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Citation: *Journal of Vacuum Science & Technology B* **22**, 2299 (2004); doi: 10.1116/1.1781660

View online: <http://dx.doi.org/10.1116/1.1781660>

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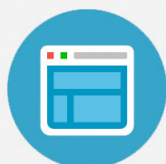
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Direct CoSi₂ thin-film formation with homogeneous nanograin-size distribution by oxide-mediated silicidation

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(Received 11 March 2004; accepted 14 June 2004; published 6 October 2004)

By annealing at 460 °C for 120 s followed by 600 °C 120 s, nanocrystalline CoSi₂ thin film with an average grain size of 5 nm can be directly formed from a Co/SiO_x/Si multilayer with the SiO_x as a mediated layer. It is found that annealing at 460 °C for enough time is crucial for generating enough diffusion channels within the SiO_x layer. After these channels are created, subsequent annealing at 600 °C keeps these channels open and is responsible for rapid grain growth. In other words, by using two-step annealing, nucleation and growth processes can be effectively controlled and, hence, the resulting microstructure. The homogeneous nanograin-size distribution is important for ultralarge-scale integration technology below 90 nm to prevent resistance degradation induced by CoSi₂ agglomeration. © 2004 American Vacuum Society. [DOI: 10.1116/1.1781660]

I. INTRODUCTION

Cobalt silicide (CoSi₂) possesses low bulk electrical resistivity and a good lattice match with Si. Therefore, CoSi₂ has been widely applied in integrated-circuit (IC) technology as the device feature size decreases. However, the normal polycrystalline-cobalt-silicide 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 limitation of linewidth and shallow source/drain junction. This agglomeration will induce large-grain CoSi₂ formation and hence resistance degradation.^{1,2}

Epitaxial CoSi₂ has been expected to resolve this problem due to its excellent thermal stability. The major methods for the fabrication of epitaxial CoSi₂ include molecular-beam epitaxy (MBE),^{3,4} mesotaxy,^{5,6} Ti-interlayer-mediated epitaxy (TIME),⁷ and oxide-mediated epitaxy (OME).^{8–10} Of the above, the MBE and mesotaxy methods are incompatible with conventional ULSI technology. The TIME method suffers from the formation of large voids in the epitaxial CoSi₂ layers near the edges of field oxides and difficulty with epitaxy on an arsenic-doped silicon.^{7,11} The OME method involves first 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 CoSi₂ layers produced by a single OME process is limited to ~11 nm. Thicker epitaxial CoSi₂ films demand repeated deposition and annealing processes using the thin CoSi₂ layer formed from the first deposition as a template. In addition, the cobalt deposition and annealing processes need to be performed in an ultrahigh-vacuum environment,^{8–10} which causes high production costs.

Alternatively, Xiao *et al.*¹² and Sun, Liaw, and Hsu¹³ report that smaller grain size and more-uniform grain size distribution have lower grain-boundary energy and larger interfacial energy. These are favorable for the thermal stability of silicide, so in other words, CoSi₂ agglomeration can be reduced. Kamal, Obeidat, and Budri¹⁴ also report that small grain size and uniform size distribution can reduce the chance for CoSi₂ recrystallization along its grain boundary. Therefore, developing polycrystalline CoSi₂ with smaller grain size and better size uniformity is still a major goal for further improvement in the current IC technology. Especially for ULSI technology below 90 nm, nanograin-size CoSi₂ is needed to prevent large-grain CoSi₂-induced resistance degradation.^{13–15} In this article, we show that homogeneous CoSi₂ with a nanograin-size of 5 nm can be achieved with the OME process by controlling the annealing temperature and time. Furthermore, the underlying mechanism is discussed.

