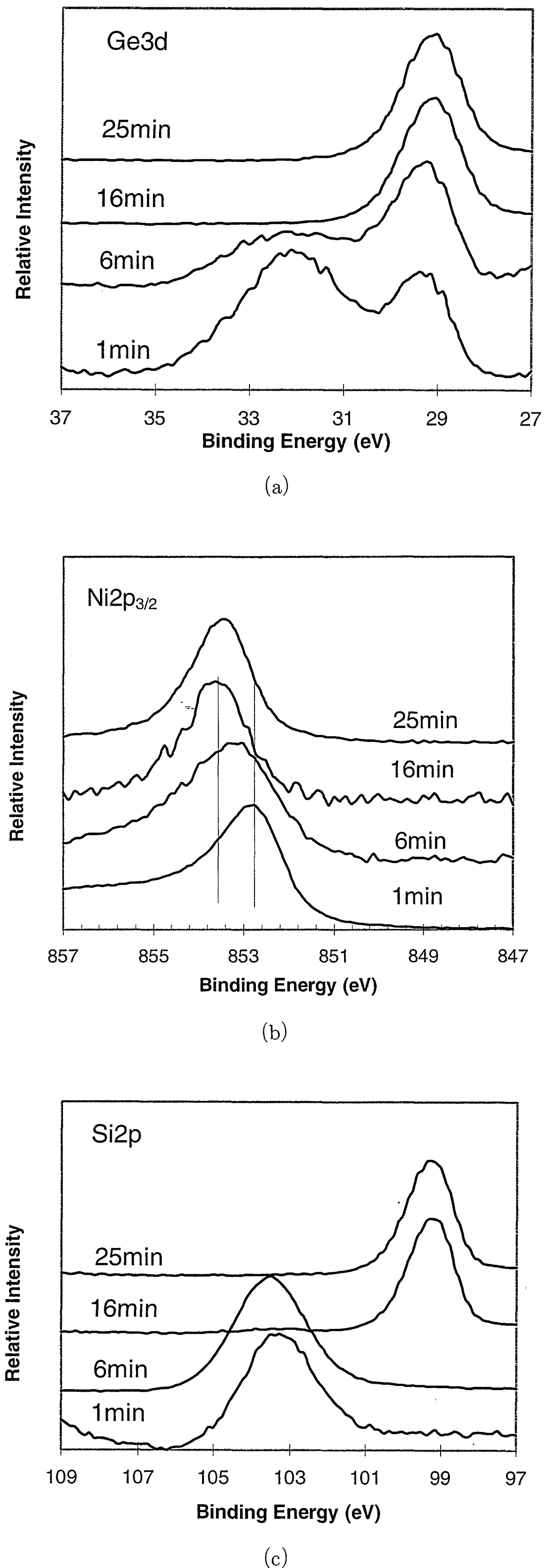


Fig. 3. The variation of the XPS spectra of (a) Ge3d, (b) $Ni2p_{3/2}$ and (c) Si2p with sputter time. The positions of $Ni2p_{2/3}$ in the bulk of metallic Ni (852.7 eV) and NiSi (853.5 eV) are respectively indicated by the left and right vertical lines.

has not been observed for normal thermal oxidation of films with a Ge content less than 50%.

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