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C49 $TiSi_2$상의 에피구조 및 상안정성

전형탁, R. J. Nemanich*
한양대학교 금속공학과
*Dept of Physics and Materials Science & Engineering, NCSU.

Phase stability and epitaxy of C49 $TiSi_2$ on Si(111)

Hyeongtag Jeon[1] and R. J. Nemanich[2].
Department of Metallurigical Engineering, Hanyang University, Seoul, Korea, 133-791.
**Departments of Physics and Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695-8202*

초 록 초청정 Si(111) 기판상에 초고진공 챔버에서 Ti을 증착하여 $TiSi_2$를 에피층으로 성장시켰다. 재구성된(reconstructed) Si(111) 표면에 상온에서 50Å 두께의 Ti을 증착한 후 100℃간격으로 800℃까지 열처리 하였다. $TiSi_2$ 박막의 구조는 전자회절 패턴 분석을 통하여 준안정상인 C49상임을 확인하였다. SEM 사진은 세가지 형태의 island를 보이고 있다. 각 island는 단결정이며 그 구조는 서로 다른 결정학적 방향을 갖는 에피구조이다. 이러한 $TiSi_2$ island는 $[1\bar{1}2]$C49 $TiSi_2$/[110]Si, (021) C49 $TiSi_2$/$(\bar{1}11)$Si의 방향관계를 가지고 있다.

Abstract Epitaxial $TiSi_2$ films have been grown by UHV deposition of Ti on atomically clean Si(111)-orientated substrates. The Ti film of 50Å was deposited on the reconstructed Si(111) surface at room temperature. The sample was annealed up to 800℃ in 100℃ increments. The structure of the $TiSi_2$ films have been identified as the C49 metastable phase by electron diffraction patterns. Scanning electron microscopy(SEM) shows three different types of Ti-silicide island morphologies. The individual island structures are single crystal and are considered to be epitaxy with different crystallographic orientations. The orientational relationships of the $TiSi_2$ islands is given by $[1\bar{1}2]$ C49 $TiSi_2$//[110] Si and (021) C49 $TiSi_2$//$(\bar{1}11)$ Si.

Introduction

Refractory metal silicides have been studied extensively due to their high temperature stability and low resistivity for the application of very-large-scale intergration(VLSI)[1, 2]. Especially, epitaxial transition metal silicides are often considered as one of the lowest resistivity contacts among the metal silicides. The growth of epitaxial silicides such as $CoSi_2$ and $NiSi_2$[3] which have a cubic crystal structure have been widely reported. Thin film reactions of Ti on Si result in the formation of two different forms of $TiSi_2$ which have been identified as the C49 and the C54 crystal structures[4]. While the $TiSi_2$ films formed by thin film reactions are already important for VLSI applications, there are only a few reports which have demonstrated $TiSi_2$ epitaxy for the C49 and the C54 $TiSi_2$ phases [5, 6, 7, 8, 9].

The metastable C49 phase of $TiSi_2$ on Si (111) has been reported as the stable phase up to 800℃ for Ti film thickness≦100Å[10]. This temperature is higher than the 650℃ temperature where the transition to C54 $TiSi_2$ occurs for thicker films (~400Å). In this study, the stability of the metastable C49 phase is explained in terms of the nucleation barrier, and pseudomorphic character of C49 $TiSi_2$ at the interface. The morphology and epitaxial growth of thin film C49 $TiSi_2$ on Si(111) are also displayed by SEM and HRTEM. Previously we have reported the relationship of the nucleation and island formation of $TiSi_2$/Si[10]. We examine the three different types of island surface and interface morphologies and the phase stability of the C49 $TiSi_2$. Most of the islands are epitaxial, and the corresponding crystallographic orientation relationships between the Si substrate and epitaxial $TiSi_2$ are determined from the selected area diffraction.

