PHASE TRANSITION AND FORMATION OF TISi₂ CODEPOSITED ON ATOMICALLY CLEAN Si(111).

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Abstract

In this study, the phase transformation and the surface and interface morphologies of TiSi₂ formed on atomically clean Si substrates are investigated. 200Å Ti and 400Å Si films on Si(111) have been co-deposited at elevated temperatures (400°C - 800°C) in ultrahigh vacuum. The phase transition of TiSi₂ is characterized with using XRD. The results distinguish the formation of the C49 and C54 crystalline titanium silicides. The surface and interface morphologies of titanium silicides have been examined with SEM and TEM. A relatively smooth surface is observed for the C49 phase while a rough surface and interface are observed for the C54 phase. The islanding of the C54 phase becomes severe at high temperature (800°C). Islands of TiSi₂ have been observed at temperatures above 700°C but no islands are observed at temperatures below 600°C. For films deposited at 400°C and 500°C, weak XRD peaks corresponding to TiSi were observed and TEM micrographs exhibited small crystalline regions of titanium silicide at the interface.

Introduction

Titanium silicide is often considered for application as contacts and interconnects due to its low resistivity and stability at high processing temperatures [1,2]. However, a significant problem in the application of titanium silicide is island formation, resulting in a rough surface morphology.

Two different phases of TiSi₂ have been reported after the reaction of Ti and Si [3]. These are TiSi₂ of the C49 and C54 phases. The C49 phase of TiSi₂ is formed at low temperatures, while higher temperature annealing leads to the transition to the C54 phase. Both structures are orthorhombic. The C49 phase is metastable forms at temperatures from 450°C to 600°C. The stable C54 phase forms after higher temperature annealing to >650°C. The initial interactions at temperatures below 450°C have also shown evidence of a disordered intermixed layer and in some cases the presence of additional silicides [4,5].

In this paper we focus on formation sequences and mechanism of the titanium silicides formed by codeposition of Ti and Si on atomically clean Si substrates at elevated temperatures. The surface and interface morphologies of the C49 and C54 TiSi₂ phases were examined by SEM and TEM. The phases of titanium silicides were identified by XRD.

Experimental

The substrates used in this study were Si(111)-oriented substrates (25 mm diam.) with resistivities of 0.8-1.2 Ω cm (n-type, P-doped). The ultrahigh vacuum deposition chamber was equipped with a turbo-pumped loading chamber, and an ion-pumped deposition chamber. The deposition chamber has a heating stage and a dual e-gun system which are Ti and Si deposition sources. The base pressure in the UHV chamber was <1x10⁻¹⁰ Torr.

The Si wafer cleaning involved exposure to UV light from a quartz Hg lamp with the sample in air. These oxidizing agents react with contaminant molecules to form ozone and atomic oxygen from the oxygen in air [6]. These oxidizing agents react with contaminant molecules to form simple volatile molecules. This oxidation process removes surface hydrocarbons while leaving an oxide layer on the Si surface. The wafer was then treated with a spin etch with HF + H₂O + ethanol, 1 : 1 : 10 at room temperature to remove the oxide from the surface [7,8]. The wafer was introduced into the loading system.

In UHV deposition chamber, the Si substrate was heated to 800°C for 10 min to desorb the residual contaminants and hydrogen. The chamber pressure was typically better than ~1x10⁻⁹ Torr while heating. After heat cleaning in UHV, the base pressure returned to $1-2x10^{-10}$ Torr. Following in-situ cleaning, 200Å Ti and 400Å Si films on Si(111) was deposited simultaneously at elevated temperatures (400°C - 800°C). The resultant silicide layer is a 500Å in thickness. The thicknesses were monitored with a quartz crystal oscillator. After films deposition, characterization of the grown titanium silicide layers was carried out with using XRD, SEM and TEM.

Results

Phase identification of titanium silicides at different substrate deposition temperatures has been carried out using X-ray diffraction. XRD shown in Fig. 1 exhibits the results of titanium silicide phases in the temperature ranges of 400°C - 800°C. Weak XRD peak corresponding to TiSi phase which was deposited at 400°C has been observed. The coexistence of the TiSi and C49 TiSi₂ phases have been detected in the sample deposited at a temperature of 500°C. But for the sample deposited at 600°C, only the C49 phase is observed. The C54 phase formation has been observed for deposition temperatures above 700°C.

The surface and interface morphologies are investigated by TEM and SEM. The changes of the surface and interface morphologies are displayed by the SEM and TEM micrographs shown in Fig. 2. The sample deposited at 400°C shows smooth surface and interface morphologies. The C49 phase of TiSi₂ formed at 600°C also exhibits a relatively smooth interface. However the C54 phase formed at 800°C shows a wavy interface. The surface of the titanium silicide shown in Fig. 2, is uniformly covered at 600°C deposition, but



Fig. 1 XRD data of titanium silicides formed at temperatures of 400°C (a), 500°C (b), 600°C (c) and 800°C (d).



(c)

Fig. 2 SEM and TEM micrographs of titanium silicide formed at temperatures of 400°C (a), 600°C (b) and 800°C (c).

it is rough at 800°C deposition. Islanding on the surface is observed after the C54 phase has formed.

