SYNTHESIS OF NiSi NANOCRYSTALS FROM Ni FILMS ON Si(111) SUBSTRATES BY LOW-TEMPERATURE MICROWAVE ANNEALING

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In this paper, we describe the formation of nickel silicide nanocrystals by physical vapor deposition of nickel on a Si(111) substrate and subsequent silicidation by microwave annealing at temperatures ranging from 250 to 350 °C. The thin films of Ni were deposited on Si(111) wafers at a pressure of 2×10^{-4} mbar. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) investigations revealed that the as-prepared NiSi nanocrystals are almost spherical with sizes in the range of 35 to 155 nm. The XRD patterns reveal the formation of NiSi and the presence of NiO. The chemical composition of the structure was determined by SEM with energy dispersive X-ray spectroscopy.

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1. Introduction

Metal-semiconductor contact properties play a critical role in every solid-state device used in electronics [1]. The silicide contact technology has transitioned from $TiSi_2$ to $CoSi_2$ and to the current NiSi to achieve properties such as low resistance, low thermal budget, and good thermal stability required for conventional Si devices [2, 3].

In thin film planar reactions (*i.e.*, Ni films reacting with bulk Si), the temperature of the reaction between Ni and Si is known to largely determine the formed Ni silicide phase. As the temperature is increased, Ni_2Si is the initial phase formed above 200 °C, which then transforms to NiSi at temperatures above 350 °C, and finally to $NiSi_2$ at temperatures above 750 °C [1, 2, 4, 5].

The application of microwave annealing (MWA) in semiconductor processing has recently gained increased attention due to the unique features of the process. MWA has been reported to yield metal silicides [6-10] and activate dopants [8–11] at a significantly lower temperature than that used with the conventional rapid thermal annealing process [12]. Several authors have reported methods to improve the morphological stability of the NiSi films. One strategy involves alloying the as-deposited Ni film with elements like Pt [13], resulting in the formation of a stable NiPtSi solid solution. The addition of other elements (*e.g.*, Pd, Ti, Ta, W, and Zr) has also been shown to stabilize the NiSi layer [11, 13].

Nanocrystallization in amorphous silicon (a-Si) has been achieved by different methods such as solid phase crystallization (SPC) [13], excimer laser annealing [14–16], and metal induced crystallization (MIC) [17].

In this study, we prepared nickel silicide nanocrystals (NCs) from thin films of Ni, ~90 nm in thickness, deposited by physical vapor deposition on Si(111) wafers *via* microwave annealing (MWA) between 250 and 350 °C. The morphology and structure of the resulting silicide was characterized by electron microscopy (SEM) and X-ray diffraction (XRD). Energy dispersive X-

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ray spectroscopy (EDS) was used to investigate the concentration of the different elements across the thickness of the films.

2. Experimental

2.1. Material preparation

Ni films were deposited on p-type boron doped (0.01–0.1 Ω cm^{-1}) Si(111) wafers (SILTRONIX), 335–405 µm in thickness. The Si wafers were cleaned with organic solvents and etched with a buffered HF solution (10%) to remove the native oxides on the Si surface before loading into the evaporation chamber. The Ni film was deposited by physical vapor deposition (PVD).

A custom-made sputtering chamber consisting of a stainless steel cylinder with a diameter of 22 cm and 25 cm height was used. A primary pump (ALCATEL 2012A) and a turbo-molecular pump (EDWARDS EXT255H) allowed a base pressure of 2×10^{-6} mbar, while the working pressure was adjusted to 2×10^{-4} mbar. The gas pressure was measured using a BOC EDWARDS gauge. The working gas (argon) was introduced into the chamber through a mass flow controller near the target. The magnetron target was a 50 mm diameter disk of pure Nickel placed at the top of the chamber and connected to the radio frequency power supply through a matching box at a distance of 50 mm from the substrate. The power density was 6 $W.cm^{-2}$.

The film was annealed within the temperature range of 250 to 350 °C. The Microwave annealing was carried out in the chamber at a frequency of 5.8 GHz. The samples were placed in the middle of the chamber between quartz wafers where the electromagnetic field is the most uniform. The temperature of the silicide film was measured by an infrared thermometer. The annealing time was 300 s, with a low annealing temperature (below 400 °C, appropriate to form the silicide). The microwave power determined the total thermal energy emitted by the microwave generator [18].

