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Effects of a Ta interlayer on the phase transition of $TiSi_2$ on Si(111)

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This study examines the effects of a thin Ta interlayer on the formation of $TiSi_2$ on Si(111) substrate. The Ta interlayer was introduced by depositing Ta and Ti films sequentially on an atomically clean Si(111) substrate in an ultrahigh vacuum (UHV) system. Samples of 100 Å Ti with 5 and 10 Å Ta interlayers were compared to similar structures without an interlayer. After deposition, the substrates were annealed for 10 min, *in situ*, at temperatures between 500 and 750 °C in 50 °C increments. The $TiSi_2$ formation with and without the Ta interlayer was analyzed with an X-ray diffractometer, Auger electron spectroscopy (AES), Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and a four-point probe. The AES analysis data showed a 1:2 ratio of Ti:Si in the Ti-silicide layer and indicated that the Ta layer remained at the interface between $TiSi_2$ and the Si(111) substrate. The *C* 49–*C* 54 $TiSi_2$ phase transition temperature was lowered by ~200 °C. The *C* 49–*C* 54 $TiSi_2$ phase transition temperature was 550 °C for the samples with a Ta interlayer and was 750 °C for the samples with no Ta interlayer. The sheet resistance of the Ta interlayered Ti silicide showed lower values of resistivity at low temperatures which indicated the change in phase transition temperature. The *C* 54 $TiSi_2$ displayed different crystal orientation when the Ta interlayer was employed. The SEM and TEM micrographs showed that the $TiSi_2$ with a Ta interlayer significantly suppressed the tendency to islanding and surface agglomeration. © *2000 American Institute of Physics.* [S0021-8979(00)02216-7]

I. INTRODUCTION

Among the metal silicides, titanium silicide has been one of the most widely used and studied silicides as an electrical contact to Si-based devices.[1–3] The $TiSi_2$ compound exhibits two polymorphic structures: a metastable *C* 49 phase (resistivity: 60–70 $\mu\Omega$ cm, base-centered orthorhombic) and a stable *C* 54 phase (resistivity: 15–20 $\mu\Omega$ cm, face-centered orthorhombic). The *C* 54 phase is noted in the Ti–Si binary phase diagram, while the *C* 49 phase does not appear in the binary phase diagram. It is, however, the first phase to form from the interface reaction of Ti deposited onto a silicon substrate. The preferential nucleation of the *C* 49 phase has been explained in terms of surface and interface energies of the two phases.[4]

A high temperature anneal (>650 °C) is required to transform the *C* 49 phase to the *C* 54 phase which is the low resistivity phase of $TiSi_2$. The *C* 49–*C* 54 transition temperature is dependent on film thickness and on the lateral linewidth of the film. In both cases, a decrease in thickness or linewidth results in a significant increase in the *C* 49–*C* 54 $TiSi_2$ transition temperature.[4–6] These problems limit the compatibility of $TiSi_2$ for applications in very large scale integrated (VLSI) device processing. Therefore, the goal of our research is to reduce the transition temperature of $TiSi_2$ and to obtain a uniform surface of *C* 54 $TiSi_2$ film at silicide formation temperatures.

There have been several research reports on methods to reduce the *C* 49–*C* 54 transition temperature of $TiSi_2$. These include refractory metal implantation and a preamorphization implant of Si substrate.[7–9] In these studies, the mechanism responsible for the lowering of the transition temperature of $TiSi_2$ has been explained as an increase in the nucleation density of the *C* 54 phase in the *C* 49 matrix and a reduction in the energy barrier to nucleate the *C* 54 phase. These processes result, to some extent, in a lowering of the transition temperature of $TiSi_2$.

A new approach to enhance the formation *C* 54 phase of $TiSi_2$ has been suggested, which is the deposition of a thin layer of a refractory metal on Si substrate before depositing the Ti film.[10] Results have established that the presence of a thin refractory metal layer such as W, Mo, or Ta can act as an interlayer between Ti and Si(100) which results in a reduction of the transition temperature. In this article, we investigated the effect of a thin Ta interlayer on the Ti-silicide formation on Si(111) substrates. The research involves deposition of 5 and 10 Å Ta films between 100 Å Ti and the Si(111) substrate. The substrates were annealed for 10 min in an ultrahigh vacuum (UHV) system at temperatures between 500 and 750 °C with 50 °C increments. The silicide formation and its physical properties were examined by using an x-ray diffractometer, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Auger electron spectroscopy (AES), and a four-point probe. It was shown that the addition of Ta interlayer to the Ti-silicide formation resulted in the significant reduction of phase transition tem-

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perature and the improvement of surface morphology at high temperatures.

