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〈연구논문〉

Growth of Ti on Si(111)-7×7 Surface and the Formation of Epitaxial C54 $TiSi_2$ on Si(111) Substrate

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Si(111)-7×7 면에서 Ti 성장과 C54 $TiSi_2$/Si(111) 정합성장에 관하여

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Abstract—The growth of Ti on Si(111)-7×7 and the formation of epitaxial C54 $TiSi_2$ were investigated by using reflection high energy electron diffraction(RHEED) and high resolution transmission electron microscopy(HRTEM). Polycrystalline Ti layer is grown on the amorphous Ti-Si interlayer which is formed at the Ti/Si interface by Ti deposition on Si(111)-7×7 at room temperature (RT). HRTEM lattice image and transmission electron diffraction (TED) showed that epitaxial C54 $TiSi_2$ grown on Si substrate with 160 ML of Ti on Si(111)-7×7 surface at RT, followed by annealing at 750℃ for 10 min in UHV. Thin single crystal Si overlayer with [111] direction is grown on $TiSi_2$ surface when $TiSi_2$/Si(111) is annealed at ~900℃ in UHV, which was confirmed by Si(111)-7×7 superstructure.

요 약—고에너지 반사 전자회절기(RHEED) 및 투과전자현미경(HRTEM)을 이용하여 Si(111)-7×7 면에서의 Ti박막의 성장 mode와 Si(111) 면에서의 C54 $TiSi_2$의 정합성장을 조사하였다. 초고진공에서 Si(111)-7×7 표면에 상온에서 Ti를 증착하면 Ti/Si 계면에서 비정질의 Ti-Si 중간막이 먼저 형성되고 그 위에 Ti 박막은 다결정으로 성장하였다. 160 ML의 Ti를 증착한 시료를 초고진공 내에서 750℃로 10분 열처리하면 C54 $TiSi_2$가 정합성장하였으며 이는 HRTEM 격자상 및 TED pattern으로 확인할 수 있었다. $TiSi_2$/Si(111) 시료를 다시 900℃로 가열하면 $TiSi_2$ 위에 단결정 Si층이 [111] 방향으로 성장하였다.

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1. Introduction

Because of needs for new material in Si-based microelectronic device application, the growth and characterization of epitaxial silicide on single crystal Si-substrate have been studied extensively for the last decade[1-3]. According to Royer[4] epitaxial silicides can be grown on Si when the crystal structure of the silicide is similar to that of Si. Recently, however, Zur *et al.*[5], demonstrated that most silicides can be grown epitaxially on Si-substrate by comparing the interface translational symmetry with the bulk materials on both sides of the interface. A number of epitaxial silicides were successfully grown on the Si(100)[6, 7] and Si(111) [8, 9] surfaces.

$TiSi_2$ has two kinds of crystal structures; base centered orthorhombic (C49 type, a_o = 0.362 nm, b_o = 1.376 nm, and c_o = 0.360 nm) and face centered orthorhombic (C54 type, a_o = 0.826 nm, b_o = 0.480 nm, and c_o = 0.853 nm). It is known that both C49 and C54 type $TiSi_2$ can be grown epitaxially on Si(111) substrate[10]. Epitaxial growth of C54 $TiSi_2$ was reported from non UHV Ti/c-Si diffusion couples prepared by both furnace annealing and rapid thermal annealing(RTA), but the dominant mode of orientation relationships and average grain size were found to be different[11, 12]. The dominant orientation relationships between epitaxial C54 $TiSi_2$ and Si were reported to be [100]$TiSi_2$| |[111]Si, (004)$TiSi_2$| |(02$\bar{2}$)Si or [001]$TiSi_2$| |[111]Si and (400)$TiSi_2$| |(02$\bar{2}$)Si, whereas those between C49 $TiSi_2$ and Si are [3$\bar{1}$0]$TiSi_2$| |[112]Si and (130)$TiSi_2$ | |(11$\bar{1}$)Si[12]. It is known that the presence of impurities can strongly influence the orientation relationships in epitaxial silicide. However, few studies have been carried out to investigate epitaxial silicide formation where impurity free metal films are deposited under UHV on atomically clean Si substrate.

