

Thin Solid Films 320 (1998) 206-210



Co-deposition of cobalt disilicide on silicon–germanium thin films¹

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Received 28 May 1997; accepted 7 October 1997

Abstract

The formation of CoSi_2 on strained epitaxial $\text{Si}_{0.8}\text{Ge}_{0.2}/\text{Si}(100)$ films has been studied as a function of the deposition method and annealing temperature. Two types of deposition processes were used: a direct method, where 5 nm of pure Co metal were deposited at room temperature onto a strained 80 nm thick $\text{Si}_{0.8}\text{Ge}_{0.2}$ layer; and a co-deposition method, where 5 nm Co and 18.2 nm Si were simultaneously deposited in a 1:2 ratio onto a strained $\text{Si}_{0.8}\text{Ge}_{0.2}$ layer at 450°C. Samples were then annealed at temperatures ranging from 500 to 800°C. Extended X-ray absorbance fine structure spectroscopy (EXAFS) and X-ray diffraction (XRD) were used to characterize the structure of the resulting films. It was found that the samples prepared via the direct deposition method did not convert to CoSi_2 at any annealing temperature up to 800°C, while the co-deposited samples formed epitaxial CoSi_2 at even the lowest annealing temperature of 500°C. These results are discussed in terms of proposed reaction mechanisms of the different deposition methods, based on consideration of the Co–Si–Ge ternary phase diagram. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt disilicide; Silicon-germanium alloys; EXAFS

1. Introduction

The development of Si–Ge based devices has created the need for stable, low thermal budget, low resistivity metal–silicide contacts to SiGe alloys. Metal/SiGe systems based on Ti, Co, Zr, Ni, Pd and Pt have previously been studied [1–7]. CoSi₂ has a low resistivity and forms epitaxial films on Si, thus it makes a promising candidate for a contact material to SiGe alloys. Previous studies with CoSi₂ contacts to SiGe have utilized the direct deposition of Co onto the SiGe alloy, however, annealing temperatures \geq 700°C have been required to form the silicide and the problem of Ge phase segregation has also been observed [4,6,7]. Thus, other methods of preparing the silicide were sought.

Some insight into the behavior of Co deposited onto SiGe alloys has been gained from inspection of the bulk Co–Si–Ge ternary phase diagram [8], shown in Fig. 1. Region C is an area in which various solid solutions of CoSi and CoGe are in equilibrium with Si_{1-x}Ge_x solid

¹ Presented at the FCMCTF Conference '97 San Diego, CA, USA. April 21-25, 1997.







Fig. 1. The Co–Si–Ge ternary phase diagram determined at 760°C for alloys below 50 at.% Co and at 950°C for alloys above 50 at.% Co [8].

solutions for $0.71 \le x \le 0.94$. It has been proposed that the reaction of pure Co with a SiGe alloy may be expected to form a meta-stable Co(Si_{1-v}Ge_v) phase. As observed by

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Wang et al. [6] and Qi et al. [9], the reaction path to CoSi_2 formation must then go through this meta-stable $\text{Co}(\text{Si}_{1-y}\text{Ge}_y)$ phase in order to form first CoSi by expulsion of Ge and then CoSi_2 . Another region of the phase diagram is relevant to the co-deposition of Co and Si onto SiGe alloys. In Fig. 1, region E is a two phase region where CoSi_2 is in bulk equilibrium with $\text{Si}_{1-x}\text{Ge}_x$ alloys for $x \le 0.71$. The presence of this region suggests that co-deposition of Co and Si onto SiGe alloys can avoid the phase segregation and lead to more stable CoSi_2 contacts to SiGe alloys than the direct deposition of Co.