II. EXPERIMENT

The Si substrates used in this study were Si(111)-oriented substrates with P doping and resistivities of 0.68–0.72 Ω cm (*n* type). Prior to loading into the UHV system, the Si substrates were cleaned by UV (ultra violet)/ozone exposure and spin etching with $HF:H_2O$: ethanol at ratio of 1:1:10.[11–13] The UHV deposition system is equipped with a turbo pumped loading chamber and a cryopumped main chamber, which was used to deposit and anneal the Ti–Ta–Si(111) samples. After loading the substrates into this system, the Si substrates were cleaned by heating in UHV to a temperature of 800 °C for 10 min. This process resulted in the desorption of the residual contaminants and hydrogen. Three sets of samples were prepared in the multi source-electron beam UHV chamber. The first set which served as reference samples was prepared by the deposition of 100 Å of Ti onto the clean Si(111) substrates. The second set of samples was produced with the introduction of a 5 Å Ta layer between the 100 Å Ti and Si(111) substrates. The third set of samples was made with the deposition of a 10 Å Ta layer between the 100 Å Ti and Si(111) substrates. The base pressure in the UHV chamber was $1-2\times10^{-10}$ Torr, and the Ta and Ti films were deposited consecutively without breaking vacuum. After the room temperature deposition, the Ti–Ta–Si samples were annealed, *in situ*, for 10 min, to temperatures in the range of 500–750 °C. Samples in each set were produced with 50 °C increments. After annealing the samples, the physical and electrical properties of the three sets of samples were examined by a four-point probe, x-ray diffraction, SEM, TEM, and AES.

III. RESULTS AND DISCUSSION

The phase formation of Ti silicide on Si(111) substrates with and without a Ta interlayer was examined. It was observed that the Ta interlayer in this Ti–Ta–Si(111) system affected the titanium silicide formation significantly. The significant aspects of this study were as follow: the Ta interlayer resulted in a reduction of the *C* 49–*C* 54 $TiSi_2$ phase transition temperature, there was an identifiable orientation change of the Ti silicide, and the tendency of $TiSi_2$ islanding was somewhat suppressed.

For each sample, the x-ray diffractometer was used for phase identification of $TiSi_2$, and the results are summarized in Fig. 1. The *C* 49 phase of $TiSi_2$ was present in the reference samples which were annealed between 500 and 700 °C [see Fig. 1(a)]. When the reference sample was annealed at 750 °C, the *C* 49 phase was completely transformed into the *C* 54 phase. The transition temperature of the 100 Å Ti on Si(111) was to some extent increased by about 100 °C as compared to the normal Ti-silicide transition temperature (of ~650 °C). This is in agreement with previous reports of the thickness dependence of the phase transition temperature of $TiSi_2$. The phase sequence for the Ta interlayer samples was quite different. For the Ta interlayer series, *C* 49 $TiSi_2$ was the dominant phase observed at 500 °C, but the *C* 54 phase

