Room temperature oxidation of $Cu/Si_{0.76}Ge_{0.24}$ annealed at 200 to 300°C

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Abstract

The Cu_3Si-catalyzed oxidation behavior of $Cu/Si_{0.76}Ge_{0.24}$ after annealing at a temperature of 200–300°C was studied using transmission electron microscopy (TEM). For the $Cu/Si_{0.76}Ge_{0.24}$ samples annealed at 200°C and followed by exposure in air for 1–4 weeks an SiO_2 layer embedded with precipitates containing Cu, Ge, Si, and O was formed on the surface of the $Cu_3(Si_{1-x}Ge_x)$ film. During exposure the Cu atoms released from $Cu_3(Si_{1-x}Ge_x)$ by oxidation diffused down to the residual $Si_{0.76}Ge_{0.24}$ film and subsequently the Si substrate to form new $Cu_3(Si_{1-x}Ge_x)$ and Cu_3Si, respectively. After exposure for 5–6 weeks not only the oxidation of the surface layer became severe but also the growth of the buried SiO_2 layer was initiated at the $Cu_3(Si_{1-x}Ge_x)/Cu_3Si$ interface. Concurrently, the Cu_3Si-catalyzed oxidation of Si by inward movement of the SiO_2/Si interface was also observed. As compared with the annealed Cu/Si samples the presence of Ge significantly lowered the oxidation rate of the annealed $Cu/Si_{0.76}Ge_{0.24}$ samples. Higher temperature annealing promoted the oxidation rate because of Ge segregation out of the $Cu_3(Si_{1-x}Ge_x)$ layer and the formation of a larger fraction of the $Cu_3(Si_{1-x}Ge_x)/Cu_3Si$ interface where the buried SiO_2 layer was initially formed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: $Cu_3(Si_{1-x}Ge_x)$; Room temperature oxidation; Ge segregation; Transmission electron microscopy

1. Introduction

As the device dimensions continue to shrink Cu is a potential material to replace Al for future metallization schemes because of its superior electrical conductivity and electromigration resistance [1]. Unfortunately, Cu is quite mobile in Si and its presence creates recombination centers which can reduce the minority-carrier lifetime [2]. The possible solution to this problem is the use of Cu_3Si or Cu_3Ge [3,4]. However, upon air exposure Cu_3Si reacts readily with oxygen at room temperature, while Cu_3Ge is stable [4–6]. Many studies on the Cu_3Si-catalyzed oxidation of Si have been made [7–13].

$Si_{1-x}Ge_x$ material offers the promise of greater carrier mobility and band gap engineering, and hence has potential applications in high-speed electronic and optoelectronic devices [14]. The formation of metal–$Si_{1-x}Ge_x$ ohmic or rectifying contacts is required for device applications. Recently, the interfacial reactions of metals such as Ni [15], Pt [16], Pd [17], Ti [18–20], Co [21,22], and Cu [23] on $Si_{1-x}Ge_x$ films have been studied. In these reactions, the growth of a ternary phase, e.g. $M(Si_{1-x}Ge_x)_2$, was generally accompanied by Ge segregation and the formation of agglomeration structure.

For the $Cu/Si_{1-x}Ge_x$ system Jaquez et al. [23] have shown that Ge plays an important role in slowing the rate of oxygen incorporation into the Cu germanosilicide. To date, as far as we know, the oxidation behavior for the $Cu/Si_{1-x}Ge_x$ system after annealing has not been detailed. In this paper, we report the evolution of room temperature oxidation in air for the $Cu/Si_{0.76}Ge_{0.24}$ system after annealing at a temperature of 200–300°C using transmission electron microscopy (TEM) in conjunction with energy dispersive spectrometry (EDS). A simultaneous study of the Cu_3Si/Si system was also conducted for comparison.

