Silicide formation process in ultra-thin Ni-silicide film for advanced semiconductor devices: mechanism of NiSi$_2$ formation at low temperature

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Abstract. Atomic-resolution high-angle annular dark-field scanning-transmission electron microscopy and ab-initio calculations were used to reveal the reaction involved in the formation of ultra-thin Ni silicide film at 300°C. We found that a Ni-adamantane structure, in which Ni atoms occupy the tetrahedral interstitial voids of Si, forms at the initial stage of the reaction. We also found that the adamantane structure is under considerable compressive stress due to lattice-mismatch at the adamantane structure-Si interface (5.6%). Then, NiSi$_2$ forms just beneath the Ni-adamantane structure at a much lower temperature than the NiSi$_2$ formation temperature reported for the reaction between a Ni layer and Si substrate (800°C). Our analyses strongly suggest that the Ni-adamantane structure acts as a precursor in the formation of NiSi$_2$.

1. Introduction

In advanced metal-oxide-semiconductor field effect transistors (MOSFETs), thin NiSi films (< 20 nm) are used as contacts in the source and drain regions [1]. A serious problem is the unexpected formation of NiSi$_2$ during the silicidation process: NiSi$_2$ raises the resistivity and roughens the silicide/Si interface, degrading device performance.

Previous studies have indicated that in the reaction between a Ni film and Si substrate, Ni$_3$Si, NiSi, and NiSi$_2$ are sequentially formed as the sintering temperature increases [2]. The formation temperature of NiSi$_2$ is about 800°C. However, the NiSi$_2$ phase is reportedly formed at a much lower temperature in some cases [3-5]. The mechanism of NiSi$_2$ formation at low temperatures, which is used in the silicidation process (< 400°C), has yet to be clarified.

We examined the atomic structure of a very thin Ni-silicide layers formed by depositing monolayers of Ni on a Si (001) surface at 300°C, using atomic-resolution high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM). We also examined the stability of these thin Ni-silicide layers using first-principle calculations. From these results, we infer that the surface layer acts as a precursor in forming NiSi$_2$ at low temperature.

2. Experiment

We prepared two samples in which 0.5-nm-thick (sample 1) and 1.0-nm-thick (sample 2) Ni films were deposited on Si (001) substrates by chemical vapor deposition. Deposition rate was 0.2 nm/min. The samples were then formed into <110> cross-sectional specimens using mechanical thinning and Ar-ion milling. In HAADF-STEM observations, the electron probe convergence angle was 20 mrad,
and the annular detector was set to collect the electrons scattered at angles between 45 and 110 mrad. First-principles calculations were carried out using the WIEN2k package [6]. STEM image simulation software xHREM was used in the STEM image analysis.

3. Results

Cross-sectional views over wide areas of the specimens are shown in Fig. 1. Thin bright surface layers were observed in both samples. In sample 2, bright triangular areas were observed just beneath the surface layer. The facets of the triangular areas were parallel to the (111) of the Si substrate. The faceted shape (Fig. 1(b)) as well as its atomic arrangement, shown in the micrograph in Fig. 3, indicated that the triangular areas were NiSi$_2$.

Figure 1. HAADF-STEM of (a) sample 1 and (b) sample 2. Bright areas are reaction products.

High-resolution observations of the surface layer revealed that Ni atoms in the surface layers occupy tetrahedral interstitial voids of the Si substrate. Figure 2(a) shows a representative image of the surface layer of sample 1. Bright dots are evident at the tetrahedral interstitial voids of Si as well as at the Si lattice sites. The image intensity distribution measured along the (110) lattice plane of Si, which is indicated by the arrow in Fig. 2(a), is shown in Fig. 2(b). Peaks are evident at some interstitial sites in the surface area (the left side of the graph), strongly suggesting that the sites are occupied by Ni atoms. Moreover, in some Si atomic column pairs, the peak intensities of individual Si atomic columns significantly differed. This difference indicates that Si atoms dissociated themselves from the lattice sites that showed smaller peak intensities.

Figure 2. (a) Close-up of surface layer in sample 1 and (b) intensity distribution measured along a lattice plane denoted by arrow in (a). Blue and red balls in (b) represent Si lattice sites and interstitial voids, respectively. Peaks at blue ball positions (denoted by red arrows) indicate that interstitial sites are occupied. Intensities of Si atomic column pairs (denoted by black arrows) significantly differ.

