Growth, structure and electrical characteristics of epitaxial nickel silicide from chemically electroless Ni deposition on Si

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The epitaxial $NiSi_2$ has been successfully grown on (1 0 0) and (1 1 1) silicon single crystals by chemical electroless deposition and isothermal annealing for the first time. Transmission electron microscopy (TEM) was applied to study the structure and orientation relationship of the films and substrates. The nickel silicide formed on both (1 0 0) and (1 1 1) Si substrates was identified to be $NiSi_2$ and was found to have epitaxial relationship with the substrates by bright field imaging and selected area diffraction pattern analysis. Square, hexagonal and irregular dislocation networks were observed. The orientation relationships of silicide phase with respect to (1 0 0)Si substrate were identified to be (2 2 0)Si ‖ (2 2 0)$NiSi_2$, (4 0 0)Si ‖ (4 0 0)$NiSi_2$ and (0 0 1)Si ‖ (0 0 1)$NiSi_2$. The orientation relationships of silicide phase with respect to (1 1 1)Si substrate were identified to be (2 2 0)Si ‖ $(0 2 \bar{2})$$NiSi_2$, $(3 \bar{1} 1)$Si ‖ $(3 1 \bar{1})$ $NiSi_2$ and $[1 \bar{1} \bar{4}]$Si ‖ $[1 \bar{1} \bar{2}]$$NiSi_2$. The average spacing of interfacial dislocations was about 90 nm for epitaxial silicide formed on (1 0 0)Si at 800° C, which is narrower than that on (1 1 1)Si. These spacings decreased with increasing annealing temperature.

Sheet resistances were measured to be lower than that of poly-$NiSi_2$ produced from electron gun evaporation with the same annealing condition. A linear relationship between resistivity and thickness was found and discussed.

1. Introduction

Metal silicides grown on silicon substrates have been widely used as ohmic contacts, Schottky barriers, electrodes and low resistance interconnects in the microelectronic devices [1, 2]. Epitaxial silicides are a special class of silicides which exhibit definite orientation relationships with respect to the Si substrate. A necessary condition for good epitaxial growth is the matching of the lattice parameters between the overgrowth and the Si substrate. The controlled formation of epitaxial silicides on silicon is of great importance for application in silicon-integrated circuits [3] as well as for fundamental studies [4-6]. The epitaxial growth of silicides is important because its resistivity is much lower than that of polycrystalline silicides. This property could be used to lower the voltage drop of the silicide interconnects and to increase the speed of devices [2]. In addition, the epitaxial growth of the silicide offers the possibility of crystalline growth on the top of these silicides leading to novel devices [7, 8] and buried contacts [9].

In the last few years, many silicides were found to grow epitaxially on Si via vacuum plating and annealing process. Recently, epitaxial Fe–Ni alloy silicides have been successfully grown on (1 1 1) Si using chemical electroless deposition technique with subsequent annealing schemes [10]. This finding should bring impetus for further investigations on formation and properties of various epitaxial silicides.

In most cases silicides have been formed under vacuum conditions. Samples have generally been prepared by depositing thin films onto chemically cleaned silicon substrate by electron-gun evaporation under vacuum of about $1 * 10^{-6}$ torr. Samples were then annealed in a vacuum or in a controlled atmosphere [2] to form epitaxial silicides. However there is an alternative approach by which the metallic thin film is deposited using chemically electroless immersion plating followed by appropriate annealing to form epitaxial silicide. This approach will have many advantages, such as mass production, fast deposition rate, almost no space limitation, evenness, fast processing rate and low cost [11, 12]. In principle, electroless deposition technique is more convenient than evaporation for selective area deposition [13]. The method is potentially applicable to the processing of commercial devices. However, the formation, structure, orientation relationship, and phase transformation of epitaxial silicides on various index planes of Si via this new alternative process should be intriguing. In addition less is known about the relationship between the thickness of the epitaxial phase and electrical property, which should be valuable in both practical application and academic understanding.

