Uniform CoSi$_2$ nano-nucleus formation by oxide mediated silicidation with a Ti capping layer

Juin-Jie Chang [a], Tsung-Eong Hsieh [a], Chuan-Pu Liu [b], Ying-Lang Wang [c],*

[a] Department of Materials Science and Engineering, National Chiao-Tung University, Hsinchu, Taiwan
[b] Department of Materials Science and Engineering, National Cheng-Kung University, Tainan, Taiwan
[c] Taiwan Semiconductor Manufacturing Company, Hsinchu, Taiwan

Available online 30 August 2005

Abstract

The nucleation stage toward CoSi$_2$ with average island size of about 4 nm and uniform island size distribution is obtained from a TiN/Co/Ti/Co/SiO$_x$/Si multilayer with the SiO$_x$ as a mediated layer by annealing at 460 °C for 240 s followed by 600 °C 240 s. It is found that Ti capping layer can enhance Co diffusion into the Si substrate at higher temperature (600 °C 240 s) annealing, which results in larger nucleus size (average grain size about 12 nm) but nonuniform nucleus size distribution. However, two-step annealing for 460 °C 240 s followed by 600 °C 240 s results in a smaller average nucleus size with better nucleus size distribution. The mechanism responsible for the discrepancy is discussed in the paper.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Oxide mediated epitaxy; Cobalt silicide; Nucleus; Annealing

1. Introduction

Cobalt disilicide (CoSi$_2$) possesses low bulk electrical resistivity, good lattice match with Si (001) and therefore CoSi$_2$ has been widely applied in integrated circuit (IC) technology as the device feature size decreases. However, normal polycrystalline cobalt disilicide process still suffers from some serious issues such as agglomeration, silicon consumption, leakage current. Especially, the agglomeration issue will become more critical for ultra-large scale integration (ULSI) technology below 90 nm because of the limitation of line width and shallow source/drain junction. The agglomeration will induce large-grain CoSi$_2$ formation and hence resistance degradation [1,2].

Epitaxial CoSi$_2$ has been expected to resolve this problem due to its excellent thermal stability. Recently, Tung [3–5] has proposed oxide mediated epitaxy (OME) technique, which can be used to form good quality of epitaxial CoSi$_2$ and is compatible with conventional ULSI processing. The OME method involves with firstly the deposition of a Co thin layer (1–3 nm) onto a Si surface covered with a thin SiO$_x$ layer grown in an aqueous peroxide solution followed by annealing at 500–700 °C. However, the thickness of the epitaxial CoSi$_2$ layers produced by a single OME process was limited to ~11nm. Thicker epitaxial CoSi$_2$ films demand repeating deposition and annealing processes using the thin CoSi$_2$ layer formed from the first deposition as a template. In addition, the cobalt deposition and annealing processes need to be performed under ultra-high vacuum environment [3–5], which then causes high cost in production.

Kim et al. [6,7] found that using Ti-capping can form a thicker epitaxial CoSi$_2$ layer directly without repeating Co deposition and annealing processes. It is because Ti can absorb oxygen in Co layer and weaken the SiO$_x$ layer to enhance Co diffusion into Si substrate [8,9]. However, this process required sequential deposition of Co and Ti without vacuum break.

In addition to epitaxial CoSi$_2$, alternatively, polycrystalline CoSi$_2$ via the same OME process in a lower vacuum

---

* Corresponding author. Tel.: +886 6 505 9688; fax: +886 6 5051262.
E-mail address: ylwang@tsmc.com (Y.-L. Wang).

environment has also been shown to provide advantages. For example, low resistive $CoSi_2$ is formed directly at a lower annealing temperature of 500–700 °C bypassing high resistive phases of CoSi and Co_2Si [1,2]. Compared to the conventional higher temperature annealing method; the $CoSi_2$ layers is dense with smooth surface [3–5]. Therefore, to produce a polycrystalline $CoSi_2$ phase via the OME process is more cost-effective.

