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Morphology and stability of $(Ti_{0.9}Zr_{0.1})Si_2$ thin films on Si(111) and Si(100) formed in UHV

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Abstract

This study explores the temperature stability and surface morphology of $(Ti_{0.9}Zr_{0.1})Si_2$ films formed from reaction of TiZr alloys on Si. Titanium and zirconium alloy films (200 Å) were deposited on atomically clean Si surfaces in an ultra high vacuum (UHV) electron beam deposition system, and the wafers were annealed in UHV to form the alloy silicide. In-situ Raman experiments were performed to identify the phases of the $(Ti_{0.9}Zr_{0.1})Si_2$ films. The surface morphologies were studied using scanning electron microscopy, and the root mean square surface roughness was measured using atomic force microscopy. Sheet resistivity measurements were also performed. The results indicate that $(Ti_{0.9}Zr_{0.1})Si_2$ films are stable in the C49 phase for temperatures up to 1000 °C. In addition, the surface roughness is substantially less than similarly prepared TiSi_2 films at high temperatures indicating that agglomeration is reduced for the C49 alloy films. The sheet resistances of the alloy films are less than those of the TiSi_2 films annealed at the same temperatures (>800 °C) because of decreased agglomeration. The $(Ti_{0.9}Zr_{0.1})Si_2$ films showed little degradation of sheet resistance for annealing temperatures up to 900 °C.

Keywords: Surface morphology; Alloys; Annealing; Titanium; Zirconium

1. Introduction

Refractory metal silicides are important materials for application in very large scale integrated circuits (VLSI) as contacts and interconnections. These materials exhibit high temperature stability, low resistivity and compatibility with current processing steps. Among refractory metal silicides, TiSi₂ is often used, because TiSi₂ exhibits the lowest sheet resistivity [1–6]. It is now well established that TiSi₂ exhibits two crystalline [1–6] structures, a C49 phase with a basecentered orthorhombic structure and a C54 phase with a facecentered orthorhombic structure. While Zr exhibits many similarities to Ti, the stable silicide formed from the Zr–Si thin film reaction is C49 ZrSi₂ [7–11].

The reaction of Ti on Si results in the nucleation and growth of C49 TiSi₂ followed by a polymorphic transformation to the low resistivity C54 TiSi₂ phase at temperatures of ~700 °C. Recent results have indicated that the C54 phase exhibits a larger surface energy than the C49 phase, and this results in severe agglomeration for thin silicide films (less than 400 Å) [3,7,12–15]. Agglomeration of the TiSi₂ films was readily observed at annealing temperatures of 800 °C or higher. The agglomeration of C54 TiSi₂ thin films significantly degrades the sheet resistance. This effect is less significant for thicker films. However, thicker silicide films consume

more silicon atoms at the source and drain regions of metaloxide semiconductor field effect transistor (MOSFET) devices. The need for shallow junctions on the source and drain regions requires thinner metal silicide layers while not sacrificing the contact resistance [16,17].

In this study, a new approach was employed to stabilize the metastable C49 phase at high temperatures (>700 °C) in order to solve the agglomeration problem for the C54 TiSi₂. The C49 silicide films were fabricated by co-deposition of Ti and Zr alloys (with small percentage of Zr) on Si in ultra high vacuum (UHV), followed by in-situ annealing [18]. The phase stability of the alloy silicide thin films was studied by in-situ Raman spectroscopy. The surface morphology of the alloy silicide thin films was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The sheet resistance measurements were performed using a four-point probe.

