Phase selective synthesis of gadolinium silicide films on Si(111) using an interfacial SiO_2 layer

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We synthesized a single phase $GdSi_2$ film on a Si(111) substrate with an interfacial SiO_2 layer. In order to take account of the role of the interfacial SiO_2 layer, systematic investigations on clean and oxidized Si substrates were done by using *in situ* reflection of high energy electron diffraction, x-ray diffraction, and atomic force microscopy of the silicides formed with post annealing. Our result showed that the interfacial SiO_2 layer enhanced the structural transformation of the initial $GdSi_{1.7}$ hexagonal phase into the $GdSi_2$ orthorhombic phase above the decomposition temperature of $SiO_2(\sim 800\,^{\circ}C)$. We proposed a reaction mechanism for the $GdSi_2$ film formation with the help of the interfacial SiO_2 layer. The measured electrical resistivity of the Gd-silicide film strongly depends on the silicide phase. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1581342]

I. INTRODUCTION

Silicides are normally formed by metal deposition on a pre-cleaned Si substrate followed by high temperature annealing. A silicide-Si interface is located inside the layer due to the solid-state reaction in the silicide formation, which results in intimate contact between the silicide and the Si substrate.[1] Rare-earth (RE) silicides have attracted considerable attention in the semiconductor industry due to their low Schottky barrier height on *n*-type Si (0.3–0.4 eV) since its initial report in the late 1980's. It makes them suitable candidates for ohmic contacts and gate electrodes in Si integrated circuits.[2–4] Moreover, their small lattice mismatch to Si(111) substrates makes epitaxial layer growth possible and ensures an ideal interface structure with minimized defect states.[5] On the other hand, it is well known that the Schottky barrier height strongly depends on atomic structure at the interface. Once a mixed silicide phase exists at the interface, the inhomogeneity of barrier height will be introduced along the contact area, which results in the degradation of device property. The importance of obtaining a single-phase silicide layer is increased as the dimension of device approaches the nano-
scale regime.[6]

The two well-known silicide phases in gadolinium thin film on silicon substrate are the hexagonal $GdSi_{1.7}$ structure and the orthorhombic $GdSi_2$ structure. The $GdSi_2$ ($a = 0.401$ nm, $b = 0.409$ nm, $c = 1.344$ nm) phase is known to be stable at high temperature, while the $GdSi_{1.7}$ phase ($a = 0.3877$ nm, $c = 0.4172$ nm) is formed at low temperature and is unstable over about 400 °C. In contrast to other RE silicides, the separation of $GdSi_{1.7}$ phase and $GdSi_2$ phase in the solid-state reaction of RE thin film formation on Si(111) substrate has not been successful.[7] The ratio of the two different phases in the gadolinium silicide film systematically changes depending on the various growth conditions.[7,8]

Another issue is that a heavily pitted rough surface results when the RE silicide layer is prepared via the solid-state reaction between deposited thin metal and Si substrate.[9,10] Such a surface condition gives increased leakage current as well as higher sheet resistance that degrades the properties of the electronic device.[11]

In this article, we report our experimental results of obtaining single phase $GdSi_2$ film with dramatically improved surface morphology on Si(111) substrate with the help of a thin oxide layer. The role of the SiO_2 layer on the Si surface is systematically studied by comparing the silicide film formed on a clean Si(111) surface. The electrical resistivity of the obtained Gd-silicide film is also examined in four-point probe electrical conductivity measurements.