Xiao et al. [10] and Sun et al. [11] reported that smaller grain size and more uniform grain size distribution exhibit lower grain boundary energy and larger interfacial energy favorable for the thermal stability of silicide. In other words, $CoSi_2$ agglomeration or recrystallization along its grain boundary can be reduced [12]. Therefore, developing polycrystalline $CoSi_2$ with smaller grain size and better size uniformity is still a main stream for the further improvement in the current IC technology. Especially for the ULSI technology below 90 nm, nano grain sized $CoSi_2$ is requested to prevent large-grain $CoSi_2$ induced resistance degradation [11–13]. In this paper, we show that uniform nano-nucleus $CoSi_2$ with nano island size of 4 nm can be achieved by using the OME process with Ti-capping in a lower vacuum environment process by controlling annealing temperature and time. The underlined mechanism is also discussed.

2. Experimental details

P-type (8–12 Ω cm) silicon substrates were chemically cleaned and dipped in a boiling $HCl/H_2O_2/H_2O = 3:1:1$ solution for 3 min to form a SiO_x layer (Shiraki Oxide) prior to loading the sample into a DC magnetron sputter. Subsequently, a TiN/Co/Ti/Co multilayer was deposited using argon (99.995% purity) as the sputtering gas after the base pressure of 3×10^{-6} Torr was reached and the target of Co or Ti (99.95% purity) had been pre-sputtered for 10 min. The multilayer deposition was intermittence, where vacuum break was performed for target exchange between layers. The thicknesses of the $TiN/Co/Ti/Co/SiO_x$ multilayer were about 10/4/10/4/2 nm, respectively, from a TEM cross sectional image. Ex-situ annealing was carried out in a vacuum chamber at 10^{-5} Torr. Upon annealing, all layers except the reactive products were stripped off by chemical etching, in order to examine the silicide layer in plan-view. The TiN/Ti, the unreacted Co and the SiO_x layers can be stripped off by $NH_4OH/H_2O_2/H_2O = 1:1:4$ solution at 50 °C, aluminum etching solution (H_3PO_4 71 wt.%, HNO_3 2.5 wt.%, CH_2COOH 12.5 wt.%, others H_2O) at 75 °C and HF solution, respectively. The phase and nucleus size of the samples were then examined by transmission electron microscope (TEM). The chemical characteristics of the SiO_x layer were analyzed by Fourier transform infrared spectrometer (FTIR).

3. Results and discussion

Fig. 1(a) shows a TEM bright field plan-view image and the corresponding diffraction pattern of the reactive silicide upon annealing at 600 °C for 120 s with all the other layers removed. The diffraction pattern shows that the silicide is $CoSi_2$, which agrees with that of Tung et al. [3–5] and proved that $CoSi_2$ can be formed directly bypassing CoSi, Co_2Si from lower temperature (500–700 °C) annealing, because the SiO_x acts as a diffusion barrier reducing Co effective concentration at the cobalt disilicide growth interface [14,15]. The image shows that the sample is still in the process of grain growth, and exhibits bimodal size distribution with the peaks centered at the grain size of 3 nm and 16 nm as shown in Fig. 1(b). According to the study of Detavernier [8,9], Ti should diffuse through the grain boundaries of the Co layer to the SiO_x layer, and reduce SiO_x to $Co_xTi_yO_z$, which then enhances the Co diffusion to form cobalt disilicide. Fig. 2(a) and (b) are TEM bright field cross-sectional images from two different areas of the sample as in Fig. 1. Both images reveal that all of the interfaces are rough with a few dark areas at the SiO_x/Si interface, corresponding to $CoSi_2$. Since the layer is thin, interface roughness may play a significant role in Ti and Co diffusion, rendering the non-uniform nucleus distribution. The bimodal nucleus size distribution may be decided by the involvement of Ti at various locations.

This bimodal size distribution can be amplified by doubling annealing time, which is exactly the case as shown in Fig. 3(a) from a TEM bright field plan-view image of the sample upon annealing at 600 °C for 240 s. Compared
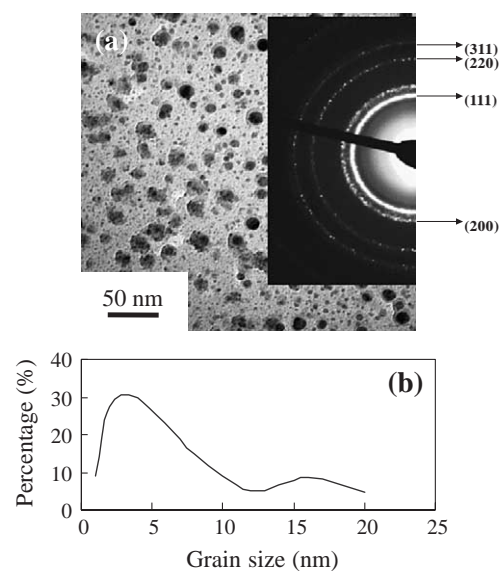

