

Arsenic 도즈 량에 따른 코발트 실리사이드 표면 위의 이상 산화

조일현, 성낙균, 최경근, 이종근, 이원규*

하이닉스 반도체, System IC 연구소, Logic 공정, 강원도 춘천시 강원대학교 화학공학과*

Effect of As Dose on Abnormal Growth of Oxide on CoSi₂

Ihl Hyun Cho, Nak Kyun Sung, Kyoung Keon Choi, Jeong-Gun Lee, Won Gyu Lee*

Hynix Semiconductor, System IC R&D Division, Logic Process, Kangwon National University*

서론

In order to obtain high-speed logic devices and to minimize chip size without shrinking contact size, cobalt silicide and borderless contact (BLC) have been extensively investigated [1]. Silicon nitride is generally used as an etch-stop barrier in BLC. The direct deposition of silicon nitride on CoSi₂ films and Si-substrates can degrade device reliability such as hot carrier lifetime because of the defects generated in Si by constrain stress [5]. In order to avoid degradation of device reliability, silicon oxide is chemically deposited on CoSi₂ and Si, prior to deposition of silicon nitride.

We found that the contact resistance (R_c) of CoSi₂ formed on n⁺ doped Si was more degraded than that on p⁺ doped Si, as shown in Fig. 1, when an Si oxide and nitride double layer structure on cobalt silicide is used as an etch barrier. The thick oxide on CoSi₂ films grew in the n⁺ doped Si region rather than in the p⁺ region, as shown in Fig. 2. Thus the contact hole for the n⁺ region was not well defined, resulting in an increase in the contact resistance. As and P were used for n⁺ dopants. Enhancements of oxide growth rate on highly n⁺ doped Si under exposure by boiling deionized water and increased deposition rates of silicon dioxide films on phosphorous-doped Si have been reported [2]. Thus we assumed that the dopants influence the oxide growth on CoSi₂ films. The oxidation kinetics of CoSi₂ on (111) Si by transmission electron microscopy (TEM) have been investigated [3]. However, no research on As concentration dependence of LPCVD oxide growth behavior on CoSi₂ has been reported. In this study, we investigated the effect of arsenic doping level on LPCVD of SiO₂ growth on CoSi₂ films and discussed the origin of abnormal growth of SiO₂.

본론

The effect of As concentration on CoSi₂ formation is shown in Fig. 3, where the XRD patterns and sheet resistances of CoSi₂ films with As dose are presented. CoSi₂ (220) peaks were observed only for the samples with As dose up to $1 \times 10^{15} \text{ cm}^{-2}$, but no peaks appeared at a dose of $1 \times 10^{16} \text{ cm}^{-2}$. The CoSi₂ (220) peak showed maximum intensity at the As dose of 1×10^{15} , suggesting that the formation of CoSi₂ significantly depends on As concentration in Si substrates. On the other hand, no peaks corresponding to a CoSi₂ phase were observed for the As dose of 1×10^{16} , which indicates that CoSi₂ formation was prevented by the high dose As in Si. Similar behavior was reported for TiSi₂ silicide systems: TiSi₂ formation was suppressed by high dose As-implanted Si substrates [4]. The sheet resistance of samples with As dose below $5 \times 10^{15} \text{ cm}^{-2}$ was as low as 6 ohm/□, but it abruptly increased to about 50 ohm/□ at a dose of $1 \times 10^{16} \text{ cm}^{-2}$. This abnormal increase in sheet resistance is probably caused by the formation of thin CoSi₂ or a different phase from CoSi₂. As mentioned above with the XRD results, this finding also supports that the heavily As-doped Si blocks the formation of uniform CoSi₂ crystallites.

Figs. 4(a)-4(b) show cross-sectional TEM images of LPCVD SiO₂/CoSi₂ films with As dose. For the As dose up to $1 \times 10^{15} \text{ cm}^{-2}$, uniform CoSi₂ films of 40 nm in thickness were obtained, and the silicon oxide thickness slightly increased with increasing dose. At a dose of $1 \times 10^{16} \text{ cm}^{-2}$, however, non-uniform CoSi₂ layers below 10 nm in thickness and thick SiO₂ were observed. This result

indicates that the highly doped As in Si suppressed the formation of uniform CoSi_2 resulting in high sheet resistance of CoSi_2 for the As dose of 10^{16} cm^{-2} . In addition, the formation of a layer silicon oxide of about 60 nm-thickness on CoSi_2 is unexpected, as approximately 15 nm-thick silicon oxide should be deposited on bare Si wafer according to our deposition rate.

