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SCIENCE DIRECT

Surface & Coatings Technology 200 (2006) 3314 – 3318

SURFACE & COATINGS TECHNOLOGY

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The study of diffusion and nucleation for $CoSi_2$ formation by oxide-mediated cobalt silicidation

Juin-Jie Chang [a], Chuan-Pu Liu [b], Tsung-Eong Hsieh [a], 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] *College of Science and Engineering, National University of Tainan, Taiwan*

Available online 10 August 2005

Abstract

The role of cobalt in oxide-mediated silicidation is studied in terms of diffusion and nucleation by varying annealing conditions, oxide thickness and implantation in Si substrate. Electroscopic imaging in transmission electron microscopy shows that SiO_x act as a one-way diffusion barrier reducing the Co effective concentration at the cobalt silicide growth interface leading to $CoSi_2$ as the first formation phase during silicidation. X-ray photoelectron spectroscopy analysis shows that unreacted Co coexists with $CoSi_2$ at the interface between the SiO_x layer and Si substrate, implying that Co diffusion rate is faster than $CoSi_2$ nucleation rate. An Si-implanted substrate can increase the $CoSi_2$ nucleation rate and reduce the Co accumulation.

Keywords: Cobalt silicide; Diffusion; Nucleation; Oxide-mediated silicidation

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, the normal process to form polycrystalline cobalt disilicide still suffers from serious issues such as agglomeration, silicon consumption and 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 et al. [3–5] has proposed oxide-mediated epitaxy (OME) technique for the epitaxial $CoSi_2$ formation, which involves with firstly the deposition of a Co thin layer (1–3 nm) onto an 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 resulting epitaxial $CoSi_2$ layer produced by the OME process was limited to ~11 nm. Thicker epitaxial $CoSi_2$ layer demands repeating the OME process using the prior thin $CoSi_2$ layer 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.

In our previous report [6], we have attempted to form $CoSi_2$ through silicidation by the slightly modified OME method. The differences were that Co was deposited by conventional sputtering and annealing was performed in lower vacuum environment, which was called oxide-mediated silicidation, and the modified OME is cost-effective and more compatible with current ULSI technology. We have shown that not epitaxial $CoSi_2$ but nano-grained (average grain size 5 nm) polycrystalline $CoSi_2$ thin film with homogeneous grain size distribution (5 ± 1.8 nm) can be obtained by properly controlling the annealing process in this method. In addition, this method also remained the advantages of the OME method in that

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

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doi:10.1016/j.surfcoat.2005.07.044

$CoSi_2$ directly formed as the first phase bypassing the CoSi and Co_2Si in lower temperature (500–700 °C) annealing with respect to the conventional process, which required >750 °C annealing temperature to ensure complete replacement of CoSi and Co_2Si with $CoSi_2$ [1,2]. The resulting $CoSi_2$ layer from this method was dense with smooth surface. All the above advantages are significant for ULSI technology because this process can reduce thermal budget, resistance and leakage current. So far, although it was believed that SiO_x acts as the diffusion barrier layer to reduce the concentration of Co that diffused to Si leading to $CoSi_2$ as the first phase [3–5], there is no direct evidence to prove it and less systematical study was carried out on the diffusion and nucleation mechanism of oxide-mediated $CoSi_2$ formation. In this paper, we attempt to investigate the formation mechanism of oxide-mediated $CoSi_2$ thin films.

2. Experimental details

P-type (8–12 Ω cm) silicon substrates without or with Si doping by Si implantation at 30 keV with a dose of 1×10^{13} atoms/cm^2 were chemically cleaned and dipped in a boiling $HCl/H_2O_2/H_2O$=3:1:1 solution for 3 min to form an SiO_x layer (Shiraki Oxide) prior to Co deposition by DC magnetron sputtering. The Co target (99.95% purity) was pre-sputtered for 10 min after the base pressure of 3×10^{-6} Torr was reached using argon (99.995% purity) as the sputtering gas. Subsequently, TiN of about 10 nm was deposited as the cap layer before exposing the sample to air. Ex situ annealing was carried out in a vacuum chamber of 10^{-5} Torr. Upon annealing, all layers except the reactive products were stripped off by chemical etching in order to examine the silicide layer on Si in plan-view. The TiN, unreacted Co and 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 of the samples was then examined by transmission electron microscope (TEM) or binding energy in X-ray Photoelectron Spectroscopy (XPS). The element distribution of the multilayered thin films was examined by energy-filtered electroscopic imaging (ESI).