2.2. Characterization

The nickel silicide film was characterized by X-ray powder diffraction (Bruker D8 Advance) with copper Kα radiation ($\lambda = 1.5406$ Å) for 2θ range of 10 to 89° in steps of 0.05°. The morphology and structure of the samples were examined by scanning electron microscopy (SEM). The depth profile of the chemical composition was obtained by SEM with energy dispersive X-ray spectroscopy

3. Results and discussion

3.1. SEM analysis

Nanocrystal growth in the thin film occurred at the temperature of 350 °C. Nanocrystals with grain sizes of 40–110 nm were clearly observed in the SEM image shown in Fig. (1a). Figure (1b) shows the method used to measure the length and height of the grains using the WXM software (for line 1 and line 2 marked in Fig. 1a), from which the average size of the grains was calculated to be 82 nm. Thermodynamically, large grains grow larger by their tendency to reduce the surface free energy [12]. This implies that the reaction of Ni and Si controls the silicide formation. Because the equilibrium phase is determined by the ratio of the Ni atoms to those of Si [19], the thinner films tend to be Si-rich silicides, while the thicker films consist of Ni-rich phase [17–19].

XRD investigations to determine the phase and composition of the Ni silicide phases revealed the formation of both NiSi (orthorhombic space group Pnma (62), with the lattice constants, a = 0.5233, b = 0.3258, c = 0.5659 nm, JCPDS# 38-0844) and NiO (face-centered cubic (FCC)) phases (JCPDS# 47-1049) (Fig. 2). SEM-EDX (Detector type: SUTW Sapphire, take-off: 35.00, and resolution: 149.30) was used to obtain the chemical composition profile. For region (a) at the surface with presence of few nanocrystals, where the surface remains rich in Si and deficient in Ni, the proportion of the constituent elements was found to be Si = 45.46%, Ni = 38.75%, and O

= 15.81%, whereas for region (b) with significant amounts of NCs, the proportion of the constituent elements is Ni = 54.06%, Si = 41.22% and O = 4.72%, as shown in (Figs. 3a and 3b). The existence of oxygen is due to the contamination of the sample when it was exposed to air.

The presence of unreacted Ni on the surface of the film is consistent with the inadequacy of the thermal energy emitted by the microwave power to transform all Ni into silicide. According to a previous report, a low microwave power (1 P) generated sufficient thermal energy to yield low-resistance NiSi films, whereas a microwave power of 4 P led to minimum sheet resistance and degraded the film [12].

When a thin film of Ni deposited on Si is annealed, Ni first diffuses into the silicon substrate to form the unstable, high-resistivity Ni_2Si phase at about 200 °C. Upon further increase in the temperature, the preferred low-resistivity monosilicide NiSi phase starts to nucleate at 350 °C and the high-resistivity phase $NiSi_2$ nucleates above 750 °C [18–19]. In our case, nanocrystalline NiSi formed at 350 °C.

3.2. Size of the nanocrystals

The size of the nanocrystals depended on the thickness of the deposited Ni film and the annealing temperature. Large bars grow inhomogeneously on surfaces deposited with thicker Ni films. However, the preference for growth orientation is independent of the thickness.

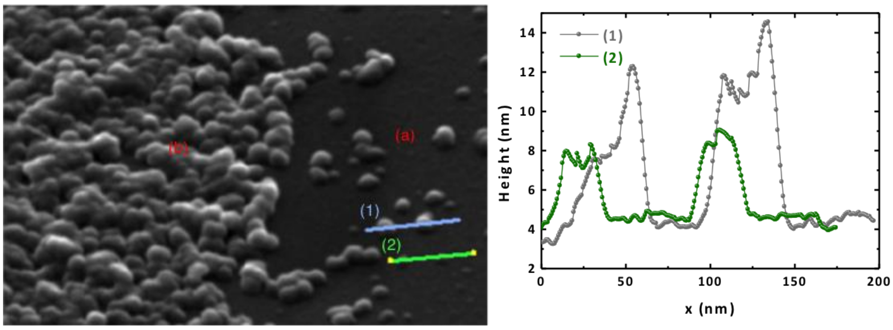
The average nanocrystal size was calculated by two methods: the first by SEM *via* direct calculation using WXM software (Figs. 1a and 1b), which yields an average size of the NCs = 82 ± 10 nm and the second is by XRD using the Scherrer's formula expressed as,

$$D = \frac{K\lambda}{\beta \cos \Theta}$$

where D is the average crystal size, λ is the wavelength of the X-ray source, β is the line broadening at the full width at half maximum (FWHM) in radians, and θ is the Bragg angle determined by fitting the Si (101) substrate crystal diffraction line, and $K = 0.89$ is the Scherrer constant.