In this paper we report our experimental findings on the growth of Ti layer on Si(111)-7×7 surface at substrate temperature of either RT or ~550℃ and the growth of epitaxial C54 $TiSi_2$ on Si(111) substrate. A thin single crystalline Si overlayer is grown on $TiSi_2$ when the $TiSi_2$/Si(111) is annealed in UHV. The orientation relationships between epitaxial $TiSi_2$ and Si(111) are characterized by using high resolution transmission electron microscopy(HRTEM) and selective area diffraction(SAD) pattern.

2. Experimentals

Phosphorus doped (ρ: ~4 Ω · cm), *n*-type Si(111) wafers of ~10 mm×30 mm were used as the substrate for the experiment. Prior to loading into the UHV chamber, the wafer was chemically cleaned by standard Si wafer cleaning procedure. The wafer was mounted to a sample holder, in which dc current can be applied directly for resistive heating. After the whole chamber was baked out at ~150℃ for 10 hours, the pressure in the chamber was low 10^{-10} Torr range. Auger electron spectrum showed that considerable amount of carbon and oxygen were present at the wafer surface. The line-shapes[13] of C_{KLL}(273 eV) and Si_{LVV} (78 eV) were characteristics of SiC and SiO_x, which might be inevitably formed at the Si surface during sample handling and baking. The Si-wafer was heated upto ~1200℃ for 2 min by applying dc current directly in order to remove any contaminants from the surface and cooled down to ~300℃. After 4 or 5 cycles of heating and cooling, well collimated electron beam (beam size; ~0.5 mm) with an energy of ~20 kV was incident to the sample surface at an angle of 2° along Si[112] or Si[110] direction. The Si(111)-7×7 reconstructed RHEED pattern clearly demonstrated that the wafer surface was atomically clean. Auger electron spectrum also showed that the impurity atoms were below the typical detection limit(~0.1 at %).

High purity (99.999%) Ti evaporated by resistive heating the Ti-coated tungsten filament was deposited onto the Si(111)-7×7 surface which was held at either RT or ~550℃. The deposition rate and the thickness were monitored by quartz crystal oscillator thickness monitor with an accuracy of 0.1 ML(1 ML≈ 7.8×10^{15} atoms/cm^2 for Si(111) surface). Typical deposition rate was ~0.5 ML/min and the RHEED pattern was monitored at the end of each deposition (by 0.1 ML interval). The base pressure in the chamber before Ti evaporation was 2×10^{-10}

Torr but it rose to ~2×10^{-9} Torr during deposition. The thickness of Ti films were in the range from 10 ML to 160 ML. After the deposition the sample was annealed *in situ* for the growth of Ti silicide. The annealing temperature was ramped from 550℃ to 750℃ by 50℃ in step and the sample was annealed for 10 min at each annealing process. The atomic compositions and the phases of the silicide were characterized by using AES depth profile and X-ray diffraction. The lattice image and the corresponding orientation relationships were obtained by using HRTEM and SAD pattern. TEM samples were prepared at LN_2 temperature by Ar^+ ion milling.

3. Results and Discussion

No structural changes is observed in RHEED pattern until Ti is deposited up to 0.4 ML at RT. Upon increasing Ti thickness up to 0.5 ML, the intensities of diffraction spots at L_{01}, L_{02}, L_{03}, L_{04}, and L_{05} Laue zone decrease, while the intensities of the spots at L_0 and L_1 Laue zone remain unchanged, which is known to be the Si(111)-α-7×7 superstructure (see, Fig. 1). The Si(111)-α-7×7 changes to Si(111)-1×1 as the Ti thickness increases to 2.6 ML. Upon further deposition the two dimensional RHEED pattern disappears and only the background is observed until 10 ML. "Texture structure" appears at ~30 ML of Ti and this pattern remains until 160 ML.

When the substrate temperature is 550℃, on the other hand, Si(111)-7×7 RHEED pattern remains unchanged until the deposited Ti thickness is up to 4.5 ML. This pattern changes to Si(111)-1×1 at 6 ML. Streaks for uniform Ti layer together with the pattern for the formation of 3 dimensional islands appears over 6 ML(Fig. 2). Upon further deposition up to 10 ML the streaks decreases whereas the 3 dimensional pattern dominates. This indicates that at 550℃ Si atoms diffuse into the Ti matrix faster than at RT and these form the silicide islands. The same pattern is obtained from Ti(10 ML)/Si(111)-7×7 sample prepared at RT by annealing at 550℃. The RHEED pattern of the sample (Ti(10 ML)/Si(111) at 550℃) transformed from 3 dimensional silicide pattern to a diffuse Si