II. EXPERIMENT

P-type (8–12 Ω cm) silicon substrates are chemically cleaned and dipped in a boiling HCl:H₂O₂:H₂O=3:1:1 so-

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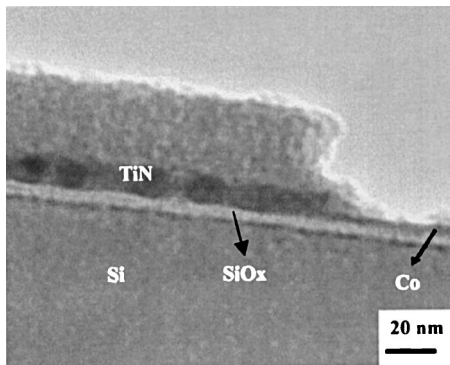


FIG. 1. Bright-field cross-section TEM image of the as-deposited sample.

lution for 3 min to form a SiO_x layer (Shiraki oxide) prior to Co deposition by dc magnetron sputtering. The Co target (99.95% purity) is pre-sputtered for 10 min after the base pressure of 3×10^{-6} Torr is reached using argon (99.995% purity) as the sputtering gas. The thicknesses of the Co and the SiO_x layers are measured to be about 4 and 2 nm, respectively, from a transmission-electron microscope (TEM) cross-sectional image. Subsequently, about 10 nm of TiN is deposited as the cap layer before exposing the sample to air. *Ex situ* annealing is carried out in a vacuum chamber at 10^{-5} Torr. Upon annealing, all layers except the reactive products are stripped off by chemical etching in order to examine the silicide layer in plain view. The TiN can be stripped off by a NH₄OH:H₂O₂:H₂O=1:1:4 solution at 50 °C. The unreacted Co is stripped off by an aluminum-etching solution (H₃PO₄ 71 wt%, HNO₃ 2.5 wt%, CH₂COOH 12.5 wt%, others H₂O) at 75 °C and the SiO_x is stripped off by a hydrofluoric acid solution. The phase and grain size of the samples are then examined by TEM. The chemical characteristics of the SiO_x layer are analyzed by Fourier-transform infrared spectrometer (FTIR).

III. RESULTS AND DISCUSSION

Figure 1 shows the bright-field TEM cross-sectional image of the as-deposited sample imaged with the Si(004) edge on condition. From the image, apparently, both the Shiraki oxide and Co layer are generally uniform, with a sharp inter-

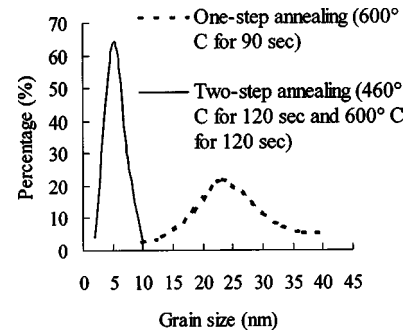


FIG. 3. Grain-size distribution between one-step annealing (600 °C for 90 s.) and two-step annealing (initially 460 °C for 120 s and then 600 °C for 120 s).

face. The thicknesses of the Shiraki oxide and Co layer are calibrated to be about 2 and 4 nm, respectively.

Figures 2(a) and 2(b) are the TEM bright-field plain-view images and diffraction patterns of the reactive silicide upon annealing with all the other layers removed, where the annealing conditions are (a) 600 °C for 90 s and (b) 460 °C for 120 s followed by 600 °C for 120 s. Both diffraction patterns show that the silicide is CoSi₂. Although Co is deposited by sputtering, the resulting phase agrees with that of Tung and Ohmi^{8–10} bypassing CoSi, Co₂Si. SiO_x acts as a diffusion barrier, the Co diffusion rate toward the Si substrate is reduced. According to Vantomme¹⁶ and Pretorius,¹⁷ if the Co effective concentration at the cobalt–silicide growth interface is low enough, this will lead to the biggest negative change in the free energy for the CoSi₂ formation. Furthermore, 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, the CoSi₂ formation needs not to break the CoSi bonding.¹⁸

Comparing Figs. 2(a) and 2(b), the most striking feature is the average grain size and the grain size distribution as shown in Fig. 3, which are 24 ± 7.0 and 5 ± 1.8 nm, which corresponds to one-step and two-step annealing, respectively. Both diffraction patterns in Fig. 2 show a strong 111-preferred orientation, while the diffraction rings in Fig. 2(b) appear to be much more diffuse than in Fig. 2(a). This con-