Fig. 1. (a) A TEM bright-field plan-view image with the corresponding diffraction pattern and (b) nucleus size distribution of the sample upon annealing at 600 °C for 120 s with the TiN capped layer, unreacted cobalt, Ti and SiO_x removed.
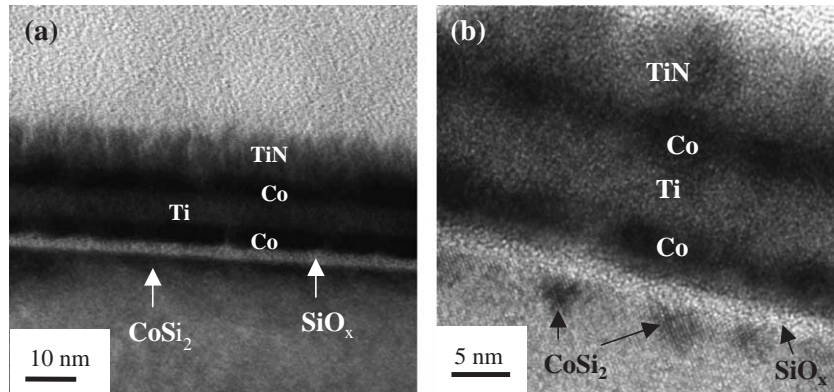
Fig. 2. (a) and (b) TEM bright-field cross-sectional images from two different areas of the sample upon 600 °C 120 s annealing.

to Fig. 1(a), nucleus grow further and bimodal distribution becomes more distinct, which will then lead to a continuous film with non-uniform grain size distribution and is not desired for real application. Thus, we employed a two-step annealing as shown in Fig. 3(b), which is a TEM bright field plan-view image of the sample upon annealing at 460 °C for 240 s followed by 600 °C for 240 s. Comparing Fig. 3(a) and (b), the most striking feature is the discrepancy for the average nucleus size and the size distribution, which are 12 ± 5.8 nm and 4 ± 0.7 nm corresponding to the one-step and two-step annealing, respectively, as shown in Fig. 3(c). Apparently, the two-step annealing produces smaller and

more homogeneous nucleus size distribution than the one-step annealing although both experience the same annealing at 600 °C for 240 s. Why the nucleus size from the two-step annealing become smaller and uniform although it experiences even additional annealing at 460 °C? According to Fitch et al. [16], they showed that the SiO_x would become denser toward more stoichiometric SiO_2 upon annealing and eventually turn into SiO_2 at 900 °C for 30 s. Therefore, the possible chemical stoichiometry was examined by FTIR in Fig. 4, which compares the result from the as-deposited sample with the sample upon annealing at 460 °C for 240 s. According to Chao et al. [17], the absorbance frequency of
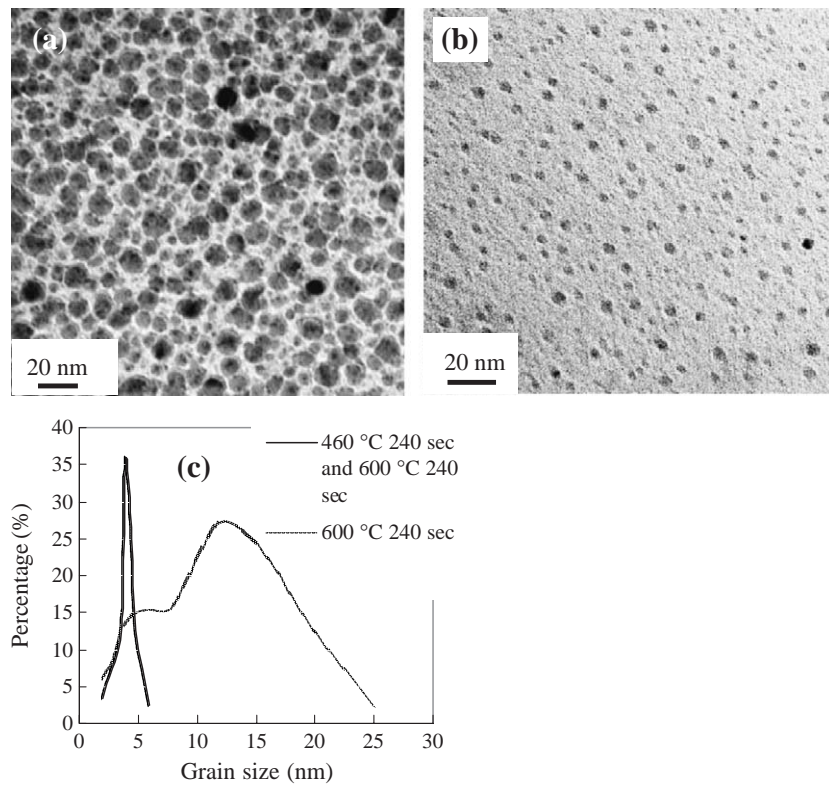