2. Experimental

In-situ experiments were carried out in an integrated UHV film growth and characterization system. Three chambers from that system used in this study included the deposition system, a chamber with low electron energy diffraction (LEED) and Auger electron spectroscopy (AES) capability, and a chamber for Raman spectroscopy. The base pressure of the transfer line of the system is $\sim 2 \times 10^{-9}$ Torr. The Si(111) and Si(100) wafers used in this study were cleaned by a three-step process: (a) UV/ozone exposure to remove hydrocarbon contamination from the surface; (2) an HFbased spin etch to remove the native oxide; and (3) an insitu heat cleaning to 850 °C for 10 min to desorb hydrogen and other residues [19,20]. The LEED pattern of the cleaned substrates exhibited 7×7 Si(111) and 2×1 Si(100) reconstructed structures, and AES showed no detectable carbon or oxygen on the surface prior to the deposition. The base pressure in the UHV chamber was $< 5 \times 10^{-10}$ Torr. The Ti and Zr alloy films were co-deposited on the atomically cleaned Si(111) and Si(100) substrates by electron beam evaporation with the substrates at room temperature. The total thickness of the alloy metal films was 200 Å. The compositions of the alloy metal films were controlled by the deposition rates of the Ti and Zr sources using quartz crystal deposition thickness and rate monitors. The films were then annealed in-situ at temperatures between 500 and 1000 °C for 20 min.

It has previously been shown that Raman spectroscopy can be used to distinguish between the C49 and C54 phases of



Fig. 1. (a) In-situ Raman spectra of 200 Å ($Ti_{0.9}Zr_{0.1}$)/Si(111) annealed at temperatures between 500 °C and 910 °C. (b) In-situ Raman spectra of 200 Å ($Ti_{0.9}Zr_{0.1}$)/Si(100) annealed at temperatures between 500 °C and 1000 °C.

TiSi₂ [21]. A series of in-situ Raman experiments were carried out to identify the phases of the alloy films after the insitu annealing. Raman spectra were excited with $\sim 200 \text{ mW}$ of 514.5 nm Ar ion laser radiation. The scattered light was first filtered with a subtractive 0.32 m double monochromator and then dispersed with a 0.64 m spectrometer. The light was detected with a liquid nitrogen cooled multichannel CCD detector. Sheet resistivity measurements were performed using a four-point probe. Surface morphologies of the alloy silicide thin films were examined using a JEOL 6400 fieldemission scanning electron microscope. Film surface roughness was measured using AFM. The AFM microscope used for this experiment was a Park Scientific SFM-BD2. The piezo scanner used for this experiment had a 10 µm scanning range in both the X and Y directions and a 2.5 µm range in the Z direction. The scan area on the sample surfaces was ~ 4 μ m \times 3.2 μ m.

3. Results

In-situ Raman spectra of the 200 Å ($Ti_{0.9}Zr_{0.1}$) alloy films on Si(111) and Si(100) annealed at high temperatures were shown in Fig. 1(a) and 1(b), respectively. The features displayed in the range of 250–350 cm⁻¹, of the 600 °C and



Fig. 2. (a) Comparison of the sheet resistance between 200 Å $(Ti_{0.9}Zr_{0.1})/$ Si(111) films and 200 Å Ti/Si(111) films as a function of temperature between 500 °C and 910 °C. (b) Comparison of the sheet resistance between 200 Å $(Ti_{0.9}Zr_{0.1})/Si(100)$ films and 200 Å Ti/Si(100) films as a function of temperature between 600 °C and 900 °C.

higher temperature spectra, in both Fig. 1(a) and 1(b) can all be assigned to the C49 TiSi2 structure [12]. No detectable signal was observed at ~ 240 cm⁻¹ where features associated with the C54 phase are located [12,21]. The Raman results indicate that the formation temperatures of the C49 phase are between 500 °C and 600 °C for the alloy silicide thin films on both Si(111) and Si(100). The phase transition from the C49 phase to the C54 phase was not observed. With the presence of Zr atoms, the C49 phase of the alloy silicide is stabilized to higher temperatures compared with TiSi2. Presumably, the transition temperatures from the C49 phase to the C54 phase are greater than 910 °C for the 200 Å $(Ti_{0.9}Zr_{0.1})/Si(111)$ film and 1000 °C for the 200 Å $(Ti_{0.9}Zr_{0.1})/Si(100)$ film. These values are more than 200 °C higher than the previously observed transition temperatures for TiSi₂ films on Si with the same thickness [12].