Experimental

The $TiSi_2$/Si structures were prepared in a system 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 UHV system was$<1\times10^{-10}$Torr. Silicon substrates, with [111] orientation and n-type phosphorous doped with 0.8~1.2Ω-cm resistivites, were cleaned by UV-ozone exposure followed by a spin-etched with $HF+H_2O$ +ethanol, 1 : 1 : 10[11]. The wafers were then transferred into the UHV deposition chamber and heated to a temperature of 800℃ for 10 minutes to desorb the residual contaminants and hydrogen. After the in situ cleaning, LEED showed the diffraction pattern associated with the 7×7 Si(111) reconstructed surface, and AES indicated no oxygen or carbon contaminants. Ti deposition was monitored by a quartz crystal oscillator. The maximum pressure was$<\sim1\times10^{-9}$Torr while depositing the Ti on the Si substrate. In this study, 50Å of Ti was deposited on the atomically clean Si substrate at room temperature. To study the reaction kinetics, the Ti film on Si(111) deposited at room temperature was annealed in 100℃ increments up to 800℃.

Results

The in situ LEED and AES characterization of the $TiSi_2$ formation process were performed first. The cleanliness of Si substrate was verified after Si wafer cleaning process by in situ AES and LEED. After in situ cleaning in UHV system, the AES shows no evidence of any contaminants such as carbon and oxygen and LEED displays the 7×7 Si(111) reconstructed pattern which is an atomically clean Si surface. Shown in Fig. 1 is the variation of AES

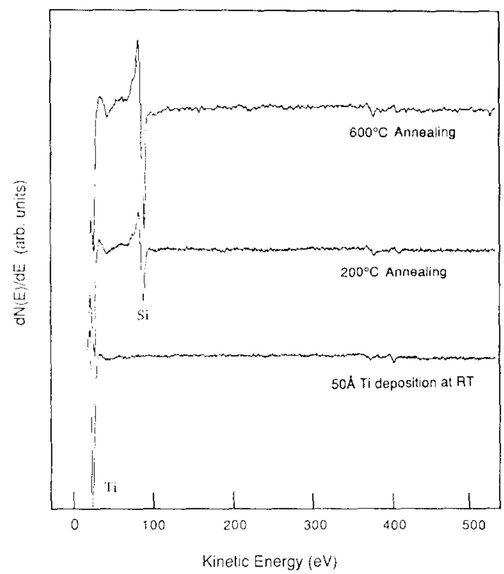

Fig. 1. The AES of the 50Å Ti deposited on Si (111) substrate as a function of the temperatures.

peaks depending on the annealing temperatures. Immediately after the 50Å Ti deposition at room temperature on the atomically clean Si substrate, the Si AES signal disappeared, and no LEED diffraction spots were observed indicating complete Ti coverage of the Si surface. After annealing to 200℃, the AES showed a weak Si signal indicating interdiffusion of Ti and Si, and the signal continually increased after each anneal up to 600℃. The signal increased slightly for annealing at the higher temperatures(600℃-800℃). The changes of the LEED patterns shown in Fig. 2

exhibited no diffraction spots for anneals up to 500℃, but at 600℃ and 700℃ anneals, a reappearance of weak diffraction peaks superimposed with the 7×7 Si(111) reconstructed surface was observed. We suggested that this indicate the onset of agglomeration of the $TiSi_2$ film with bare Si regions between $TiSi_2$ islands and also indicates the overgrowth of $TiSi_2$ is ordered with respect to Si(111) substrate. Further annealing up to 800℃ resulted in a sharp 7×7 diffraction pattern(see Fig. 2(c)). This suggests that the opening of bare Si regions is extended.

