Coexistance of C40 and C54 $TiSi_2$ during the solid state reaction of Ti/Mo/Si system

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Abstract The effect of a 0.9 nm Mo interlayer at the interface of Ti film deposited on a Si substrate on phase formation of $TiSi_2$ during annealing has been studied by using transmission electron micro-diffraction technique. When Ti/Mo/Si was annealed at low temperature as 550°C for 30 min in Ar ambient, a metastable phase, i.e., hexagonal C40 $TiSi_2$, and the equilibrium phase, i.e., orthorhombic C54 $TiSi_2$, were both detected. The experimental patterns of the C40 and C54 compare well with the simulated ones.

Keywords Transmission electron micro-diffraction, Phase of $TiSi_2$, C54, C40

CLC numbers TN304.1+2, TN304.2+6, TN305.3, O472+.1

1 INTRODUCTION

The so called "fine line effect" would raise the temperature of the C54 $TiSi_2$ formation in submicron Si line (<0.5 μm), in which the density of nucleaton sites is lower than that in bulk Si material. It was well established[1~5] that the introduction of refractory metals (RMs) such as Mo, Ta, Nb, W into Ti-Si system can eliminate such "fine line effect" of C54 $TiSi_2$ formation by reducing the formation temperature of C54 $TiSi_2$ phase by 100-150°C. However, the mechanism of the enhancement of refractory metals remains to be unclear. Intensive studies[1~7] of the enhancement mechanism were carried out in the past several years. The template mechanism proposed based on sheet resistance measurements in combination with XRD[1,2] has become one of the most probable candidates for the effect of refractory metal on C54 $TiSi_2$ based on the similarity of crystallographic structure between C54 $TiSi_2$ and C40 or C11b $(RM_x, Ti_{1-x})Si_2$, which acts as the seeds for the direct formation of C54 $TiSi_2$. C54 is a $TiSi_2$-type orthorhombic structure with unit-cell dimensions (in 0.1 nm) of a=8.27, b=4.8 and c=8.55, C40 is a $CrSi_2$-type hexagonal of a=4.43 and c=6.38 and C11b is a $MoSi_2$-type tetragonal of a=3.21 and c=7.83.[3]

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The most characteristic features of the C54, C40 and C11b structures are the "close packed" hexagonal plane of atoms. If the hexagonal plane is stacked with different sequences of ABCDA$\cdots$, ABCA$\cdots$, ABA$\cdots$, respectively, the crystalline structures of C54, C40, C11b will be generated.[3] Thus the growth of C54 $TiSi_2$ on C40 or C11b (RM_x, Ti_{1-x})Si_2 is expected. Apart from the observation of direct formation of C54 $TiSi_2$ on C40 (RM_x, Ti_{1-x})Si_2 interlayer, direct growth of metastable C40 $TiSi_2$ on C40 $TaSi_2$ or (Ta, Ti)Si_2 interlayer was also detected by XRD[8] at lower annealing temperature of 525°C. Coexistance of C54 and C40 $TiSi_2$ was also observed by HRTEM[7] in the Ti-Si system with Ta interlayer by rapid thermal annealing at 650°C. The observation of the C40 $TiSi_2$ at low temperature and the coexistance of the C40 and C54 $TiSi_2$ at higher temperature were both attributed to the template phenomenon mentioned above. Since (Mo,Ti)Si_2 shares the same structure as (Ta, Ti)Si_2, i.e., C40, C40 $TiSi_2$ and/or coexistance of the C54 and C40 $TiSi_2$ should be possible also in a Ti-Si system with Mo interlayer if the template mechanism governs the kinetic process. However, no previous C40 $TiSi_2$ was reported in Ti-Si system with Mo interlayer up to now. By replacing Ta with Mo interlayer, we will show the coexistance of C54 and C40 $TiSi_2$ in the vicinity of interfacial C40 (Mo,Ti)Si_2 at low temperature of 550°C by cross-sectional transmission electron microscopy (XTEM) in combination of electron micro-diffraction analysis. Therefore, the results here confirm the template mechanism governing the enhancement effect of the refractory metals on C54 $TiSi_2$ formation.

