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Initial Reactions of Ti on the Atomically Clean Si Substrates

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초청정한 Si 기판 위에서 Ti의 초기 반응

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요 약. Ti과 Si의 초기 반응이 Titanium Silicide의 표면 거칠기 (Surface roughness)를 고찰하기 위해 연구하였다. 형성기구는 In−situ AES와 LEED의 측정장비로 연구하였다. Ti의 하나나 두 원자층이 초고진공에서 원자적으로 깨끗한 Si 기판 위에 증착되었다. Reconstruction이 된 7×7 Si(111) 표면이 초 고진공하에서 얻어졌으며 박막의 증착은 Quartz Crystal Oscillator로 측정되었다. In−situ 측정 결과 Ti과 Si의 초기 반응이 실온에서 일어났으며 Disorder막을 형성하였다. 낮은 온도(200°C∼300°C)에서 Ti과 Si의 Intermixing이 고찰되었고 400°C 근처에서 1×1 Si(111) LEED 패턴이 관찰되었다. 이것은 Disorder막이 Order막으로 변화가 생긴 것을 나타낸다. 더 높은 온도에서 7×7 Si(111) LEED 패턴이 재관찰되었는데 이것은 3차원적인 $TiSi_2$의 형성을 증명하는 것이다.

Abstract. Initial reactions of Ti and Si have been studied to examine the surface roughness of titanium silicide. Formation mechanism has been explored with in-situ measurement tools such as AES(Auger electron spectroscopy) and LEED (low energy electron diffraction). One or two monolayers of Ti films have been deposited in ultrahigh vacuum on atomically clean Si(111) substrates. Atomically clean Si substrates which are reconstructed 7×7 Si(111) have been obtained after in-situ heat cleaning in ultrahigh vacuum. Deposition of the films were monitored by a quartz cuystal oscillator and the Ti films were analyzed with in-situ AES and LEED. The in-situ measurements show that the initial reactions of Ti and Si occur at room temperature and form a disordered layer. At low temperatures(200°C∼300°C) intermixing of Ti and Si is detected by AES. Substrate 1×1 LEED patterns are displayed after 400°C anneal. This indicates that the disordered layer has transformed to form an ordered surface. The reappearance of the 7×7 LEED pattern in observed with further high temperature anneals and indicates three dimensional titanium silicide island formation.

Key Words: Surface roughness, Reconstruction, Disordered layer

1. Introduction

The primary direction in the development of Si MOS technology is device miniaturization. The continued development of small devices results in needs of the metallization schemes for low resistivity contacts and interconnects [1, 2]. The application of aluminum and polysilicon in VLSI devices will become limited as demands increase for low resistivity, small structures, and temperature stability [1]. As the miniaturization of devices progress, forming metal silicides by thin film reaction with the Si substrate offers the possibility of stable, low resistivity contacts and interconnects. For many years, among refractory metal silicides titanium silicide has been studied and examined for use as contacts and interconnects on Si MOS devices [1, 3, 4]. The primary reasons why titanium silicide is so attractive for the application of Si MOS devices are its low resistivity (metallic) and its stability to high temperatures processing [2, 5, 6]. One of the drawbacks, however, is a rough surface after formation of titanium silicide [5]. Three dimensional islands formation of titanium silicide has been studied extensively by several authors. But few authors show the interest on the very few monolayers of coverage Ti on Si. In this study, we focus on the initial reactions of Ti and Si with thicknesses less than two monolayers of coverage of Ti on atomically clean Si substrates. The phase in the formation of $TiSi_2$ proceeds with the initial reactions to form a disordered layer by interdiffusion at low temperatures, followed by the extension of this disordered layer, the formation of the C49 metastable $TiSi_2$, and finally stable C54 phase formation at high temperatures [4, 6, 7]. Surface morphologies of these layers are examined with using in-situ AES and LEED. Uniform, rough surface, and intermixing of Ti and Si have been investigated with using in-situ measurement tools.

In this study, we have examined the initial reactions of Ti and Si at several different temperatures with using in-situ AES and LEED in ultrahigh vacuum. The intensity variation of the AES peak and a series of changes in LEED patterns have been carefully monitored to detect the atomic interdiffusion between Ti and Si, and the surface structural transition from the disordered phase to the ordered phase, which is epitaxial with the substrate. A series of changes in the LEED patterns and variations of the AES peaks indicate the sequential formation of disordered layer at room temperature, intermixed layer at temperatures of 200°C~300°C, and ordered layers of Ti and Si at further annealing [4, 6, 7]. This uniform ordered layer formation may be used as a template to grow the epitaxial titanium silicide. Three dimensional islands of titanium silicide at high temperature anneals (>500°C) are observed with LEED and same as the Ti films thickness greater than 50Å. The observation of the change of surface morphology of titanium silicide is a strong indication of the possibility of the two dimesional growth of titanium silicide.