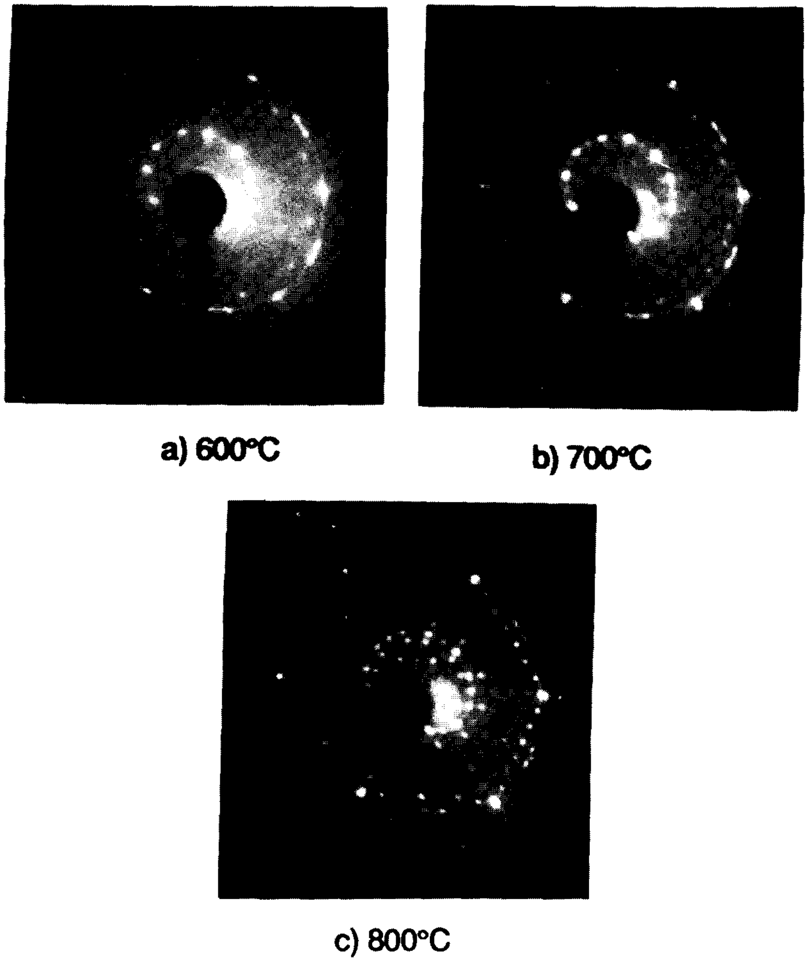

Fig. 2. The changes of the LEED patterns as a function of the annealing temperatures of (a) 600℃, (b) 700℃, and (c) 800℃

The morphologies of the $TiSi_2$ film were obtained from SEM, and a typical region is shown in Fig.3. Three different morphological regions of $TiSi_2$ island structures are displayed ; nearly uniform coverage(two dimensional-like), connected intermediate size islands and randomly spread small islands. The cross sectional TEM examination indicates different types of recessions of these islands into the Si substrate ; totally recessed, partially recessed, and small partially recessed islands. Shown in Fig.4 is a cross-sectional TEM micrograph of three differently recessed islands. The totally recessed islands correspond to the two dimensional-like surface morphology while the smaller islands show the least recess into the substrate. The totally recessed and the partially recessed islands show extremely smooth and flat interfaces.