II. EXPERIMENT

The samples were prepared on (111) oriented *p*-type Si wafers with two different surface conditions: a clean silicon surface and an oxidized silicon surface. Si surfaces were cleaned chemically first by using the standard reduced calcium aluminate (RCA) method, which removed organic and metallic residues from the surface and resulted in the formation of 4–6 ML of SiO_2 (20–30 Å) at the substrate surface.[12,13] Right after the RCA cleaning, Si wafers were divided into two groups. One group was introduced into the vacuum chamber without additional surface treatments and used as substrates with oxide layer. The other group was dipped in a dilute HF solution before introduction into the chamber. For obtaining a clean surface, these wafers were flashed above 1000 °C and the well-ordered $Si(111)-7\times7$ surface was confirmed by observing high energy electron diffraction (RHEED) pattern. Gd was evaporated on the prepared Si surface via ionized beam assisted deposition from a W crucible at 1×10^{-9} Torr. The deposition rate was controlled to 0.4 Å/s and the substrate temperature was maintained at 400 °C. The Gd film thickness was measured using a RUMP simulation of Rutherford backscattering data, with a

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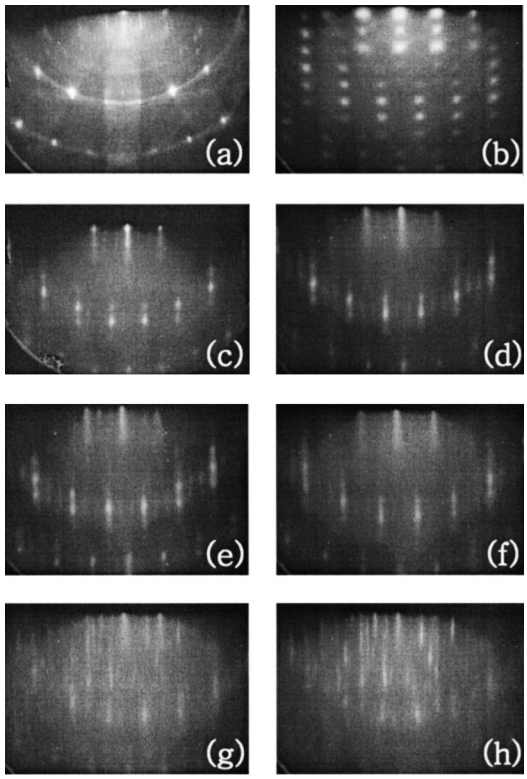

FIG. 1. RHEED patterns observed from the (a) Si(111)-7×7 surface before Gd deposition, (b) as-deposited Gd film on Si(111), Gd-silicide layer grown on the clean Si surface after annealing for (c) 20 min, (d) 40 min, (e) 120 min, Gd-silicide layer grown on the oxidized Si surface after annealing for (f) 20 min, (g) 40 min, (h) 120 min. The incident electron beam is along the [112] direction.

result of 20 nm for our experiment. Immediately after Gd deposition, the sample was heated *in situ* under 5×10^{-10} Torr via electron bombardment to form the silicide. The sample temperature below 500 °C was measured by reading the applying current in the current source which was carefully calibrated with a chromel–alumel thermocouple contacting the backside of a sample. Higher sample temperature was measured directly with an optical pyrometer. To investigate the evolution of Gd-silicide phase on Si substrate, samples were annealed at 800 °C for different annealing periods of 20, 40, and 120 min, respectively.

The accompanying phase change of the epitaxial layer during sample annealing was monitored by using *in situ* reflection of high energy electron diffraction. The formed silicide phases were identified with x-ray diffraction (XRD) technique. The chemical state of the films was investigated by the depth profile of x-ray photoelectron spectroscopy. Atomic force microscopy (AFM) was used for examining surface morphology of the resulting film. The electrical resistivity of the film was measured by using the four-point probe method.

