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Citation: *Journal of Vacuum Science & Technology B* **23**, 1952 (2005); doi: 10.1116/1.2006132

View online: <http://dx.doi.org/10.1116/1.2006132>

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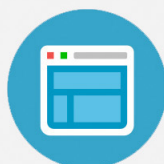
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Study of diffusion and quality control for CoSi₂ formation by oxide-mediated cobalt silicidation with Ti capping

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(Received 22 February 2005; accepted 20 June 2005; published 12 September 2005)

The mechanism for the enhancement of CoSi₂ thin film formation and film quality control by oxide-mediated cobalt silicidation with a Ti-capping layer is discussed. It is found that Ti absorbs oxygen from the SiO_x layer, which induces weak points in the SiO_x layer and then enhances Co diffusion as well as CoSi₂ formation. The control of the reactions between Ti and SiO_x is significant because a low reaction rate cannot form a suitable thickness of CoSi₂ film, whereas a high reaction rate tends to form the highly resistive CoSi phase. In addition, to maintain the SiO_x layer still existing after annealing is also important because if no SiO_x layer remains, unreacted Co would react with Si directly to form the highly resistive phase of CoSi, leading to the smooth interface between CoSi₂ and Si and dense bulk CoSi₂ thin film being destroyed. © 2005 American Vacuum Society. [DOI: 10.1116/1.2006132]

I. INTRODUCTION

Cobalt disilicide (CoSi₂) possesses low bulk electrical resistivity and a good lattice match with Si (001) so it has been widely applied in integrated circuit technology as the device feature size decreases. However, the normal polycrystalline cobalt disilicide process still suffers from some serious issues such as agglomeration, silicon consumption, and leakage current. In particular, the agglomeration issue will become more critical for ultralarge scale integration (ULSI) technology below 90 nm because of the limitations of the linewidth and shallow source/drain junction. This agglomeration will induce large-grain CoSi₂ formation and hence resistance degradation.^{1,2}

Epitaxial CoSi₂ has been considered as one candidate to solve this problem due to its excellent thermal stability. Recently, Tung^{3,4} and Jung and Ohmi⁵ proposed an oxide mediated epitaxy (OME) technique, which can be used to form good quality epitaxial CoSi₂. The OME method involves the deposition of a Co thin layer (1–3 nm) onto a Si surface capped with a thin layer of SiO_x grown in an aqueous peroxide solution followed by annealing at 500–700 °C. However, the thickness of the epitaxial CoSi₂ layers produced by a single OME process is limited to about 11 nm. Thicker epitaxial CoSi₂ films demand repeated depositing and annealing processes using the previously formed thin layer of CoSi₂ as the template. In addition, the cobalt deposition and

annealing processes need to be performed in an ultrahigh vacuum environment,^{3–5} which then results in higher production costs.

In our previous study,⁶ we found that smooth interfaces and dense bulk CoSi₂ thin films with homogeneous nanograin size (5±1.8 nm) distribution can be formed by an oxide-mediated silicidation process using a SiO_x layer as the diffusion barrier in the OME method. The formation of a sharp interface and homogeneous nanograin size distribution of a CoSi₂ thin film can reduce junction leakage and resistance, respectively, which are important for ULSI technology.^{1,2} However, the thickness of the CoSi₂ thin film formed by this method is still limited as the OME process.

A thicker epitaxial CoSi₂ film of 40–50 nm formed by the OME method with a Ti-capping layer has been reported by Kim *et al.*^{7,8} However, the detailed mechanism was not provided in their study. For the same structure, Detavernier *et al.*^{9,10} have ascribed the enhancement of cobalt silicide formation to the reduction of SiO_x to Co_xTi_yO_z by Ti. In this study, we find that Ti can absorb oxygen from the SiO_x layer and decompose it, a conclusion which is different from that of Detavernier *et al.*^{9,10}

II. EXPERIMENTAL DETAILS

p-type (8–12 Ω cm) silicon substrates were chemically cleaned and dipped in a 60 °C HCl:H₂O₂:H₂O=3:1:1 solution for 1 min to form a SiO_x layer. Subsequently, a Co layer was deposited by magnetron sputtering followed by a

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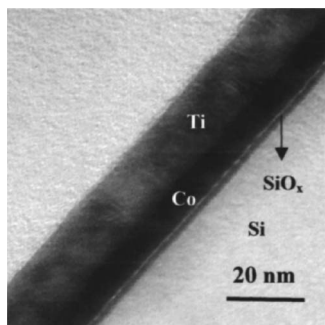


FIG. 1. Bright-field TEM cross sectional image of the as-deposited Ti/Co/SiO_x sample.