Figs. 5(a)-5(b) show the SIMS depth profiles of the same samples used for TEM analysis. The depth profiles of Co and Si atoms show an uniform CoSi_2 phase for As dose up to $1 \times 10^{15} \text{ cm}^{-2}$, which is consistent with the TEM results. As shown in Fig. 5(b), for As dose of 10^{16} cm^{-2} , the uniform CoSi_2 layer disappeared, and a thick SiO_2 layer larger than 60 nm in thickness was observed. The Co depth profiles extended to the oxide film and its depth profile shows similar behavior with As, rather than with Si, in the whole range, suggesting the formation of a Co-As compound for the As dose of $1 \times 10^{16} \text{ cm}^{-2}$. Since the formation energy is comparable between CoAs and CoSi_2 [5], some reaction of As with Co might take place for the As dose of 10^{16} cm^{-2} , resulting in the formation of a Co-As compound during the silicidation. The limited solid solubility of As in Si also encourages Co-As compound formation. A stable tie line exists between CoSi_2 and the Co-As compound according to the phase diagram; thus the Co-As compound is stable with respect to an overlaying CoSi_2 film. However, there is no experimental evidence for any Co-As compound formation.

As shown in Figs. 5(a), the As depth profiles change at the interface of $\text{CoSi}_2/\text{SiO}_2$ with As dose, which may result from the usual matrix effect; i.e., the degree of ionization and sputtering yield of As dopants increase at the interface. For the As dose of $1 \times 10^{16} \text{ cm}^{-2}$ (Fig. 5(b)), some As dopant diffused out into the cobalt silicide films and even into the SiO_2 layer from the Si-substrates. Out-diffusion of As into silicide was also revealed by X-ray photoelectron spectroscopy (XPS) (not shown in this paper). According to the phase diagram of CoSi_2 and As in Si, no tie line exists between CoSi_2 and As. Thus As doped Si is unstable with respect to an overlaying CoSi_2 film. During the CoSi_2 formation and SiO_2 deposition by LPCVD, the small amount of As in the Si-substrates diffused into silicide and oxide.

Fig. 6 shows the thickness of SiO_2 grown on both CoSi_2 film and bare Si as a function of As dose. The oxide thicknesses on CoSi_2 rapidly increased with As dose, while the thickness on bare Si increased negligibly. This result suggests that As on the CoSi_2 films accelerates the decomposition of TEOS and then increases the deposition rate of SiO_2 . As-doped Si was reported to enhance oxide growth in steam oxidation [2]. Thus, we can conclude that As on the CoSi_2 surface increased the decomposition rate of TEOS, resulting in abnormal oxide growth, especially for high As doses.

결론

The abnormal growth of SiO_2 on CoSi_2 films was mainly caused by highly doped As in Si. In addition, the highly doped As in Si interrupted the formation of CoSi_2 and increased contact resistance. Thus, we have carefully to control the As concentration in Si to prevent abnormal oxide growth on CoSi_2 and to obtain low contact resistivity for the interconnection lines to Si substrates when we use a oxide and nitride layered structure as a etch barrier. For stable process control, the suppression of rapid growth of oxides on CoSi_2 is essential. This point will be addressed in future work.

참고문헌

- [1] K. Maex, Materials Science and Engineering, R11 (1993) 53.
- [2] E. Biermann, H. H. Berger, P. Linke, B. Muller, J. Electrochem. Soc. 143 (1996) 1434.
- [3] G. J. Huang, L. J. Chen, J. Appl. Phys. 76 (1994) 865.
- [4] H. Fang, M. C. Ozturk, E.G. Seebauer, D.F. Batchelor, J. Electrochem. Soc., 146 (1999) 4240.
- [5] K. Maex, G. Ghosh, L. Delaey, V. Probst, P. Lippens, L. Van den hove, R.F. De Keersmaecker, J. Mater. Res. 4 (1989) 1209.