2. Experimental

$Si_{0.76}Ge_{0.24}$ films, about 150 nm thick, were grown at 550°C in an ultrahigh vacuum chemical vapor deposition system. A Cu layer, about 70 nm thick, was deposited onto the $Si_{0.76}Ge_{0.24}$ films at a rate of 0.1 nm/s in an electron gun deposition system. The base pressure was about 2.0×10^{-6} Torr. An amorphous Si overlayer, 10 nm thick, was subsequently deposited onto the Cu layer to protect the unreacted samples from oxidation during storage in a cham-

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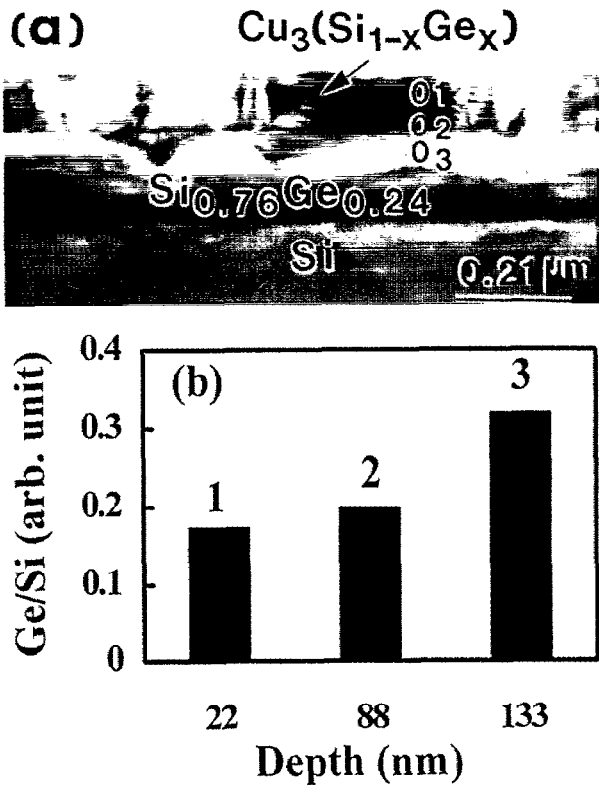*E-mail address:* wtlin@mail.ncku.edu.tw (W.T. Lin)

Fig. 1. (a) XTEM image and (b) the depth profile of Ge for the Cu/Si$_{0.76}$Ge$_{0.24}$ sample after annealing at 200°C. Ge/Si is the atomic concentration ratio, $x/(1 - x)$, in the Cu$_3$(Si$_{1-x}$Ge$_x$) and Si$_{1-x}$Ge$_x$ films.

Fig. 3. (a) XTEM image and (b) the Ge distribution in the Cu/Si$_{0.76}$Ge$_{0.24}$ sample after annealing at 300°C showing Ge segregation out of the Cu$_3$(Si$_{1-x}$Ge$_x$) grains to the surrounding Si$_{1-x}$Ge$_x$. Ge/Si is the atomic concentration ratio, $x/(1 - x)$, in the Cu$_3$(Si$_{1-x}$Ge$_x$) and Si$_{1-x}$Ge$_x$ films.

