Vol.12 No.3 NUCLEAR SCIENCE AND TECHNIQUES August 2001

Annealing behavior of ultrathin Mo layer located at interface or on surface of Ti-Si system

ZHANG Zhi-Bin[1], ZHANG Shi-Li[2], ZHU De-Zhang[1], XU Hong-Jie[1]

[1] *(Laboratory of Nuclear Analyses and Techniques, Shanghai Institute of Nuclear Research, The Chinese Academy of Sciences, Shanghai 201800)*

[2] *(Kungliga Tekniska Högskolan, Department of Electronics, Electrum 229, SE-164 40 Kista, Sweden)*

Abstract Annealing behavior, at different annealing temperatures, of an ultrathin Mo layer located between a Ti film and Si substrate or deposited on the top of surface of a Ti film was investigated by Rutherford backscattering spectrometry (RBS), cross-sectional transmission electron microscopy (TEM) and energy dispersive X-ray spectrometry (EDS). In a Ti/Mo/Si structure, partially reacted film with layer structure of Ti-rich silicide/$TiSi_2$/(Mo, Ti)Si_2 on a Si substrate was formed after 550°C annealing for 30 min. The ratio of Mo to Ti in (Mo, Ti)Si_2 layer decreases from near Si substrate upwards and becomes zero at about 20 nm away. In a Mo/Ti/Si structure, the surface Mo layer enhances the Si diffusion from the substrate during annealing. Mo bearing Ti rich silicide exists on the surface until 600°C and then converts to (Mo, Ti)Si_2 after 650°C annealing, and the atomic ratio of Mo to Ti decreases from the top surface into Ti silicide film, and becomes zero at about 30 nm away from the surface. In both cases of interface Mo and surface Mo layer, the atomic ratio of Mo to Ti in the region of (Mo, Ti)Si_2 was found to be very low, with an average value of less than 0.2. Low content of Mo in Mo containing ternary silicide leads easily to the formation of the stable phase of C54 (Mo, Ti)Si_2, which acts as a template for the formation of C54 $TiSi_2$ beneath when Mo is deposited on the surface.

Keywords Silicidation, $TiSi_2$, (Mo,Ti)Si_2

CLC numbers TN304.1$^+$2, TN304.2$^+$6, TN305.3, O485 A

1 INTRODUCTION

$TiSi_2$ has been widely used in Si-based very large scale integration (VLSI) technology owing to its low resistivity, high thermal stability and technological maturity[1,2]. $TiSi_2$ usually exists in two phases. One is the metastable base-centered orthorhombic crystallographic structure (C49) with resisitivity of 50~70 $\mu\Omega$cm and the other is the equilibrium face-centered structure (C54) with resistivity of 15~20 $\mu\Omega$cm. The C54 $TiSi_2$

Supported Partly by the National Natural Science Foundation (No. 19910131370)

Manuscript received date:2001-02-01

of low resistivity is desired in microelectronic devices. Metastable C49-$TiSi_2$ forms first at 300°C~550°C and higher temperature of about 700°C is needed for the formation of equilibrium C54 $TiSi_2$ through transition of C49-C54. However, the temperature for the transition of C49-C54 will be increased in narrow Si line with width smaller than 0.5μm due to reduced density of C54 $TiSi_2$ nucleation sites[3]. It is well known that the formation of C54 $TiSi_2$ will be enhanced by the introduction of refractory metal (such as Mo, Ta and Nb) into a Ti-Si system, either by ion implantation into Si prior to Ti deposition, by deposition as an interposed layer between Ti and Si, or by co-deposition with Ti as an alloy film[4~7]. Intensive studies including experimental and theoretical works have been focused on mechanisms of the enhancement effect of refractory metal on the formation of C54 $TiSi_2$ [5,8~11]. Template effect was proposed to account for the enhancement effect by refractory metal on C54 $TiSi_2$ formation, in which the formation of C40 (Mo, Ti)Si_2 is invoked for the direct formation of C54 $TiSi_2$ since C40 and C54 lattices share the same atomic arrangement in their stacking planes[5,6]. It is obvious that the structure of (Mo, Ti)Si_2 is the critical factor for its role as seeds for C54 $TiSi_2$ nucleation. The thermodynamic equilibrium phase of (Mo, Ti)Si_2 is either C40 or C54, which is related to the atomic ratio of Mo to Ti[12,13]. Both C40 and C54 (Mo, Ti)Si_2 will enhance the formation of C54, $TiSi_2$ due to the template effect, even a Mo layer locates at surface[9,11]. On the other hand, phases of Ti rich silicide, such as Ti_5Si_4, Ti_5Si_3 and TiSi, existing in partially reacted film formed at low temperature, are also important for the formation of $TiSi_2$ [14-16].