III. RESULTS AND DISCUSSION

The RHEED patterns shown in Fig. 1 were taken with incident electron beams along the [112] direction. Figure 1(a) is taken from the Si(111)-7×7 reconstructed surface of the clean Si substrate before depositing Gd layer. The observed sharp streaks and Kikuchi lines indicate an atomically flat and contamination free Si surface. Figure 1(b) obtained right after the deposition of the Gd layer on the clean Si substrates at 400 °C shows hexagonal symmetry and the formation of Gd silicide between the deposited Gd layer and the Si(111) surface at this stage is confirmed in x-ray diffraction data. The appearance of the blurred diffraction spots indicates its imperfection of crystallinity. The RHEED patterns in Figs. 1(c)–1(e) and 1(f)–1(h) show the evolution of Gd-silicide film prepared on the clean surface and the oxidized surface, respectively, as a function of the annealing period at 800 °C. These patterns indicate that the Gd silicides initially have the same hexagonal structure on both surface conditions. As the sample annealing continues, additional streaks start to appear beside the initial streaks. The appearance of the secondary streaks is more easily recognizable with the incident electron beam along the [112] direction in comparison with the [110] direction. This change happened much faster in the film grown on the oxidized silicon substrate where the change was clearly observed from the sample annealed longer than 40 min. Even though the RHEED pattern implies that the annealing results in a structural change in the silicide film, it is not easy to characterize details of the accompanying structural change with the RHEED pattern alone.

Figure 2 shows x-ray diffraction (XRD) data collected after each annealing step with theta-2theta x-ray diffractometer for these samples. The Bragg's peaks of each XRD pattern were compared with those of the known hexagonal $GdSi_{1.7}$ and the orthorhombic $GdSi_2$ phases[7,14] and assigned carefully to decide the corresponding phase. Figures 2(a)–2(d) show the evolution of the Gd-silicide layer prepared on the clean silicon surface upon the postannealing, where each sample was (a) as deposited, (b) annealed for 20 min, (c) annealed for 40 min, (d) annealed for 120 min at 800 °C, respectively. We observed only the hexagonal $GdSi_{1.7}$ phase in the early stage of annealing from XRD data. As the sample was annealed further at 800 °C, the (112) peak of the orthorhombic $GdSi_2$ phase starts to appear and finally we observe a mixed phase of $GdSi_{1.7}$ and $GdSi_2$. A different behavior is clearly observed in the XRD patterns collected from the Gd-silicide grown on the oxidized Si surface as represented in Figs. 2(e)–2(h). The (112) peak of $GdSi_2$ phase is already appearing after 20 min annealing at 800 °C. As the sample annealing continues, the intensities of the (001) and (002) peaks of the hexagonal $GdSi_{1.7}$ phase decrease dramatically and the (112) peak of the orthorhombic $GdSi_2$ phase increases rapidly. After the extended annealing at 800 °C, the $GdSi_{1.7}$ phase disappeared and the $GdSi_2$ single phase silicide layer remained. XRD measurement clarifies the structural change of the Gd silicide during the annealing, which corresponds to the phase transition from the hexagonal $GdSi_{1.7}$ phase to the orthorhombic $GdSi_2$ phase. Our experimental result shows that the existence of interfacial SiO_2 layer between Gd and Si substrate facilitates the formation of the $GdSi_2$ phase from the beginning of sample annealing and finally results in single phase $GdSi_2$ film on a Si(111) substrate.