ber which was kept in a vacuum of approximately 2×10^{-2} Torr [12]. Furnace annealing was carried out in a vacuum of approximately 2.0×10^{-6} Torr. Phase formation and microstructures were observed by plan-view TEM and cross-sectional TEM (XTEM). The distribution of chemical species in the films was analyzed using EDS which was equipped with a field emission gun with an electron probe 1.2 nm in size. In order to minimize heating during XTEM sample preparation, which could promote the oxidation of
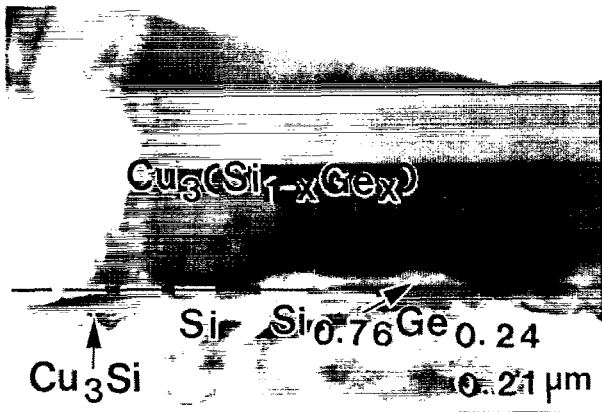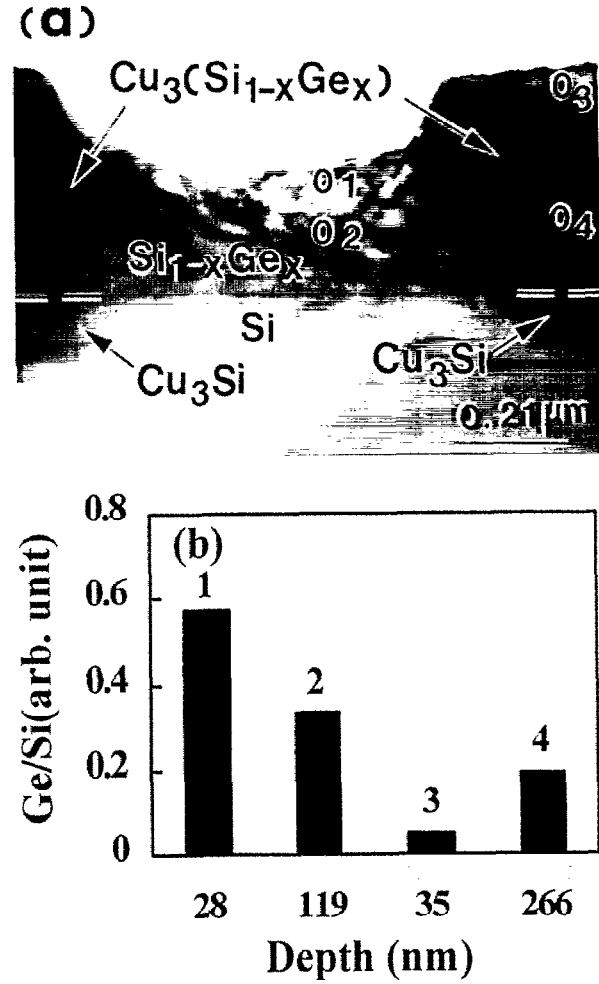
the samples, the epoxy for bonding the sample stack was cured at room temperature and ion milling of the samples was performed using the substrate holder cooled by liquid N$_2$.

