Room temperature oxidation of Cu/Si$_{0.76}$Ge$_{0.24}$ annealed at 200 to 300°C

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Abstract

The Cu$_x$Si$_{1-x}$-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$_x$Si$_{1-x}$Ge$_x$ film. During exposure the Cu atoms released from Cu$_x$(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$_x$(Si$_{1-x}$Ge$_x$) and Cu$_x$Si, 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$_x$(Si$_{1-x}$Ge$_x$)/Cu$_x$Si interface. Concurrently, the Cu$_x$Si-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$_x$(Si$_{1-x}$Ge$_x$) layer and the formation of a larger fraction of the Cu$_x$(Si$_{1-x}$Ge$_x$)/Cu$_x$Si interface where the buried SiO$_2$ layer was initially formed. © 1999 Elsevier Science S.A. All rights reserved.

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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$_x$Si or Cu$_x$Ge [3,4]. However, upon air exposure Cu$_x$Si reacts readily with oxygen at room temperature, while Cu$_x$Ge is stable [4-6]. Many studies on the Cu$_x$Si-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$_x$Si/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-
3. Results and discussion

3.1. Vacuum annealing

For the samples annealed at 200°C, \( \eta'' \)-\( \text{Cu}_3(\text{Si}_{1-x}\text{Ge}_x) \) was formed from analysis of the electron diffraction pattern. EDS/XTEM analysis showed that the Ge/Si concentration ratio, \( x/(1 - x) \), in the \( \text{Cu}_3(\text{Si}_{1-x}\text{Ge}_x) \) film was reduced, ranging from 0.14 to 0.22 along the film depth, while that in the unreacted \( \text{Si}_{0.76}\text{Ge}_{0.24} \) 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 (\(~10 \text{ nm}\)). During annealing the capping Si layer was involved in the reactions between Cu and \( \text{Si}_{0.76}\text{Ge}_{0.24} \) and hence
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$_3$Si. This result is reasonable since Cu is the dominant moving species in the formation of Cu$_3$Si and Cu$_3$Ge 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$_{1-y}$Ge$_y$) and Cu$_3$Si 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$_{1-y}$Ge$_y$. Similar results have been observed in the Ti/Si$_{1-y}$Ge$_y$, Co/Si$_{1-y}$Ge$_y$, and Ni/Si$_{1-y}$Ge$_y$ systems [19,22,26]. The Ge/Si ratio of the Cu$_3$(Si$_{1-y}$Ge$_y$) layer grown at 300°C ranged from 0.05 to 0.24 along the film depth. The heats of formation for Cu$_3$Si and Cu$_3$Ge 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$_3$Si move readily to the Cu$_3$Si/Si or SiO$_2$/Si interfaces to form new Cu$_3$Si [7]. In the present study, the Cu atoms released from Cu$_3$(Si$_{1-y}$Ge$_y$) by oxidation moved downward to the unreacted Si$_{0.76}$Ge$_{0.24}$ and Si to form Cu$_3$(Si$_{1-y}$Ge$_y$) and Cu$_3$Si, 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$_{1-y}$Ge$_y$)/Cu$_3$Si 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...
followed by exposure in air for 1 week. A buried SiO$_2$ layer may possibly decrease the diffusion flux of atomic oxygen and the formation of buried SiO$_2$ is initiated at the Cu$_3$(Si$_{1-x}$Ge$_x$)/Si substrate to form new Cu$_3$(Si$_{1-x}$Ge$_x$)/Cu$_3$Si interface. For 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$_{0.76}$-Ge$_{0.24}$) system is not as dense as that formed in the Cu/Si system. Besides, the oxidation rate for the Cu/(Si$_{0.76}$-Ge$_{0.24}$) 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 rates 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$_x$)/Cu$_3$Si interface, (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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References