Fig. 3. TEM bright-field plan-view images of the samples upon annealing with the TiN capped layer, unreacted cobalt, Ti and SiO_x removed, where the annealing condition are (a) 600 °C 240 s, (b) firstly 460 °C 240 s and then 600 °C 240 s; (c) nucleus size distribution for one-step annealing (600 °C 240 s) and two-step annealing (firstly 460 °C 240 s and then 600 °C 240 s).
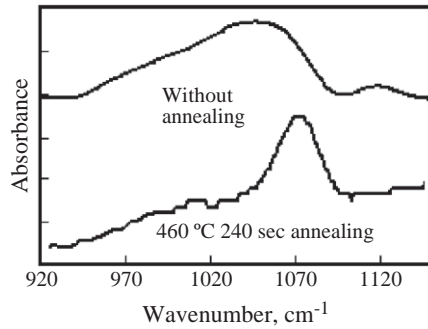
Fig. 4. FTIR spectra of the as-deposited SiO_x layer and that upon 460 °C annealing for 4 min.

SiO_x is in a range between 940 and 1075 cm^{-1} and that of stoichiometric SiO_2 is about 1075 cm^{-1}. While a broad peak representing SiO_x for the as-deposited sample in Fig. 4, a more definite peak at 1075 cm^{-1} reveals the evidence of forming SiO_2 upon annealing at 460 °C. Therefore, the Ti diffusion rate to the SiO_x layer is slowed down due to the densified SiO_2 microstructure and the transformation to SiO_2. In the one-step higher temperature annealing, SiO_x should still be able to transform to SiO_2 but the ability of Ti diffusion to SiO_x increases more significantly and help stabilize the SiO_x layer, which causes the larger nucleus size (see Fig. 1(a)). In the two-step annealing process, the SiO_2 formation becomes dominant and the induced slow inter-diffusion may effectively render the nucleus size uniform distribution.

To further justify our supposition, another two-step annealing experiment was performed for 460 °C 120 s followed by 600 °C 240 s, where the annealing time at 460 °C was half of that used in Fig. 3(b). Fig. 5(a) shows a TEM bright field plan-view image from this sample. Compared to Fig. 3, apparently, the nucleus size magnitude and uniformity degree are just between Fig. 3(a) and (b). This is because the shorter 460 °C annealing time renders looser SiO_x network than Fig. 3(b), which is consistent with our previous supposition. The average nucleus size of 7 ± 2.9 nm (see Fig. 5(b)) is still smaller than that from the one-step

annealing and the nucleus size distribution is also more homogeneous than one-step annealing.

In addition, Detavernier et al. [8] found that at even higher annealing temperature of 850 °C, high resistive CoSi phase forms by a lateral growth phenomenon where Si from the substrate diffuses through the $CoSi_2$ and reacts with the remaining Co to form CoSi following $CoSi_2$ nucleation directly underneath the weak regions of SiO_2. Therefore, smaller grain size with less lateral growth phenomena will inhibit the formation of CoSi. It means two-step annealing will have less chance to form CoSi than one-step annealing.