3. Results and discussion

3.1. Vacuum annealing

For the samples annealed at 200°C η''-Cu$_3$(Si$_{1-x}$Ge$_x$) was formed from analysis of the electron diffraction pattern. EDS/XTEM analysis showed that the Ge/Si concentration ratio, $x/(1 - x)$, in the Cu$_3$(Si$_{1-x}$Ge$_x$) film was reduced, ranging from 0.14 to 0.22 along the film depth, while that in the unreacted Si$_{0.76}$Ge$_{0.24}$ layer remained unchanged, i.e. 0.32 as seen in Fig. 1. The reduction of Ge concentration in the germanosilicide was attributed to the capping Si layer (~ 10 nm). During annealing the capping Si layer was involved in the reactions between Cu and Si$_{0.76}$Ge$_{0.24}$ and hence
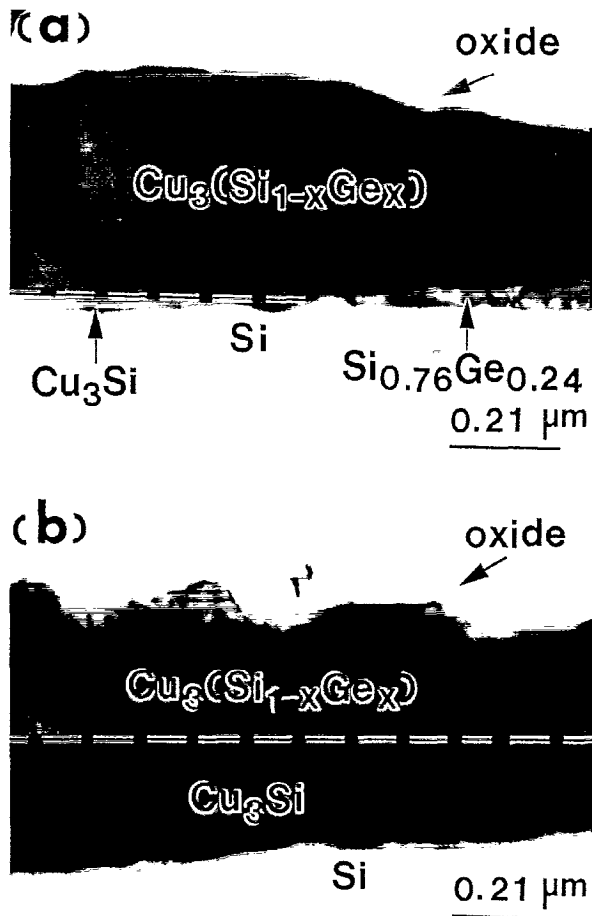

Fig. 2. XTEM image of the Cu/Si$_{0.76}$Ge$_{0.24}$ sample after annealing at 250°C.

Fig. 4. XTEM image of the Cu/$Si_{0.76}Ge_{0.24}$ sample annealed at 200°C and followed by exposure in air for (a) 2 and (b) 4 weeks showing that some Cu atoms released from $Cu_3(Si_{1-x}Ge_x)$ by oxidation moved to the Si substrate to form Cu_3Si and the thickness of the reacted region increased with the exposure time.

diluted the Ge concentration of the germanosilicide. For the samples annealed at 250°C most of the $Si_{0.76}Ge_{0.24}$ film was consumed and the reacted layer somewhat penetrated to the Si substrate as shown in Fig. 2. From EDS/XTEM analysis
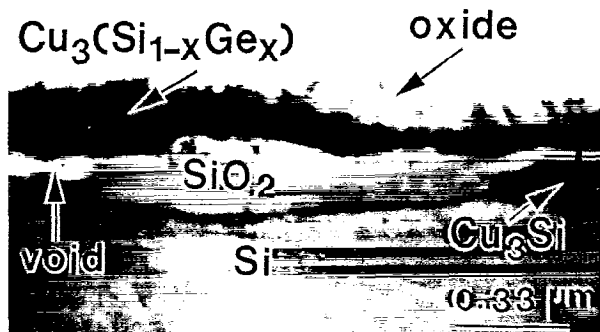
the reacted areas in Si were Ge free, revealing the formation of Cu_3Si. This result is reasonable since Cu is the dominant moving species in the formation of Cu_3Si and Cu_3Ge by thermal reactions of Cu on Si and Ge. respectively [24,25]. The Ge/Si ratio of the germanosilicide ranged from 0.14 to 0.39 along the film depth. For the samples annealed at 300°C most of the reacted layer penetrated to the Si substrate, forming $Cu_3(Si_{1-x}Ge_x)$ and Cu_3Si layers. Meanwhile, agglomeration occurred as shown in Fig. 3; Ge segregated out of the germanosilicide and diffused into the grain boundaries of the germanosilicide to react with Si and Ge from the substrate, forming Ge-rich $Si_{1-x}Ge_x$. Similar results have been observed in the Ti/$Si_{1-x}Ge_x$, Co/$Si_{1-x}Ge_x$, and Ni/$Si_{1-x}Ge_x$ systems [19,22,26]. The Ge/Si ratio of the $Cu_3(Si_{1-x}Ge_x)$ layer grown at 300°C ranged from 0.05 to 0.24 along the film depth. The heats of formation for Cu_3Si and Cu_3Ge are about −24 and −16 kJ/mol, respectively [27]. Those values suggest that Cu tends to react preferably with Si.