2. Experimental

All samples were prepared using 25 mm n-type Si $\langle 100 \rangle \pm 0.5^{\circ}$ wafers, 0.5 mm thick, with a resistivity of 5–10 Ω cm (Virginia Semiconductor). The wafers were spin etched [1] with a solution of HF:H₂O:C₂H₅OH (1:1:10) immediately prior to loading into the UHV electron beam evaporation chamber. The base pressure of the chamber was 2.7×10^{-8} Pa. After loading, the wafers were heated to >900°C for 10 min to thermally desorb any remaining oxide. A 20-nm Si buffer layer was then deposited onto the wafers at 550°C, from which a sharp 2×1 RHEED pattern was observed along the [110] azimuth, indicating a well ordered surface. Next, an 80 nm thick Si_{0.8}Ge_{0.2} layer was deposited onto the wafers while maintaining the substrate at 550°C. Two different methods were then utilized to produce the subsequent silicide layer: direct deposition, where 5 nm of Co were directly deposited onto the Si_{0.8}Ge_{0.2} layer at room temperature ('direct' deposited samples); and co-deposition, where 5 nm of Co and 18.2 nm of Si were co-deposited onto the Si_{0.8}Ge_{0.2} layer at 450°C ('co-deposited' samples). Samples of each type were then annealed at temperatures ranging from 500 to 800°C for 10 min. The heating and cooling rate used in all cases was 40°C/min. One 20 nm and one 5 nm direct sample were prepared as above excepting they were annealed at 700°C for 20 min.

The structural properties of the films were studied using XRD and EXAFS. EXAFS data were collected in total electron yield (TEY) mode at the Co K-edge at beamline X-11A at the NSLS. A Rigaku Geigerflex diffractometer using Cu K_{α} radiation and a (0001) graphite monochromator was used to collect the XRD data in the θ -2 θ mode.

3. Results

XRD patterns for 20 nm and 5 nm direct deposited samples annealed for 20 min each are shown in Fig. 2a. The Si $\langle 001 \rangle$ 'ghost' reflection, which is due to the

substrate itself, is observed when the substrate has good crystallinity and is well aligned within the goniometer. The 'ghost' reflection consists of two peaks, a strong one at 33.0° and a weaker one at 33.6° , superimposed on a broad background peak which covers a 2θ range from approximately 32° to 37° . The smaller substrate peak at 33.6° is obscured by the CoSi₂ (200) peak in the scan of the 20 nm sample in Fig. 2a, but it is observed in the patterns in Fig. 2b,c. The EXAFS results, discussed below, indicate the absence of CoSi₂ in the direct deposited samples, therefore it is clear that the small peak appearing at 33.6° in the XRD patterns of the direct deposited samples in Fig. 2b cannot be due to CoSi₂. The pattern of the 20 nm direct deposited sample contains reflections due to the CoSi₂ (111), (200) and (220) planes. A peak corresponding to the CoSi (210) reflection is also observed as well as small peaks due to the CoSi (211) and CoSi (110) reflections. The pattern for the 5 nm direct deposited sample in Fig. 2a shows only a CoSi (210) reflection and a just discernible CoSi (211). Fig. 2b shows the XRD patterns for 5 nm direct deposited samples annealed for 10 min at temperatures ranging from 500 to 800°C. The evolution of the CoSi (210) reflection with increasing annealing temperature is observed. Fig. 2c shows the XRD spectra of the 5 nm co-deposited samples annealed for 10 min at temperatures of 500, 600 and 700°C. No peaks other than the substrate ghost peak are observed in any of the co-deposited sample diffraction patterns.

The Fourier transforms of the EXAFS data are shown in Fig. 3. No phase correction was performed. Shown in Fig. 3a are the EXAFS spectra of the 5 nm direct deposited samples annealed for 10 min. All of these spectra indicate Co-Si bonding characteristic of the CoSi structure. Fig. 3b shows the spectra of the 5 nm co-deposited samples annealed for 10 min, as well as a CoSi₂ standard spectra formed by co-depositing Co and Si onto a pure Si $\langle 100 \rangle$ substrate and annealing to 700°C. In each case, the characteristic CoSi₂ structure is observed. The appearance of the higher shells indicates the presence of long range order. Shown in Fig. 3c are the spectra of the 20 nm and 5 nm direct deposited samples annealed for 20 min at 700°C. The EXAFS spectra of the 20 nm sample indicates a transition from the CoSi structure to the CoSi₂ structure while the 5 nm sample shows bonding characteristic of CoSi.

4. Discussion

The XRD pattern of the thicker 20 nm direct deposited sample in Fig. 2a indicates that this sample contains CoSi and CoSi₂ after annealing to 700°C. Previous work by Wang et al. [6,7] on samples prepared similarly to the 20 nm direct deposited sample in this study suggested that the reaction path to CoSi₂ formation began with the formation of a Co(Si_{1-v}Ge_v) phase at low annealing temperatures.



