REDUCTION OF THE PHASE TRANSITION TEMPERATURE OF $TiSi_2$ ON Si(111) USING A Ta INTERLAYER

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ABSTRACT

The effect of a thin Ta interlayer on the C49 to C54 phase transition of $TiSi_2$ on Si(111) was examined. The Ta interlayered samples were prepared by depositing Ta and Ti films sequentially on Si(111) substrates in a UHV system. As control samples, 100Å Ti films were deposited directly on clean Si(111) substrates. The deposited substrates were annealed for 10 min, in-situ, at temperatures between 500°C and 750°C using 50°C increments. The $TiSi_2$, which formed in this UHV process, was analyzed with XRD, AES, SEM, TEM, and four-point probe measurements. The control samples exhibited the C49 to C54 transition at a temperature of 750°C. However, the $TiSi_2$ samples with 5Å and 10Å Ta interlayers displayed a significant reduction of the phase transition temperature. The XRD analysis indicated that the C49 to C54 transition temperature of $TiSi_2$ was lowered by ~200°C. The sheet resistance measurement showed a low resistivity characteristic of C54. The SEM and TEM micrographs showed that the Ta interlayer also suppressed the surface agglomeration of the C54 $TiSi_2$ film. The AES analysis data indicated that the composition of the titanium silicide showed the expected Ti:Si stoichiometry of 1:2.

INTRODUCTION

Among the refractory metal silicides, titanium silicide is one of the most widely used and studied silicides because of its importance in the technology of Si based semiconductor devices. The low resistivity and high thermal stability of $TiSi_2$ are of significant value in the application of this material to current device structures. However, titanium silicide exhibits a significant surface roughening when it forms C54 $TiSi_2$ at high temperatures (>650°C). The $TiSi_2$ compound exhibits two polymorphic structures: a metastable C49 phase (resistivity: 60-70 μΩ-cm, base-centered orthorhombic) and a stable C54 phase (resistivity: 15-20 μΩ-cm, face-centered orthorhombic) [1, 2]. The metastable, higher resistance C49 phase is observed to form initially in reactions of Ti on Si. To achieve low resistivity phase $TiSi_2$, higher temperature anneals (>650°C) are required to transform the C49 phase to the C54 phase [3]. The C49 to C54 transition temperature of $TiSi_2$ has been reported to depend on the Ti film thickness, linewidth, dopant concentration and Si substrate orientations [4, 5, 6]. The goal of this research is to form a uniform and low resistance film of C54 $TiSi_2$ [7, 8]. There have been several research reports on methods to reduce the transition temperature of $TiSi_2$. These include refractory metal implantation and a preamorphization implant of the Si substrate [9, 10, 11]. In these studies, the mechanism responsible for the lowering the transition temperature of $TiSi_2$ has been explained as an increase in the nucleation density of the C54 phase in the C49 matrix and a reduction in the energy barrier to nucleate the C54 phase. These processes result, to some extent, in a lowering of the transition temperature of $TiSi_2$. Another approach, which has resulted in a reduction of the phase transformation temperature, is the deposition of a thin layer of Ta between the Ti film and the Si substrate [12]. A possible mechanism to explain the observed reduction of the C54 phase formation temperature involves the crystallographic orientation matching between two silicide phases. The $TaSi_2$ phase which is a C40 phase (hexagonal) has a basal plane exhibiting a similar atomic array with the (001) plane of C54 $TiSi_2$. It has been proposed that this crystallographic similarity enhances the formation of C54 $TiSi_2$ and may also improve the surface morphology [12].

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In this study, we deposited 5Å and 10Å Ta films, which act as an interlayer between 100Å Ti film and the Si(111) substrate. The structures were annealed for 10 min. in an ultrahigh vacuum system at temperatures between 500°C and 750°C using 50°C increments. We investigated the effect of this Ta interlayer on the $TiSi_2$ C49 to C54 transition temperature. The physical and electrical properties of the $TiSi_2$ films were examined using SEM, AES, XRD, TEM and four-point probe techniques. The presence of the Ta interlayer resulted in the reduction of phase transition temperature, and a smooth surface morphology. We attempt to develop an understanding of the correlation of the C54 formation temperature and the Ta layer thickness.