4. Conclusions

Homogeneous nucleus size of 4 nm prior to a $CoSi_2$ thin film can be obtained by oxide mediated silicidation with Ti capping in which cobalt was deposited by DC magnetron sputtering on SiO_x/Si with the SiO_x as a mediated layer followed by ex-situ two-step annealing (460 °C 240 s and 600 °C 240 s). Lower temperature annealing at 460 °C can alter the microstructure of the SiO_x layer toward more stoichiometric SiO_2, which then reduces Co and Ti diffusion rate and thus $CoSi_2$ nucleus size leading to homogeneous nucleus size distribution. The homogeneous nucleus morphology remains unchanged even experiencing subsequent annealing at higher temperatures to increase Co diffusion rate.
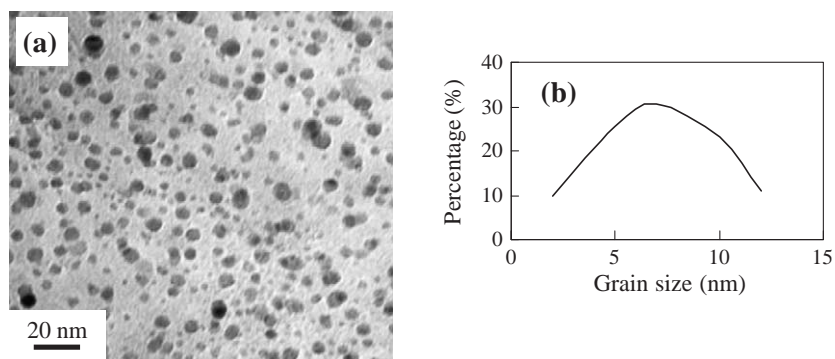
Fig. 5. (a) A TEM bright-field plan-view image and (b) nucleus size distribution of the sample upon annealing at 460 °C for 120 s followed by 600 °C 240 s with TiN capped layer, unreacted cobalt and SiO_x removed.

References

[1] S. Vaidya, S.P. Murarka, T.T. Sheng, J. Appl. Phys. 58 (1985) 971.
[2] C.Y. Ting, F.M. d'Heurle, S.S. Iyer, P.M. Fryer, J. Electrochem. Soc. 133 (1986) 2621.
[3] R.T. Tung, Appl. Phys. Lett. 68 (1996) 3461.
[4] R.T. Tung, Jpn. J. Appl. Phys. 36 (1997) 1650.
[5] R.T. Tung, S. Ohmi, Thin Solid Films 369 (2000) 233.
[6] Gi Bum Kim, Joon Seop Kwak, Hong Koo Baik, J. Vac. Sci. Technol., B 17 (1999) 162.
[7] Gi Bum Kim, Joon Seop Kwak, Hong Koo Baik, J. Appl. Phys. 85 (1999) 1503.
[8] C. Detavernier, R.L. Van. Meirhaeghe, F. Cardon, K. Maex, Thin Solid Films 386 (2001) 19.
[9] C. Detavernier, R.L. Van. Meirhaeghe, F. Cardon, R.A. Donaton, K. Maex, Microelectron. Eng. 50 (2000) 125.
[10] Z.G. Xiao, G.A. Rozgonyi, C.A. Canovai, C.M. Osburn, Mater. Res. Soc. Symp. Proc. 202 (1991) 101.
[11] W.T. Sun, M.C. Liaw, C.C. Hsu, IEEE Electron Device Lett. 19 (1998) 163.
[12] A.H.M. Kamal, A.T. Obeidat, T. Budri, J. Vac. Sci. Technol., B 20 (2002) 173.
[13] D.K. Sarkar, I. Rau, M. Falke, H. Giesler, S. Teichert, G. Beddies, H.J. Hinneberg, Appl. Phys. Lett. 78 (2001) 3604.
[14] A. Vantomme, S. Degroote, J. Dekoster, G. Langouche, Appl. Phys. Lett. 74 (1999) 3137.
[15] R. Pretorius, J.W. Mayer, J. Appl. Phys. 81 (1997) 2448.
[16] J.T. Fitch, E. Kobeda, G. Lucovsky, E.A. Irene, J. Vac. Sci. Technol., B 7 (1989) 153.
[17] S.S. Chao, J.E. Tyler, Y. Takagi, P.G. Pai, J. Vac. Sci. Technol., A 4 (1986) 1574.