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Growth behavior of self-formed barrier at Cu–Mn/SiO$_2$ interface at 250–450 °C

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A diffusion barrier layer was self-formed at the interface between Cu–Mn alloy and tetraethylorthosilicate oxide layers at 250–450 °C. No interdiffusion occurred across the self-formed barrier layer during annealing at these temperatures up to 100 h. The growth of the barrier layer obeyed a logarithmic law and depended on manganese concentration. The barrier thickness could be controlled in the range of 2–8 nm. © 2007 American Institute of Physics. [DOI: 10.1063/1.2750402]

Copper has been accepted as an advanced interconnect material. Tantalum and tantalum nitride have been widely employed as conventional barrier materials to prevent interdiffusion between Cu interconnect and dielectric insulating layer. However, the barrier formation with the conventional materials and technique has become gradually difficult as the technology node is reduced from 90 to 65 nm and further to 45 nm. An alternative method is self-forming barrier process by using Cu alloy metallization. In this process, an alloying element was supposed to migrate to the interface and form an oxide layer as a diffusion barrier.[1] However, previous investigations found it difficult to form a thin barrier layer and to reduce simultaneously the resistivity of the metallization.[2]

Recently, Cu–Mn alloy process was proposed by Koike and co-workers.[3,4] An excellent barrier layer was self-formed by annealing the Cu–Mn alloy at 450 °C. Using this alloy as a seed layer of dual-damascene interconnect structure, Usui *et al.*[5] reported that a self-formed barrier layer was formed without the conventional Ta barrier. They also demonstrated excellent resistance against stress-induced voiding and electromigration failure. However, the growth behavior and thermal stability of the self-formed barrier layer are not clear. In order to control the barrier layer thickness, it is indispensable to understand their growth kinetics.

In the present work, the growth behavior of the self-formed barrier was studied at 250–450 °C with various Mn concentrations. Obtained results were analyzed on the basis of theoretical concept of low temperature oxidation kinetics and diffusion coefficient of Mn in Cu. Thermal stability of the self-formed barrier was also studied by annealing at 450 °C up to 100 h. The barrier thickness could be controlled by controlling annealing temperature, time, and Mn concentration.

Experiments were performed as follows. A film of Cu–10 at. % Mn alloy was deposited to a thickness of 150 nm on a plasma tetraethylorthosilicate (TEOS) oxide. Deposition was carried out at room temperature by cosputtering of pure Cu (6*N* in purity) and pure Mn (3*N* in purity) with a suitable rf power. This was followed by the deposition of a Ta cap layer to a thickness of 50 nm. The Ta cap layer was necessary to avoid Mn atoms to segregate on the film surface and to form oxide during subsequent annealing. We confirmed that approximately 6 at. % of Mn remained in the alloy film after annealing at 450 °C for 100 h with the Ta cap layer. Annealing was performed in a vacuum level of 1.5×10^{-5} Pa at 250–450 °C for various time lengths from 10 min to 100 h. Cross-sectional image of the annealed samples was observed by a transmission electron microscope (TEM). Concentration of Mn was also measured using an x-ray energy dispersive spectrometer (EDS) attached to the TEM.

Figure 1 shows cross-sectional TEM images after annealing at 450 °C. The sample annealed for 1 h shows a self-formed barrier layer of 4.5 nm thickness. The sample annealed for 100 h shows the growth of the barrier layer to a thickness of 6.9 nm. The barrier layer is uniform in thickness and has an amorphous structure that is favorable for a diffusion barrier layer. EDS analysis confirmed no intermixing between the alloy film and the SiO$_2$ layer after annealing for 100 h. Variation of the barrier thickness (x) is plotted in Fig. 2 as a function of annealing time (t). The barrier thickness increases rapidly in an initial annealing stage up to 5 h, followed by slow growth. It is noted that when the samples are annealed at 250 and 350 °C, the barrier thickness remains less than 3.3 nm even after annealing for 100 h. In order to identify the growth mechanisms, the data points in Fig. 2 are replotted in a parabolic form of x^2-t in Fig. 3(a) and in a
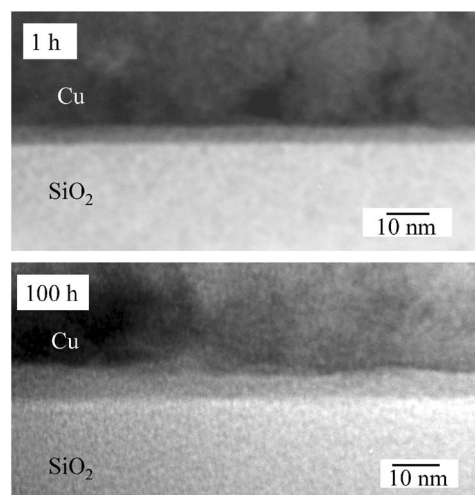