3.2. Room temperature oxidation

For the samples annealed at 200°C and then exposed in air for 1 to 4 weeks, an SiO_2 layer with precipitates containing Cu, Ge, Si, and O was formed on the surface of the germanosilicide. Both the average thicknesses of the oxide and of the reacted layer increased with the exposure time as shown in Fig. 4. Evidently, after exposure for 2 weeks the reacted layer had already moved to the Si substrate. It has been reported that the Cu atoms released by oxidation of Cu_3Si move readily to the Cu_3Si/Si or SiO_2/Si interfaces to form new Cu_3Si [7]. In the present study, the Cu atoms released from $Cu_3(Si_{1-x}Ge_x)$ by oxidation moved downward to the unreacted $Si_{0.76}Ge_{0.24}$ and Si to form $Cu_3(Si_{1-x}Ge_x)$ and Cu_3Si, respectively.

After exposure for 5–6 weeks, not only the oxidation of the surface layer became severe but also the formation of buried SiO_2 was initiated at the $Cu_3(Si_{1-x}Ge_x)/Cu_3Si$ interface as shown in Fig. 5. Concurrently, the oxidation of Si proceeding by inward movement of the SiO_2/Si interface was also observed. It is worth noting that voids are usually present in the buried SiO_2 layer. They may be formed by

Fig. 5. XTEM image of the Cu/$Si_{0.76}Ge_{0.24}$ sample annealed at 200°C and followed by exposure in air for 6 weeks showing that the buried SiO_2 was initially formed at the $Cu_3(Si_{1-x}Ge_x)/Cu_3Si$ interface and subsequently the oxidation of Si proceeded by inward movement of the SiO_2/Si interface.
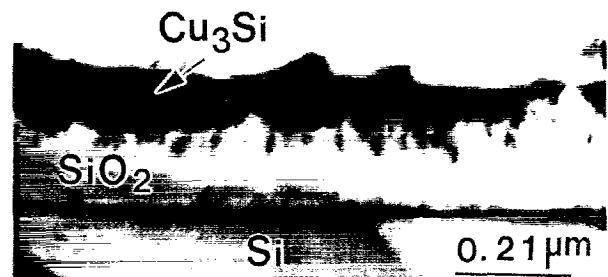

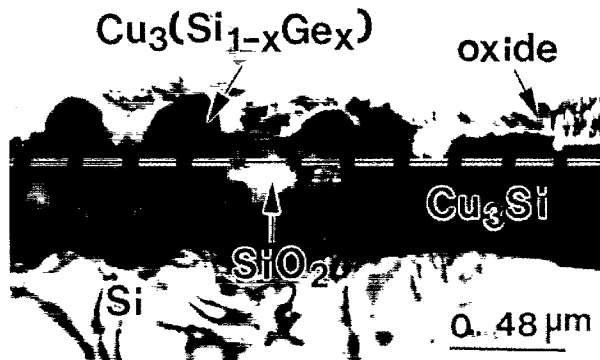Fig. 6. XTEM image of the Cu/Si sample annealed at 200°C and followed by exposure in air for 1 week.

Fig. 7. XTEM image of the Cu/Si$_{0.76}$Ge$_{0.24}$ sample annealed at 300°C and followed by exposure in air for 1 week.