2. Experimental Procedure

The substrates used in this study were Si(111)-oriented substrates (25 mm diam) with resistivities of 0.8-1.2 Ωcm (n type, P doped). The ultrahigh vacuum (UHV) system was equipped with a turbo-pumped loading chamber, and an ion-pumped UHV chamber with two stations for deposition and analysis. The deposition stage has a heating stage and a filament Ti deposition source, and the anaylsis stage has LEED and AES characterization. The base pressure in the UHV chamber was $<1\times10^{-10}$Torr.

The ex-situ clean involved exposure to UV light from a quartz Hg lamp with the sample in air [8]. These oxidizing agents react with contaminant molecules to forms ozone and atomic oxygen from the oxygen in air. These oxidizing agents react with contaminant molecules to form simpler 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 $HF+H_2O$

+ethanol, 1:1:10 at room temperature to remove the oxide from the surface [9, 10, 11]. The wafer was introduced into the UHV system.

In UHV system, 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 ~ 1×10^{-9} Torr while heating. After heat cleaning in UHV, the base pressure returned to $1\text{-}2\times10^{-10}$ Torr. Following in-situ cleaning, the LEED showed 7×7 Si (111) reconstructed patterns and AES indicated no evidence of oxygen or carbon. One to two monolayers of Ti films were then deposited on the atomically clean Si substrates by evaporation from a Ti filament, and the thicknesses were monitored with a quartz crystal oscillator. After Ti film deposition, samples were annealed for 10 min. at temperatures from 100°C up to 800°C in 100°C increments. After each anneal, the sample was cooled to room temperature, and LEED and AES measurements were carried out.

3. Results

The sequential change of LEED patterns shown in *Fig.* 1 was found after about two monolayers of Ti was