2. Experimental procedure

The silicon substrate used in this work were 3–5 ohm cm phosphorus-doped (1 1 1) and (1 0 0) wafers. These

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were cleaned ultrasonically in soap solution, rinsed in deionized water, immersed in 1:1 H_2O_2/HCl solution, followed by etching in dilute HF and rinsing again in deionized water. The etched wafers were immersed into a special nickel hypophosphite-based electroless plating bath for a few minutes at about 90° C. The pH value of the bath was maintained at about 9. Nickel thin films were deposited autocatalytically. The various thicknesses of the films were controlled by the immersion time and measured by the chemical analytical method with Atomic Emission Spectroscopy, and further calibrated by cross-sectional transmission electron microscopy.

As-deposited samples were then annealed in dry N_2 ambient in a three zone diffusion furnace at temperatures between 800 and 900° C. The N_2 gas was purified by first passing it through a titanium getter tube maintained at 850° C to reduce the O_2 content. The annealing time at each temperature was 1 h.

The sheet resistances were measured by Van der Pauw method [19]. The specimens for TEM examinations were prepared by mechanically cutting the samples into discs about 3 mm in diameters and then chemical polishing from the silicon side; the deposited side was covered with an electronic wax for protection during polishing. The polishing solution consisted of one part of solution A (0.25 g of iodine and 110 cc of CH_3COOH) and two parts of solution B (1 HF–3 HNO_3) [14]. TEM examinations were performed with JEOL-200CX transmission electron microscopy.

3. Results and discussion

In order to accurately control the relationship between the thickness of electroless depositing thin film and time, studies on the relationship between film thickness and immersion time were carried out. The electroless deposition thickness was found to increase linearly with time as soon as the deposition was initiated on the silicon surface.

Hypophosphite was used as the main reducing agent for the reduction of nickel cations to the nickel atom in the solution. During the deposition process hydrogen bubbles were observed to continuously evolve from the surface as a reaction by-product. Catalytic dehydrogenation of hypophosphite with an active hydride transfer to the catalytic surface, is considered to be the first step in the deposition process. The hydride ions then react with nickel ions which are probably a hydrolized species adsorbed on catalytic sites to produce the deposit [15]. For the same immersion time the thickness of deposited nickel film on (1 0 0) was found to be thicker than that on (1 1 1).

For samples annealed at temperatures higher than 800° C, the silicide were found to grow epitaxially with respect to both (1 0 0) and (1 1 1) Si substrate. This is consistent with the known fact that epitaxial silicides are faceted with (1 0 0) and (1 1 1) interfaces [16], in which the epitaxial silicides were prepared under vacuum conditions. Figure 1 shows a bright field micrograph of a typical epitaxial region, about 10 μm in size, on the (1 0 0) Si substrate. The characteristic right angles interfacial dislocation networks [17, 21] indicate an epitaxial relationship taking place. The

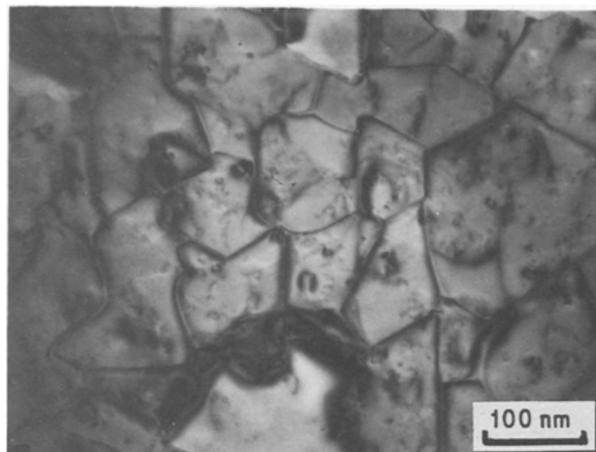

Figure 1 Bright field micrograph showing the epitaxial regions for Ni/Si(1 0 0). After 1 h, N_2 furnace annealed at 800° C.