EXPERIMENTAL

The substrates used in this study were Si(111)-oriented substrates with resistivities of 0.68-0.72 Ωcm (*n* type, P doped). Prior to loading into the UHV system, the wafers were cleaned by room temperature UV/ozone exposure and spin etching with $HF:H_2O$:ethanol at relative concentrations of 1:1:10. The UHV system is equipped with a turbopumped 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 heat cleaned by annealing 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. A set of control samples was prepared by the deposition of 100Å of Ti on the Si(111) substrates. The second set of samples was made with the introduction of a 5Å Ta layers between the 100Å Ti and the Si(111) substrate. The third set of samples were made with the deposition of a 10 Å Ta layer between the 100Å Ti and Si(111) substrate. The base pressure in UHV chamber was 1-2 x 10^{-10} Torr, and the Ta and Ti films were deposited consecutively without breaking vacuum. After the room temperature metal depositions, the Ti-Ta-Si samples were annealed, in situ, for 10 min., to the temperatures in the range of 500 to 750°C using 50°C increments. After annealing the physical and electrical properties of three sets of samples were examined by a four-point probe, XRD, SEM, TEM and AES.

RESULTS AND DISCUSSION

The XRD was used for phase identification of $TiSi_2$ and the results are summarized in Fig. 1. The C49 phase of $TiSi_2$ was found in all of the control samples, which were annealed between 500°C and 700°C (see Fig. 1(a)). When the control sample was annealed at 750°C, the C49 phase is completely

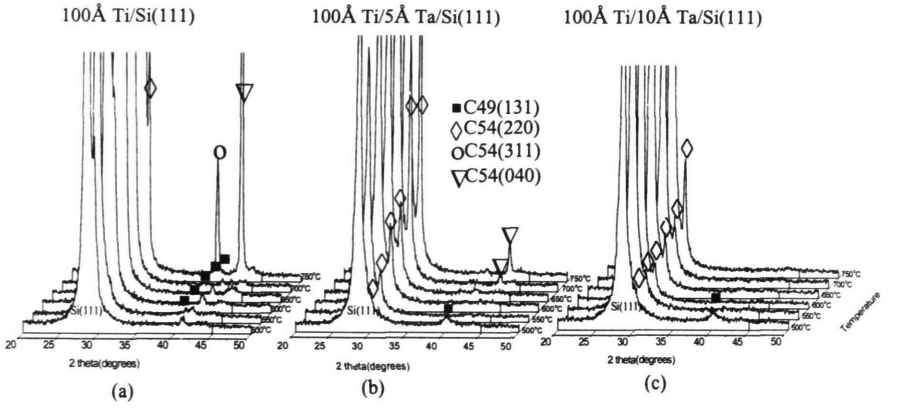

Fig. 1. XRD patterns of Ti-silicide formed without (a), with (b) 5Å Ta and with (c) 10Å Ta on Si(111) as a function of temperatures.