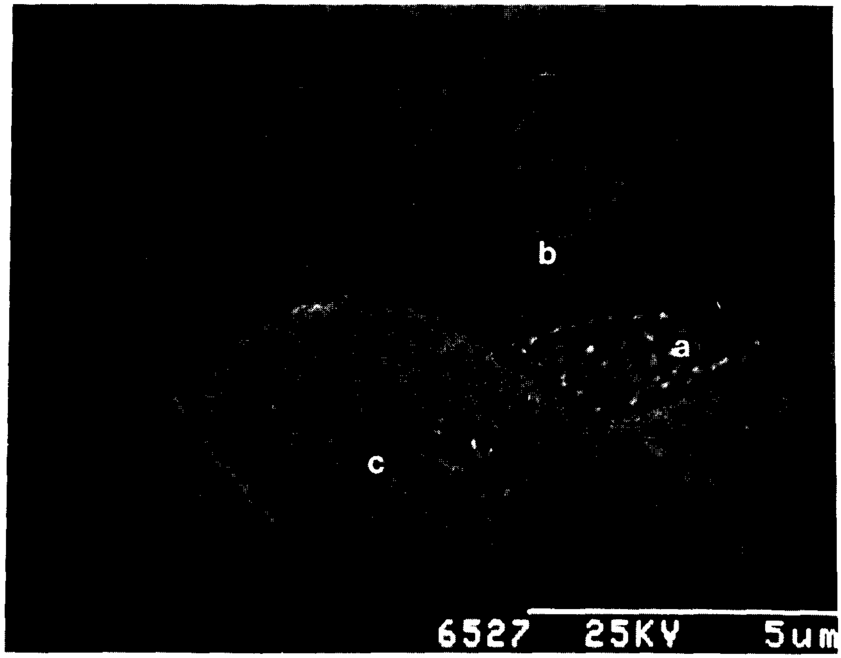

Fig. 3. SEM micrograph of the three different types morphologies of the C49 $TiSi_2$, which are (a) randomly spread small islands, (b) connected intermediate size islands, and (c) uniform coverage(two dimensional-like) islands.

The epitaxial relationship was found previously to be [$3\bar{1}0$] C49 $TiSi_2$//[112] Si and (130) C49 $TiSi_2$//($11\bar{1}$) Si[7]. New epitaxial C49 $TiSi_2$ showing atomic steps at the interface is shown in Fig. 5. The orientation relationship was found to be [112] C49 $TiSi_2$//[110] Si and (021) C49 $TiSi_2$//($\bar{1}$ 11) Si.

Discussion

Most of silicides epitaxies such as $CoSi_2$ and $NiSi_2$ exhibit the same structure with the Si substrate which are cubic [3]. These materials satisfy the general requirements for the high quality epitaxial growth which are the same structure and the good lattice matching across the interface. However, for $TiSi_2$ on Si(111) system, the conventional criterion of lattice mismatch, by comparing the lattice parameters, is not applicable because they exhibit totally different structures ; orthorhombic(C49) and diamond cubic[5, 12]. Rather, if there is a similar atomic array for both structures such as an hexagonal array of the C49 $TiSi_2$ structure which can match the six fold symmetry of Si(111), or alternatively if there is a match of the interplanar spacing on both sides of the interface, then it is possible to grow the epitaxy of the C49 $TiSi_2$ on Si substrate. The (001) plane of C49 $TiSi_2$ exhibits pseudohexagonal arrays of Si atoms which are similar to the six fold symmetry of Si(111). Other planes may also exhibit hexagonal arrays. The epitaxial relationship found from selected area diffraction patterns is [$3\bar{1}0$] C49 $TiSi_2$//[112] Si and (130) C49 $TiSi_2$//(111) Si which is the same as reported by M. S. Fung, et al. [7]. Another orientation relationship examined in this study is [$1\bar{1}2$] C49 $TiSi_2$//[110] Si and (021) C49 $TiSi_2$//(111) Si. Planes of $TiSi_2$ and Si show similar interplanar spacings along the axis