selected area diffraction pattern of these silicide regions is shown in Fig. 2 in which the extra regular diffraction spots beside the spots of Si indicate only epitaxial $NiSi_2$ formed without any other phases present. From a detailed Miller indices analysis of the diffraction pattern, as shown in Fig. 3, the orientation relationships with respect to (1 0 0)Si were identified as (2 2 0)Si ‖ (2 2 0)$NiSi_2$, (4 0 0)Si ‖ (4 0 0)$NiSi_2$ and [0 0 1]Si ‖ [0 0 1]$NiSi_2$.

As shown in Fig. 1, the average spacing between interfacial dislocations was found to be about 90 nm. These spacings were found to increase by decreasing the formation temperature of the silicide. Although the mechanism by which interfacial dislocations of the silicide form at different temperatures is known to be complicated, a tentative explanation is proposed as follows. The spacing between interfacial dislocations is considered to correlate with the lattice mismatch to the strain induced from formation conditions. The mismatch can be accommodated by both semicoherent interfacial dislocations and elastic strain throughout the lattice. In fact, the thermal expansion coefficients of $NiSi_2$ and Si are considerably different. Consequently, the lattice mismatches between $NiSi_2$ and Si are the function of the annealing temperature. For instance, in the case of isotropic thermal expansion, the mismatches from theoretical calculation are 0.588% and 0.735% at 800° C and 900° C, respectively

Figure 2 Selected area diffraction pattern of the same region as shown in Fig. 2.

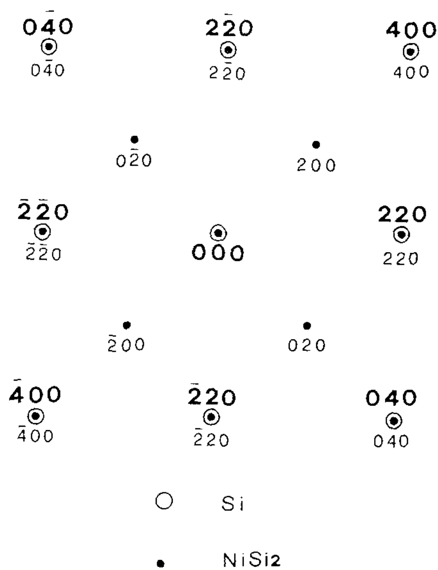

Figure 3 Detailed Miller indices analysis of the diffraction pattern shown in Fig. 3.

[21]. Thus it is not surprising that on the condition of the same annealing time, sufficient to form semicoherent dislocation arrays, the average spacing between interfacial dislocations was found to decrease with increasing annealing temperature.

It is apparent that the transformation of solid state epitaxy in our case is complete within 1 h at high annealing temperatures. This transformation time seems no longer than that of $NiSi_2$ prepared by electron gun evaporation technique [17], although the expected impurity, phosphorus, in the electroless deposited nickel thin film is considered to be about 5% [20]. The small amount of phosphorus does not appear to have any retardation effect on the formation rate of silicon-rich silicide phase. Moreover there is no apparent difference in epitaxial relationship between these two different processes.

Figure 4 shows a bright field micrograph of typical epitaxial region of Ni/Si(1 1 1) after 800° C 1 hr N_2 furnace annealing. The configuration of interfacial dislocation networks, such as hexagonal and few irregular types were found. The average spacing of interfacial dislocations on Si(1 1 1) seems wider than

