CHIN.PHYS.LETT. Vol.11,No.4(1994)231

Slow Positron Annihilation in Silicide Films Formed by Solid State Interaction of Co/Ti/Si and Co/Si*

LIU Ping, LIN Chenglu, ZHOU Zuyao, ZOU Shichang
Ion Beam Laboratory, Shanghai Institute of Metallurgy, Academia Sinica, Shanghai 200050
WENG Huiming, HAN Rongdian
Department of Modern Physics, University of Science and Technology of China, Hefei 230026
LI Bingzong
Department of Electronic Engineering, Fudan University, Shanghai 200433

(Received 5 October 1993)

Slow positron beam was used to investigate the solid state reaction of Co/Si and Co/Ti/Si. Variable-energy (0–20 keV) positrons were implanted into samples at different depths. The Doppler broadening of the annihilation γ-ray energy spectra measured at a number of different incident positron energies is characterized by a line-shape parameter, S. It was found that the measured S parameters are sensitive to thin film reaction and crystalline characteristics. In particular, the S parameter of epitaxial $CoSi_2$ formed by the ternary reaction is quite different from that of the polycrystalline $CoSi_2$ formed by direct reaction of Co with Si.

PACS: 68.55.–a, 68.55.Eg, 68.35.–p

Epitaxial silicide films have received growing attention because of their promising applications in fabricating new structural and high-performance microelectronic devices.[1] A new approach to solid phase epitaxy of $CoSi_2$ on Si substrate through a reaction of ternary Co/Ti/Si system has been investigated.[2–6] Slow positron annihilation technique (SPAT) has been developed to be used as an effective way to study near-surface defects in solid and the phase transition of materials.[7–10]

A positron implanted into materials annihilates with an electron, producing two antiparallel annihilating γ photons with energy of 511 keV. A Doppler-broadened profile of these γ photons can provide information about the existence of defects. In particular, positrons are very sensitive to vacancy-like defects. The width of the spectrum becomes narrow as the density of defects increases due to the positron trapping and its annihilation at these defects. A slow positron beam consists of monoenergetic positrons of which the energy can be varied by adjusting the accelerating voltage. Variable-energy positrons could be implanted into the films at different depths. Detecting the annihilation photons, one can obtain information about defects, structure and phase-transition of the films at different depths.

We have reported the epitaxial $CoSi_2$ films with minimum channeling backscattering yields of 10–14% grown on both (100)- and (111)- oriented Si substrates by a multi-step annealing of ternary Co/Ti/Si system.[5,6] In this work, the slow positron annihilation technique was used to characterize the epitaxial $CoSi_2$ growth during the thin film reaction of Co/Ti/Si.

A set of 5–8 Ω·cm, p-type (100) Si wafers with ion beam sputtering deposited thin films of 20 nm Ti followed by 36 nm Co were multi-step annealed from 550 to 900°C in nitrogen

*Supported by Chinese Postdoctoral Science Foundation.

ambient to grow epitaxial $CoSi_2$. The details of reaction process were described in our earlier publication.[5] Six samples as listed in Table 1 were prepared for the slow positron annihilation measurement. For comparison, $CoSi_2$ film was also formed by direct reaction of Co with Si, defined as sample 6 in Table 1; and an arsenic doped Si substrate was also used for reaction of Co/Ti/Si, defined as sample 5 in Table 1. The $5\times10^{15}/cm^2$ arsenic was implanted into Si at 40 keV, followed by an activation anneal.

Table 1. Processes of samples prepared for slow positron annihilation measurements.

Sample number	Process of samples
1	Co/Ti/Si, as-deposited
2	Co/Ti/Si, 550°C, 2′
3	Co/Ti/Si, 550°C, 2′+700°C, 5′
4	Co/Ti/Si, 550°C, 2′+700°C, 5′+(750–900°C), 4′
5	Co/Ti/Si(As), 550°C, 2′+700°C, 5′+(750–900°C), 4′
6	Co/Si, 850°C, 1′

Positrons from a ^{22}Na source were thermalized in a well-annealed tungsten-vane (positron converter). The monoenergetic positrons emitted from the converter were focused and accelerated by a voltage between the grid and the tungsten-vane to 24 eV. Then they were transported to a target chamber in a longitudinal magnetic field produced by a solenoid. The final positron energy could be varied from 0 to 20 keV by adjusting the voltage applied to the target. An energy-sensitive γ-ray germanium detector was used to determine the Doppler-broadened annihilation spectra caused by the momentum of the annihilating positron-electron pairs. The shape of the spectra is characterized by a line-shape parameter, defined as

$$S = \frac{\int_{-a}^{a} C(E)dE}{\int_{-\infty}^{\infty} C(E)dE},$$

where $C(E)$ is the measured spectra taken at the incident energe E, $(-a, a)$ is central region of the spectra around 511 keV. We took an energy shift $a = 1$ keV at both sides of the peak energy of 511 keV. 2 keV He^+ Rutherford backscattering (RBS) channeling measurement was used to determine the epitaxial characteristics of $CoSi_2$.