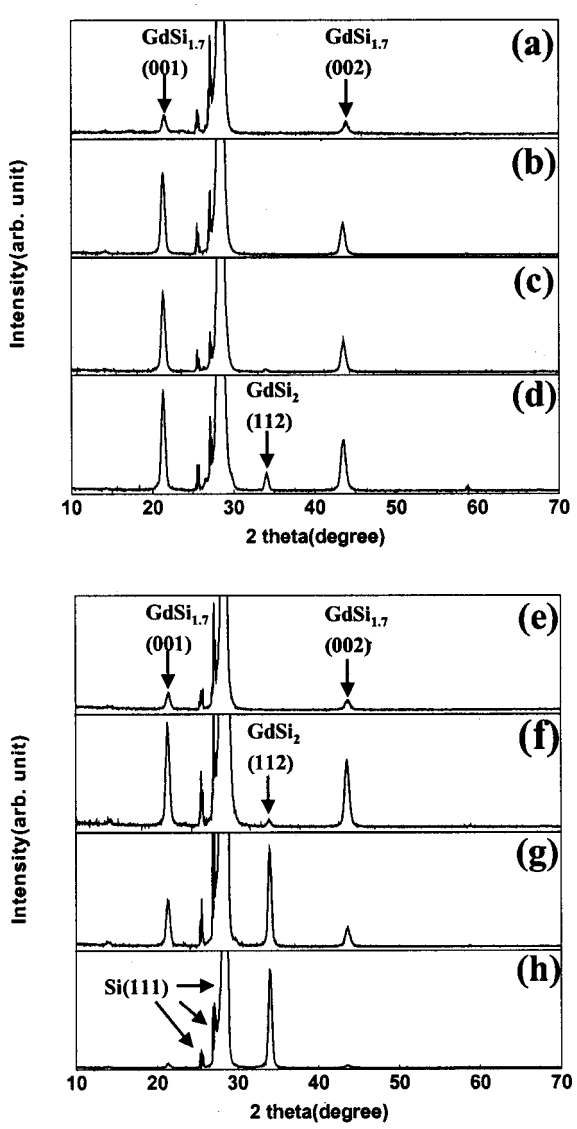

FIG. 2. XRD data collected from the sample with Gd layer on the clean Si surface after (a) deposition, annealing at 800 °C for (b) 20 min, (c) 40 min, (d) 120 min, from the sample with Gd layer on the oxidized Si surface after (e) deposition, annealing at 800 °C for, (f) 20 min, (g) 40 min, (h) 120 min.

We suggest a reaction pathway for the formation of Gd silicide in Fig. 3 to explain our observations. Si has been known to be the faster diffusing species in rare-earth silicide formation via solid-state reaction.[15] In Gd-silicide formation, the $GdSi_{1.7}$ phase should be formed first due to the slow diffusion rate of Si atoms in the solid-state reaction, where the $GdSi_{1.7}$ phase has a defect structure based on the AlB_2 hexagonal lattice with about 15% random vacancies in the Si sublattice plane.[5,14] The Si rich $GdSi_2$ phase can be formed initially only at the $Si/GdSi_{1.7}$ interface as the annealing continues, suggested in Fig. 3(a). We observed this result in the Gd-silicide film prepared on the Si substrate without the interfacial SiO_2 layer. The same reaction mechanism should be applicable to the Gd-silicide film prepared even on a thin SiO_2 interfacial layer if the annealing temperature is not high enough to break the SiO_2 domains. In this temperature range, SiO_2 domains act as diffusion barriers and the diffusion of Si atoms is possible only through the domain boundaries of the

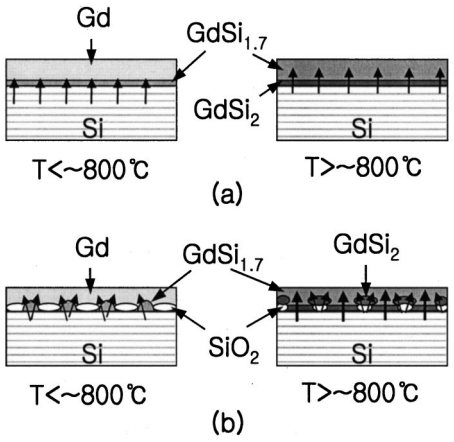

FIG. 3. The schematic diagrams representing the reaction pathway of the Gd-silicide layer via solid-state reaction in postannealing. (a) Gd-silicide film formation on the clean Si surface, (b) Gd-silicide film formation on the Si surface with interfacial SiO_2 layer.

SiO_2.[16] Once the annealing temperature is higher than the decomposition temperature of SiO_2, additional Si atoms will be supplied from the boundaries of the decomposing SiO_2 domains and the Si rich $GdSi_2$ phase can be formed as indicated in Fig. 3(b).