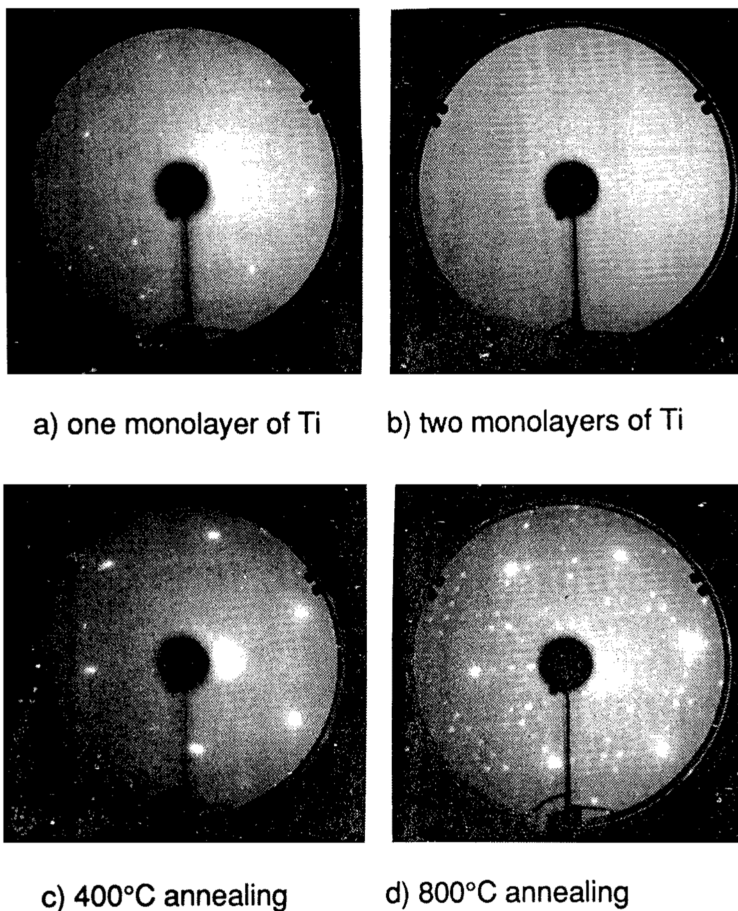

***Fig*. 1. The sequential changes of LEED patterns on Si(111) as a function of Ti films thickness and temperatures.**

deposited on Si(111). After ~1 monolayer deposition, the LEED shows the 1×1 Si(111) bulk pattern. This indicates that the ordered reconstructed surface has been destroyed. The 1×1 LEED pattern disappears completely after ~two monolayers of Ti deposition on Si(111). After 300°C annealing, the LEED displayed a 1×1 diffraction pattern which become sharper after annealing at 400°C for 10 min. This 1×1 LEED pattern changes to a dim 7×7 pattern after a 500°C anneal and becomes brighter after further anneals. AES shown in *Fig*. 2 shows the results for half, one, and two monolayers of Ti deposited on Si(111). The Ti peak at 27 eV and the Si peak at 92 eV are detected at the same time. The AES signal variations of Si and Ti peaks depend on the annealing temperature, as is shown in *Fig*. 3.

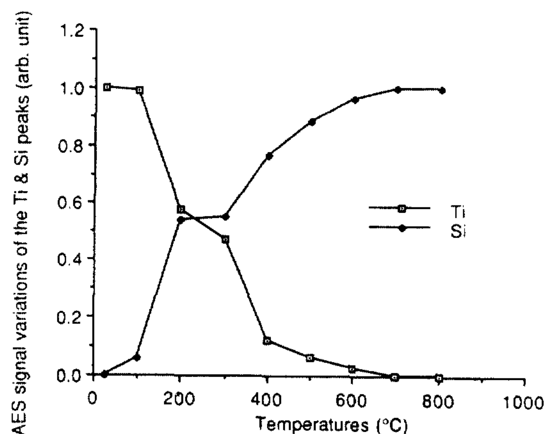

Fig. 3. Signal variations of AES for the Ti and Si peaks as a function of the temperature for two monolayers Ti deposited on the 7×7 Si(111).

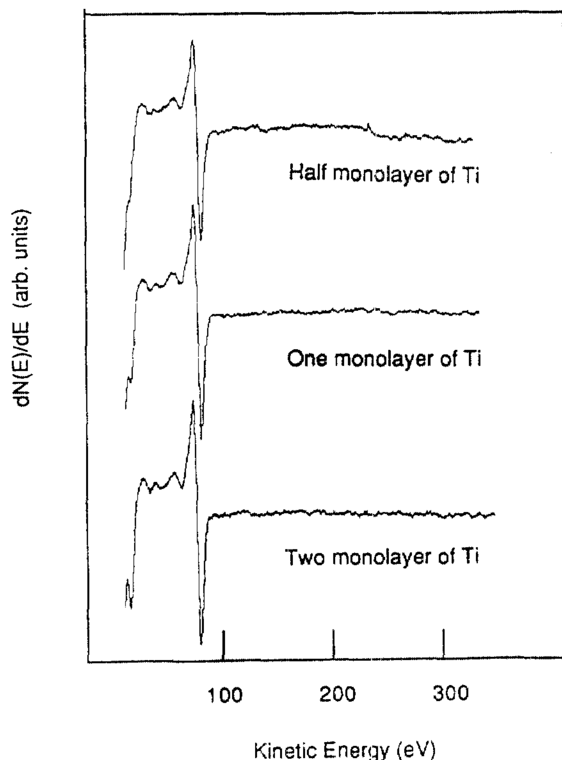

Fig. 2. AES of half, one, and two monolayers of Ti deposited on Si(111) showing the Ti peak at 27 eV and Si peak at 92 eV.

4. Discussion

In-situ AES and LEED studies of the initial growth of Ti on Si surface lead to some interesting results. The fact that one monolayer of Ti on Si substrate is enough to cause the surface reconstruction to completely disappear and that Ti films less than two monolayers result in no LEED patterns at all indicates that the initial reaction of Ti and Si begins even at room temperature. Nemanich et al. inferred this disordered layer was due to interdiffusion between the deposited Ti film and the Si substrate [4]. There are many other results reported by other authors. Butz et al. have reported from the Auger experiments that no Ti-Si reaction occurs at room temperature [12]. On the other hand, Franciosi et al. have observed such a reaction with photoemission studies [13]. Van Loenen et al. with results of high resolution medium energy ion scattering [14, 15] have in- terpreted this result to be due to intermixing at the Ti-Si interface at room temperature.

One-two monolayers Ti film thickness is not enough to disappear the LEED pattern completely if there is

no reaction between the Ti film and the Si substrate. When reactions occur between Ti and Si, this layer will be thick enough to vanish the LEED pattern completely. From LEED results of this study for less than two monolayers deposition, it can be concluded that there is an indication of a Ti-Si reaction even at room temperature.