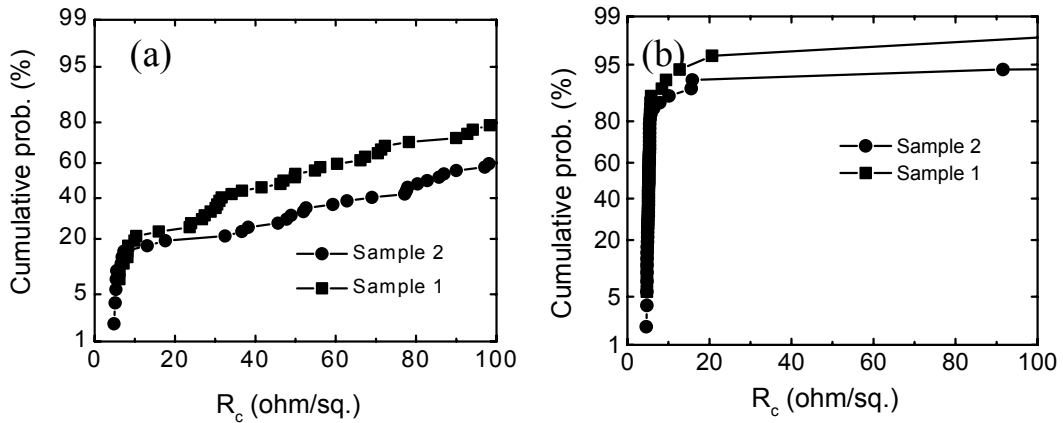


Fig.1. Cumulative plot for contact resistances for two samples of (a) n+ and (b) p+ doped Si with a Si₃N₄/SiO₂ etch stop layer.

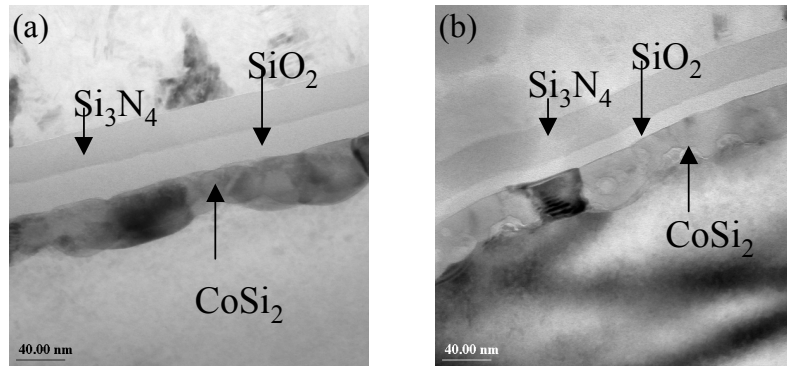


Fig. 2. Cross-sectional TEM images of Si₃N₄/SiO₂/CoSi₂ structures on (a) n+ and (b) p+ doped Si. The nitride (30 nm) and oxide (10 nm) films were deposited by low-pressure chemical vapor deposition method

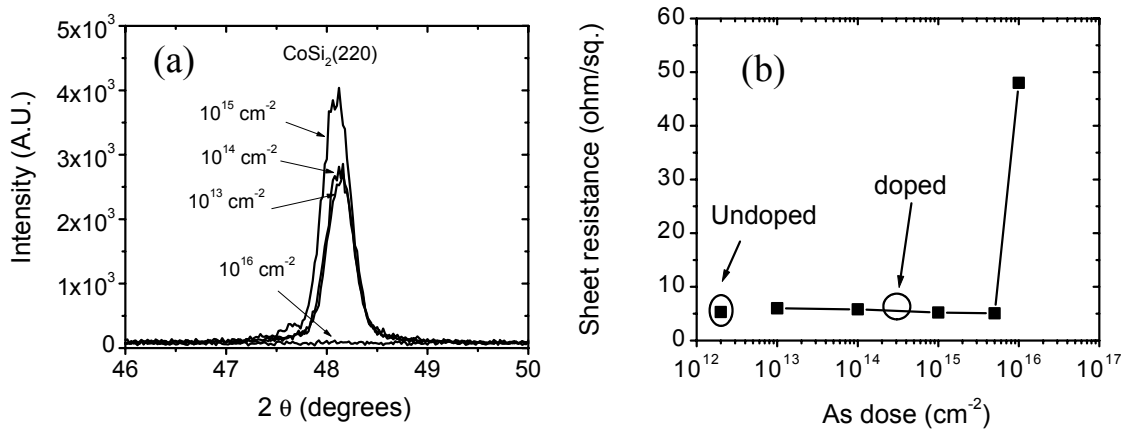


Fig. 3. (a) XRD patterns and (b) sheet resistances of CoSi₂ films as a function of As dose in Si.