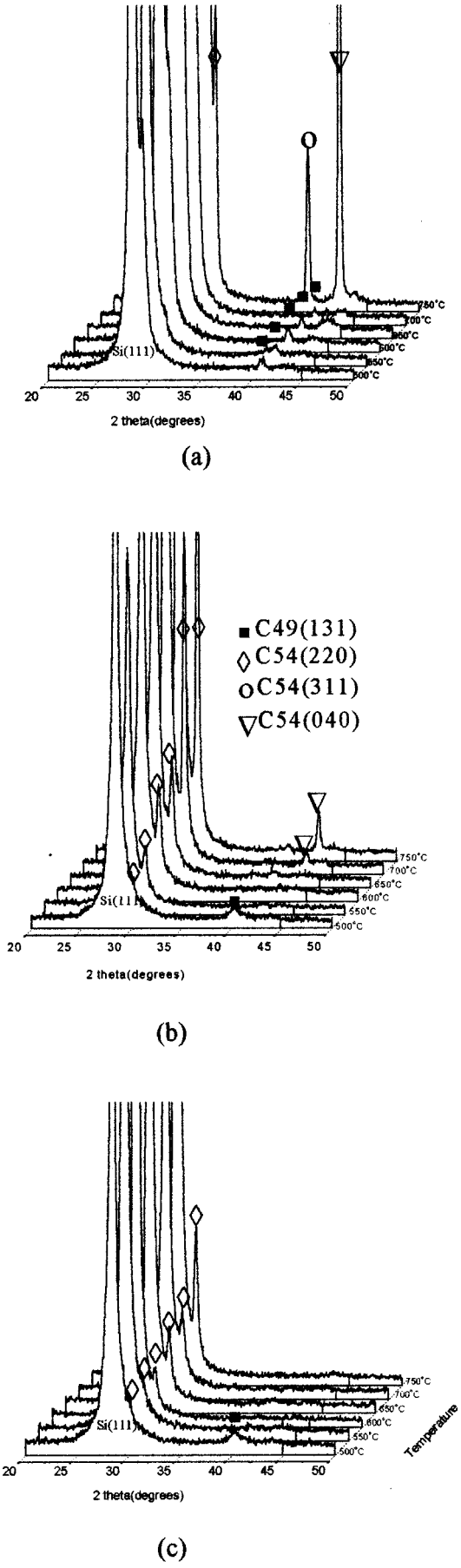

FIG. 1. X-ray diffractometer patterns of Ti silicide formed without (a), with (b) 5 Å Ta and with (c) 10 Å Ta on Si(111) as a function of temperatures.

was also evident. The *C* 49 phase could not be identified in the x-ray diffractometer after 550 °C annealing.

It is interesting to explore the changes in x-ray diffractometer peak intensities for the different series. For the reference series, only *C* 49 peaks are observed up to 700 °C. The *C* 54 phase is evident after 750 °C, and three different peaks are clearly detected. The strongest *C* 54 $TiSi_2$ peak was from the (040) plane. For the Ta interlayer samples, the dependence is again considerably different. For the 5 Å Ta interlayer, both phases of *C* 49 and *C* 54 $TiSi_2$ were observed after the 500 °C anneal, but the dominant peak was the (131) of the *C* 49 phase. However, after the 550 °C anneal, the peaks related to the *C* 49 $TiSi_2$ phase were not observed, and the (220) peak of *C* 54 $TiSi_2$ appeared clearly at $2\theta = 30.1°$. The intensity of the (220) peak of $TiSi_2$ increased as the annealing temperature increased. The (040) peak of *C* 54 $TiSi_2$ was observed at temperatures greater than 700 °C, but the strongest peak of *C* 54 $TiSi_2$ was the (220) peak. Figure 1(c) shows the x-ray diffractometer patterns of the samples with a 10 Å Ta interlayer. In these samples, the diffraction peaks of the Ti silicide were similar to the patterns of the samples with a 5 Å Ta interlayer. However, at each temperature, the peak intensity of the sample with the 10 Å Ta interlayer was relatively lower than that of the sample with the 5 Å Ta interlayer. The x-ray diffractometer results indicated that the thin Ta interlayer of *C* 54 $TiSi_2$ reduced the transition temperature by about 200 °C. In addition, by introducing the Ta interlayer, the main diffraction peak of the *C* 54 $TiSi_2$ changed from the (040) plane to the (220) plane.

The surface and interface morphologies of $TiSi_2$ at 750 °C were examined by SEM and cross-sectional TEM. The results are shown in Fig. 2. In the reference sample without a Ta interlayer, the SEM micrograph exhibits agglomerated islands of Ti silicide and the bare Si surface which was exposed between the islands. Cross-sectional TEM also showed $TiSi_2$ islands that were separated and agglomerated in agreement with SEM. In contrast, as shown in Figs. 2(b) and 2(c), the samples with a Ta interlayer showed significant changes in the surface and interface morphologies. Although the grains grew larger as the annealing temperature increased, the Ta interlayered $TiSi_2$ samples were not agglomerated and showed continuous and smooth surface morphologies. In the 10 Å Ta interlayered Ti-silicide sample, the grains were not coalesced, as in the 5 Å Ta interlayered sample. This SEM and TEM examination indicated that the Ta interlayer between the Ti and Si(111) substrate significantly improved the surface morphology by suppressing the islanding of the *C* 54 $TiSi_2$ phase at the higher annealing temperatures. We propose that this suppression of agglomeration of $TiSi_2$ is closely related to the change in orientation of the *C* 54 $TiSi_2$ which was observed by the x-ray diffractometer.

