# Atomic diffusion in annealed $Cu/SiO_2/Si$ (100) system prepared by magnetron sputtering*

Cao Bo(曹 博)[a)b)], Jia Yan-Hui(贾艳辉)[a)],
Li Gong-Ping(李公平)[a)†], and Chen Xi-Meng(陈熙萌)[a)]

[a)] *School of Nuclear Science and Technology, Lanzhou University, Lanzhou* 730000, *China*
[b)] *School of Nuclear Science and Engineering, North China Electric Power University, Beijing* 102206, *China*

(Received 7 October 2008; revised manuscript received 4 August 2009)

Cu thin films are deposited on p-type Si (100) substrates by magnetron sputtering at room temperature. The interface reaction and atomic diffusion of $Cu/SiO_2/Si$ (100) systems are studied by x-ray diffraction (XRD) and Rutherford backscattering spectrometry (RBS). Some significant results can be obtained. The onset temperature of interdiffusion for $Cu/SiO_2/Si(100)$ is 350 °C. With the annealing temperature increasing, the interdiffusion becomes more apparent. The calculated diffusion activation energy is about 0.91 eV. For the $Cu/SiO_2/Si$ (100) systems copper silicides are not formed below an annealing temperature of 350 °C. The formation of the copper silicides phase is observed when the annealing temperature arrives at 450 °C.

**Keywords:** diffusion, interface reaction, copper silicides

**PACC:** 6610C, 6822

## 1. Introduction

The metal-semiconductor interface has been extensively investigated in the past few decades in order to better understand the corrosion resistance of microelectronic devices, and for the understanding of catalytic materials.[1−7] Cu has low electrical resistivity, high and stress migration resistance, and high melting point. These properties make Cu a promising candidate as microelectronic interconnection. Moreover, when Cu is deposited on Si substrate, the interface reactions between Cu and Si contacts have attracted even more interest. However, under thermal annealing, the high reactivity between Cu and Si and its easy diffusion of Cu into Si substrate,[8,9] make device deteriorated and capability worsened. Therefore, it is necessary to find appropriate materials as an effective diffusion barrier between Cu and Si.

There are quite a number of materials which have been adopted as diffusion barriers against Cu, such as W, Ta, WN, TaN, TiN, TiSiN and TaC.[10−15] The diffusion and interface reaction of $Cu/SiO_2/Si$ (111) have been studied by our group.[16] In the present paper, the Si (100) surface covered with a thin native silicon oxide layer is used. The thickness of the native silicon oxide ($SiO_2$) layer is about 4 nm measured by ellipse polarization. The Cu thin films are prepared by magnetron sputtering followed by annealing at different temperatures. The behaviour of Cu atoms and the formation of copper silicides in Cu thin films are studied, by Rutherford backscattering spectrometry (RBS) and x-ray diffraction (XRD) analysis respectively.

## 2. Experiment

The p-type Si wafers with a resistivity of 8–13 $\Omega\cdot$cm were used as substrates for the deposition of Cu. The wafers were first boiled in a cleaning solution ($H_2O_2:H_2SO_4$ = 1:3) for 30 min and washed thoroughly with distilled water; then boiled in cleaning solution ($H_2O$:$H_2O_2$:HCl = 5:2:1) for 5 min and washed thoroughly with distilled water; finally the wafers were boiled in the aqua regia (HCL:$HNO_3$ = 3:1) for 20 min and washed with cold water and hot water (in cold water ten times, followed by washing in hot water ten times and in cold water fifteen times). The substrates were pull-dried at 200 °C for 2 h. The thickness of the $SiO_2$ layers on substrates was about 4 nm measured by ellipse polarization.

The Cu films were deposited on p-type Si (100) substrates by magnetron sputtering (Open Laboratory of Applied Magnetism, Lanzhou University).

*Project supported by the National Natural Science Foundation of China (Grant No. 10375028).
†Corresponding author. E-mail: ligp@lzu.edu.cn
© 2010 Chinese Physical Society and IOP Publishing Ltd

The system was pumped down to a pressure of $5.3\times10^{-5}$ Pa by molecular pump prior to deposition. During the deposition, the argon flow rate and rf power were maintained at about 14.0 SCCM and 50 W, respectively. The duration of the deposition was about 10 min, and the thickness of the resulting Cu films was controlled at about 100 nm. The samples were then annealed for 30 min in high-purity (99.999%) argon atmosphere at temperatures ranging from 300 °C to 700 °C, in a tubular annealing furnace.