By investigating the annealing behavior of Mo layer within the Ti-Si system, the present paper focuses on the Mo redistribusion after annealing. The result here will be beneficial to shed a light on the formation of Mo containing ternary silicide.

2 EXPERIMENTAL

In this experiment, Ti and Mo films were deposited with different sequences on lightly doped Si (100) by electron-beam evaporation without breaking the vacuum. Two sets of samples with different structures were prepared. One is 50 nm Ti/0.9 nm Mo/Si which is denoted as sample I (Mo at interface) and the other is 1 nm Mo/44 nm Ti/Si which is denoted as sample S (Mo on surface). A 48 nm Ti on Si substrate without Mo deposition was also prepared as a reference sample denoted as sample N. All the samples were annealed in a diffusion furnace in purified Ar at 550°C to 650°C for 30 min. Solid-state interactions of Ti, Mo and Si were then characterized mainly by Rutherford backscattering spectrometry (RBS) with a 2 MeV $^4He^+$ beam with large incident angles, such as 50°, 70°, to improve depth resolution and avoid the plane channeling effect. By resorting to cross-sectinal transmission electron microscopy (TEM) and energy dispersive

X-ray spectrometry (EDS) with an electron beam of 6~9 nm in diameter, a study of the local change of the atomic ratios of (Ti+Mo) to Si and of Mo to Ti inside the silicide film was carried out.

3 RESULTS AND DISCUSSION

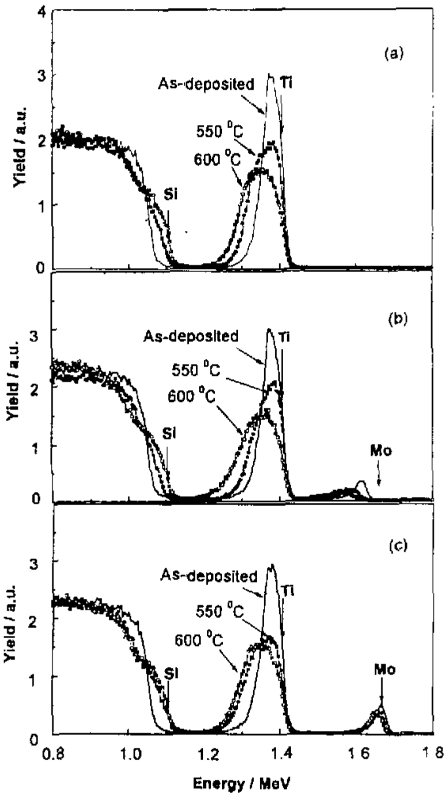

Fig.1 RBS spectra for the silicide formation in (a) sample N, (b) sample I, (c)sample S The spectra for the samples annealed at 650 and 700°C for 30 min (not shown) are almost identical to that for the sample at 600°C for 30 min

During annealing of the Ti/Si sample, formation of the Ti riched silicides begins, followed by the growth of $TiSi_2$, through the continuous diffusion of Si atoms from the substrate. Ti silicide formation in the three sets of samples (N, I and S) with respect to annealing temperature could be drawn from RBS, shown in Fig.1. The formation of $TiSi_2$ has not completed at 550°C in the three sets of samples, leading to partially reacted silicide films. If increasing the temperature to 600°C, the $TiSi_2$ formation seems to be almost completed through the entire film because the curve of RBS remains unchanged when annealing temperature was further increased (not shown in Fig.1).

By measuring the Si signal in the RBS spectra of the partially reacted silicide film at 550°C, the thickness of the $TiSi_x(x \approx 2)$ layer in sample I is calculated to be about 65 nm. For simplicity the $TiSi_x(x \approx 2)$ is denoted as $TiSi_2$ layer in sample I which is thinner than those of sample N and sample S. The $TiSi_2$ layer in sample I is thinner because of the hindrance of Si diffusion from silicon substrate to react with Ti by the interfacial Mo containing silicide layer. By comparing the Si to Ti signals in Fig.1, it was found that the Si diffusion seems to have been greatly enhanced by the Mo surface layer in sample S, resulting in a thicker layer of the $TiSi_2$ layer in this sample.