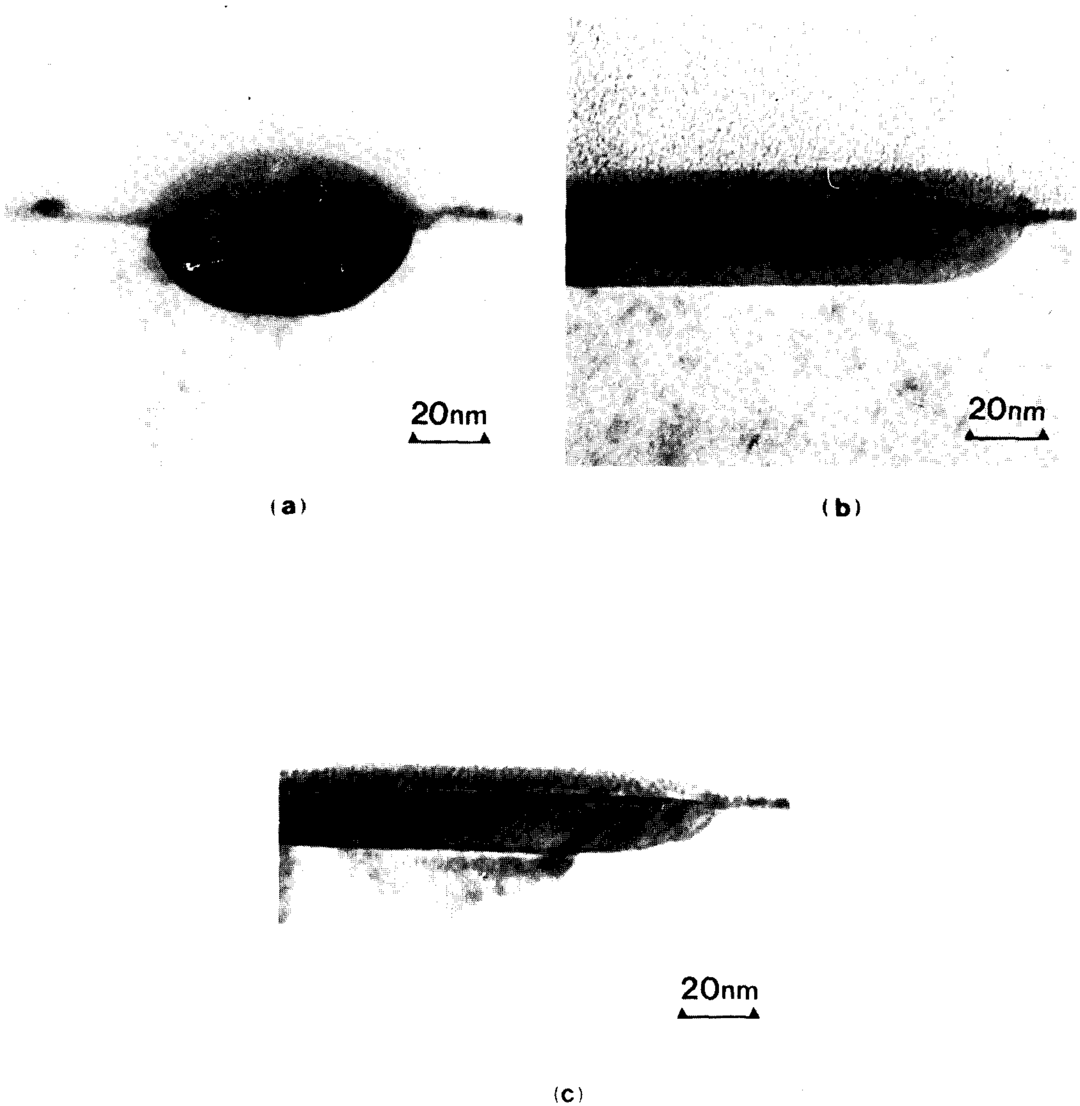

Fig. 4. Cross sectional TEM of the three different type of C49 $TiSi_2$ islands which are (a) small partially recessed, (b) partially recessed, and (c) totally recessed islands.

normal to the interface. The Si(111) plane spacing is 0.313nm, and the C49 $TiSi_2$ (021) plane spacing is 0.319nm which results in a misfit normal of ~2.0%. Atomic steps in the C49 $TiSi_2$ epitaxy on Si(111) are shown in Fig. 5. These steps may be related to the character of the interface matching.