The interdiffussion of Cu and Si was studied by RBS technique. The RBS measurement for all samples was carried out by using a 2×1.7 MV serial static accelerator (The Opening Laboratory of Ministry of Education in the Institute of Heavy Ions, Peking University). A beam of 2.0 MeV $^4He^+$ ions was used in the present work. An Au–Si surface barrier detector with an energy resolution of 18 keV was placed at a scattering angle of 165° to detect the scattered particles. Interface reaction was also investigated by XRD analysis (Philips, X'pert automated diffractometer) using monochromated Cu K–alpha radiation of 1.5406 Å (1 Å = 0.1 nm) for phase identification. The x-ray tube was operated at a voltage of 40 kV and a current of 60 mA.

## 3. Results and discussion

The RBS spectra for the samples before and after annealing at different temperatures are shown in Fig. 1. In the RBS spectra, the mark of Si denotes the highest energy of backscattering $^4He^+$ obtained from the surface where the collision between $^4He^+$ and Si occurred, the marked channel of Si is about 280. For as-deposited sample a clear separation of Cu (above channel No. 320) and Si (below channel No. 260) signals with practically zero yields in between is observed. The Cu/Si interface is very abrupt, which indicates that no reaction and/or formation of phase occurred during the preparation of the samples. The spectra features remain practically unchanged for the sample annealed at 300 °C. For the sample annealed at 350 °C, it is evident from the figure that broadening occurs in Cu and Si parts of the spectrum, that is, the Cu part of the spectrum extends below channel No. 320 and the Si part above channel No. 260. This shows that the interdiffusion of Cu and Si atoms occurs, though to a very small extent, after annealing at 350 °C for 30 min. Interdiffusion at the Cu/Si interface has also been observed at an annealing temperature of ∼ 230 °C in the case of ionized Cu cluster beam deposition on Si.[17] And compared with the Cu films deposited on Si (111) surface with native silicon oxide in our previous work,[16] the Cu films in the present work manifest the interdiffusion of Cu and Si that can be observed after annealing at 450 °C for 30 min. The RBS spectra of the samples annealed at 450 °C and 500 °C show that the Cu part of the spectrum broadens more towards below channel No. 320, and the Si part extends more towards above channel No. 260. Moreover, the intensity of Cu peak gradually becomes smaller with annealing temperature increasing. This is because more Cu atoms diffuse into Si substrates, react with Si atoms and form more copper silicides. This is also confirmed by XRD (below in Fig. 3). When the samples are annealed at 650 °C and 700 °C separately, an apparent step is seen in the channel of about No. 270. More copper silicides are formed when the samples are annealed at higher temperatures. This step arises from Si component in copper silicides.[16,18]

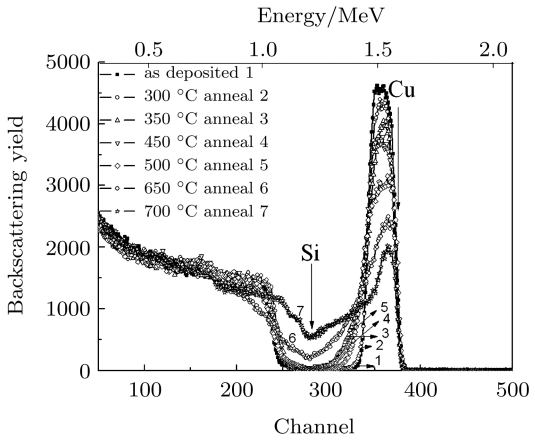



**Fig. 1.** 2.0 MeV $^4He^+$ backscattering spectra of Cu layer deposited on Si (100): (■) as-deposited; (○) annealed at 300 °C for 30 min; (△) 350 °C for 30 min; (▽) 450 °C for 30min; (◇) 500 °C for 30 min ; (⊙) 650 °C for 30 min; (☆) 700 °C for 30 min.

The diffusion coefficient ($D$) was calculated by using the relation $L^2 = Dt$, where $t$ is the annealing time and $L$ is the diffusion distance.[16,17,19] The average thickness of the Cu films was about 115 nm calculated from RBS spectra. The diffusion coefficients of the $Cu/SiO_2/Si$ (100) samples annealed at different temperatures were calculated. These results are shown in Table 1.

**Table 1.** Diffusion coefficients at different annealing temperatures.

| $T$/°C | 350 | 450 | 500 | 650 | 700 |
|---|---|---|---|---|---|
| $D$/cm$^2$·s$^{-1}$ | $1.296\times10^{-16}$ | $1.162\times10^{-15}$ | $6.330\times10^{-15}$ | $1.709\times10^{-14}$ | $1.202\times10^{-13}$ |

The diffusion coefficient can be expressed as

$$D = D_0 \exp(-\Delta E/K_{\rm B}T), \tag{1}$$

where $\Delta E$ is diffusion activation energy, $K_{\rm B}$ is the Boltzmann constant, $D_0$ is the diffusion constant, and $T$ is the annealing temperature. The relation between diffusion coefficient and annealing temperature can be obtained in Fig. 2. The calculated diffusion activation energy is 0.91 eV. It can be seen that the value is in the range (0.81–1.81 eV) reported by other groups.[20–23] Moreover, the value of Cu/$SiO_2$/Si (100) sample is smaller than that of the Cu/$SiO_2$/Si (111) sample reported.[16]