The resulting sample was examined with AFM. The surface morphology of the Gd-silicide film grown on the oxidized Si surface shows smaller pinholes in comparison with that grown on the clean Si surface. The AFM images taken from the same samples used in XRD in Figs. 2(e)–2(h) are shown in Figs. 4(a)–4(d). The large pinholes observed on the as-deposited film surface gradually decreased in size with an increased number density of pinholes as the sample annealed, which corresponds to the diffusion limited kinetic growth. The AFM image from the sample annealed for 40 min at 800 °C shows deeper pinholes and a rougher surface, which is believed mainly due to the existence of a mixed

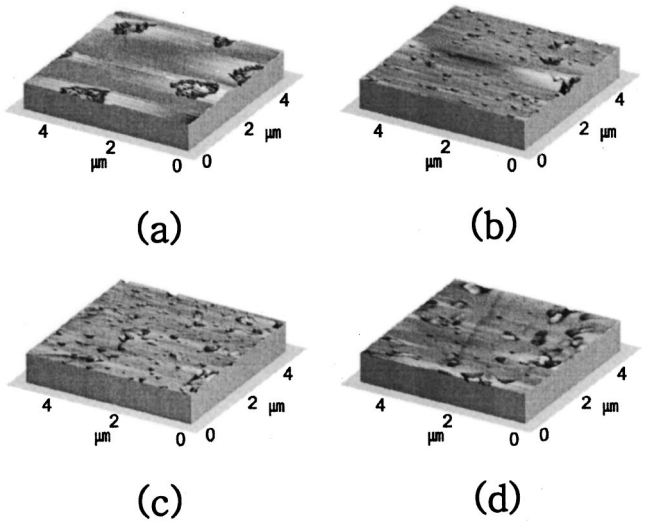

FIG. 4. AFM images collected on the sample prepared on the oxidized Si surface after (a) Gd layer deposition, annealed at 800 °C for (b) 20 min, (c) 40 min, and (d) 120 min, respectively.

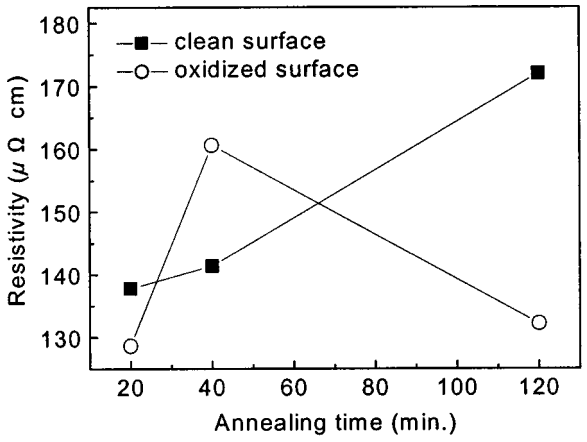

FIG. 5. Measured electrical resistivity of the Gd-silicide films grown on the clean Si surface and the oxidized Si surface as a function of annealing time.

phase of the hexagonal $GdSi_{1.7}$ and the orthorhombic $GdSi_2$. After the sample annealed for a longer time, surface pinholes healed and the surface roughness was reduced as shown in Fig. 3(d). This is expected from the XRD data where the Gd-silicide film forms a single-phase $GdSi_2$ layer.

Figure 5 shows the measured electrical resistivity of the Gd-silicide films grown on the clean Si surface and the oxidized Si surface as a function of annealing time at 800 °C. The resistivity of the Gd-silicide film grown on the clean Si surface increases continuously with the annealing time and reaches 172 $\mu\Omega$ cm. However, the resistivity of films grown on the oxidized Si surface increases initially and hits a maximum value and then decreases as the sample is annealed further. This change in the measured resistivity can be explained with the structural transition of the Gd-silicide film. As the silicide film transforms from the mixed phase of $GdSi_{1.7}$ and $GdSi_2$ to the single-phase $GdSi_2$, film resistivity should be decreased. This result implies that obtaining single-phase metal-silicide films will be an important issue for obtaining reliable interconnects in silicon devices.

IV. CONCLUSION

A high quality single-phase $GdSi_2$ film on a Si(111) surface was obtained with the help of an interfacial SiO_2 layer. We also suggested a reaction mechanism that can explain our experimental observation in the postannealing of Gd-silicide formation. The improved surface morphology of the resulting Gd-silicide film was confirmed in AFM images. The measured electrical resistivity of Gd-silicide film shows a strong dependence on the existing structural phase.

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