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초청정한 실리콘 기판상에서 Titanium Silicide 의 초기성장

한양대학교 금속공학과 전 형 탁
N C S U 물리과 R.J.Nemanich

Initial growth of $TiSi_2$ on atomically clean Si substrates.

Hyeongtag Jeon[1] and R. J. Nemanich[2]
[1] Dept. of Metallurgical Engineering, Hanyang University. Seoul, Korea.
[2] Dept. of Physics, North Carolina State University, Raleigh, N.C., U.S. A.

Introduction:

Titanium silicide among the transition metal silicides has received considerable attention as low resistivity contacts in very large scale integration device applications [1,2]. $TiSi_2$ has several unique properties including its low sheet resistivity and high temperature stability. However, a significant problem in the $TiSi_2$ material system is the nucleation of islands, resulting in a rough surface morphology . In this study, we focus on the silicide formation in films thickness between less than two monolayers and 50A 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 at temperatures around 200°C - 300°C, the formation of the C49 metastable $TiSi_2$ (450°C - 600°C), and finally stable C54 phase formation at temperatures ≥650°C.

The formation mechanisms of $TiSi_2$ deposited on atomically clean silicon substrates have been investigated. The initial reactions of $TiSi_2$ have been monitored with in-situ Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) to analyze the surface contaminants and the surface structures. Phase identification of the $TiSi_2$ is characterized by Raman spectroscopy. High resolution transmission electron microscope (HRTEM) is utilized to verify the epitaxy of $TiSi_2$.

Experimental:

The UHV system has equipped with a turbo molecular-pumped load chamber and an ion-pumped main chamber with two stations; one for Ti deposition and the other one for in-situ LEED and AES analysis. The base pressure of the system was better than mid-10^{-10} Torr. Silicon substrates, with <111> orientation and n-type phosphorous doped with 0.8~1.2 Ω-cm resistivities, were cleaned by UV-ozone exposure and spin-etched with $HF+H_2O$+ethanol, 1:1:10 [3]. They were then loaded into the UHV system and heated to 800°C for 10 min to desorb the residual oxide and hydrogen. After the in-situ cleaning, the LEED showed the pattern associated with the 7x7 Si(111) reconstructed surface, and the AES indicated no oxygen and carbon contaminants. Ti thickness was monitored by a quartz crystal oscillator. The maximum pressure was better than $\sim 1 \times 10^{-9}$ Torr while depositing the Ti on the Si substrate. To study the reaction kinetics, the substrate was annealed with 100°C increments up to 800°C, and after each anneal in-situ LEED and

AES were carried out after cooling to room temperature. Post preparation Raman scattering, TEM, HRTEM, electron diffraction and SEM were used to characterize the resulting island structures.

Results and Discussion:

The sequential change of LEED patterns was found after about two monolayers of Ti was deposited on Si (111). After ~1 monolayer deposition, the LEED shows the 1x1 Si(111) bulk pattern. This indicates that the ordered reconstructed surface has been destroyed. The 1x1 LEED pattern disappears completely after ~ two monolayers of Ti deposition on Si(111). After 300°C annealing, the LEED displayed a 1x1 diffraction pattern which become sharper after annealing at 400°C for 10 min. This 1x1 LEED patten changes to a dim 7x7 pattern after a 500°C anneal and becomes brighter after further anneals. AES 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.

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.

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.

This initial phase is reported 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 surface morphology after initial phase formation is believed to be smooth according to the in-situ results of sharp 1x1 LEED patterns. Further anneals at higher temperatures result in the reappearance of the 7x7 reconstructed patterns, which are an indication of the titanium silicide island formation.

Summary:

The initial reactions of formation of $TiSi_2$ on Si substrates have been studied in-situ by AES and LEED. The reconstructed surfaces of the Si(100) and Si(111) have been examined prior to Ti deposition. Deposition of 1-2 monolayers of Ti results in a disordered surface layer. This is an indication of reaction of Ti and Si 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 1x1 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 patterns corresponding to the reconstructed Si(100) and Si(111) substrates. This indicates the formation of islands with atomically clean Si substrate regions between the islands.

References:

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