During annealing of sample I, the Si atoms diffusion from the Si substrate through the interface Mo layer to react with Ti led to the consecutive shifts of the Mo peak to lower energy (Fig.2). The change of Mo peak shape is due to the redistribution of Mo during the formation of Mo containing ternary silicide.

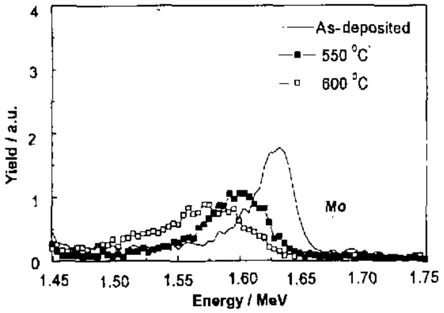

Fig.2 Partial RBS spectra which is the Mo signal of Fig.1b showing Mo redistribution in sample I after annealing at 550°C and 600°C for 30 min

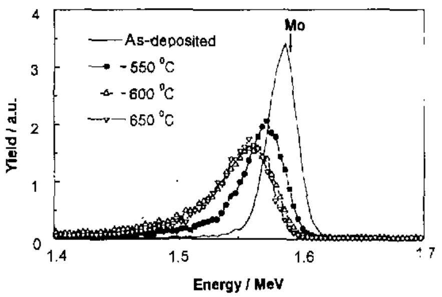

Fig.3 Partial RBS spectra showing Mo redistribution after annealing (a) at 550°C~650°C for 30 min. To enhance the depth resolution for the Mo signal, an incident angle of 70° was used

For sample S, Si and Ti are believed to have reached the top surface since their signals stem from their surface positions after annealing, but the Mo peak leaves away a little from its surface position to lower energy (Fig.3). The phenomenon indicates that a very thin layer containing Si and Ti but free of Mo was formed on the surface, which was confirmed by XPS results, whereas the oxidation layer consisting of SiO_2 and TiO_2 but free of Mo element was formed on free surface[17]. The shape of Mo peak also indicates the Mo redistribution in the surface Mo containing ternary silicide after annealing. The Mo distribution is found to keep almost steady after 600°C annealing.

Fig.4 shows the cross-sectional transmission bright field morphology of partially reacted film of sample I after 550°C annealing. The whole silicide film is measued to be about 90 nm. An EDS measurement was performed vertically and laterally in the film at the positions marked by the white points in Fig.4 to obtain the composition information, as summarized in Table 1. It is found that Si content in the entire silicide layer reduces consecutively from the interface near to Si substrate to the top surface. In the bright region from A to C of about 60 nm thick, $TiSi_2$ formation has been almost completed, which is in agreement with the RBS result presented above. The Ti rich silicide layer exists above the $TiSi_2$, i.e., in the dark region in the film in Fig.4 exists the Ti rich silicide layer. At position A, the effect from the Si substrate leads to a smaller value of the atomic ratio of metal (Mo+Ti) to Si. Increasing the anealing temperature to 600°C, the entire silicide layer grew to be about 110 nm thick due to the further formation of $TiSi_2$.

Mo was found to stay still at the interface region close to the Si substrate after annealing, and the Mo content varied greatly when measured at position A1 to A3 with atomic ratio of Mo to Ti between 0.04 and 0.23. The atomic ratio of Mo to Ti has a decreasing tendency with 0.13 at the interface close to the substrate and 0 at about 20 nm away. The average ratio of Mo to Ti is very low, estimated to be less than 0.2 in the region containing Mo.