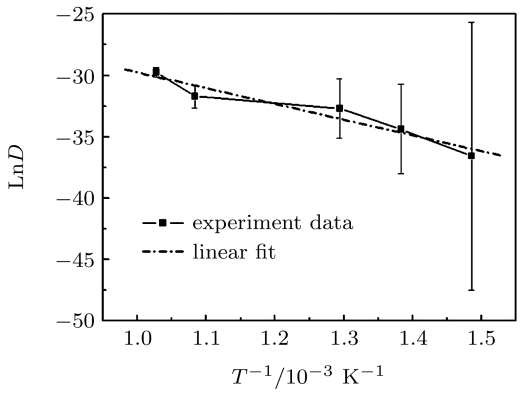



**Fig. 2.** Relationship between diffusion coefficient $D$ and annealing temperature.

The XRD patterns of the samples annealed at different temperatures are shown in Fig. 3. It is seen that there exist only Cu (111) and Cu (200) peaks, but no other peaks appeared when the annealing temperature was below 350 °C. It shows that the continuous Cu films were formed without forming copper silicides. As depicted in this figure, it can be seen that two new diffracted rays are present, corresponding to $Cu_3Si$ (300) and $Cu_3Si$ (030) after annealing at 450 °C for 30 min. It reveals that copper silicides were formed due to the reactions between the Cu layers and Si substrates. The Cu peaks disappeared when the sample was annealed at 500 °C, which meant that Cu was used up and followed by the formation of copper silicides. There are three peaks of copper silicides, i.e. $Cu_3Si$ (030), $Cu_3Si$ (300) and $Cu_3Si$ (311). When the annealing temperature reached 650 °C, the intensity of $Cu_3Si$ (012) peak became stronger. The samples annealed at 700 °C are found to form no other new phase comparing with that annealed at 650 °C. However, the intensities of $Cu_3Si$ (012) and $Cu_3Si$ (311) peaks become stronger than their original ones, which suggests that more interface reactions of Cu and Si took place than at lower annealing temperatures, and therefore more copper silicides were formed on their interface.

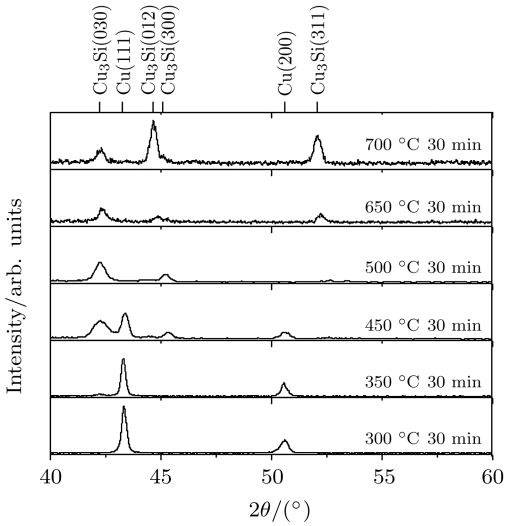



**Fig. 3.** XRD patterns of the samples annealed at 300 °C, 350 °C, 450 °C, 500 °C, 650 °C, and 700 °C, respectively.

For the Cu/$SiO_2$/Si (100) system, when it was annealed below 450 °C no copper silicides were formed. Copper silicides were formed only when the annealing temperature was 450 °C or more. But for the Cu/$SiO_2$/Si (111) system, when its annealing temperature was 500 °C, copper silicides were formed. And for the Cu/Si (100) system its annealing temperature was below 230 °C. It is determined by the orientations of the films and the substrates.[8,17] It is observed that there are $Cu_3Si$ (030) and $Cu_3Si$ (300), besides Cu peaks, when the annealing temperature was 450 °C. The Cu peak disappeared when the annealing temperature was 500 °C and above 500 °C. When the annealing temperature was 700 °C, there still existed $Cu_3Si$(030), $Cu_3Si$(012), $Cu_3Si$(300) and $Cu_3Si$(311) peaks. And the peak intensities of $Cu_3Si$ (012) and

$Cu_3Si$(311) annealed at 700 °C is larger than those annealed at lower temperatures. So $Cu_3Si$ is confirmed to be the dominant stable phase in the Cu/Si interface, among the annealing temperatures.