3. Results and discussion

Fig. 1(a) shows a cross-sectional TEM image from the sample of the unimplanted Si substrate after 600 °C 90 s annealing with the ESI elemental maps of (b) Co and (c) Si. The thickness of the Co and SiO_x layers is about 4 and 2 nm, respectively. Fig. 1(d) is a bright-field plan-view TEM image of this sample and the corresponding diffraction pattern. The diffraction pattern shows that the characteristic rings correspond to polycrystalline $CoSi_2$. Although Co was deposited by sputtering, the resulting phase agrees well with the study of Tung et al. [3–5]. Hence, the blobs of dark contrast on Si side at the Si/SiO_x interface as indicated in Fig. 1(a) are $CoSi_2$. Fig. 1(b) exhibits that while Co diffuses into the Si substrate after annealing, Si diffuses less out due to inhibition from the SiO_x layer as shown in Fig. 1(c). This is a direct evidence in that the SiO_x acts as a one-way diffusion barrier to inhibit Si and Co interdiffusion from forming CoSi and Co_2Si [1,2]. According to Vantomme et al. [7] and Pretorius and Mayer [8], if the Co effective concentration at the cobalt silicide growth interface is low enough, the biggest negative change in the free energy would lead to the $CoSi_2$ formation. In addition, direct $CoSi_2$ formation can effectively reduce the formation temperature because the reaction path is $Co+2\ Si\rightarrow CoSi_2$ rather than $CoSi+Si\rightarrow CoSi_2$, in other words, it needs not to break the CoSi bonding [9]. In the oxide-mediated silicidation process, SiO_x not only acts as a diffusion barrier to reduce the concentration of Co diffusing into Si but also inhibits Si from out-diffusion. Because $CoSi_2$ forms directly bypassing CoSi and Co_2Si, the formation temperature is effectively reduced to 600 °C. Vantomme et al. [7] even reported an even lower formation temperature of 360 °C.

But what is the diffusion path of Co in the SiO_x layer to Si? Baten et al. [10] and Fedorovich [11] have found that cobalt diffuses through SiO_2 without any chemical interaction with the SiO_2 networks but only occupies interstices of the very open SiO_2 structure and migrates along the interstices as diffusion channels without affecting the regular lattices. The SiO_x microstructure is more porous than SiO_2, thus more interstices channels exist in the SiO_x. Detavernier et. al. [12] also found the $CoSi_2$ formation has taken place underneath the weak points of SiO_2. Fig. 2(a) is a cross-sectional TEM image of the same unimplanted Si sample annealed at 600 °C for 60 s. In Fig. 2(a), the microstructure of the SiO_x layer is apparently still intact after annealing, which supports the previous results in that Co diffuses through the interstices as diffusion channels without affecting the regular lattices. The $CoSi_2$ grains formed discontinuously underneath the SiO_x layer, which implies that the SiO_x networks in these areas are more porous leading to the faster Co diffusion rate here. These areas are apparently "weak points" of the SiO_x layer. The corresponding bright-field plan-view TEM image in Fig. 2(b) shows discontinuous grain distribution, which is also characterized by Co diffusing only through the weak points of the SiO_x layer leading to island morphology rather than a continuous film. Besides, from the Co ESI map in Fig. 1(b), the Co signal over the SiO_x layer is not uniform but concentrates more on some diffusion channels, which provide further evidence. Hence, a uniform SiO_x layer is crucial for a uniform $CoSi_2$ thin film formation. In order to visualize the effect of oxide thickness on Co diffusion, Fig. 3 shows a bright-field cross-sectional TEM image of the sample with a thinner SiO_x layer of about 0.8 nm annealed at a lower temper-