Ti-capping layer deposition in the same chamber with vacuum breaking to change targets. The Co and Ti targets (99.95% purity) were presputtered for 10 min after the base pressure of 3×10^{-6} Torr was reached using argon (99.995% purity) as the sputtering gas. The thicknesses of the Ti/Co/SiO_x layers in the stack were determined to be about 14/7/0.8 nm from a transmission electron microscope (TEM) cross sectional image. In addition, another multilayer sample of TiN/Co/Ti/Co/SiO_x was also prepared using the same method except that the time and temperature to form the SiO_x layer were increased to 3 min and 90 °C to increase the thickness. The thicknesses of the TiN/Co/Ti/Co/SiO_x layers in the stack were determined to be about 8/3/6/3/2 nm. *Ex situ* annealing was carried out in a vacuum chamber of 10^{-4} Torr. Upon annealing, all layers of the latter sample except for the reactive products were stripped off by chemical etching, in order to examine the silicide layer in plan view. TiN, unreacted Co and SiO_x layers can be stripped off by $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:1:4$ 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 of the samples was then examined by TEM. The atomic redistribution of the TiN/Co/Ti/Co/SiO_x multilayer was examined by Auger electron spectroscopy (AES) depth profiling.

III. RESULTS AND DISCUSSION

Figure 1 shows a bright-field TEM cross sectional image of the as-deposited Ti/Co/SiO_x sample. This image clearly shows that the SiO_x layer was 0.8 nm in thickness and sandwiched between Co and Si, whereas the thicknesses of the Co and Ti layers are about 7 and 14 nm, respectively. Figure 2(a) shows a bright-field TEM cross sectional image of the sample after annealing at 460 °C for 120 s. In Fig. 2(a), Co diffused through the SiO_x layer and a wavy layer of cobalt silicide formed, indicating that the Co diffusion may be only through some weak points in the SiO_x layer, which agrees with the results of Detavernier *et al.*^{9,10} One can also easily see that the SiO_x layer is more discontinuous than in the as-deposited sample in Fig. 1, implying that some SiO_x disappears. Figure 2(b) is a closeup high resolution TEM image of Fig. 2(a). Apparently, lattice fringes and dark contrast in the SiO_x layer verify that part of the layer has been reacted

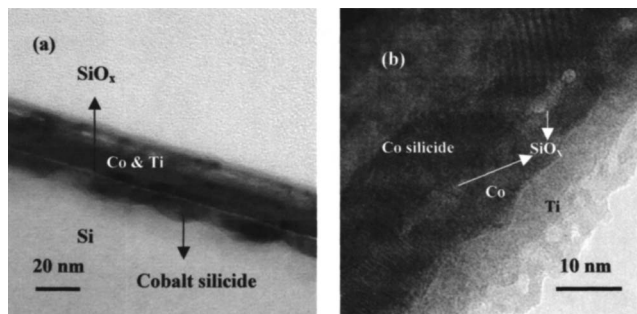


FIG. 2. (a) Bright-field TEM cross sectional image of the Ti/Co/SiO_x sample after annealing at 460 °C for 120 s and (b) magnified high resolution TEM image of (a).

and crystallized. If the annealing time is further prolonged, the entire SiO_x layer disappears, as shown in Fig. 3, which is a bright-field TEM cross sectional image of the sample after 460 °C 300 s annealing. According to the study of Baten and Fedorovich,^{11,12} Co diffuses through SiO₂ without any chemical interaction with the SiO₂ networks, but only occupies interstices of the very open SiO₂ structure and migrates along the interstices as diffusion channels without affecting the regular lattices. This indicates that the SiO_x layer would not react with Co and would not be destructed by the Co diffusion. But why does the SiO_x layer disappear? Detavernier *et al.* have reported^{9,10} that Ti should diffuse through the grain boundaries of the Co layer to the SiO_x layer, and reduce SiO_x to $\text{Co}_x\text{Ti}_y\text{O}_z$, which then enhances the Co diffusion to form cobalt silicide. However, in their study, the SiO_x layer was still left after annealing because of a thicker SiO_x layer, so this cannot explain our results either. It is also noted that another white line appears between the Ti and Co layers in Fig. 3, which according to Detavernier *et al.*^{9,10} should be a Ti-oxide layer resulting from absorbing oxygen from the environment and the Co layer. The residual oxygen in the Co layer is due to exposure to air prior to the deposition of the Ti-capping layer. Could the SiO_x layer also be decomposed by Ti because Ti has a larger negative oxide formation enthalpy than Si and Co? (see Table I)^{11,13} In order to prove this assertion, another multilayered sample of the TiN/Co/Ti/Co/SiO_x/Si structure was prepared without a vacuum

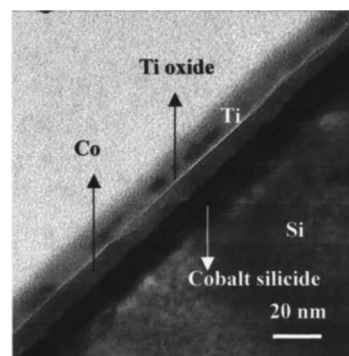


FIG. 3. Bright-field TEM cross sectional image of the Ti/Co/SiO_x sample after annealing at 460 °C for 300 s.