transformed to the C54 phase. The transition temperature of the 100Å Ti film on Si(111) was to some extent increased with respect to prior reports for thicker Ti films. This is in agreement with the previously observed thickness dependence of the phase transition temperature of $TiSi_2$[13]. It is noted that the highest intensity XRD peak of the C54 $TiSi_2$ phase is from the (040) planes. Figure 1(b) shows the change in XRD patterns of the samples of 100Å Ti / 5Å Ta on the Si(111) substrates. Both phases of C49 and C54 were observed after the 500°C anneal, and the dominant peak was the (131) of C49 $TiSi_2$. However, after the 550°C anneal the peaks related to the C49 $TiSi_2$ phase were not observed, and the (220) peak of C54 $TiSi_2$ was shown clearly at $2\theta=30.1°$. The intensity of (220) peak of C54 $TiSi_2$ increased as the annealing temperature increased. The (040) peak of C54 $TiSi_2$ was observed at temperatures greater than 700°C, but the strongest peak for all anneals was the (220) peak of C54 $TiSi_2$. Figure 1(c) shows the XRD patterns of the samples with a 10Å Ta interlayer. The diffraction peaks of the silicide were similar to the patterns of the samples with a 5Å Ta interlayer. However, at each temperature, the peak intensity of the sample with the 10Å Ta interlayer was relatively lower than that of the sample with the 5Å Ta interlayer. The results of the XRD indicate that the thin Ta interlayer between the 100Å Ti film and Si(111) substrate resulted in a lowering of the formation temperature of C54 $TiSi_2$ by about 200°C. In addition, the main diffraction peak of the C54 $TiSi_2$ changed from the (040) plane to the (220) plane. We suggest that this variation of $TiSi_2$ orientation may be related to the surface morphology of the C54 $TiSi_2$.

The surface and interface morphologies of $TiSi_2$ were shown in Figs. 2 and 3. The control samples without a Ta interlayer exhibited surface agglomeration at 700°C (Fig. 2(a)). But, as shown in Figs. 2(b) and (c), the samples with a Ta interlayer showed a suppression of the surface agglomeration at high temperatures (>700°C). Cross-sectional TEM micrographs, shown in Fig. 3, were obtained to display the Ti-silicide interface. Separated and agglomerated islands were observed in the control sample (Fig. 3(a)). In contrast, flat and sharp interfaces of the C54 $TiSi_2$ were obtained in the samples with a Ta interlayer (Fig. 3(b) and (c)). This SEM and TEM examination indicated the Ta interlayer between Ti and Si substrate significantly suppressed the surface agglomeration of C54 $TiSi_2$ phase at high temperatures.

Figure 4 shows the change in sheet resistance as a function of annealing temperatures for the Ti-silicide layers formed with and without a Ta interlayer. The resistance of the control samples of $TiSi_2$

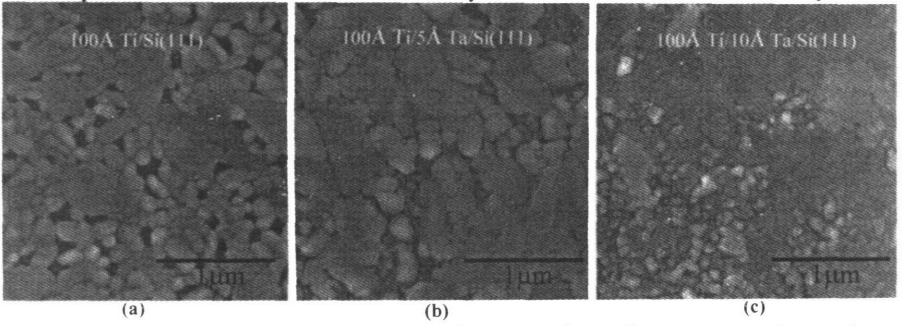

Fig. 2 SEM micrographs of $TiSi_2$ formed with (a) 100Å Ti. (b) 100Å Ti/ 5Å Ta, and (c) 100Å Ti/ 10Å Ta on Si(111) and in-situ annealed at 700°C for 10 min.

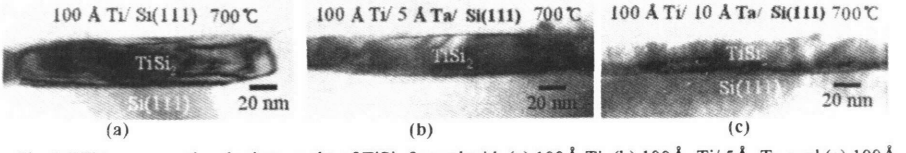

Fig. 3 TEM cross-sectional micrographs of $TiSi_2$ formed with (a) 100Å Ti, (b) 100Å Ti/ 5Å Ta, and (c) 100Å Ti/ 10Å Ta on Si(111) and in-situ annealed at 700°C for 10 min.