FIG. 1. Cross-sectional TEM images of an interface region after annealing at 450 °C.

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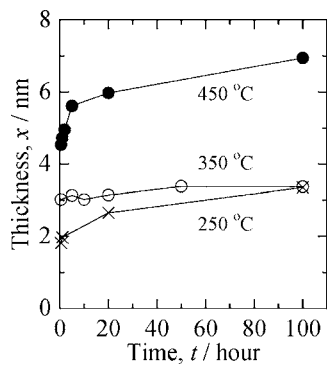**90**, 252107-1

FIG. 2. Growth behavior of the self-formed barrier layer.

TABLE I. Diffusion coefficients of Mn in Cu and oxygen in SiO_2.

	250 °C	350 °C	450 °C	Reference
Diffusion coefficient of Mn in Cu (m^2/s)	1.1×10^{-24}	1.7×10^{-21}	3.6×10^{-19}	9
Diffusion coefficient of oxygen in SiO_2 (m^2/s)	2.9×10^{-29}	5.7×10^{-27}	2.6×10^{-25}	10

logarithmic form of x-log t in Fig. 3(b). A linear relation can be found in Fig. 3(b) but not in Fig. 3(a). This indicates that the logarithmic form describes the growth behavior adequately. We assumed that manganese diffuses from the Cu–Mn alloy into the Cu–Mn alloy/SiO_2 interface and forms an oxide barrier layer by reacting with SiO_2. It is noted that the above equations can be used for the oxidation reaction between a metal and an oxygen-containing atmosphere. Although the present self-forming barrier process is a solid-state reaction, it is worthwhile to find out if the general oxidation approach can explain the kinetic aspects of the growth behavior of the self-formed barrier. Growth mechanism of an oxide layer at high temperatures in an oxygen-containing atmosphere has been well known to obey the following Wagner's parabolic law that is the diffusion-controlled growth[6] where thermal energy is sufficient for ions to diffuse through an oxide layer:

$$x^2 = K_1 t. \tag{1}$$

Here t is the annealing time and K_1 is the rate constant. The present case does not obey the parabolic law, as shown
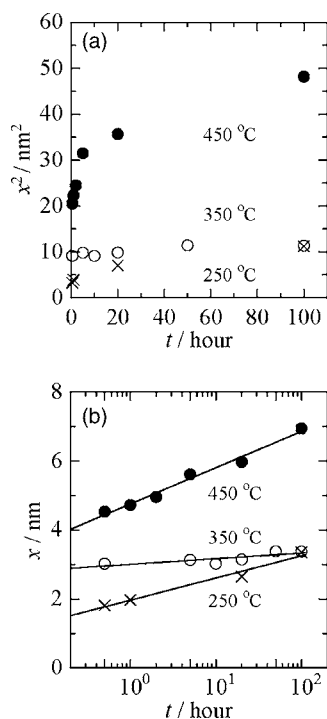

FIG. 3. (a) Parabolic growth plot and (b) logarithmic growth plot of the barrier thickness.

in Fig. 3(a), because thermal energy is not high enough for ions to diffuse through the oxide layer below 450 °C. On the other hand, at low temperatures, a logarithmic rate law, proposed by Mott and Cabrera,[7,8] has been known to describe the oxidation kinetics and is given by

$$x = K_2 \ln(at + b). \tag{2}$$

Here K_2, a, and b are constants. This model is based on a mechanism in which a space charge layer is formed owing to tunneling of metallic electrons through a thin oxide layer to reaction surface. The resultant electric field enhances mass transport through the oxide layer. The growth rate is limited by the field-assisted cation migration in the developing oxide film. Consequently, the barrier thickness could be controlled within the range of 2–7 nm by controlling annealing temperature and time.