TABLE I. Free enthalpies of oxide formation at 1030 K in kJ/mol O_2 .

TiO_2	SiO_2	CoO
-1069	-1020	-714

break between layers in order to prevent oxygen contamination, and the thickness of the SiO_x layer was increased to about 2 nm so as to more easily monitor oxygen diffusion from the SiO_x layer.

Figure 4(a) is a bright-field TEM cross sectional image of this multilayered sample after 240 s annealing at 600 °C, a significantly higher temperature than for the previous stack. First of all, no extra white line was found in the Ti and Co interface, which illustrates the residual oxygen in the Co layer has been eliminated by this deposition process. Figure 4(b) is a TEM bright field plan-view image with a diffraction pattern from the reactive silicide of the same sample as in Fig. 4(a) after all the other layers have been removed. The diffraction pattern shows that the silicide is CoSi_2 , in agreement with our previous results⁶ in that the CoSi_2 is the first phase from the oxide-mediated cobalt silicidation, which also confirms that the dark contrast in Si adjacent to SiO_x is cobalt silicide in Fig. 4(a). Figure 4(c) shows the AES depth profiles of the sample in Fig. 4(a), where every layer is clearly distinct and oxygen from the SiO_x layer was largely

absorbed in the Ti layer after annealing. This finding directly supports our supposition above and is different from the mechanism proposed by Detavernier *et al.*^{9,10} The fact that the SiO_x layer can be decomposed by Ti, even to the point of disappearing, overthrows the impression that SiO_x should always remain upon annealing in the OME process.³⁻⁶ This can also explain why a CoSi_2 layer from a Ti-capped multilayer produced by a single OME process can be thicker than ~11 nm.^{7,8} That is because the Ti capping layer thins the SiO_x layer to increase the Co diffusion rate while the SiO_x layer can reduce the Co diffusion rate to form a CoSi_2 layer from a non-Ti-capped multilayer. By comparing Fig. 3 with Fig. 4(a) for both samples comprised of the Ti capping layer, the thicker SiO_x layer in Fig. 4(a) more effectively deters the Co diffusion rate, resulting in a thinner cobalt silicide layer than Fig. 3, although the sample in Fig. 4(a) experiences annealing at a higher temperature.

The sample in Fig. 3 was annealed further at 600 °C for 300 s and the result is shown in Fig. 5. Apparently, because the SiO_x barrier layer is gone, Co reacts directly with the Si substrate as in the convectional cobalt silicide formation process, which induces a rough interface due to Co and Si interdiffusion.^{1,2} Moreover, in this case, if the annealing temperature is lower than 750 °C, the highly resistive phase CoSi will be formed.^{1,2} Comparing Figs. 3 and 5, we find that if the annealing process is well controlled, a smooth