Figure 3 shows the variation of the sheet resistance as a function of annealing temperature for the Ti silicide formed with and without a Ta interlayer. The resistance of $TiSi_2$ without Ta interlayer decreases as the annealing temperature is increased from 500 to 650 °C. However, the resistance increases at temperatures above 700 °C. This increase in resistance is attributed to the islanding and surface agglomeration of the *C* 54 phase as shown in Fig. 2. In contrast, the $TiSi_2$ phase formed with a Ta interlayer showed a different dependence of the resistance versus temperature. The Ta interlayer samples displayed a low resistance for all annealing temperatures above 550 °C corresponding to the formation of

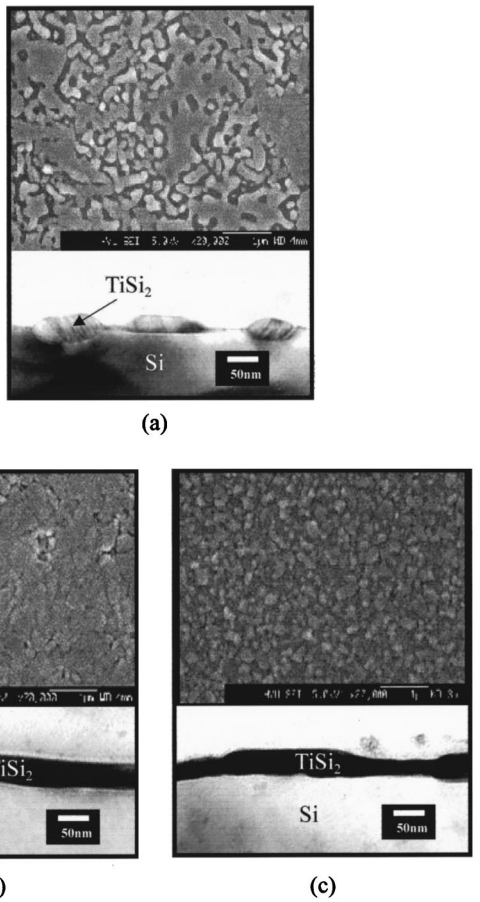

FIG. 2. SEM and cross-sectional TEM micrographs of $TiSi_2$ formed with (a) 100 Å Ti, (b) 100 Å Ti/5 Å Ta, and (c) 100 Å Ti/10 Å Ta on Si(111) and *in situ* annealed at 750 °C for 10 min.

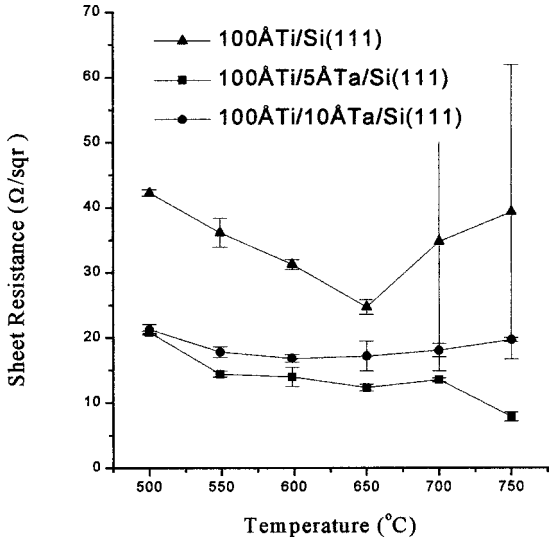

FIG. 3. The change in sheet resistance of three different sets of Ti silicide formed on Si(111) substrate as a function of annealing temperatures.