Fig. 2. XRD patterns of (a) 20 nm and 5 nm direct deposited samples annealed at 700°C for 20 min; (b) 5 nm direct deposited samples annealed at 500–800°C for 10 min; and (c) 5 nm co-deposited samples annealed at 500–700°C for 10 min.

The Ge *y* index was initially lower than that of the $Si_{0.8}Ge_{0.2}$ substrate and decreased with increasing annealing temperature. Upon annealing to higher temperatures, the $Co(Si_{1-y}Ge_y)$ converted to CoSi and then $CoSi_2$. Evidence for this reaction mechanism was given by XRD data which showed that the CoSi (210) and (211) reflections appeared at lower angles than those of pure CoSi at annealing temperatures around 400°C. Upon progressive annealing to 700°C, the (210) and (211) peaks gradually shifted up to the angles corresponding to those of pure

CoSi. Wang et al. proposed that expansion of the interplane spacing of the (210) and (211) planes, attributed to formation of Co(Si_{1-y}Ge_y), was responsible for the initially lower 2θ values. Expulsion of the Ge by annealing to higher temperatures caused 2θ for the (210) and (211) planes to shift up to the pure CoSi values. Based on polarization dependent EXAFS measurements of these samples at the Co K-edge, which indicated the films were not strained, Wang et al. [7] ruled out straining of the CoSi as the cause of the shift. In the present study, the CoSi



Fig. 3. Fourier transforms of k^2 -weighted EXAFS data for (a) direct deposited samples annealed at 500–800°C for 10 min; (b) co-deposited samples annealed at 500–700°C for 10 min; and (c) 20 nm and 5 nm direct deposited samples annealed at 700°C for 20 min.

reflections for the 20 nm sample, which was annealed to 700°C, were not shifted and thus it was concluded that the $Co(Si_{1-y}Ge_y) \rightarrow CoSi$ transition was complete and that the sample was undergoing the transition from CoSi to $CoSi_2$. This conclusion is also supported by the EXAFS measurements for this sample (Fig. 3c) which indicate the presence of both CoSi and CoSi₂ type bonding.

The 5-nm direct deposited samples prepared in this study behaved differently than the 20 nm sample upon annealing. The EXAFS results in Fig. 3a indicate that no transition to $CoSi_2$ occurred at any annealing temperature from 500 to 800°C for these samples, which were annealed for 10 min. A 5 nm direct deposited sample annealed for 20 min (Fig. 3c) at 700°C began to show some evidence of a transition to $CoSi_2$ type bonding by the slight change in the relative amplitude of the first shell Si and first shell Co peaks. No $CoSi_2$ reflections were observed in the XRD

patterns. However, EXAFS is more sensitive to short range order than XRD, and the initial CoSi₂ which forms may be disordered. A 'thin film effect' is also observed in the reaction of Ti on Si where the C49 to C54 transition temperature is shown to increase as the Ti thickness decreases [10–12]. It was proposed by Jeon et al. [11] that decreasing Ti film thickness may cause a change in the equilibrium shape of the C54 TiSi₂ nucleus resulting in an increase in the nucleation barrier of the C54 phase. A similar mechanism may be at work in the direct deposited samples in the present study. The cobalt film thickness may have an effect on the equilibrium shape of the CoSi₂ nucleus, where thinner Co films distort the CoSi₂ nucleus shape and increase its surface-to-volume ratio, thus increasing the activation energy barrier for nucleation of CoSi₂.

The co-deposited samples were observed to form CoSi₂ at all annealing temperatures used in this work. The EX-AFS spectra in Fig. 3b are indicative of crystalline CoSi₂ and compare quite well with the standard CoSi₂ spectra plotted in the same figure. The absence of the $CoSi_2$ (111) and (220) XRD reflections are evidence that the $CoSi_2$ is epitaxial to the $Si_{0.8}Ge_{0.2}$ layer. A $CoSi_2$ film epitaxial to a $Si_{0.8}Ge_{0.2}/Si \langle 100 \rangle$ substrate would be expected to show only the CoSi₂ (200) and (400) reflections, however, due to the thinness of the 5 nm co-deposited silicide films, the (200) and (400) peak intensities are low. The (200) reflection cannot be resolved from the Si 'ghost' peak and the $CoSi_2$ (400) peak cannot be resolved from the broad and intense Si (400) substrate peak (not shown). The stable formation of CoSi₂ in contact with Si_{0.8}Ge_{0.2} is predicted by region E in the phase diagram of Fig. 1. By co-depositing in this region, CoSi2 formation can take place immediately upon annealing without the $Co(Si_{1-y}Ge_y) \rightarrow CoSi \rightarrow$ CoSi₂ reaction mechanism required by the direct deposition method which leads to Ge segregation. Thus, co-deposition appears to lead to stable, epitaxial silicide formation at lower annealing temperatures than the direct deposition method.