The formation of silicides is controlled by the interdiffusion of Cu and Si. Compared with the Cu/Si (100) system, the Cu/$SiO_2$/Si (100) system has a native silicon oxide layer. For the Cu/Si (100) system, copper silicides were formed at an annealing temperature of ∼200 °C.[8,9] For the Cu/$SiO_2$/Si (100) system, the existence of the native silicon oxide layer suppresses the interdiffusion of Cu and Si. It is because the native silicon oxide layer acts as a diffusion barrier and prevents the interdiffusion of Cu and Si. The Cu/$SiO_2$/Si (100) system needs more energy to surmount the diffusion barrier than the Cu/Si (100) system. That is to say, the diffusion and the interface reaction of Cu and Si in the Cu/$SiO_2$/Si (100) system are harder than in the Cu/Si (100) system at the same annealing temperatures. In fact, it is because the bond energy of Si–O bond (425 kJ/mol) is bigger than Si–Si bond (222 kJ/mol). It suggests that the interface reaction of Cu and Si in the Cu/$SiO_2$/Si (100) system takes the following steps: the Cu atoms meet the layer $SiO_2$, when the annealing temperature was high enough, the Si–O bond can break and the reaction of Cu and Si can take place. If the annealing temperature is not high enough, the Si–O bond will not break, and the reaction of Cu and Si will not occur.[24]

## 4. Conclusions

The Cu films on p-type Si (100) substrates are prepared by magnetron sputtering at room temperature. The interface reaction and the atomic diffusion of Cu/$SiO_2$/Si (100) are studied by RBS and XRD. The onset temperature of interdiffusion is 350 °C for the Cu/$SiO_2$/Si (100) system. With the increase of the annealing temperature, the interdiffusion becomes more apparent. The calculated diffusion activation energy for the Cu/$SiO_2$/Si (100) system is about 0.91 eV. The Cu/$SiO_2$/Si (100) system has a native silicon oxide layer compared with the Cu/Si system. The existence of the native silicon oxide layer suppresses the interdiffusion of Cu and Si. For Cu/$SiO_2$/Si (100) system, no copper silicides are formed when annealing temperature is below 350 °C. From XRD, the formation of the copper–silicide phase is observed when the annealing temperature reaches 450 °C.

## References


[1] Barth J V, Costantini G and Kern K 2005 *Nature* **437** 671
[2] Tsay J S, Fu T Y, Lin M H, Yang C S and Yao Y D 2006 *Appl. Phys. Lett.* **88** 102506
[3] Wu Y, Xiang J, Yang C, Lu W and Lieber C M 2004 *Nature* **430** 61
[4] Guo H, Zhang Y M and Zhang Y M 2006 *Chin. Phys.* **15** 2142
[5] Cao Y R, Ma X H, Hao Y, Zhang Y, Yu L, Zhu Z W and Chen H F 2007 *Chin. Phys.* **16** 1140
[6] Guo H, Zhang Y M, Qiao D Y, Sun L and Zhang Y M 2007 *Chin. Phys.* **16** 1753
[7] Ahn C H, Rabe K M and Triscone J M 2004 *Science* **23** 488
[8] Chang C A 1990 *J. Appl. Phys.* **67** 566
[9] Soltz L and D'Heurle F M 1990 *Thin Solid Films* **189** 269
[10] Imahori J, Oku T and Murakami M 1997 *Thin Solid Films* **301** 142
[11] Song S X, Liu Y Z, Mao D L, Ling H Q and Li M 2005 *Thin Solid Films* **476** 142
[12] Moriyama M, Kawazoe T, Tanaka M and Murakami M 2002 *Thin Solid Films* **416** 136
[13] Liu Y Z, Song S X, Mao D L, Ling H Q and Li M 2004 *Microelectron. Eng.* **75** 309
[14] Kuchuk A V, Ciosek J, Piotrowska A, Kaminska E, Wawro A, Lytvyn O S, Nowicki L and Ratajczak R 2004 *Vacuum* **74** 195
[15] Benouattas N, Mosser A, Raiser D, Faerber J and Bouabellou A 2000 *Appl. Surf. Sci.* **153** 79
[16] Cao B, Bao L M, Li G P and He S H 2006 *Acta Phys. Sin.* **55** 6550 (in Chinese)
[17] Takaoka G H, Fujita K, Ishikawa J and Takagi T 1989 *Nucl. Instr. Meth.* B **37/38** 882
[18] Sekar K, Satyam P V, Kuri G, Mahapatra D P and Dev B N 1993 *Nucl. Instr. Meth. B* **73** 63
[19] Poate J M, Turner P A and Debonte W J 1975 *J. Appl. Phys.* **46** 4275
[20] Stolt L and Dheurle F M 1990 *Thin Solid Films* **189** 269
[21] Chromik R R, Neils W K and Cotts E J 1999 *J. Appl. Phys.* **86** 4273
[22] Becht J G M, Van Loo F J J and Metselaar R 1988 *Reactivity of Solids* **6** 45
[23] Hong S Q, Comrie C M, Russel S W and Mayer J W 1991 *J. Appl. Phys.* **70** 3655
[24] Chang C A 1989 *J. Appl. Phys.* **66** 1163