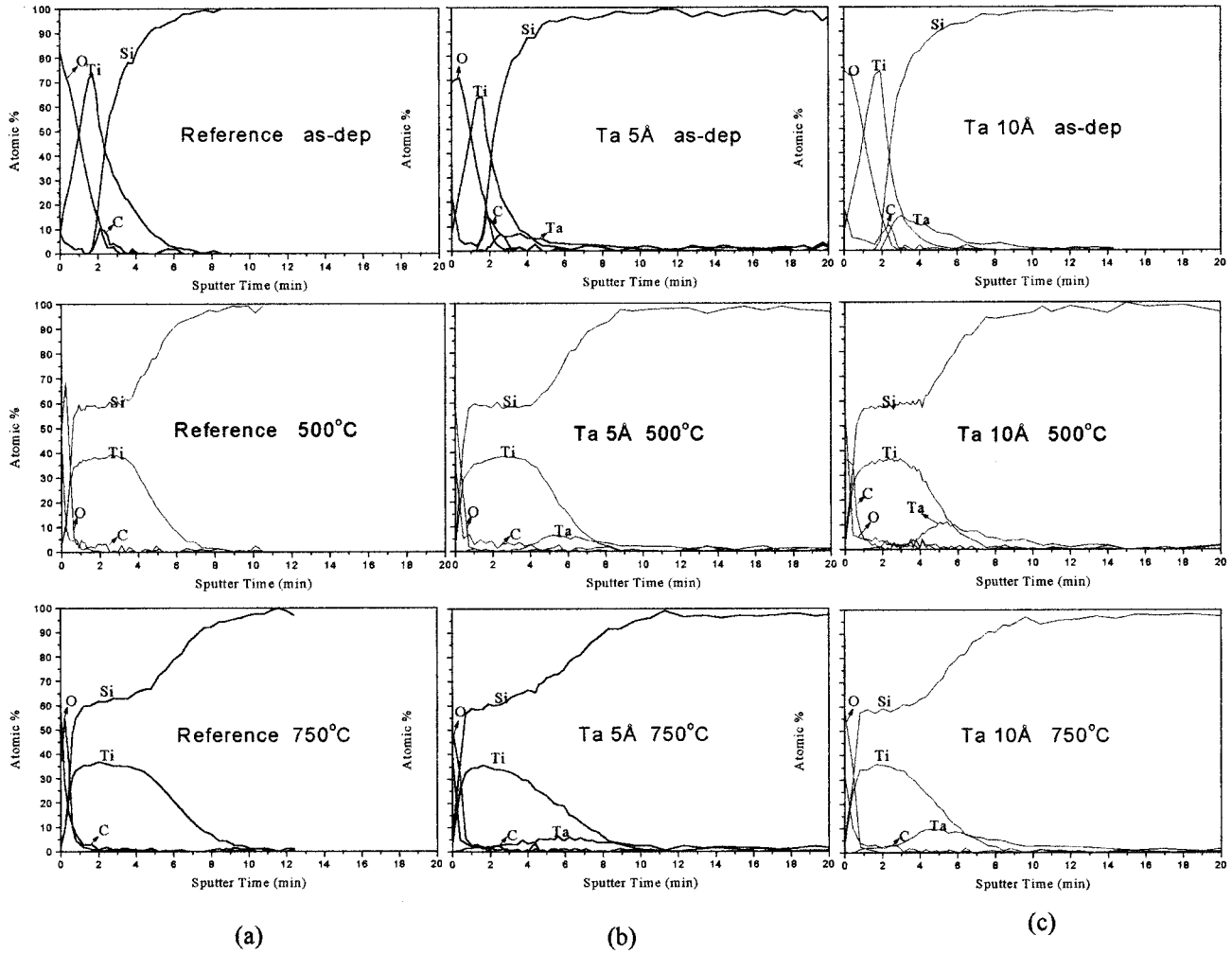

FIG. 4. AES depth profiles of (a) 100 Å Ti, (b) 100 Å Ti/5 Å Ta, and (c) 100 Å Ti/10 Å Ta deposited on Si(111) as deposited and annealed at 500 and 750 °C for 10 min.

the *C* 54 $TiSi_2$ phase. Moreover, the resistance did not show a sudden increase at higher annealing temperatures. The low resistance at high temperatures is attributed to a suppression of the surface islanding and agglomeration as shown in Fig. 2. Comparing the two Ta interlayer series, the samples prepared with a 5 Å Ta interlayer displayed a lower resistance than the 10 Å Ta interlayered samples. This difference may be due to an increase in the content of Ta impurities in the *C* 54 $TiSi_2$ and to the smaller grain size of *C* 54 $TiSi_2$.