2 EXPERIMENTS

In this experiment, 0.9 nm Mo film and then 50 nm Ti film were deposited by means of electron-beam evaporation without breaking the vacuum on lightly doped Si (100) followed by furnace annealing in purified Ar at 550°C for 30 minutes. Cross-sectional transmission electron microscopy (XTEM) and energy dispersive x-ray spectrometry (EDS) with an electron beam diameter of 6−25 nm were carried out to determine the phase of individual crystals and their composition. The crystals having diameters of at least 20 nm are chosen for a micro-diffraction study. Phase identification was carried out by comparing experimental patterns with the simulated ones generated by the plane section of all the possible reciprocal lattices of C49, C54, C40, C11b and $Ti5Si_3$ phases.

3 RESULTS AND DISCUSSION

During annealing Ti/Mo/Si at 550°C for 30 min, the Mo interlayer reacts with Si together with Ti to form Mo containing ternary silicide at the interface firstly and then the formation of binary Ti silicide occurs through continuous Si supply from the Si substrate. Fig.1 shows a typical cross-sectional bright-field image for this sample.

The layer structure has been determined to be Ti-rich silicide/$TiSi_2$/(Mo,Ti)Si_2/Si.[9] The EDS result[9] shows that the bright part corresponds to $TiSi_2$ and (Mo,Ti)Si_2, whereas the dark part to the Ti-rich silicide. The dark part in Fig.1 is due to higher electron scattering amplitude of Ti comparing to that of Si.[10]

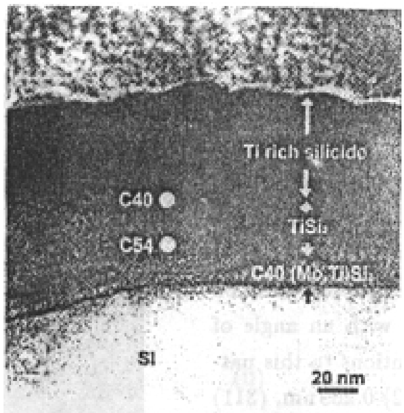


Fig.1 Cross-sectional bright-field image showing the structure of the silicide layers in the sample after annealing at 550°C for 30 min

Fig.2a shows a micro-diffraction pattern obtained at a particular crystal with 0.1 atomic ratio of Mo to Ti located in the region of (Mo,Ti)Si_2. The two marked diffraction spots in Fig.2a were measured to be 0.191 and 0.234 nm with an angle of about 65° between them, corresponding to the reflections ($2\overline{1}\overline{2}$) (0.191 nm) and (110) (0.235 nm) of

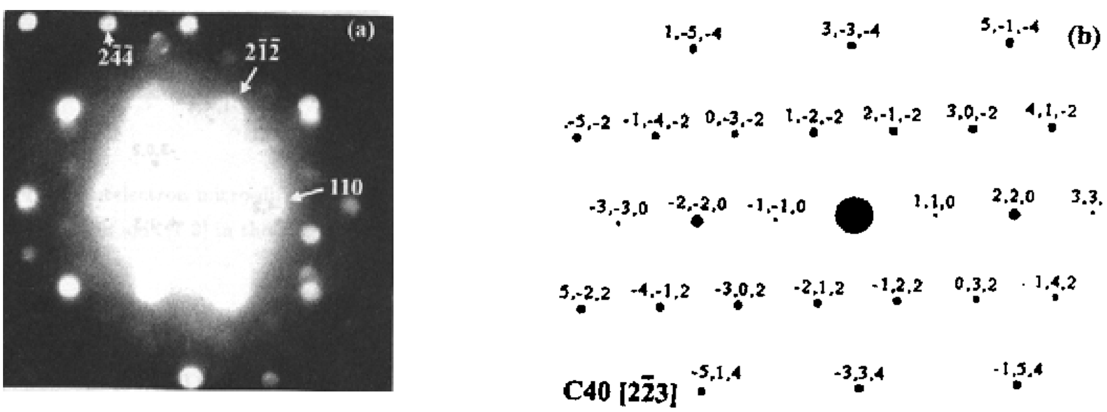
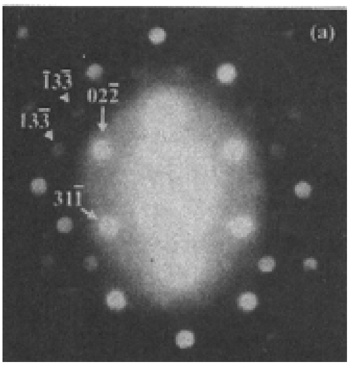
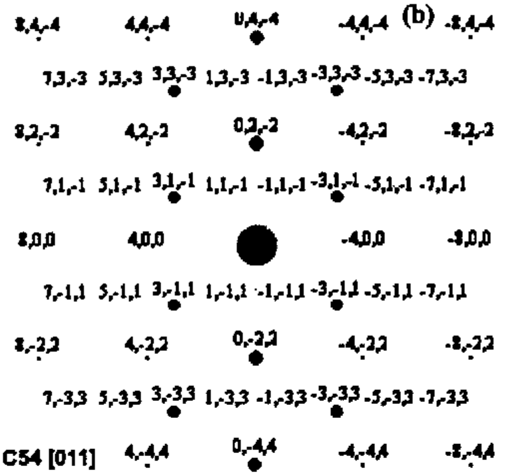