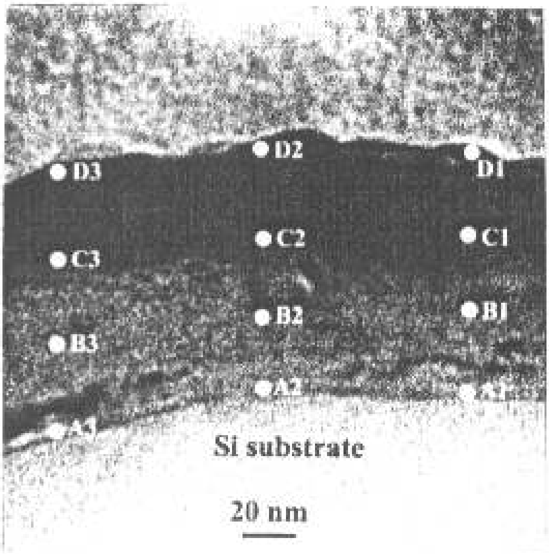

Fig.4 Transmission bright field morphology of sample I annealed at 550°C. An EDS measurement was carried out vertically and laterally to show the distribution of Mo, Ti and Si in the film (see text) at the position marked by the letters from A to D and by the Arabic numerals from 1 to 3 thickness

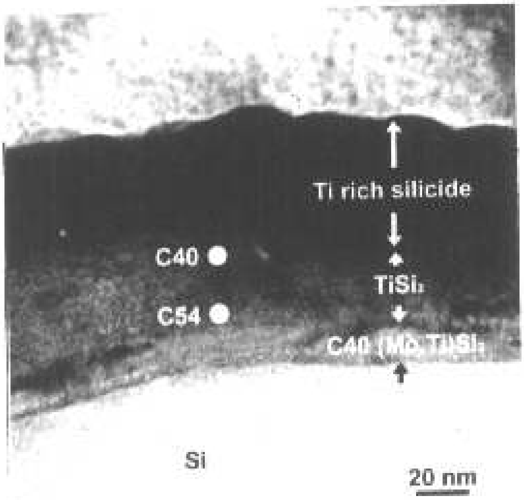

Fig.5 Transmission bright field morphology of sample S annealed at 600°C. An EDS measurement was carried out vertically to show the ratio of Mo to Ti in selected areas close to the surface (see text) at the position marked by the letters from A to C. In a similar selected area close to surface of sample S at 650°C, the EDS was performed vertically at the similar position from A to D

Fig.5 shows the layer structures of sample S after annealed at 600°C. An oxidation layer of about 10 nm forms on top of the silicide layer. The entire silicide film is about 120 nm thick. At the positions marked by A, B and C near to the surface, the ratios of (Ti+Mo) to the Si and of Mo to Ti are also summarized in Table 1. The measured value of the atomic ratio of metal to Si at position A is 0.4, which is the indication of $TiSi_2$. In the region between point B and C, the EDS result shows about 15 nm thick metal rich silicide layer close to the surface oxidation layer. A Ti_5Si_3 phase has been detected by glancing angle XRD in the same sample[11]. Therefore, the value of 1.25 of the ratio of (Ti+Mo) to Si at position C indicates that about 10 nm (Mo, Ti)$_5$Si$_3$ remains at the region close to the surface oxidation layer.

The ratio of Mo to Ti between position B and C is low, i.e., 0.08~0.09, and reduces drastically to be 0.01 at position A. Therefore, while most of Mo locate in metal riched silicide just beneath the surface oxidation layer, a small amount of Mo is imbedded into underneath $TiSi_2$.

If the annealing temperature is raised to 650°C, the change of Mo content has a similar tendency as that of sample S annealed at 600°C. (see Table.1) However, the atomic ratio of (Mo+Ti) to Si becomes over 0.4 from A to C, indicating the conversion of the remaining (Mo, Ti)$_5$Si$_3$ layer at 600°C to (Mo,Ti)Si$_2$ at 650°C. At positions from C to D, the ratio of Mo to Ti reduces obviously from 0.16 to 0.08. This result is in agreement with both the RBS result presented above and XPS result. Similarly, all values of Mo to Ti ratios measured were found to be very low, which possibly makes the (Mo,Ti)Si$_2$ with C54 structure a stable phase due to thermordynamic reason[13]. Once formation of C54 (Mo, Ti)Si$_2$ occurs firstly, transition of C49 to C54 $TiSi_2$ is expected to take place downwards induced by the surface C54 (Mo, Ti)Si$_2$ [11]. C54 (Mo, Ti)Si$_2$ acts as a templete for the enhanced transition of C49 to C54 $TiSi_2$.