Using the Scherrer equation, the average crystallite size is calculated to be 87 nm from the FWHM of the broad peak of the (101) plane of nickel silicide, at $2\theta = 54.8°$.

The formation of the silicide NCs occurs by the preservation of the size of the smallest object that originates immediately after the formation of these interfaces. The growth of primary particles occurs by the addition of soluble species from the solid solution of nickel and silicon. These species bind to the surface and possibly diffuse through the surface to the position corresponding to the minimum energy. The modification of the surface/interface energy of the nano-grains results in the compaction of the nanoparticles or their coating. We can therefore imagine that the characteristic size can be maintained (by stopping growth in time) and thus enable the formation of nanometric objects probably caused by the change in temperature; the nucleation/growth process then begins as a result of this increment in temperature. Owing to the presence of electrical charges in our case, due to MWA, a repulsive interaction develops between two approaching particles and prevents their coalescence or aggregation.



(a) (b)

Fig. 1. (a) SEM images of NiSi NCs produced on the surface, (b) the measured length and height of the grains in two different regions; for line 1, the height of the NC is ~12–14 nm and the length is 50 nm and for line 2, the height is 8–12 nm and the length is 40 nm.

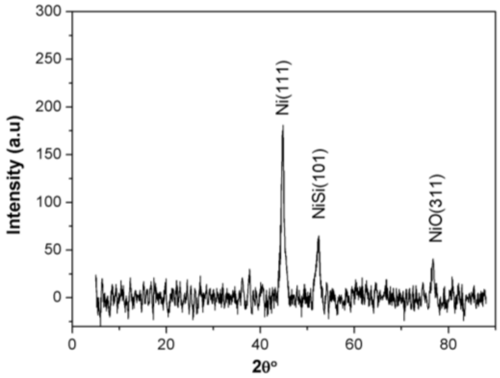


Figure 2: XRD spectra of the Ni silicide film fabricated by microwave annealing of a Ni film on Si substrate at 350 °C for 300 s

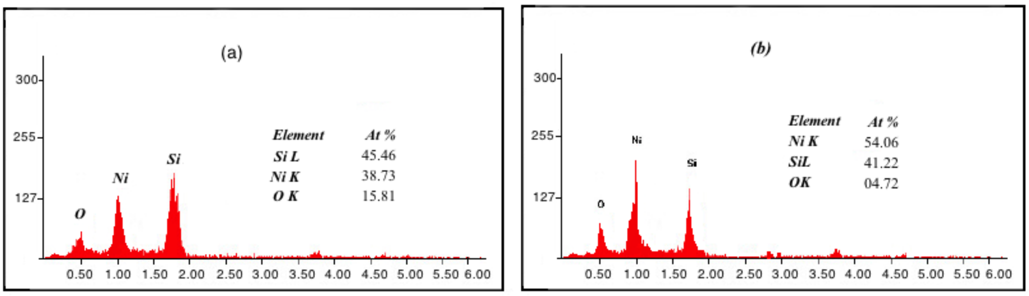


Fig. 3. Energy-dispersive X-ray spectral mapping of Ni, Si, and O in the sample annealed at 350 °C

4. Conclusions

We successfully fabricated nickel silicide nanocrystals by PVD of a thin nickel film on Si(111) wafer followed by microwave annealing. The XRD profile shows the formation of NiSi phase with the presence of NiO, because the surface is rich in Ni and deficient in Si and the thermal energy emitted by the microwave power used for annealing was insufficient to transform all Ni into silicide. The average size of the silicide NCs determined by SEM, as calculated using the WXM software, is 72 ± 10 nm and agrees well with that calculated by XRD using the Scherrer's formula, 87 nm. To our knowledge, this is the first report on the formation of silicide NCs by PVD followed by microwave annealing.

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