5. Conclusion

Direct and co-deposition methods for the preparation of $CoSi_2$ films on strained $Si_{0.8}Ge_{0.20}/Si$ (100) layers were compared in regards to the formation and structure of the resulting silicide film. EXAFS and XRD measurements indicated that 5 nm direct deposited samples did not convert to $CoSi_2$ even at 800°C, the highest annealing temperature used in this study. Co-deposited films prepared using the same amount of Co, however, showed a complete conversion to $CoSi_2$ even at 500°C and exhibited epitaxy to the substrate. A 20 nm direct deposited sample indicated partial conversion from CoSi to $CoSi_2$ when annealed for 20 min at 700°C. This study suggests that

co-deposition of Co and Si may be a better method than direct deposition of Co for producing thin, epitaxial silicide contacts to SiGe layers at low annealing temperatures.

Acknowledgements

This work was funded by the Department of Energy under contracts DE-FG05-93ER79236 (D.E.S., instrumentation), DE-FG05-89ER45384 (D.E.S., X-11 Operations at the NSLS), and by the National Science Foundation under contract DMR-9633547 (R.J.N.). The authors gratefully acknowledge use of beamline X-11A at the National Synchrotron Light Source. The NSLS is funded by the Department of Energy under contract DE-AC02-76CH00016.

References

 D.B. Aldrich, Y.L. Chen, D.E. Sayers, R.J. Nemanich, S.P. Ashburn, M.C. Öztürk, J. Mater. Res. 10 (1995) 2849–2863.

- [2] O. Thomas, F.M. d'Heurle, S. Delage, J. Mater. Res. 5 (1990) 1453–1461.
- [3] R.D. Thompson, K.N. Tu, J. Angillelo, S. Delage, S.S. Iyer, J. Electrochem. Soc. 135 (1988) 3161.
- [4] M.C. Ridgway, R.G. Elliman, N. Hauser, J.-M. Baribeau, T.E. Jackman, Mater. Res. Soc. Symp. Proc. 260 (1992) 857–861.
- [5] D.B. Aldrich, F.M. d'Heurle, D.E. Sayers, R.J. Nemanich, Phys. Rev. B 53 (1996) 16282–16297.
- [6] Z. Wang, D.B. Aldrich, Y.L. Chen, D.E. Sayers, R.J. Nemanich, Thin Solid Films 270 (1995) 555–560.
- [7] Z. Wang, D.E. Sayers, R.J. Nemanich, Physica B 208–209 (1995) 567–568.
- [8] F. Wald, J. Michalik, J. Less Comm. Met. 24 (1971) 277-289.
- [9] W.J. Qi, B.Z. Li, W.N. Huang, Z.G. Gu, H.Q. Lu, X.J. Zhang, M. Zhang, G.S. Dong, D.C. Miller, R.G. Aitken, J. Appl. Phys. 77 (1995) 1086–1092.
- [10] D.B. Aldrich, Characterization of the Solid Phase Reaction of Titanium with Silicon Germanium Alloys: Interface Reactions, Phase Formation, and Stability, PhD thesis, North Carolina State University (1995) 283 pp.
- [11] H. Jeon, C.A. Sukow, J.W. Honeycutt, G.A. Rozgonyi, R.J. Nemanich, J. Appl. Phys. 71 (1992) 4269–4276.
- [12] H.J.W. van Houtum, I.J.M.M. Raaijmakers, in: R.J. Nemanich, P.S. Ho, S.S. Lau (Eds.), Thin Films-Interfaces and Phenomena, Vol. 54, Materials Research Society, Pittsburgh, PA, 1986, pp. 38–42.