4 CONCLUSIONS

Different effects of an ultrathin Mo layer located between a Ti film and Si substrate or on the free surface of a Ti film on the diffusion of Si and on the annealing behavior of the Mo layer were investigated by Rutherford backscattering spectrometry (RBS), cross-sectional transmission electron microscopy (TEM), and energy dispersive X-ray spectrometry (EDS). It was found that the interface Mo layer hinders the diffusion of Si during annealing, whereas the surface Mo layer enhances the diffusion of Si. In Ti/Mo/Si structure, partially reacted film with a layer structure of Ti-rich silicide/$TiSi_2$/(Mo,Ti)Si$_2$ on Si substrate was formed after 550°C annealing for 30 min. The ratio of Mo to Ti in (Mo, Ti)Si$_2$ layer decreases continuously from near Si substrate upwards in the region of (Mo, Ti)Si$_2$. In Mo/Ti/Si structure, Mo bearing Ti-rich silicide exists on the surface until 600°C and then converts to (Mo, Ti)Si$_2$ after 650°C annealing. The atomic ratio of Mo to Ti decreases continuously from the surface into Ti silicide film and becomes zero at about 30 nm away from the surface. In both cases of interface Mo and surface Mo layers, atomic ratio of Mo to Ti in the region of (Mo, Ti)Si$_2$ was found to be very low, with average value of less than 0.2.

Table 1 Atomic ratios of Metal, i.e., (Mo+Ti), to Si, and those of Mo to Ti obtained by EDS measurements vertically and laterally at positions marked by letters from A to D and Arabic numerals from 1 to 3 of sample I at 550°C shown in Fig.4. Ratios of Mo to Ti in a selected area close to the surface of sample S at 600°C as shown in Fig.5 and at the similar positions in a selected area close to the surface of sample S at 650°C were also obtained by EDS.

Sample	Atomic ratio		Position			
			A	B	C	D
I (550°C)	Metal/Si	1	0.29	0.45	0.87	11
		2	0.37	0.43	1.34	11
		3	0.34	0.41	0.93	12
	Mo/Ti	1	0.04	0	0	0
		2	0.19	0	0	0
		3	0.23	0	0	0
S(600°C)	Metal/Si		0.40	0.80	1.25	
	Mo/Ti		0.01	0.08	0.09	-
S(650°C)	Metal/Si		0.44	0.46	0.43	0.38
	Mo/Ti		0.01	0.12	0.16	0.08

References

1 Roy R A, Cabral Jr C, Lavoie C. In:Advanced interconnects and contacts, edited by Edelstein D C, Kikkawa T, ÖztürkM C *et al.* Warrendale, Pennsylvania: Materials Research Society, 1999, 35~45

2 Gambino J P, Colgan G E. Mater Chem Phys, 1998, **52**:99

3 Lasky J B, Nakos J S, Cain O J *et al.* IEEE Trans. Electron Dev, 1991, **ED-38** 262

4 Mann R W, Miles G L, Knotts T A *et al.* Appl Phys Lett, 1995, **67**:3729

5 Mouroux A, Zhang S L, Kaplan W *et al.* Appl Phys Lett, 1996, **69**:975

6 Mouroux A, Zhang S L, Kaplan W *et al.* In: Advanced metallization for VLSI, ed by Tu K N, Mayer J W, Poate J M *et al.* Pittsburgh: Materials Research Society, 1996, 511~516

7 Cabral Jr C, Clevenger L A, Harper J M E *et al.* Appl Phys Lett, 1997, **71**:3531

8 Mouroux A, Zhang S L, Petersson C S. Phys Rev, 1997, **B56**:10614

9 Zhang S L. d'Heurle F M. Appl Phys Lett, 2000, **76**:1831

10 Ohmi S, Tung R T. J Appl Phys, 1999, **86**:3655

11 Zhang S L, Zhang Z B, Zhu D Z *et al.* J Appl Phys, 2001, **89**:1641

12 Goldschmidt H J. Interstitial alloys. London: Butterworths, 1967, 322-330.

13 Bónoli, F, Lannuzzi M, Leo Miglio. Appl Phys Lett, 1998, **73**:1964

14 Robert Beyers and Robert Sinclair, J Appl Phys. 1985, **57**:5240

15 Ma J S, Lin J C, Liu J H. Thin Solid Films, 1979, **64**:439

16 Zhang S L, Lavoie M, Cabral Jr C *et al.* J Appl Phys, 1999, **85**:2617

17 ZHANG Z B, Zhang S L, Zhu D Z *et al.* Nucl Sci Tech (China), 2002, **13**: *to be published*