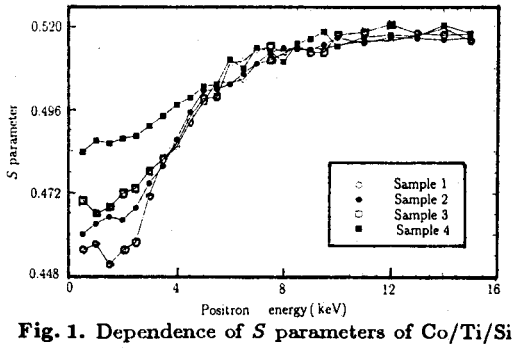

Fig. 1. Dependence of S parameters of Co/Ti/Si samples annealed at each step on incident positron energies.

Figure 1 shows dependence of the measured S parameters of Co/Ti/Si samples annealed at each step on the incident positron energies. Corresponding to implant energies higher than 5 keV the S parameters of all samples have similar values for Si substrates. The S parameters of overlayer on Si corresponding to the lower implant energies have obvious difference because of the different surface structures of the four samples caused by the reaction. Figure 2 shows variation of the S parameter at the positron implant energy $E = 2$MeV and the sheet resistance during the multi-step annealing of Co/Ti/Si system. The sheet resistance slightly increases during the early step annealing because of the interdiffusion of Co and Ti films, and decreases

down when the $CoSi_2$ starts to form inside the film. It reaches the lowest value of $1.6\Omega/\square$ after complete formation of $CoSi_2$ by the final annealing. It is notable that the S parameter in Fig. 2 gradually increases with the process of Co/Ti/Si reaction, indicating that some vacancy-like defects have been produced in the near-surface region by the reaction. Figure 3 compares the positron annihilation results of samples 4, 5 and 6 which were formed by the reaction of Co/Ti/Si, Co/Ti/Si(As), and Co/Si, respectively. The surfacial Ti containing layers above $CoSi_2$ of samples 4 and 5 were removed before the measurement. There are remarkable differences for the S parameters of near-surface regions ($CoSi_2$ films) of the three samples. The $CoSi_2$ film of sample 4 has much lower S parameters than those of samples 5 and 6.

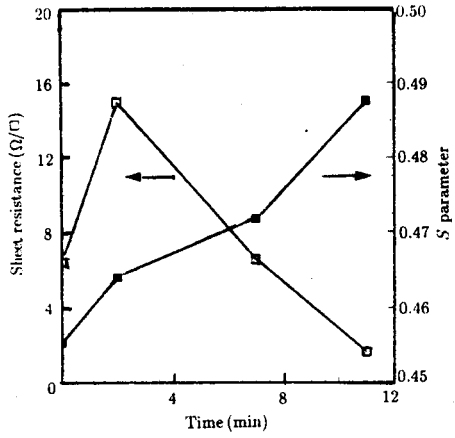

Fig. 2. Variation of the S parameter at $E = 2\,\text{keV}$ and the sheet resistance during multi-step annealing of Co/Ti/Si.

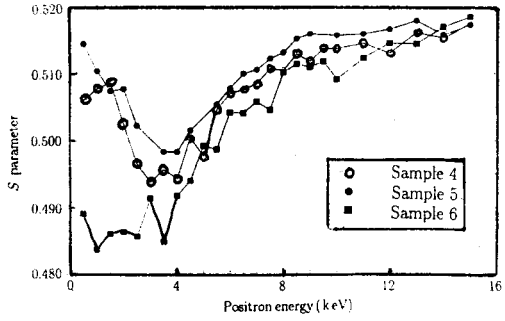

Fig. 3. Dependence of S parameters of samples 4, 5 and 6 on incident positron energies.