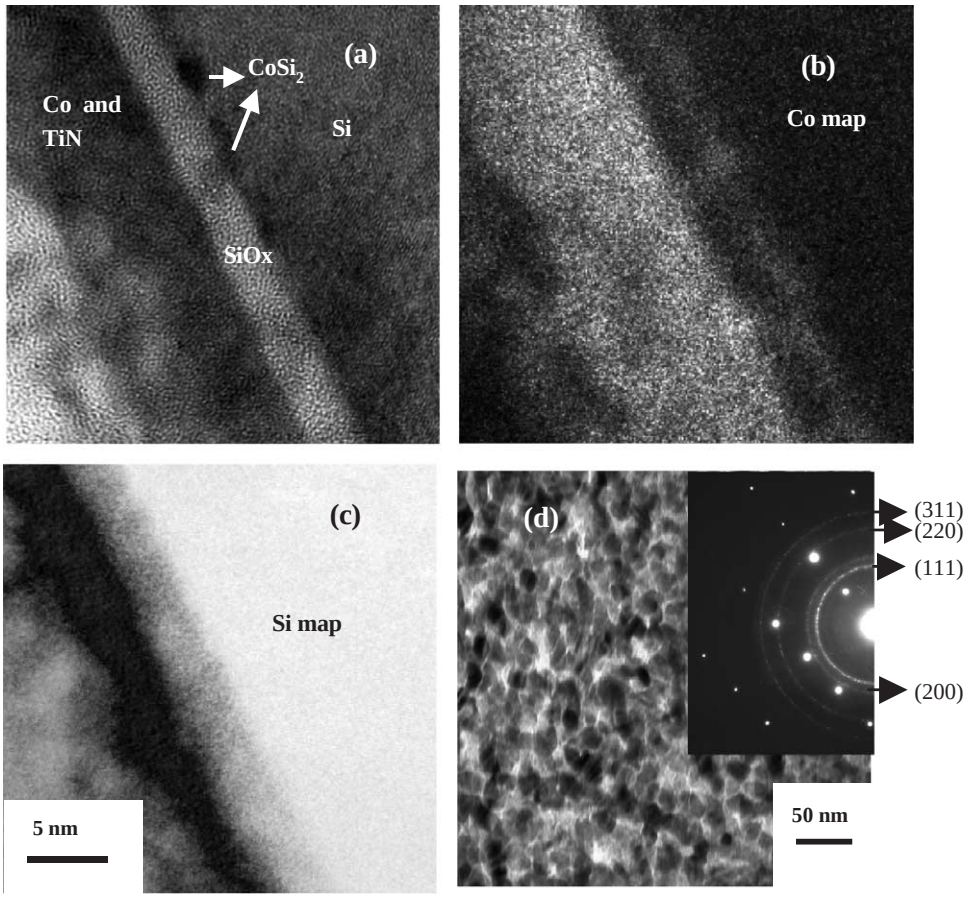

Fig. 1. (a) A cross-sectional TEM image of the sample without Si implantation annealed at 600 °C for 90 s, with ESI elemental maps for (b) Co and (c) Si; (d) a bright-field plan-view TEM image and diffraction pattern of the reactive silicide.

ature of 460 °C for 120 s. Even annealed at a lower temperature, the island morphology was enhanced and shown to be bigger (~10 nm) compared to that in Fig. 2(a) (~2 nm). It was estimated that the time required for the same diffusion distance at 460 °C is about 80 times than 600 °C [6]. This justifies that the Co diffusion is non-uniform diffusion only through the weak points. Therefore, from Fig. 3, Co diffuses through the SiO_x layer and forms a wavier cobalt silicide, more apparently indicating that Co easily diffuses through the weak points in the SiO_x layer. The thicker $CoSi_2$ thin film in Fig. 3 also implies that Co can more easily diffuse through a thinner SiO_x layer.