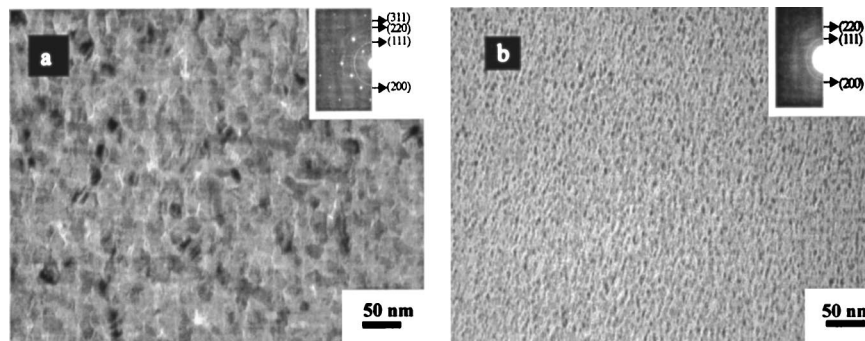


FIG. 2. TEM bright-field plain-view images and diffraction patterns of the samples upon annealing with the TiN-capped layer, unreacted cobalt, and SiO_x removed, where the annealing conditions are (a) 600 °C for 90 s, (b) initially 460 °C for 120 s, and then 600 °C for 120 s.

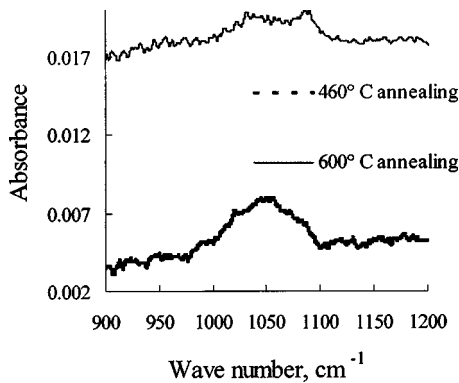


FIG. 4. FTIR spectra of the SiO_x layer after 460 and 600 °C annealing for 5 min.

firmes the much smaller grain size in Fig. 2(b). Apparently, two-step annealing produces smaller and more-homogeneous grain-size distribution than one-step annealing, although the sample for the two-step annealing also experiences higher-temperature annealing (600 °C) for an even longer time of 120 s. The difference in grain size and its distribution must be due to the number of nucleation sites, which is closely related to the temperature. Due to its kinetic limitation, the nucleation site should be determined largely by the diffusion process through the SiO_x layer. Therefore, we speculate that the number of nucleation sites is closely related to the microstructure of the SiO_x, which could be a function of the annealing temperature. In the study of Fitch *et al.*,¹⁹ they show that the SiO_x becomes denser toward more stoichiometric SiO₂ upon annealing and eventually turns into SiO₂ at 900 °C for 30 s. Baten and Fedorovich^{20,21} have found that cobalt 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. The SiO_x microstructure has more interstices than SiO₂, thus more interstitial channels exist in the SiO_x. Therefore, it is supposed that because of more stoichiometric SiO₂ network, higher annealing temperatures, such as 600 °C, will reduce the number of interstitial channels and hence the CoSi₂ nucleation sites. Figure 4 shows two FTIR spectra from the SiO_x layers of two samples upon annealing at 460 °C for 5 min and at 600 °C for 5 min, respectively, with all the other layers on top of the SiO_x layers removed. From Fig. 4, the frequency spectrum from the 460 °C annealing sample exhibits a peak at about 1050 cm⁻¹, the spectrum from the 600 °C annealing sample reveals another peak at about 1075 cm⁻¹. According to Chao *et al.*,²² the absorbance frequency of SiO_x is from 1025 to 1060 cm⁻¹ and that of stoichiometric SiO₂ is 1075 cm⁻¹. Therefore, the FTIR results support our supposition because, upon 600 °C annealing, the SiO_x layer gradually turns to SiO₂. However, given that two-step annealing also includes 600 °C annealing at the second step, why are the nucleation sites not reduced? The reason is that once the diffusion channels have been formed and completely stuffed with cobalt atoms at the