Manganese diffuses from the Cu–Mn alloy to the Cu–Mn/SiO_2 interface and forms an oxide barrier layer by reacting with SiO_2. If the supply of manganese and oxygen atoms at the reaction interface is sufficient, the oxide layer grows continuously. At 450 °C the layer thickness increases up to 100 h. On the other hand, the layer growths at 250 and 350 °C were found to almost saturate at a thickness near 3.3 nm. The oxidation is due to the reaction of manganese and oxygen atoms near the interface. However, after exhaustion of these atoms near the interface, the growth rate of the oxide decreases. Let us consider if the supply of reaction elements to the interface is sufficient. The diffusion coefficient of Mn in Cu estimated with the preexponential factor $D_0 = 1.02 \times 10^{-4}$ $m^2 s^{-1}$ and the activation energy Q = 200 kJ mol^{-1} is listed in Table I. The diffusion coefficient of oxygen in SiO_2 obtained with $D_0 = 5.54 \times 10^{-15}$ $m^2 s^{-1}$ and Q = 143 kJ mol^{-1} is also listed in Table I.

Then, for example, the mean diffusion distances, $2(Dt)^{1/2}$, of manganese atom in Cu are 1.3 nm at 250 °C, 49 nm at 350 °C, and 720 nm at 450 °C for 100 h, whereas the corresponding values of oxygen atom in SiO_2 are 0.006 nm at 250 °C, 0.09 nm at 350 °C, and 0.6 nm at 450 °C for 100 h. Thus, it is very difficult that oxygen atoms diffuse in SiO_2 at all temperatures. The supply of Mn to the reaction interface is sufficient at 450 °C. On the other hand, it would be difficult that manganese atoms reach the reaction interface at 250 and 350 °C. After the consumption of manganese atoms near the reaction interface, the growth rate of the barrier layer slows down. Consequently, the layer growths were found to almost saturate at a thickness near 3.3 nm at 250 and 350 °C. Therefore, Mn concentration near the interface affects the growth rate of the barrier layer.

Here, an investigation of Mn concentration dependence of oxidation kinetics may provide useful information on the control of the barrier thickness as well as the oxidation mechanism. Figure 4 shows the barrier thickness as a function of Mn concentration after annealing at 450 °C for 30 min. The layer thickness increases with Mn content up to
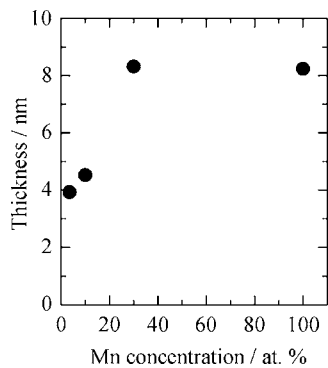
FIG. 4. Barrier layer thickness as a function of Mn concentration at 450 °C for 30 min.