The $TiSi_2$ formed from 50Å Ti deposition at room temperature followed by in situ annealing identified as having the C49 phase is unusual because the typical transition temperature of the C49 phase to the C54 phase is ~650℃ for Ti thicknesses ~400Å. It has been proposed that the high temperature stability of the metastable C49 phase is maintained instead of the formation of the stable C54 phase because of the unusual phase stability of the C49 $TiSi_2$[10]. Once the C49 phase is formed as a first phase due to its low free energy barrier, it is stabilized at the interface because of

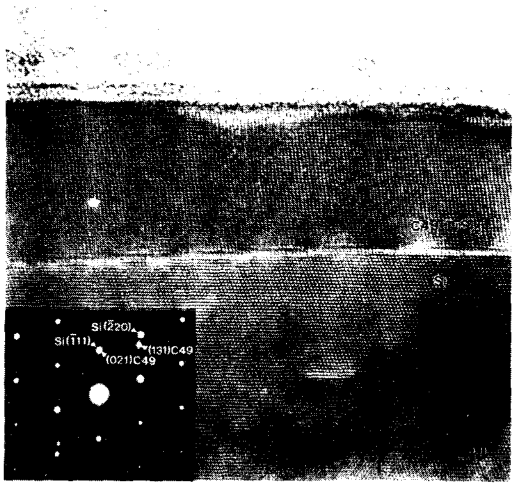

Fig. 5. HRTEM and SAD patterns of C49 $TiSi_2$ on Si(111).

its similar atomic arrangement. The C49 phase of $TiSi_2$ exhibits the pseudomorphic hexagonal array of Si atoms on its(001) plane which is similar to the six fold symmetry of Si(111). To form the C54 phase from the stabilized C49 phase, the structures must overcome a high nucleation barrier. In the case of the thin film formation, the effect of the positive energy terms such as surface energy and strain energy is enhanced. The formation of the C54 phase from the C49 phase creates a new surface areas and the atomic rearrangement, which contribute to increase the nucleation barrier. The free energy barrier to nucleate the C54 phase of the very thin film will be higher than that of the thick film due to the enhancements of positive energy terms. A more extensive study of the transition indicates that the transition temperature of C49 phase to the C54 phase increases with decreasing the film thickness[10].

We have previously modeled the island formation in terms of a liquid-liquid model to explain the island recession into the substrate [10]. Then by measuring the contact angle, the relative surface and interface energies could be determined. After $TiSi_2$ forms on the Si substrate it acts like an immiscible liquid on the top of another liquid because the titanium disilicide($TiSi_2$) is the most Si-rich silicide and it is stable in contact with Si. Therefore the degree of resession of the $TiSi_2$ island into the Si substrate strongly depends on the interface and surface energies of $TiSi_2$. Those energies can be calculated from the contact angle if the surface energy of Si is known. The surface energy of Si substrate is same as that of the clean surface since the Si surface regions show a reconstructed surface. The interface energy and the surface energy of $TiSi_2$, however, is also dependent on the orientation of $TiSi_2$. The different depths of $TiSi_2$ island recession into the Si substrate can then be attributed to the different interface energies of the different epitaxial growth orientations. Therefore the surface morphologies and interface shapes are dependent on the surface and interface energy attributed to the orientation relationship between the epitaxial $TiSi_2$ and Si(111). The TEM results show that different $TiSi_2$ morphologies occur with different epitaxial orientations. Therefore it can be proposed that the different island types are due to the different interface and surface energies which are attributed to the different orientation of the island structures.

Summary

Epitaxial C49 $TiSi_2$ and its phase stability formed on Si(111) substrates have been studied. The epitaxial orientation was identified as [112] C49 $TiSi_2$//[110] Si and (021) C49 $TiSi_2$ //(111) Si. The epitaxial C49 $TiSi_2$ is stable up to 800℃ which is higher than the C54 transition temperature for thicker films(~400Å). This unusual phase stability of the metastable C49 $TiSi_2$ is ascribed to the pseudomorphic epitaxial interface of $TiSi_2$ on Si, the stabilization of the C49 phase due to the similar atomic arrangement between the C49 $TiSi_2$ and Si (111), and the nucleation barrier consideration based on the surface and interface energies.

SEM micrographs show three different is-

land shapes for a sample deposited at room temperature followed by annealing up to 800 ℃ by 100℃ increments. The different island structures also show different epitaxial relations to the Si(111) substrate. It is proposed that the different types of island growth are related to the interface and surface energies which are dependent on the orientaion of the epitaxial growth.

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