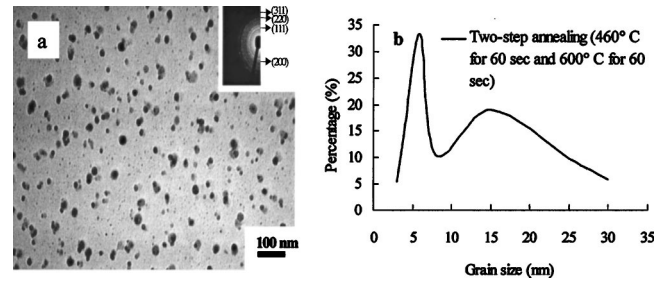


FIG. 5. (a) TEM bright-field plain-view image with diffraction pattern and (b) the grain-size distribution of the sample upon annealing with the TiN-capped layer, unreacted cobalt, and SiO_x removed where the annealing conditions are initially 460 for 60 s and then 600 °C for 60 s.

lower temperature (460 °C), the channels impede oxygen diffusion and cause the SiO_x microstructure to remain continuously open for cobalt diffusion at higher temperatures.

To further justify the assertion made for the mechanism responsible for the homogeneous nanograin-size distribution formed in Fig. 2(b), another two-step annealing experiment was performed. In this experiment, the annealing time is half that used in Fig. 2(b) to study nucleation and growth in the earlier stage. Figure 5(a) is the TEM bright-field plain-view image of this sample, where the annealing condition is 460 °C for 60 s followed by 600 °C for 60 s. 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 6 and 15 nm, as shown in Fig. 5(b). Based on the above discussion, we presume that the large-sized grains have undergone nucleation at 460 °C and grew further at 600 °C, while the small-sized grains only undergo nucleation at 460 °C and experience no further growth at 600 °C. The annealing time of 60 s at 460 °C apparently is inadequate to let enough Co diffuse through the SiO_x layer and form enough Co-stuffed channels. Therefore, the subsequent 600 °C annealing closes up some uncompleted Co diffusion channels by forming a more-stoichiometric SiO₂ network, which results in the bimodal size distribution. Fedorovich²¹ measured the diffusion coefficient of Co diffusion in SiO₂ film as $D=10^{-7} \exp[(-1.7 \pm 0.05)/kT] \text{ cm}^2/\text{s}$. Based on this equation, for Co to diffuse through a 2-nm-thick SiO₂ layer at 460 and 600 °C, it requires 3000 and 40 min respectively. However, because the SiO_x microstructure is looser, the activation energy should be smaller and the required time is expected to be much less.

In addition, Detavernier *et al.*²³ found that at the even-higher annealing temperature of 850 °C, a highly resistive CoSi phase forms by a lateral-growth phenomena where Si from the substrate diffuses through the CoSi₂ and reacts with the remaining Co. Following CoSi₂ nucleation directly underneath the weak regions of SiO₂ this process forms CoSi. Therefore, the higher-temperature annealing tends to cause bigger grain size, and also CoSi, which can be eliminated by two-step annealing.

IV. CONCLUSIONS

CoSi₂ thin film with the homogeneous nanograin size of 5 nm can be obtained by oxide-mediated silicidation in which cobalt is 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 for 120 s and 600 °C for 120 s). The microstructure of the CoSi₂ film can be altered by controlling nucleation and growth conditions. It is found that enough annealing time at the lower temperature of 460 °C facilitates Co diffusion through the SiO_x layer and forms the diffusion channels, which result in more nucleation sites and homogeneous nanograin-size distribution. Once the diffusion channels have been formed at 460 °C, they will remain open for subsequent annealing at higher temperatures.

ACKNOWLEDGMENTS

The work is supported by the National Science Counsel, Taiwan, under Project No. NSC91-2120-E006-003. The authors are also grateful for the use of the sputter equipment in the Semiconductor Lab, which is supported and maintained by the Department of Materials Science and Engineering at National Cheng-Kung University, Taiwan.

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