Figure 3 reveals that the three samples have quite different crystalline structures of $CoSi_2$. The solid state reaction Co and Si with a thin interposing Ti layer has led to growth of epitaxial $CoSi_2$ film on Si. During the early stage annealing of Co/Ti/Si, the thin Ti layer played an effective role to getter the residual oxygen at Si surface, providing an atomically clean Si surface for the following reaction of Co with Si. And the Ti moved to the surface to form TiN(O) on top of $CoSi_2$.[5] The epitaxial $CoSi_2$ has a single crystalline nature with a small lattice mismatch with Si and a low density of defects. The direct reaction of Co with Si, however, resulted in a polycrystalline $CoSi_2$ which contained a large amount of grain boundaries and higher density of defects than the epitaxial $CoSi_2$. In general, atoms have a lower activation energy of motion in the grain boundaries and vacancy formation is easier because of the excess volume in the boundaries.[11] The polycrystalline $CoSi_2$ with many grain boundaries can provide much more sites for positron annihilation. Table 2 lists the S parameters and RBS channeling (Si⟨100⟩ aligned) minimum yields of samples 4, 5

and 6. The dopant arsenic implanted into Si substrate significantly degrades epitaxial growth of $CoSi_2$ in the reaction Co/Ti/Si, resulting in a higher S-parameter than that of sample 4. It can be derived from Table 2 that the S-parameter of $CoSi_2$ has a close relation with the extent of epitaxial growth of $CoSi_2$.

Table 2. Measured S parameter and RBS minimum channeling yields of samples 4, 5 and 6.

Sample number	S parameter at $E = 2$keV	RBS minimum channeling yields
4	0.4876	12%
5	0.5024	50%
6	0.5076	No channeling effect

In conclusion, the slow positron technique provides a nondestructive way to detect the thin film reaction and crystalline characteristics. The S parameter of Doppler-broadened annihilation line-shape for the Co/Ti/Si samples was increasing with the reaction procedure due to the generation of vacancy-like defects in near-surface region. Without the effect of grain boundaries, the epitaxial $CoSi_2$ grown by the reaction of Co/Ti/Si has much lower S parameters than the polycrystalline $CoSi_2$ grown by the direct reaction of Co/Si. Arsenic initially implanted into Si substrate degrades the epitaxial growth of $CoSi_2$ in the reaction of Co/Ti/Si, resulting in an increase of S parameters.

Acknowledgements: The authors would like to thank Dr. Y. H. Yu for his helpful discussion, and Z. X. Lin, Z. P. He, Z. Sun and L. L. Di for their assistance in sample preparation.

REFERENCES

[1] T. Ohshima, N. Nakamura, K. Nakagawa, K. Yamaguchi and M. Miyao, 1991 IEDM Technical Digest, p. 33.
[2] M. L. A. Dass, D. B. Fraser and C. S. Wei, Appl. Phys. Lett. 58 (1991) 308.
[3] S. L. Hsia, T. Y. Tan, P. Smith and G. E. McGuire, J. Appl. Phys. 70 (1991) 7579.
[4] A. Vantomme, M. A. Nicolet, G. Bai and D. B. Fraser, Appl. Phys. Lett. 62 (1993) 243.
[5] P. Liu, B. Z. Li, Z. Sun, Z. G. Gu, W. N. Huang, G. B. Jiang, Z. Y. Zhou, R. S. Ni, C. L. Lin, S. C. Zou, F. Hong and G. A. Rozgonyi, J. Appl. Phys. 74 (1993) 1700.
[6] B. Z. Li, Z. Sun, P. Liu, Z. G. Gu and W. N. Huang, in *10th International IEEE VLSI Multilevel Interconnection Conference*, June, 1993.
[7] K. G. Lynn, D. M. Chem, B. Nielsen, R. Paraja and S. Myers, Phys. Rew. B34 (1986) 1949.
[8] C. Corbel, M. Stucky, P. Hautojarvi, K. Saarinen and P. Moser, Phys. Rew. B38 (1988) 8192.
[9] J. L. Lee, L. Wei, S. Tanigawa and M. Kawabe, J. Appl. Phys. 68 (1990) 5571.
[10] H. M. Weng, X. Z. Guo, R. D. Han, X. J. Shi, J. S. Zhu, T. X. Zhao and X. P. Wang, Nuclear Instruments and Methods in Physics Research, A307 (1991) 577.
[11] K. N. Tu, J. W. Mayer and L. C. Feldman, *Electronic Thin Film Science*, (Macmillan Publishing Company, 1992) Chap. 13.