Fig.2 (a) Electron micro-diffraction pattern for a C40 grain with the zone axis[2,3] in the Mo-bearing region close to the interface of silicide/Si and (b) its simulated pattern generated by the plane section of C40 reciprocal lattice perpendicular to the electron beam

C40 (Mo,Ti)Si_2, respectively, with an angle of 66.06°.[10] A simulated pattern is shown in Fig.2b. Thus, the pattern in Fig.2a is assigned to C40 (Mo,Ti)Si_2 oriented in the $[2\bar{2}\bar{3}]$ direction. The appearance of the reflection $(2\bar{4}\bar{4})$ is due to the double diffraction effect. C11b $MoSi_2$, which acts as a template for epitaxial formation of C54 $TiSi_2$, was detected by HRTEM in the case of Mo implantation into Si substrate prior to Ti deposition followed by the rapid thermal annealing process.[3] However, no C11b $MoSi_2$ has been found by micro-diffraction pattern in the (Mo,Ti)Si_2 region.

Two types of $TiSi_2$ crystals, i.e., C54 and C40 $TiSi_2$ have been found in the bright region marked in Fig.1. Fig.3a shows an electron micro-diffraction pattern obtained at a crystal located in the $TiSi_2$ region near to the C40 (Mo,Ti)Si_2. Two bright spots were measured to be 0.213 nm and 0.233 nm with an angle of 55.9°. Two possible solutions to this pattern are C54 [011] {(022) 0.209 nm, (311) 0.230 nm, 56.6°}[11] and C40 [213]{(213) 0.221 nm, (120) 0.234 nm, 56.12°}[10]





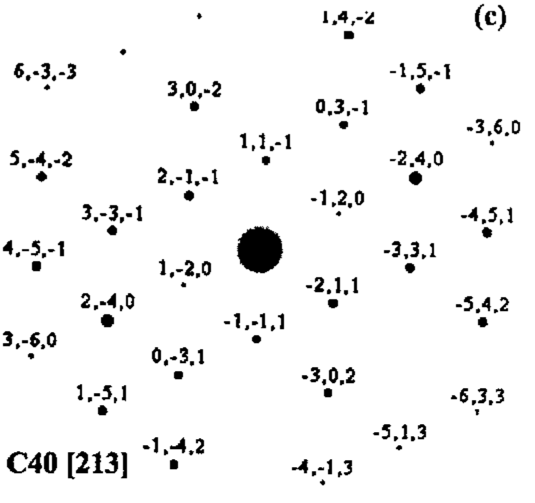


Fig.3 (a) Electron micro-diffraction pattern for a C54 TiSi2 grain with the zone axis [011] in the bright region of Fig.1 close to the interfacial Mo-bearing silicide and (b) its simulated pattern. (c) Other possible solution to the experimental pattern is C40 [213]. If the dark spots and the bright ones are considered, C54 [011] is the only solution to the experimental pattern

within the systematic error of micro-diffraction (<10%). Their simulated patterns are shown in Fig.3b and 3c, respectively. However, if the whole experimental pattern, including the bright and dark sports, is considered, C54 [011] becomes the only suitable solution. Therefore, the pattern of the observed crystal is assigned to be C54 phase oriented along [011] direction.