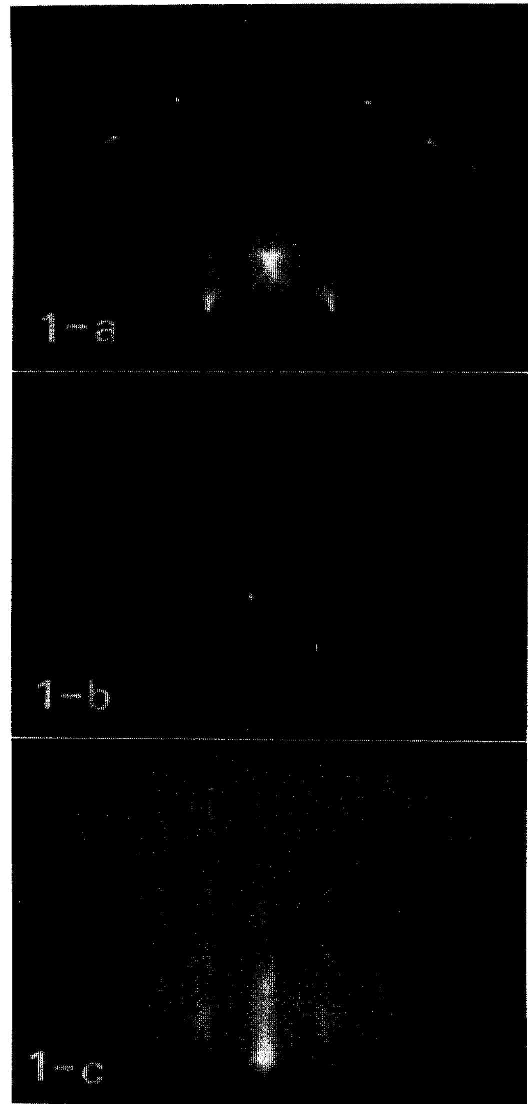

Fig. 1. Evolution of RHEED pattern as Ti is deposited on Si(111)-7×7 at RT, (a) Si(111)-α-7×7 at 0.5 ML, (b) Si(111)-1×1 at 2.6 ML, (c) texture structure at 30 ML.

(111)-α-7×7 after annealing at 800℃ for 10 min. A clear Si(111)-7×7 pattern is obtained after annealing further up to 900℃. This demonstrates that the Si overlayer on the silicide surface is single crystalline with (111) plane. Because 7×7 superstructure is known to be the most clean surface of (111)Si[14].

Fig. 3 shows the HRTEM image of the as-deposited sample (Ti(160 ML) on Si) prepared at RT.

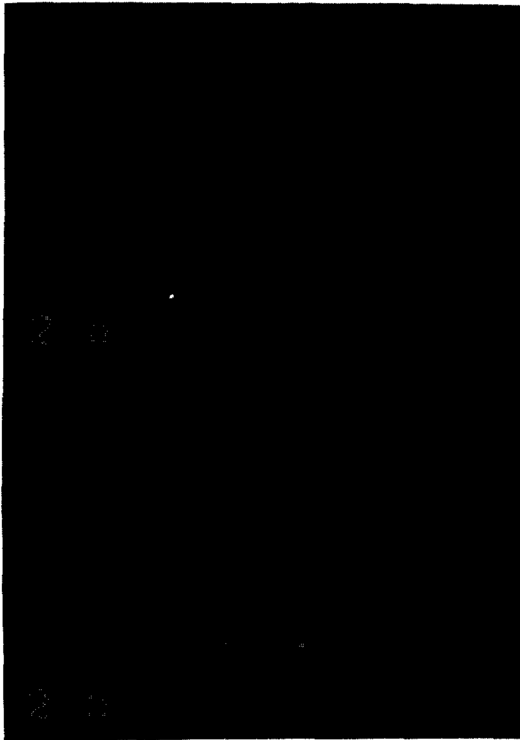

Fig 2. Evolution of RHEED pattern as Ti is deposited on Si(111)-7×7 at 550℃, (a) 6 ML, and (b) 10 ML. The same pattern was obtained 10 ML of Ti deposited on Si(111)-7×7 at RT followed by annealing at 550℃ for 10 min.