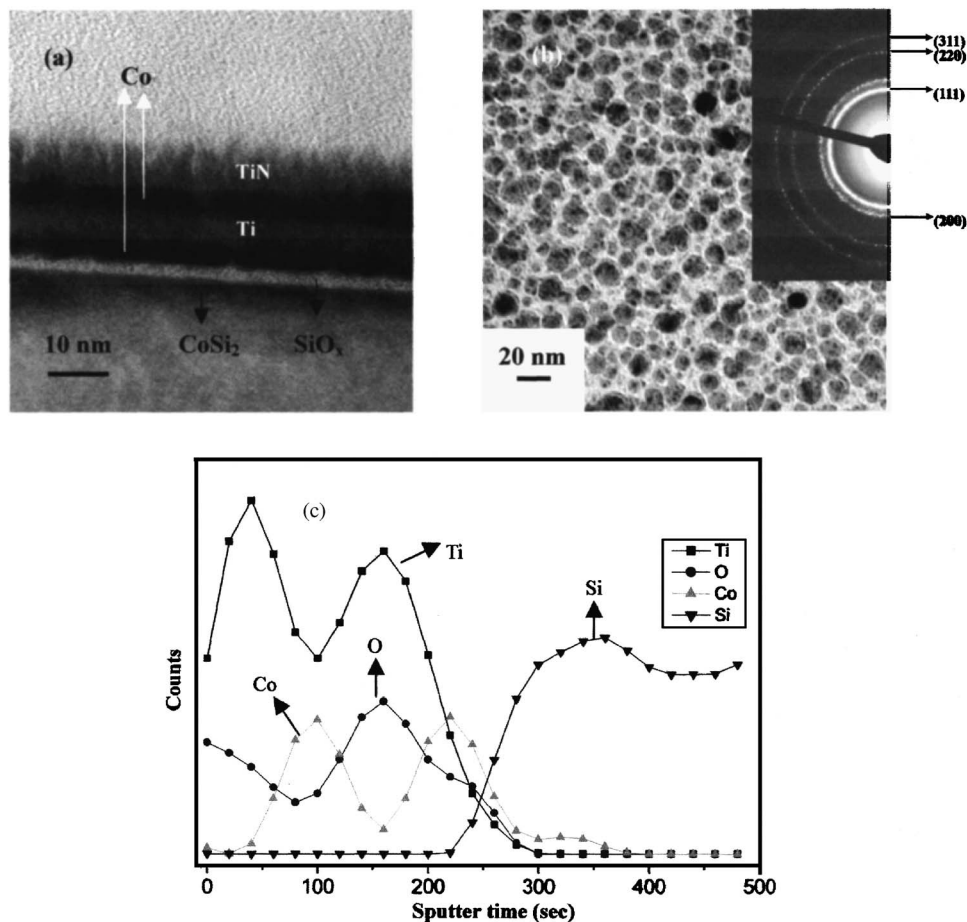


FIG. 4. (a) Bright-field TEM cross sectional image of the TiN/Co/Ti/Co/ SiO_x /Si multilayered sample after 600 °C 240 s annealing, (b) Bright-field TEM plan-view image and diffraction pattern of the reactive silicide of the sample in (a) with all the other layers removed, and (c) AES depth profiles of the sample in (a).

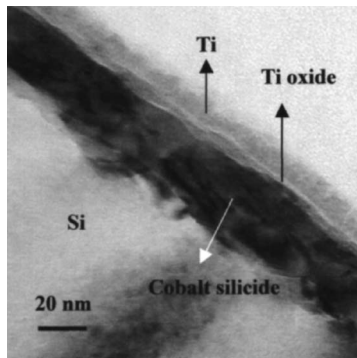


FIG. 5. Bright-field TEM cross sectional image of the Ti/Co/SiO_x sample after annealing at 460 °C for 300 s followed by 600 °C 300 s.

interface and dense bulk cobalt silicide can be formed, which is the characteristic of the oxide-mediated silicidation process³⁻⁶ as in Fig. 3. However, overannealing can destroy the cobalt silicide quality as in Fig. 5. Vantomme¹⁴ and Pretorius¹⁵ reported that if the Co effective concentration at the cobalt silicide growth interface were low enough, this would lead to the biggest negative change in the free energy for the CoSi₂ formation. In addition, the direct CoSi₂ formation can effectively reduce the formation temperature because the reaction path is $\text{Co} + 2\text{Si} \rightarrow \text{CoSi}_2$ rather than $\text{CoSi} + \text{Si} \rightarrow \text{CoSi}_2$. In other words, it does not need to break the CoSi bonding.¹⁶ Therefore, a faster reaction rate of Ti with SiO_x will enhance the Co diffusion rate and Co effective concentration at the cobalt silicide growth interface, which then induces the formation of highly resistive CoSi. The control of the reaction rate between Ti and SiO_x is crucial in oxide mediated silicidation with a Ti-capping process. Following this argument, whereas a higher reaction rate can increase cobalt silicide thickness but more easily form highly resistive CoSi, a lower reaction rate can ensure CoSi₂ as the first and only phase but reduce thickness. Furthermore, the SiO_x layer must remain after annealing for a dense bulk cobalt silicide film with a smooth interface between cobalt silicide and Si. Of course, the original thicknesses of the Co, Ti, and SiO_x layers must be optimized before annealing to yield a high quality CoSi₂ thin film.

IV. CONCLUSION

The fact that a Ti-capping layer can increase cobalt silicide thickness in an oxide-mediated silicidation process is because Ti can absorb oxygen from the SiO_x layer and then dissipate or completely decompose the SiO_x layer. Proper control of the reaction rate between Ti and SiO_x during annealing to maintain the SiO_x layer of a specified thickness for a diffusion barrier will form a high quality CoSi₂ thin film of appropriate thickness. In addition, the SiO_x layer that remains also serves to prevent the direct reaction of Co with Si, which then ensures a dense bulk cobalt silicide film with a smooth interface between cobalt silicide and Si.

ACKNOWLEDGMENTS

The work is supported by NSC, Taiwan under Project No. NSC92-2120-E006-003. The authors thank Yung-Lung Hsu for analysis assistance. They are also grateful for the use of the high-resolution electron microscopy, which is supported and maintained by the Center for Micro/nano Technology Research at National Cheng Kung University, Taiwan.

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