Ar$^-$ milling. For the Cu/Si system annealed at 200°C and followed by exposure in air for 1 week a buried SiO$_2$ layer about 200 nm thick was formed as shown in Fig. 6. No voids were observed in the buried SiO$_2$ layer. The buried SiO$_2$ layer formed in the Cu/(Si$_{0.76-x}$Ge$_{0.24}$) system is not as dense as that formed in the Cu/Si system. Besides, the oxidation rate for the Cu/(Si$_{0.76-x}$Ge$_{0.24}$) system is evidently lower than that for the Cu/Si system. All these results may be explained in terms of the high stability of Cu$_3$Ge with respect to oxygen [4–6]. Molecular oxygen may be dissociated into atomic oxygen in the surface of Cu$_3$Si, allowing more rapid diffusion through the Cu$_3$Si and SiO$_2$ layers [7,9]. The presence of Cu$_3$Ge in the Cu$_3$(Si$_{1-x}$Ge$_x$) film may possibly decrease the diffusion flux of atomic oxygen and Cu through the Cu$_3$(Si$_{1-x}$Ge$_x$), Cu$_3$Si, and buried SiO$_2$ layers, and hence reduce the Cu$_3$Si-catalyzed oxidation rate. A clear explanation remains to be discovered.

For the Cu/Si system Liu and Chen [12] have reported that the Cu$_3$Si-catalyzed oxidation rate decreases with increasing annealing temperature because of grain size effects. In the present study, however, the Cu$_3$Si-catalyzed oxidation for the Cu/Si$_{0.76}$Ge$_{0.24}$ system was enhanced after higher temperature annealing. One example is shown in Fig. 7. This result is not surprising since after annealing at 250°C some Cu atoms had already moved to the Si substrate to form Cu$_3$Si as shown in Fig. 2, eliminating the time required for the release of Cu from Cu$_3$(Si$_{1-x}$Ge$_x$) by oxidation and the subsequent diffusion of the released Cu to the Si substrate to form new Cu$_3$Si, both of which were involved in the process of room temperature oxidation for the Cu$_3$(Si$_{1-x}$Ge$_x$) films grown at 200°C. Furthermore, the aforementioned results have shown that Cu$_3$Ge is stable against oxygen and the formation of buried SiO$_2$ is initiated at the Cu$_3$(Si$_{1-x}$Ge$_x$)/Cu$_3$Si interface. In the present study, 300°C annealing yielded the lowest Ge concentration in the Cu$_3$(Si$_{1-x}$Ge$_x$) layer because of Ge segregation and the largest fraction of the Cu$_3$(Si$_{1-x}$Ge$_x$)/Cu$_3$Si interface as shown in Fig. 3, resulting in the fastest rate of Cu$_3$Si-catalyzed oxidation.

4. Summary and conclusions

For the Cu/Si$_{0.76}$Ge$_{0.24}$ samples annealed at 200°C and exposed to air for 1 to 4 weeks, an oxidation layer appeared on the surface of the Cu$_3$(Si$_{1-x}$Ge$_x$) film. The Cu atoms released from Cu$_3$(Si$_{1-x}$Ge$_x$) by oxidation diffused down to the Si$_{0.76}$Ge$_{0.24}$ film and the Si substrate to form new Cu$_3$(Si$_{1-x}$Ge$_x$) and Cu$_3$Si, successively. Upon exposure for 5 to 6 weeks, a buried SiO$_2$ layer was initially formed at the Cu$_3$(Si$_{1-x}$Ge$_x$)/Cu$_3$Si interface; then the oxidation of Si proceeded by inward movement of the SiO$_2$/Si interface. The presence of Cu$_3$Ge lowered considerably the oxidation rate of the annealed Cu/Si$_{1-x}$Ge$_x$ samples. Annealing at higher temperatures such as 300°C resulted in (a) Ge segregation out of the Cu$_3$(Si$_{1-x}$Ge$_x$) layer, (b) a larger fraction of the Cu$_3$(Si$_{1-x}$Ge$_x$)/Cu$_3$Si interface where the buried SiO$_2$ layer was initially formed, and (c) an enhanced rate of oxidation catalyzed by Cu$_3$Si.

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