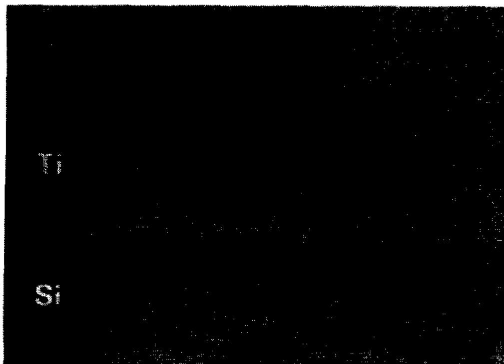

Fig. 3. High resolution transmission electron micrograph of Ti layer grown on Si(111)-7×7 at RT. Well developed polycrystalline Ti is grown on amorphous Ti-Si interlayer.

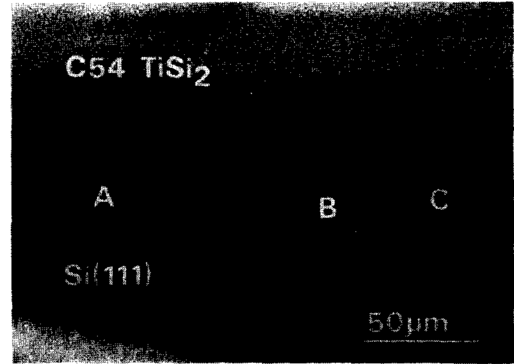

Fig 4. Cross sectional transmission electron micrograph of Ti(160 ML)/Si(111) after annealed at 750℃ in UHV.

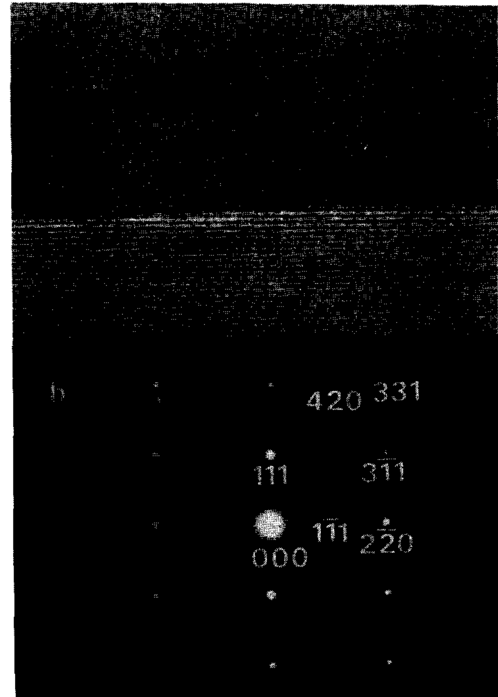

Fig 5. (a) HRTEM lattic image of region A in Fig. 3 and (b) the corresponding TED pattern, in (b) (000), (420) and ($1\bar{1}1$) correspond to Si, and (111), (331), ($3\bar{1}1$) and ($\bar{1}11$) correspond to C54 $TiSi_2$, respectively.

An amorphous glassy Ti-Si interlayer with average thickness of ~1.8 nm is observed at Ti/Si interface. The grown Ti layer on this membrane is polycrystalline structures but the grains are highly oriented to the substrate. The interplanar spacing of the lattice image is 0.26 nm using a $d_{Si(111)}=0.313$ nm as an internal standard. This plane can be assigned as Ti(010) plane, thus the orientation

relationship between Ti and Si(111) in our case is Ti(002)||Si(111) and is mainly oriented to be vertical to the Si(111) surface with ~10° of deviation. This result is also consistent with the X-ray diffraction as Ti(002) plane is parallel to Si(111) because the angle between Ti(010) and Ti(002) plane is 90°.

160 ML of Ti on Si(111)-7×7 prepared at RT was annealed at 750℃ for 10 min in UHV. Three kinds of well developed crystallites are confirmed at region. A, B and C (Fig. 4). The lattice images taken from A, B and C demonstrate that each crystallite is a single crystal of C54 $TiSi_2$ without any amorphous membrane at the silicide/silicon interface.