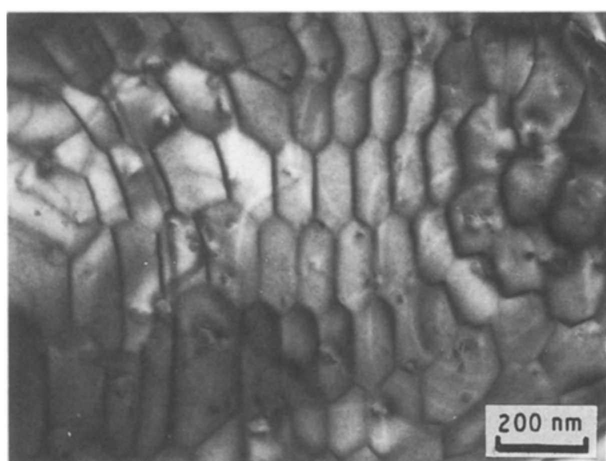

Figure 4 Bright field micrograph showing the epitaxial regions for Ni/Si(1 1 1) after 800° C, 1 h, N_2 furnace annealed.

Figure 5 Selected area diffraction pattern of the same region as shown in Fig. 5.

that on Si(1 0 0). The interface of $NiSi_2$ with Si(1 0 0) appears to be rougher than those on Si(1 1 1). The selected area diffraction pattern of these epitaxial regions is shown in Fig. 5. The orientation relationships with respect to (1 1 1)Si substrate were identified to be (2 2 0)Si ∥ $(0 2 \bar{2})NiSi_2$, $(3 \bar{1} 1)$Si ∥ $(3 1 \bar{1})NiSi_2$ and $[1 \bar{1} \bar{4}]$Si ∥ $[1 \bar{1} \bar{2}]NiSi_2$ by detailed Miller indices analysis of diffraction pattern, as shown in Fig. 6.

The sheet resistances as a function of the thickness of nickel silicides formed on Si(1 1 1) at 800° C are shown in Fig. 7. Sheet resistances were found to decrease rapidly with increasing thickness as thickness of the silicide is smaller than 150 nm. It is considered that the excellent quality of the new process silicide film improves markedly with thickness providing useful physical reference in practical application. Above 150 nm, they become steady and only decrease slightly with increasing thickness. This steady trend offers a good basis to convert sheet resistance to resistivities with apparent equivalent data from realistic and practical aspects. In particular, the sheet resistance of epitaxial $NiSi_2$ with the thickness of 500 nm is about 1Ω/□. This value is lower than that of Murarka's value [18]. It is considered to attribute to the epitaxial growth of single crystalline nickel silicide.

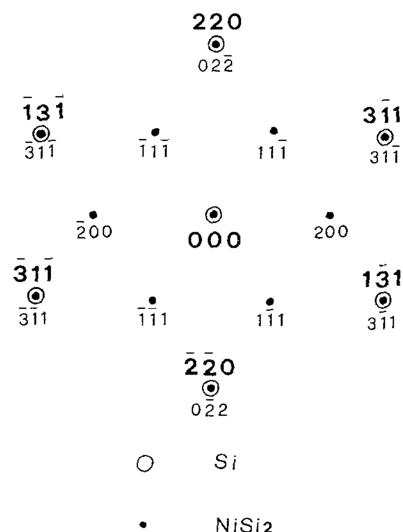

Figure 6 Detailed Miller indices analysis of the diffraction pattern shown in Fig. 6.

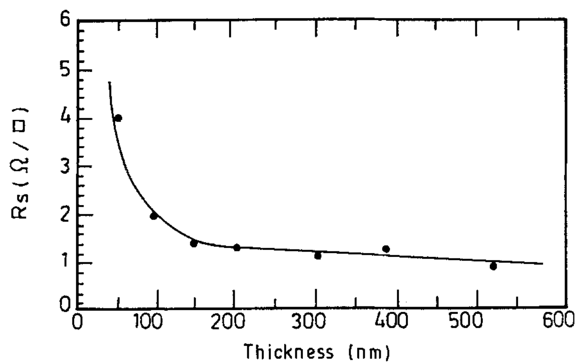

Figure 7 Variation of sheet resistance with changes thickness of $NiSi_2$, on (1 1 1)Si 800° C. 1 h annealed.