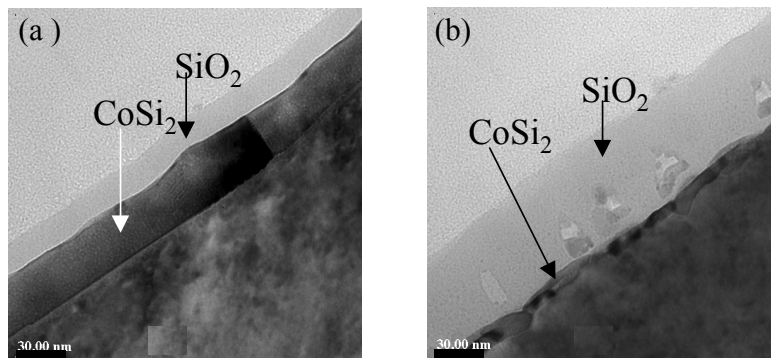


Fig. 4. Cross-sectional TEM micrographs of LPCVD SiO₂/CoSi₂ at As dose of (a) 1×10¹⁵, and (b) 1×10¹⁶ cm⁻².

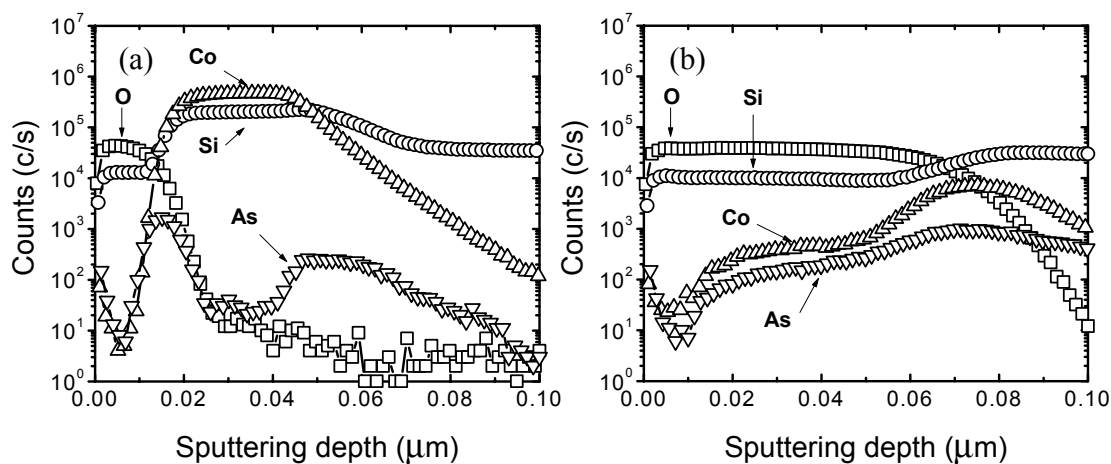


Fig. 5. SIMS depth profiles for LPCVD SiO₂ and CoSi₂ films at As dose of (a) 1×10¹⁵, and (b) 1×10¹⁶ cm⁻².

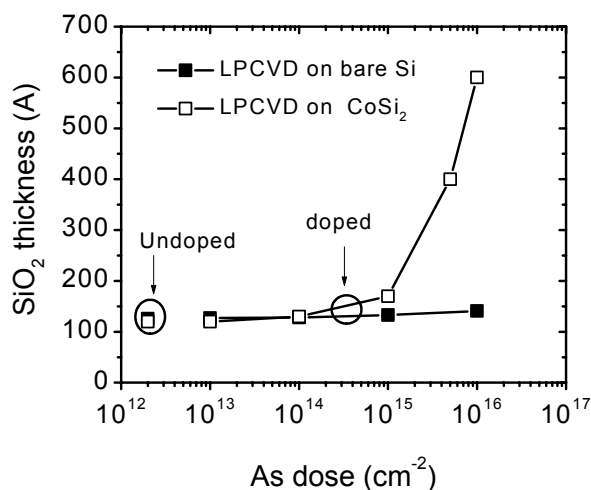


Fig. 6. The thickness of SiO₂ grown by LPCVD at 680°C for 150 s as a function of As dose. The oxide thickness was obtained by TEM.