Fig. 2(a) shows the comparison between the sheet resistances of the $TiSi_2/Si(111)$ and $(Ti_{0.9}Zr_{0.1})Si_2/Si(111)$ films annealed at different temperatures, and Fig. 2(b) shows the sheet resistance comparison between the $TiSi_2/Si(100)$ and $(Ti_{0.9}Zr_{0.1})Si_2/Si(100)$ films. The $TiSi_2$ films exhibit a low sheet resistance at 700 °C, following the formation of the C54 phase. The resistivity was calculated to be 13–18 $\mu\Omega$ cm. At high temperature (>800 °C), the sheet resistances of

the C54 TiSi₂ films on both Si(111) and Si(100) increase dramatically, presumably as a result of agglomeration. The lowest measured resistivity of the C49 (Ti_{0.9}Zr_{0.1})Si₂ films was ~46 μ \Omega cm, which is lower than the reported values for C49 TiSi₂ (60–300 μ Ω cm) [8,9]. This implies that the effect of scattering by the Zr atoms on the resistivity of the alloy silicide films is negligible. Although the lowest resistivity of the C49 (Ti_{0.9}Zr_{0.1})Si₂ films is about three times higher than that of the C54 TiSi₂ films, the sheet resistances of the alloy silicide thin films are quite stable over the temperature range of 600–900 °C. At 900 °C, the alloy silicide thin films exhibit much lower sheet resistances than the TiSi₂ films.

Scanning electron microscopy images of the alloy silicide films and the TiSi₂ films are shown in Fig. 3(a)-3(d). There are randomly distributed regions in the 200 Å Ti/Si(100) film annealed at 800 °C (Fig. 3(a)), where the Si substrate is exposed to the surface. These regions are often 5 ~ 10 μ m long and ~ 0.5 μ m wide. It is evident that the film is discontinuous. As shown in Fig. 3(b), severe agglomeration was observed for the 200 Å Ti/Si(111) films annealed at 900 °C. In contrast, the 200 Å (Ti_{0.9}Zr_{0.1})/Si(100) film annealed at 800 °C (Fig. 3(c)) and the 200 Å (Ti_{0.9}Zr_{0.1})/Si(111) film annealed at 910 °C (Fig. 3(d)) exhibit full areal coverage of



Fig. 3. (a) SEM images of silicide films annealed at high temperatures. (a) 200 Å Ti/Si(100), 800 °C; (b) 200 Å Ti/Si(111), 900 °C; (c) 200 Å $(Ti_{0.9}Zr_{0.1})/Si(100)$, 800 °C; and (d) 200 Å $(Ti_{0.9}Zr_{0.1})/Si(111)$, 910 °C.



Fig. 4. (a) Surface roughness comparison between 200 Å $(Ti_{0.9}Zr_{0.1})/Si(111)$ films and 200 Å Ti/Si(111) films as a function of temperature. (b) Surface roughness comparison between 200 Å $(Ti_{0.9}Zr_{0.1})/Si(100)$ films and 200 Å Ti/Si(100) films as a function of temperature.

the Si substrate. Both films consist of many faceted small grains. The sizes of the grains are smaller than 0.4 μm in diameter.

Atomic force microscopy was used to obtain the root mean square (RMS) surface roughness and the results are shown in Fig. 4(a) and 4(b). The surface roughness of $(Ti_{0.9}Zr_{0.1})Si_2/Si(111)$ is less than that of C54 TiSi₂/Si(111) at high temperatures (>700 °C). A similar trend was observed for the films on Si(100) substrates as shown in Fig. 4(b). The alloy silicide films exhibit reduced surface roughness at high temperatures because of less agglomeration.

4. Discussion

It is well established that the stable phases for Ti–Si and Zr–Si solid phase reactions are the TiSi₂ C54 phase and ZrSi₂ C49 phase respectively, although Ti and Zr share many chemical and electrical similarities [7–11]. The C49 phase is the first TiSi₂ crystalline structure formed in the Ti–Si solid phase reaction sequence. The presence of Zr atoms in the alloy silicide thin films tends to stabilize the C49 phase. The nucleation of the C54 phase was not observed in $(Ti_{0.9}Zr_{0.1})Si_2$ on either Si(111) or Si(100) substrates.