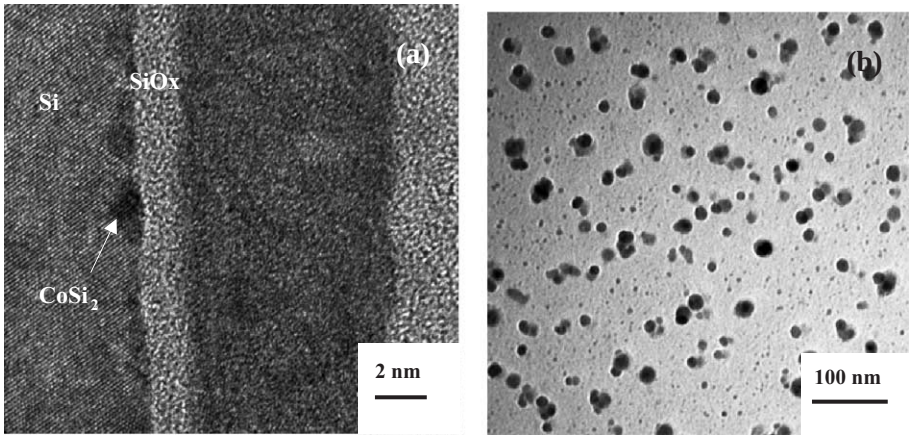

Fig. 2. (a) A bright-field cross-sectional TEM image of the sample without Si implantation for the annealing condition of 600 °C for 60 s with the corresponding plan-view TEM image in (b).

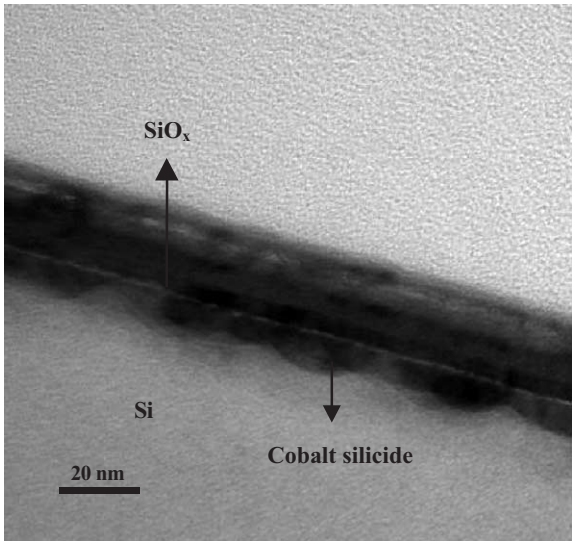

Fig. 3. A bright-field cross-sectional TEM image of the sample without Si implantation for the annealing condition of 460 °C for 120 s.

Fig. 4 shows XPS results from two samples with and without Si implantation in the Si substrate with unreacted TiN, Co and SiO_x removed, where the annealing condition was 460 °C 60 s followed by 600 °C 60 s annealing. The two-step annealing applied here is intended for growing thicker and continuous $CoSi_2$ in order to obtain enough signals for XPS. Given that the annealing conditions are the same for both samples, the qualitative interpretation in the following should be still valid. The cobalt binding energy in $CoSi_2$ and Co is about 778.7 and 778 eV, respectively [13,14]. Therefore, they tend to overlap as shown in Fig. 4(a). The sample with the substrate implanted with Si should provide a more negative free energy change for $CoSi_2$ formation due to the amorphorized Si-rich surface [15]. Therefore, the peak from the sample with Si implantation becomes sharper and shifts to 778.7 eV for more $CoSi_2$ formation compared to 778 eV from the sample without Si implantation. If the peaks were de-convoluted by Gaussian distribution fitting, it is more clearly that except $CoSi_2$, excess Co of about 79% was also found in the sample without Si implantation (Fig. 4(c)), which can be largely reduced to 38% Co accumulation in the sample with Si implantation (Fig. 4(b)). This suggests that $CoSi_2$ nucleation rate is lower than Co diffusion rate resulting in Co accumulation at the interface. Vantomme et al. [7] mentioned that the effective Co concentration at the interface is determined by metal supply as well as silicide reaction rate. In other words, reducing metal supply rate can lower the effective concentration but lower silicide reaction rate can raise the effective concentration. In order to maintain $CoSi_2$ as the first formation phase, silicide reaction rate must be raised. This is the reason why the reactive deposition epitaxy and high-temperature sputtering need to be performed at an elevated substrate temperature for higher silicide reaction rate [7,16]. This also explains why the Co thickness, more than 3 nm in the OME, tends to form CoSi