The micro-diffraction pattern shown in Fig.4a obtained in the bright region of Fig.1 is assigned to the C40 phase along the zone axis.[1,3,4] The marked spots were measured to be 0.222 nm and 0.201 nm with 78.44° angle between them, which correspond to the reflections from the plane (111) (d=0.221 nm) and plane (212) (0.191 nm)[10] with an angle of 79.4° of C40 phase oriented along.[1,3] Fig.4b shows the simulated pattern of C40.[1,3] The metastable C40 $TiSi_2$ was also identified in a similar system but with a Ta interlayer between Ti and Si,[7,8] where the growth of C40 $TiSi_2$ occurred as a result of epitaxy on C40 (Ta,Ti)Si_2. These results show that in the presence of a 0.9 nm thick interfacial Mo, C40 (Mo,Ti)Si_2 forms first at the interface and then both C54 and C40 $TiSi_2$ grow as a result of the template effect, after 550°C annealing. At the same time, we can not find C49 $TiSi_2$ in the sample.

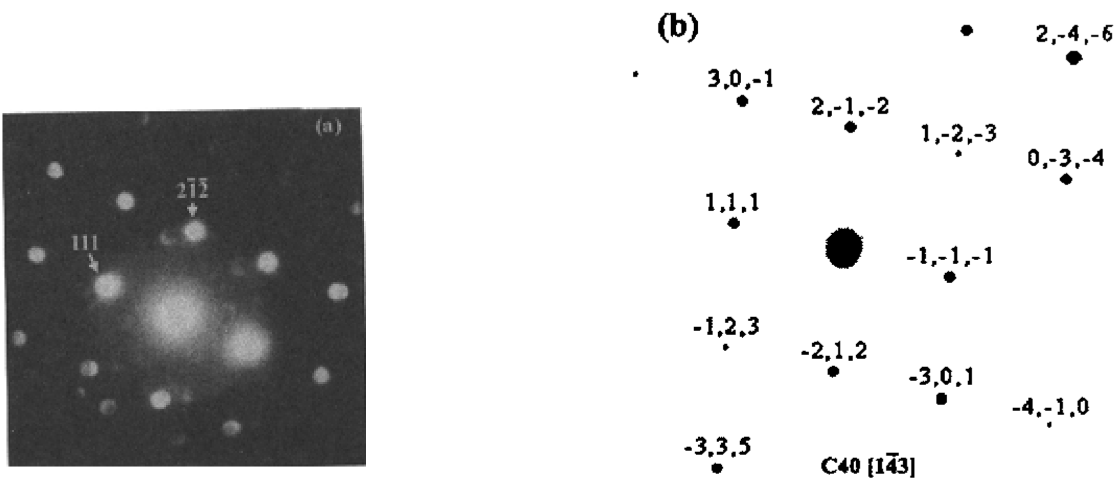


Fig.4 (a) An electron micro-diffraction pattern for an intermediate C40 TiSi2 grain with the zone axis [1 3] in the bright region of Fig. 1 and (b) its simulated pattern

4 DISCUSSION

After annealing the sample of 50 nm Ti/ 0.9 nm Mo/ Si (100) at 550°C for 30 min, C40 (Mo,Ti)Si_2 was found at the interface of silicide/Si in the partially reacted sample. Both metastable C40 $TiSi_2$ and equilibrium C54 $TiSi_2$ were detected near to the C40

$(Mo,Ti)Si_2$ without C49 $TiSi_2$ detected. The obtained locally findings here confirm the template mechanism.

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12 Standard JCPDS diffraction pattern 35-785 (orthorhombic $TiSi_2$), JCPDS-International Center for Diffraction Data, PDF-2 Database. 12 Campus Boulevard, Newton Square, PA 19073-3273, USA