Discussion

The results of this study on the titanium silicide formation from the reaction of Ti and Si on Si(111) surfaces indicate the phase transition and the changes of the surface and interface morphologies of titanium silicide. The titanium silicide formation process involves the interdiffusion of Ti and Si at low temperatures, <400°C, the formation of metastable TiSi₂ (C49) phase at ~450°C - 650°C and the transition to the stable TiSi₂ (C54) phase at ~700°C [3,9,10]. Islanding of the titanium silicide occurs when the C49 phase transforms to the C54 phase.

The cross sectional TEM micrograph of titanium silicide formed at 400°C indicates very small crystalline areas at the interface with the Si substrate. The initial interactions at this temperature have shown the evidence of a disordered interdiffused layer and the presence of additional titanium silicide. XRD indicates that the weak peak of the titanium silicide sample formed at 400°C corresponds to the TiSi phase. The results of TEM and XRD show that the first crystalline titanium silicide phase from co-deposited layer forms at the interface with the Si substrate, and is the phase close to the TiSi structure. This TiSi phase coexists with the metastable C49 phase deposited at 500°C. Similar results have been reported by other authors [5]. They reported the coexistence of TiSi and C49 TiSi₂ at the interface of the amorphous interlayer and Si annealed at 500°C. In the case of silicide formation, only one silicide phase is energetically favorable by the surface and interface energy consideration. Couple of reasons can be considered to explain the coexistence of the metastable phase of TiSi₂ and the TiSi. But one consideration we suggest is that at low temperatures, the nucleation barrier for the titanium silicide phase is altered by the presence of the interdiffusion between Ti and Si and also by the differently oriented titanium silicide growth.

The TEM and SEM results show the relatively smooth interface of the C49 phase and the rough and island formation of the C54 phase. The thin film reaction of Ti and Si on Si surfaces at elevated temperatures leads to the change in both the surface and interface morphologies, a smooth interface of the C49 phase and island formation of C54 phase. The smooth interface of C49 phase is due to the codeposition of Ti and Si. For the formation of titanium silicide by thin film reaction, Si is the primary diffusing species. But in codeposition of Ti and Si, Si atoms are supplied by the evaporation source not by the Si substrate. This results in the relatively smooth interface of the C49 phase. However, as presented previously the C49 phase formed by single Ti deposition shows a rough interface [9]. The rough interface indicates that the Si has not diffused uniformly across the interface of the Ti and Si substrate. This nonuniform interdiffusion is due to the different character for the differently oriented Ti microcrystalline grains and grain boundaries. But the codeposited thin film exhibits a significantly different interface morphology of the C49 TiSi₂ phase. The change in the interface and surface morphologies of TiSi₂ is observed when the phase transition occurs. The island formation of TiSi₂ has been observed when the C54 phase of TiSi₂ is formed. The rough interface is due to the nucleation of the C54 TiSi₂ and the significant interdiffusion of TiSi₂ and Si. At temperatures above 700°C, the C49 phase transforms to the C54 phase due to the enough energy to form the stable phase. Once nuclei of the stable C54 phase are formed, the island formation of TiSi₂ proceeds to reduce the surface and interface area between the TiSi₂ and Si. This results in a decrease in the surface-to-volume ratio of the C54 TiSi₂ islands and an increase in the exposed Si surface.

Summary

In this study we examined the phase transition of and the surface and interface morphologies of the titanium silicides. XRD data show the phase transition of the C49 phase to the C54 phase at temperatures above 700°C, and also show weak peaks corresponding to TiSi at temperatures of 400°C and 500°C. Coexistence of TiSi and C49 TiSi₂ is observed at 500°C. The C49 phase of TiSi₂ formed at 600°C exhibits a relatively smooth surface and uniform interface. The change in the surface and interface morphologies of TiSi₂ is examined when the phase transition occurs. The islanding of TiSi₂ has been observed when the C54 phase of TiSi₂ is nucleated.

References

- 1. S. P. Murarka, and D. B. Fraser, J. Appl. Phys. 51,350 (1980).
- 2. F. M. d'Heurle, J. Mater. Res. 3,167 (1988).
- 3. R. Beyers, and R. Sinclair, J. Appl. Phys. 57, 5240 (1985).
- 4. R. Butz, G. W. Rubloff, T. Y. Tan, and P. S. Ho, Phys. Rev. B30, 5421 (1984).
- 5. M. H. Wang and L. J. Chen, Appl. Phys. Lett. 59, 2460 (1991).
- 6. J. R. Vig, J. Vac. Sci. Technol. A3, 1027 (1985).
- 7. D. B. Fenner, D. K. Biegelsen, and R. D. Bringans, J. Appl. Phys. 66, 419 (1989).
- 8. T. Takahagi, I. Nagai, A. Ishitani, and H. Kuroda, J. Appl. Phys. 64, 3516 (1988).
- H. Jeon, C. A. Sukow, J. W. Honeycutt, G. A. Rozgonyi, and R. J. Nemanich, J. Appl. Phys. 71, 4269 (1992).
- 10. K. Holloway, and R. Sinclair, J. Appl. Phys. 61, 1359 (1987).