HRTEM image of region A (Fig. 5(a)) with an electron beam direction along [112]Si clearly shows that epitaxial C54 $TiSi_2$ is formed. Vertical plane image is $TiSi_2$(111) with interplanar spacing of 0.37 nm and the angle between the $TiSi_2$(111) and Si (111) plane is measured ~84°. From the SAD pattern (Fig. 5(b)) of the corresponding region, the orientation relationships have been found to be $[1\bar{2}3]$$TiSi_2$||$[11\bar{2}]$Si, $(\bar{1}11)$$TiSi_2$||$(2\bar{2}0)$Si, (420)$TiSi_2$||(111)Si and (242)$TiSi_2$||(402)Si with misorientations ~6°, 3.5° and 0.3°, respectively. The misorientation angle of 6° for $(\bar{1}11)$$TiSi_2$ and $(2\bar{2}0)$Si is consistent well with the result of HRTEM image, because the interplanar angle between (111) and $(2\bar{2}0)$ in Si lattice is measured to be 90°.

The HRTEM lattice image of region B in Fig. 3 aligned along Si$[\bar{1}10]$ beam direction corresponds to $TiSi_2$(311) plane having 0.23 nm interplanar spacing. This plane deviates 2° from Si(002) plane. SAD pattern of the same region shows the orientation relationship of $[\bar{1}36]$$TiSi_2$||$[\bar{1}10]$Si, $(3\bar{1}1)$$TiSi_2$||(002)Si and (620)$TiSi_2$||(111)Si with misorientations about 2°, 4.2° and 0.2°, respectively.

From the HRTEM image of region C in Fig. 3 aligned along Si$[0\bar{1}1]$ beam direction, the orientation relationships were found to be $[2\bar{3}3]$$TiSi_2$||$[0\bar{1}1]$Si, (022)$TiSi_2$||(200)Si, (331)$TiSi_2$||$(3\bar{1}1)$Si and $(31\bar{1})$$TiSi_2$||$(1\bar{1}\bar{1})$Si with misorientation ~14.7°, 5.3° and 3.9°, respectively.

The growth of Ti on Si(111)-7×7 can be understood on the basis of kinetic constraint[15]. The amorphous glassy membrane grows until the accomodated interfacial energy can balance the energy for Si diffusion. Then this membrane serves as a diffusion barrier for further reaction[16]. Ti grows as a layer by layer type[17] on this membrane, but as the thickness increases (over ~2.6 ML) the deposited Ti atoms coalesce to form Ti islands. As Kern *et al.*[18], pointed out, this kinds of changes of the RHEED pattern is a characteristics of Stransky-Krastanov type growth mode. If the deposited film becomes thick, this forms isolated islands to lower the total energy and these islands are relaxed by the interfacial misfit dislocations[19].

Epitaxial growth of C54 $TiSi_2$ was studied by many authors. Fung *et al.*[10], reported that the crystallographic orientation relationship of (004)$TiSi_2$||(022)Si, [100]$TiSi_2$||$TiSi_2$$[11\bar{1}]$Si for C54 $TiSi_2$ could be obtained by annealing Ti/Si(111) couple in vacuum. Wu *et al.*[20], found that (313)$TiSi_2$||(220)Si and $[10\bar{1}]$$TiSi_2$||$[\bar{1}11]$Si or (004)$TiSi_2$||(022)Si, [100]$TiSi_2$||$[11\bar{1}]$Si could also be obtained. All the relationships may happen, but it is pointed out that the epitaxial growth of $TiSi_2$ is dependent on the annealing temperature, time and cleanness of the substrate[21, 22] and on the microstructure of the substrate. Because we could not find the same orientation relationships obtained by another authors[10, 20, 23] in spite of carrying out a number of TEM analysis on wide region of our specimens.

4. Summary

The growth of Ti on Si(111)-7×7 and of C54 $TiSi_2$ investigated by RHEED and HRTEM are summarized as follows:

1) An amorphous glassy Ti-Si interlayer of ~1.8 nm is grown at the Ti/Si interface by depositing Ti on Si(111)-7×7 surface at RT. The grown Ti is a polycrystalline, but highly oriented with the substrate.

2) C54 $TiSi_2$ can be grown on Si(111) by *in situ* annealing at 750℃ for 10 min.

3) A thin single crystal-like Si overlayer with [111] direction can be grown on silicide by *in situ*

annealing Ti(10 ML)/Si sample prepared at 550℃ at ~900℃.

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