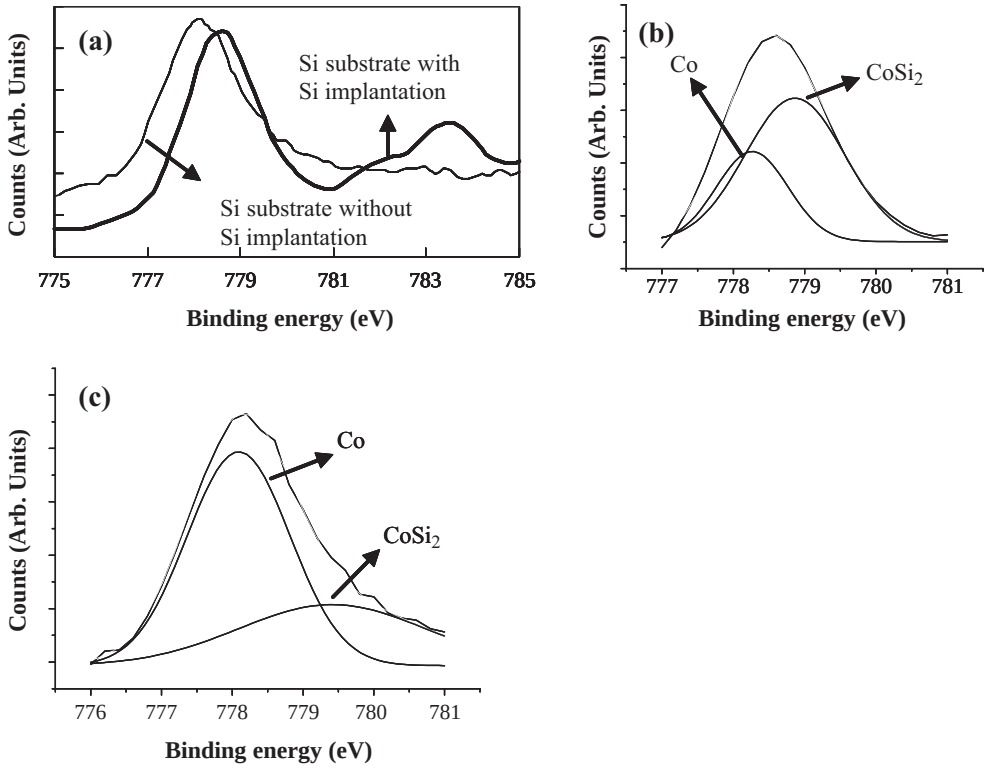

Fig. 4. (a) XPS results from two samples with and without Si implantation in the Si substrate with unreacted TiN, Co and SiO_x removed, where the annealing condition was 460 °C for 60 s followed by 600 °C for 60 s annealing. The deconvolution of the main peak in (a) is shown in (b) for the sample with Si implantation and (c) for the sample without Si implantation.

and Co_2Si instead [3–5], because a thicker Co layer increases Co diffusion rate.

4. Conclusions

The diffusion and nucleation mechanisms of the oxide-mediated cobalt silicidation are studied in this paper. Co diffuses through the weak points of the SiO_x layer and then reacts with Si to form cobalt disilicide. The SiO_x layer acts as a one-way diffusion barrier to reduce the Co concentration and increase Si concentration in the cobalt silicide growth interface, which induces $CoSi_2$ formation as the first phase in lower annealing temperature. The Co diffusion rate is higher than the $CoSi_2$ nucleation rate at 600 °C, so that excess Co coexists with the reacted $CoSi_2$. An Si-implanted Si substrate can increase the $CoSi_2$ nucleation rate and reduce the residual Co accumulation. The understanding of diffusion and nucleation mechanisms of the oxide-mediated cobalt silicidation is essential for the formation of a high-quality $CoSi_2$ thin film.

Acknowledgements

The work is supported by NSC, Taiwan under the project number of NSC92-2120-E006-003. The authors thank Mr. Wen-Chu Hsiao for analysis assistance. We are also grateful for the use of the high-resolution electron microscopy in the paper, which is supported and maintained by the Center for Micro/Nanotechnology Research at National Cheng-Kung University, Taiwan.

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