Shown in Fig. 4. is the AES depth profiles of the samples as deposited and annealed at the temperatures of 500 and 750 °C, respectively. For the as-deposited samples, the Ta layer was observed to be between the Ti film and the Si(111) substrate. After annealing the samples, Ti silicide was formed with an atomic ratio of approximately Ti:Si $=1:2$ whether a Ta interlayer was present or not. The Ta interlayer remained at the interface between the Ti film and Si substrate after the annealing. For reactive silicide formation from Ti–Si and Ta–Si reactive couples, Si has been reported to be the dominant diffusing element. In this Ti–Ta–Si system, the AES data indicate that the reactive silicide formation also progresses by the diffusion of Si from substrate through the Ta interlayer and into the Ti layer. It is evident that the Ta interlayer affected the $TiSi_2$ phase formation while remaining at the interface between the Ti film and Si(111) substrate.

In this study, a change in the orientation of the *C* 54 $TiSi_2$ was observed by the x-ray diffractometer and the effect was also analyzed in detail by selected area diffraction (SAD). The SAD pattern is shown in Fig. 5. From this pattern it is quite clear that the (220) crystal plane of *C* 54 $TiSi_2$ is parallel to (111) plane of the Si(111) substrate. The zone axes are [334] for *C* 54 $TiSi_2$ and [110] for the Si substrate. Therefore, the orientation relationship between the *C* 54 $TiSi_2$ and Si is given by

$$C\ 54\ TiSi_2[334](220)\|Si[110](111).$$

The in-plane lattice match between the *C* 54 $TiSi_2$ and Si(111) will also lead to a reduced interface energy. This reduced interface energy will result in a more stable interface with a reduced tendency to islanding or agglomeration. This can be related to the surface morphology results shown in Fig. 2. The *C* 54 $TiSi_2$ phase formed by introducing a Ta interlayer exhibited a significantly smoother surface. In this study, we observed that the Ta interlayer enhanced the phase

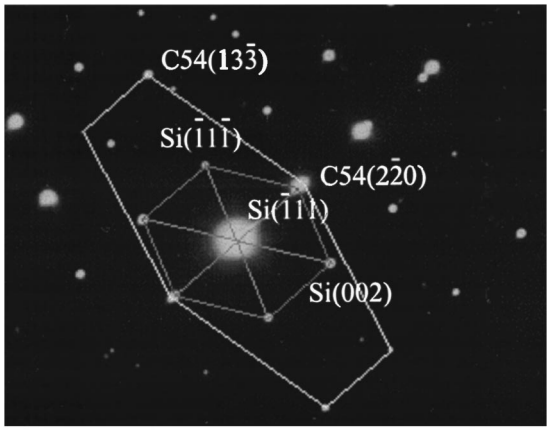

FIG. 5. SAD patterns from the Ta interlayered $TiSi_2$ and Si(111).

transition of *C* 54 $TiSi_2$ on Si(111) resulting in a reduced transition temperature. An orientation change of the *C* 54 $TiSi_2$ was observed which was related to a suppression of the *C* 54 $TiSi_2$ agglomeration.

IV. SUMMARY

The effects of a thin Ta interlayer on titanium silicide formation on Si(111) substrates have been studied. AES depth profile showed that the Ta layer remained at the interface between the Ti silicide and the Si substrate during the silicide formation. Compared to films with no interlayer, the *C* 49–*C* 54 $TiSi_2$ phase transition temperature was lowered by ~200 °C. The introduction of the Ta interlayer resulted in the predominant crystal orientation of the *C* 54 phase to change from (040) to (220). The surface and interface morphologies of the Ti silicide became significantly improved with the introduction of the Ta interlayer. The $TiSi_2$ with a Ta interlayer displayed a suppression of islanding and surface agglomeration at high temperatures. The sheet resistance of the films with an interlayer exhibited lower values at temperatures of 500–650 °C indicating the low temperature formation of *C* 54 $TiSi_2$. The $TiSi_2$ with a 5 Å Ta interlayer exhibited a lower sheet resistance than $TiSi_2$ with a 10 Å Ta. We propose that the change in interface energy due to the interlayer is closely related to the improved surface morphology characteristics. With these results, we can conclude that the addition of a Ta interlayer between Ti and Si(111) significantly affects the phase transition temperature, the surface morphology, and the crystal orientation of *C* 54 $TiSi_2$.

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