Jeon et al. and Sukow and Nemanich proposed a "solid state capillarity" model to explain agglomeration from the energetics point of view [12,13]. This model suggests that the driving force for agglomeration is the tendency of the thin films towards decreasing surface-to-volume ratio such that the structure approaching to a lower energy state. Films with lower surface and interface free energies would have a smaller driving force for agglomeration and therefore would be expected to exhibit smoother surfaces and increased areal coverages. The surface and interface free energies of the C49 TiSi₂/Si films were measured to be lower than those of the C54 TiSi₂/Si films by Sukow and Nemanich, and Kropman [13,22]. Presumably, the surface and interface free energies of the C49 $(Ti_{0.9}Zr_{0.1})Si_2$ films have almost the same values as those of the C49 TiSi₂ films. The C49 $(Ti_{0.9}Zr_{0.1})Si_2$ films should, therefore, have a smaller driving force for agglomeration and would be expected to exhibit smoother surfaces and increased areal coverages on Si substrates than the C54 TiSi2. This corresponds very well with SEM and AFM experiment results shown above.

The C49 phase exhibits a higher resistivity than the C54 phase. However, electrical properties of the silicide films are related to their morphologies. The rougher films have a higher sheet resistance. As shown in Fig. 2(a) and 2(b), the severely agglomerated $TiSi_2$ films exhibit much higher sheet resistance than the alloy silicide thin films annealed at the same temperature (~900 °C).

As shown in Fig. 3(a), there are many regions observed in the C54 TiSi₂ film on Si(100) annealed at 800 °C, where the Si substrate is exposed to the surface. The sizes of these regions are often $5 \sim 10 \,\mu\text{m}$ long and $\sim 0.5 \,\mu\text{m}$ wide during the initial stage of agglomeration. However, the film does not exhibit much degradation of the sheet resistance. The sheet resistance measurements were carried out using a four-point probe. The spacing between the four probes used in the sheet resistance measurements are on the order of one millimeter. Even with the exposed regions, a complete path will exist between the two probes. These micron-size Si substrate exposure regions do not have a significant effect on the film sheet resistance measurements. However, this effect is anticipated to be more significant when the silicide films are smaller in lateral dimensions. Present feature sizes of the CMOS devices are 0.4-1.0 µm, and for future CMOS devices the feature sizes will be 0.25 μ m and below [23,24]. When feature sizes of the devices are scaled down, the interconnection lines are required to have compatible linewidths [25]. The micronsize Si substrate exposure regions may result in discontinuous interconnections. Thus, for sub-micron linewidths, the alloy silicide with continuous areal coverage should be more electrical conductive than TiSi₂ at temperatures of 800 °C or higher. On the other hand, the micron-size substrate open regions in the C54 TiSi₂ films formed at the shallow junctions on the source and drain regions of MOSFET devices will result in significant increases of leakage currents [3]. The alloy silicide thin films, which exhibit stable sheet resistance and continuous areal coverage up to annealing temperatures

of 800 °C or higher, will also be more suitable for the thin layers (several hundred angstroms) required at shallow junctions.

5. Conclusions

Thin films of $(Ti_{0.9}Zr_{0.1})Si_2$ formed on both Si(111) and Si(100) are stable in the C49 phase at temperatures higher than 900 °C. In contrast, the C49 phase of TiSi₂ transforms to the C54 phase at ~700 °C. The C49 $(Ti_{0.9}Zr_{0.1})Si_2$ thin films exhibit better areal coverage on the Si surfaces than C54 TiSi₂. The surface roughness of the alloy silicide thin films are lower than those of the agglomerated C54 TiSi₂ films formed at the same temperatures. While the sheet resistivity of the alloy silicide thin films is about three times higher than the lowest value of the C54 TiSi₂ films, we anticipate that the contact resistance will be similar. For smaller dimensions and for higher temperature processing, Ti–Zr alloy silicides may be a better candidate for contacts and interconnections than C54 TiSi₂.

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