Consider the AES signal variations of the Si and Ti peaks which are illustrated on *Fig.* 3, Reduction of the Ti peak intensity after 100°C annealing has been observed, and further reduction of the Ti AES peak is seen after 200°C~400°C annealing. This is an indication of the interdiffusion of Ti and Si at temperatures of 200°C~400°C. Changes in the LEED patterns shown in *Fig.* 1 were detected. as well. The sharp 1×1 bulk pattern of LEED is shown after 400°C annealing for Si(111). The 1×1 pattern of the Ti/Si(111) gets brighter after further anneals. The 1×1 LEED patterns of Ti/Si(111) indicate the formation of the ordered surface layer.

This initial phase is reported by other authors [12, 15] to have a composition close to TiSi which is different to the initial phase of the thicker films. This initial phase of titanium silicide exhibits the ordered phase. which indicates an epitaxial overgrowth of titanium silicide. The LEED pattern can be affected by the smoothness of the overgrowth. If the surface of overgrowth is smooth, elastically scattered electrons. which are related to diffraction patterns, bounce back onto a fluorescent screen to display sharp LEED patterns. For rough surface, LEED reveals increase in background because of random scattering. The surface morphology after initial phase formation is believed to be smooth according to the in-situ results of sharp 1×1 LEED patterns. This ordered 1×1 surface can be used as a template for MBE growth. $TiSi_2$ growth on a 1×1 surface instead of a reconstructed surface is suggested to study the different surface and interface morphologies. Further anneals at higher temperatures result in the reappearance of the 7×7 reconstructed patterns, which are an indication of the titanium silicide island formation [3, 5]. In *Fig.* 4, the titanium silicide formation of less than two monolayers of Ti deposition is explained schematically. It shows sequential formation of a disordered layer, an ordered layer and three dimensional islands of titanium silicide.

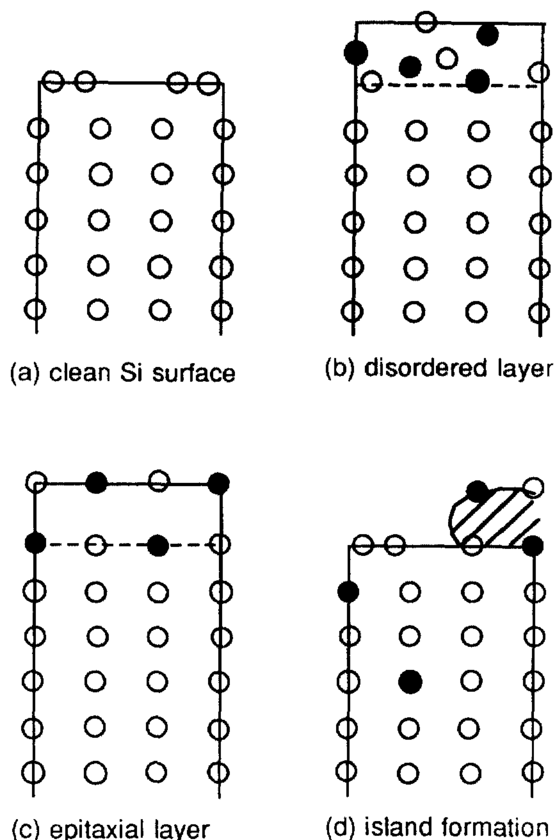

Fig. 4. The schematic illustration of the titanium phase formation : (a) an atomically clean Si substrtate, (b) formation of disordered layer, (c) epitaxial silicide formation, and (d) island formation of titanium silicide.

5. Summary

The initial reactions of formation of $TiSi_2$ on Si substrates have been studied in-situ by AES and LEED. The reconstructed surface of the Si(111) has

been examined prior to Ti deposition. Deposition of 1-2 monolayers of Ti results in a disordered surface layer. No LEED pattern after two monolayers deposition of Ti is an indication of reaction of Ti and Si even at room temperature. The AES signal variations of the Si and Ti peaks show the intermixing of Ti and Si by interdiffusion at between 200°C and 300°C. After annealing to 400°C 1×1 LEED patterns are interpreted as an ordered titanium silicide layer which is epitaxial with the Si substrate. In situ LEED measurements also show the reappearance of diffraction pattern corresponding to the reconstructed Si(111) substrate. This indicates the formation of islands with atomically clean Si substrate regions between the islands.

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