varied depending on the annealing temperatures. The increased resistance above 700°C is attributed to the surface agglomeration of the C54 phase as shown in Fig. 2. However, the Ti-silicide phase formed with a Ta interlayer showed a low resistance at low temperatures characteristic of C54 $TiSi_2$ and also exhibited low resistance at high temperatures due to the suppression of surface agglomeration. The resistance of the 10Å Ta interlayer samples was slightly higher than that of the 5Å Ta samples. This is, we suspect, due to an increased content of Ta impurities in the C54 $TiSi_2$ and due to smaller grain size. We note that the XRD of the 10Å Ta interlayer samples showed a lower peak intensity of C54 $TiSi_2$. Therefore, the electrical properties and the surface morphology of the Ti-silicide improved significantly with a Ta interlayer. For the two interlayer thicknesses examined here, it was found that the 5Å Ta interlayer was sufficient to lower the C54 transition temperature and improve the surface morphology while still maintaining a low resistance.

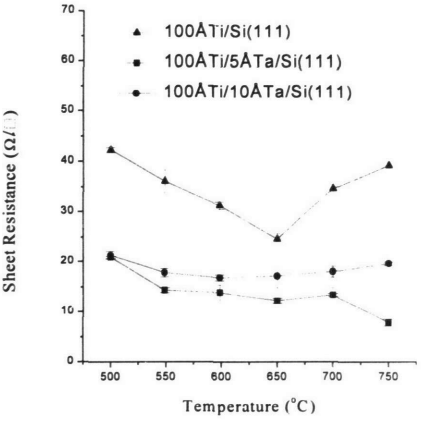

Fig. 4 The change in sheet resistance of three different sets of Ti-silicide formed on Si(111) substrate as a function of annealing temperatures.

Shown in Fig. 5 are the AES depth profiles of the Ti-silicide formed at a temperature of 500°C. In all samples, a Ti-silicide was formed with an atomic ratio of approximately Ti:Si = 1:2 whether a Ta interlayer was present or not. For the silicide formation of Ti-Si and Ta-Si bilayer systems, Si was reported to be the dominant diffusing element [14]. In this Ti-Ta-Si system the AES data showed that the Ta interlayer remained at this interface between the Ti and Si. Therefore, it is suggested that the Ta interlayer remains at the interface during the titanium silicide formation and enhances the formation of C54 $TiSi_2$.

In this study, we have observed that the introduction of a thin Ta interlayer results in a reduction of the C54 $TiSi_2$ phase transition temperature by ~200°C and the surface agglomeration of the film is also suppressed. The influence of the Ta interlayer on Ti-silicide formation is very positive, but the enhanced formation mechanism by a Ta interlayer remains to be understood. We have previously reported that the C54 $TiSi_2$ transition temperature was dependent on the Ti film thickness and the Si substrate orientation. The effect was discussed in terms of surface and volume free-energy considerations [13]. In the

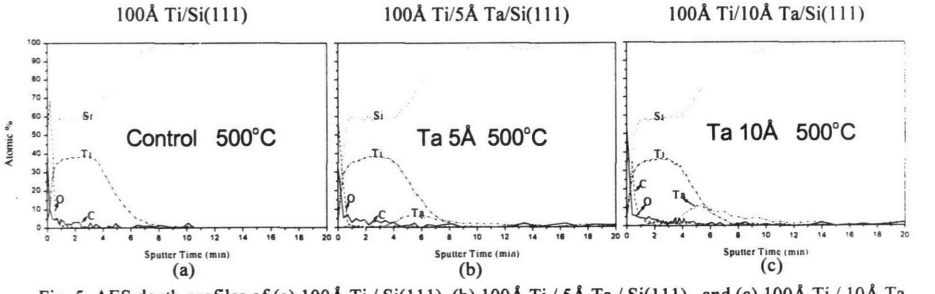

Fig. 5 AES depth profiles of (a) 100Å Ti / Si(111), (b) 100Å Ti / 5Å Ta / Si(111), and (c) 100Å Ti / 10Å Ta / Si(111). All samples were annealed at 500°C for 10 min.