A close-up view of the interface between the surface layer and the bright triangular areas in sample 2 is shown in Fig. 3(a). To determine the atomic arrangement in the surface layer, we first performed STEM image simulations (Fig. 3(b), (c)). In the simulations of the surface layer, we assumed that Ni
atoms occupy tetrahedral interstitial voids at a certain occupancy factor on the basis of the findings in Fig. 2 (the structure is referred to as adamantane structure [7, 8]). The simulated images showed that the intensities at the Si lattice sites and interstitial voids (i.e., Ni sites) were similar at the Ni occupancy factor of 0.55 (Fig. 3(d)), reproducing the observed image. In addition, the simulated image of a CaF$_2$-type NiSi$_2$ (Fig. 3(c)) well reproduced the observed image of the triangular area in Fig. 3(a).

Moreover, despite the different atomic arrangement in the surface layer and that in the triangular areas, no crystal lattice discontinuities, such as dislocations, were noticeable at the interface. That is, NiSi$_2$ was formed epitaxially beneath the surface layer, strongly suggesting that the surface layer plays a crucial role in NiSi$_2$ formation.

To examine the stability of the Ni-adamantane structure formed on a Si substrate, we calculated the total energies of its unit cell as a function of their lattice constants. In the calculation, we set the Ni occupancy factor to 1.0, for simplicity. The calculated total energy curves are shown in Fig. 4 together with that of Si. The reference energy of each curve, $E_{\text{min}}$, was set to the calculated minimum energy of each structure. The calculated Si equilibrium lattice constant, at which the total energy was minimized, was 0.534 nm, which agreed well with the measured one [9]. The calculated equilibrium lattice constant of the Ni-adamantane structure was 0.565 nm, which was 5.8% larger than that of Si. Hence, the Ni-adamantane structure should be under compressive stress when it is formed epitaxially on a Si substrate.
This considerable lattice mismatch and resulting interfacial stress possibly prevents the surface layer from becoming thicker.

4. Discussion

According to the first-phase rule [10], the Ni$_2$Si phase is the first silicide phase in the reaction between a Ni film and Si substrate: an atomic diffusion at the Ni/Si interface generates an interface layer with a eutectic composition (Ni:Si = 2:1) and a silicide crystal whose composition is congruent with the interface layer nucleates. In our samples, the Ni diffusion from the thin Ni layer may be too small to form a Ni-rich (Ni$_2$Si) interface layer, but the penetration of a small amount of Ni atoms into Si forms a Ni-adamantane structure instead.

Hence, the thin Ni film (~ 1 nm thick) and/or the small Ni deposition rate (0.2 nm/min) used in this experiment would be necessary for adamantane structure formation and following low temperature NiSi$_2$ formation. This is because large Ni film thickness and/or large Ni deposition rate would cause a large Ni diffusion and result in Ni-rich interface layer formation.

Considerable stress (5.8%) of the Ni-adamantane structure may be the cause of the low-temperature NiSi$_2$ formation. This is because the stress of the Ni-silicide layer should be reduced by NiSi$_2$ formation, which is more lattice matched to Si (the lattice constant is 0.5395, 0.6% smaller than Si [9]). Thus, we observed a NiSi$_2$ region below an initial adamantane surface layer in sample 2 (1.0-nm-thick Ni sample), in which sufficient Ni diffused to form NiSi$_2$, while only a surface adamantane layer was observed in sample 1 (0.5-nm-thick Ni sample). In addition, the decrease in the covalency of the Si-Si bonds in the surface layer possibly allows the changing of atomic arrangement at the temperatures as low as 300°C.

5. Summary

The mechanism of the NiSi$_2$ formation at a low temperature (300°C) was investigated using HAADF-STEM and ab-initio calculations. STEM analysis showed that a Ni-adamantane structure was formed at the initial stage of the reaction. In addition, NiSi$_2$ was formed just beneath the surface layer with the Ni-adamantane structure. Our computational results indicated that the equilibrium lattice constant of the Ni-adamantane structure was larger than that of Si, indicating that the stress at the Ni-adamantane structure/Si interface should be considerably larger than that at the NiSi$_2$/Si interface. We thus infer that the Ni-adamantane structure may act as a precursor in NiSi$_2$ formation.

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