30 at. % and takes a constant value of 8.3 nm from 30 to 100 at. % Mn. Figure 5 shows the layer thickness as a function of annealing time with different Mn concentrations of 3.5, 10, and 30 at. % at 450 °C. The barrier thickness growth rate became slow after annealing for 5 h at Mn concentrations of 10 and 30 at. %. Let us compare this concentration dependence of the barrier layer growth with diffusion experiment on Cu–Mn alloys. Interdiffusion experiment on Cu–Mn alloys in the concentration range between 0 and 88.6 at. % Mn has been reported.[11] The interdiffusion coefficient increases with manganese content up to 30 at. % Mn and decreases remarkably with further increase of manganese. The concentration dependence of the interdiffusion coefficient is in agreement with a generally recognized trend for the self-diffusion coefficient of alloys to increase with decreasing melting temperature.[12] Thus, the excellent agreement between the Mn concentration dependence of the barrier layer growth and the concentration dependence of the interdiffusion coefficient in Cu–Mn alloys is shown. Although the diffusion distance of manganese atom in Cu at 30 at. % Mn is longer than at 100 at. % Mn according to the report, the supply of Mn near the reaction interface is sufficient at 100 at. % Mn. The supply of oxygen from SiO_2 to
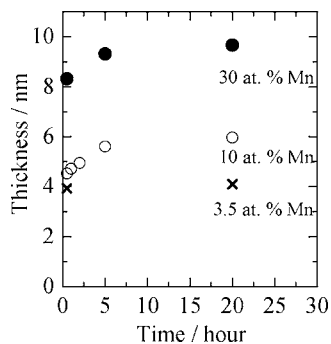
the reaction interface is insufficient. As a result, the layer thickness takes a constant value at 30 and 100 at. % Mn.

As shown above, the barrier layer growth kinetics obeys the logarithmic law. Previous researchers reported that the rate-determining step is taken to be the surface reaction at the gas-oxide interface on the logarithmic law.[13–15] This indicates that oxidation is an oxygen pressure-dependent process. In the present case, the rate-determining step is found to be a Mn oxidation reaction at the Cu–Mn alloy/SiO_2 interface because the reaction is a manganese-concentration-dependent process. Consequently, the barrier thickness could be controlled not only by annealing temperature and time but also by the Mn concentration.

In the present work, Cu–Mn alloy film was deposited on TEOS substrate and annealed at 250–450 °C. A diffusion barrier layer was self-formed during annealing. The barrier thickness can be controlled in the range of 2–8 nm. The barrier layer was thermally stable after annealing at 450 °C up to the annealing time of 100 h. The growth of barrier layer obeys the logarithmic law and depends on Mn concentration. The layer thickness increases with Mn content up to 30 at. %, corresponding to the concentration dependence of the interdiffusion coefficient in Cu–Mn alloys. The barrier thickness could be controlled by annealing temperature, time, and Mn concentration.

FIG. 5. Time-dependent barrier layer thickness with different Mn concentrations at 450 °C.

[1] P. J. Ding, W. A. Lanford, S. Hymes, and S. P. Murarka, Appl. Phys. Lett. **64**, 2897 (1994).
[2] K. Barmak, A. Gungor, C. Cabral, and J. M. E. Harper, J. Appl. Phys. **94**, 1605 (2003).
[3] J. Koike and M. Wada, Appl. Phys. Lett. **87**, 041911 (2005).
[4] J. Iijima, M. Haneda, and J. Koike, Proceedings of the IEEE International Interconnect Technology Conference, 2006, p. 246.
[5] T. Usui, H. Nasu, S. Takahashi, N. Shimizu, T. Nishikawa, M. Yoshimaru, H. Shibata, M. Wada, and J. Koike, IEEE Trans. Electron Devices **53**, 2492 (2006).
[6] C. Wagner, Z. Phys. Chem. Abt. B **21**, 25 (1933).
[7] N. F. Mott, Trans. Faraday Soc. **35**, 1175 (1939).
[8] N. Cabrera and N. F. Mott, Rep. Prog. Phys. **12**, 163 (1948).
[9] K. Hoshino, Y. Iijima, and K. Hirano, Metall. Trans. A **8A**, 469 (1977).
[10] J. D. Kalen, R. S. Boyce, and J. D. Cawley, J. Am. Ceram. Soc. **74**, 203 (1991).
[11] Y. Iijima, K. Hirano, and K. Sato, Trans., JIM **18**, 835 (1977).
[12] C. E. Birchenall, *Atom Movements*, edited by J. H. Hpllomon (ASM, Cleveland, OH, 1951), p. 112.
[13] J. E. Boggio, J. Chem. Phys. **70**, 5054 (1979).
[14] D. D. Eley and P. R. Wilkinson, Proc. R. Soc. London, Ser. A **254**, 327 (1960).
[15] A. P. Grosvenor, B. A. Kobe, and N. S. McIntyre, Surf. Sci. **565**, 151 (2004).