crystallographic orientation consideration, the C54 phase of $TiSi_2$ exhibits a face-centered orthorhombic structure, which has a hexagonal atomic array with a stacking order of ABCD. As shown in Fig. 6, the C40 phase of $TaSi_2$ also exhibits a hexagonal atomic array with a stacking order of ABC. In addition, these two phases have very close lattice matching conditions. The atomic distances of Ti-Si and Si-Si in the C54 $TiSi_2$ phase are 2.74Å and 2.75Å, respectively. And those of Ta-Si and Si-Si in the C40 $TaSi_2$ phase are 2.76Å. Therefore, the interlayer of Ta between Ti and Si substrate can enhance the nucleation and growth of the C54 $TiSi_2$.

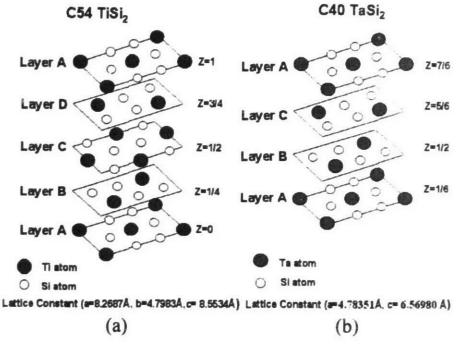

Fig. 6 The structures of (a) C54 $TiSi_2$ phase and (b) C40 $TaSi_2$ phase.

The orientational relation between the C54 $TiSi_2$ phase and the Si(111) substrate was characterized by x-ray diffraction. In our experiments we found that the introduction of the Ta interlayer resulted in a distinct change in the main diffraction peak of the C54 phase. This change in diffraction peak was from the C54 (040) plane (for no interlayer) to the (220) plane (for Ta interlayer). This orientation change indicates that most of the C54 grains on the Ta interposed Si substrate grow along the (220) orientation. The interplanar spacing of this plane is believed to be very close to that of Si(111). Interplanar spacings of Si(111) and C54 $TiSi_2$ (220) are 3.135Å and 2.969Å, respectively, which indicates some possibility of plane matched growth between Si(111) and C54 $TiSi_2$(220).

The plane matched C54 $TiSi_2$ on Si(111) will also lead to a reduced interface energy. The reduced interface energy results in an increased thermal stability of the C54 phase. Therefore, the C54 $TiSi_2$ phase formed by introducing a Ta layer can resist surface agglomeration at higher temperatures and can result in a relatively smooth surface. We attempted to detect a Ta-silicide phase at the interface between the Ti-silicide and the Si substrate, but it was not observable. We suggest that if a Ta-silicide region exists in the interface it would be very difficult to detect with XRD. With these results, we can conclude that the Ta interposed layer enhances the phase transition of $TiSi_2$ and changes the grain growth orientation of C54 $TiSi_2$. This orientation change of the C54 $TiSi_2$ resulted in a suppression of the C54 $TiSi_2$ agglomeration.

SUMMARY

We have studied the reduction of the transition temperature of the C54 $TiSi_2$ phase with the introduction of 5Å and 10Å Ta interlayers between a 100Å Ti film and Si(111) substrate. The Ta interlayer evidently affected the titanium silicide formation process. The C54 $TiSi_2$ transition temperature was lowered by ~200°C and the agglomeration of the C54 phase (>700°C) was significantly suppressed. The C54 $TiSi_2$ formed with the Ta interlayers showed excellent electrical and physical characteristics. The role of the Ta interlayer is considered to promote the nucleation and growth of the C54 phase of $TiSi_2$ and to suppress the surface agglomeration of $TiSi_2$. Our results suggest that the mechanisms responsible for the suppression of surface agglomeration and reduction of the transition temperature are related to the similarity of the C40 and C54 crystal structures and with the change in the orientation of C54 $TiSi_2$ domains caused by the addition of Ta interlayer.

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