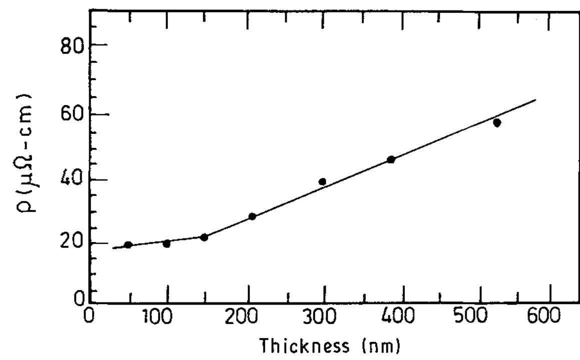

Figure 8 Variation of resistivity with changes thickness of $NiSi_2$, on (1 1 1)Si, 800° C, 1 h annealed.

On the other hand, the resistivity of epitaxial $NiSi_2$ with the thickness of 2000 nm is 27 micro ohm cm. This value is comparable with epitaxial silicide prepared from the vacuum process reported by Hou *et al.* [21]. There small amounts of phosphorous were thought to have no harmful effect on epitaxial nickel silicide formation and its resistivity.

Figure 8, shows the relationship between resistivities and the thickness of the silicides. The resistivities of the silicon-rich silicides were found to be nearly the same as the film thickness smaller than 150 nm. Above 150 nm, the resistivities increase slightly and linearly with the thickness. The reason is possibly related to the extent of the tensile strain, which gives rise to an increased resistivity, within the film [22]. The interfacial dislocations form during epitaxial silicide formation. As the silicide becomes thicker, the number of interfacial dislocations does not increase more by TEM characterization. Moreover, the strain accumulated within the thicker silicide is expanded more than that within the thinner silicide at high formation temperature. Therefore, as the temperature is reduced to room temperature, the residual strain within the thicker silicide film rises, so that higher resistivity is anticipated. These findings are valuable since few studies on the relationship between resistivities and the thickness of epitaxial $NiSi_2$ have been reported. The results provide a critical reference to practical application.

4. Conclusions

By using chemically electroless deposition technique and isotherm annealing method, epitaxial $NiSi_2$ has been successfully grown on low index planes of Si substrates.

1. In the particular range of annealing temperature the newly formed silicide was found to be a silicon-rich silicide, $NiSi_2$. The orientation relationships of the epitaxial silicide phase with respect to (1 0 0)Si substrate were identified to be (2 2 0)Si ∥ (2 2 0)$NiSi_2$, (4 0 0)Si ∥ (4 0 0)$NiSi_2$ and [0 0 1]Si ∥ [0 0 1]$NiSi_2$.

2. The orientation relationships of the silicide phase with respect to (1 1 1)Si substrate were identified to be (2 2 0)Si ∥ $(0 2 \bar{2})NiSi_2$, $(3 \bar{1} 1)$Si ∥ $(3 1 \bar{1})NiSi_2$ and $[1 \bar{1}\bar{4}]$Si ∥ $[1 \bar{1} \bar{2}]NiSi_2$.

3. The average spacing of interfacial dislocations was found to be about 90 nm for $NiSi_2$ formed on (1 0 0)Si at 800° C, which is narrower than that on (1 1 1)Si, and decreased with increasing annealing temperature. A tentative explanation is proposed. Small amounts of phosphorus were thought to have no harmful effect on epitaxial silicide formation on low index planes of Si.

4. The sheet resistance of the epitaxial silicide was found to be lower than polycrystalline silicide and comparable to the epitaxial silicide prepared from the vacuum process of e-gun evaporation followed by the same annealing. The linear relationship of resistivity against film thickness is attributed to the strain accumulated within the silicide film as the environment temperature decreases from high formation temperature.

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Received 31 January
and accepted 24 July 1989