Nitride-mediated epitaxy of $CoSi_2$ on Si(001)

R. K. K. Chong
Department of Electrical and Computer Engineering, National University of Singapore, Singapore 119260

M. Yeadon[a)]
Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602 and Department of Materials Science, National University of Singapore, Singapore 119260

W. K. Choi
Department of Electrical and Computer Engineering, National University of Singapore, Singapore 119260

E. A. Stach
NCEM, Lawrence Berkeley National Laboratory, Berkeley, California 94720

C. B. Boothroyd
Department of Materials Science, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ United Kingdom

(Received 5 August 2002; accepted 3 January 2003)

Epitaxial layers of $CoSi_2$ have been grown on Si(100) by the technique of nitride-mediated epitaxy. An ultrathin layer of silicon nitride was formed on the Si(001) surface by exposure to ammonia gas at 900 °C, followed by the deposition of a layer of Co ~20 Å in thickness at room temperature. The sample was then annealed at 600 °C and the microstructure monitored by *in situ* transmission electron microscopy and diffraction. The formation of epitaxial islands of $CoSi_2$ was observed directly, with no evidence of the formation of intermediate phases. The $CoSi_2$ islands were found to be elongated along the in-plane Si⟨110⟩ directions, consistent with reports of the deposition of Co by molecular beam epitaxy on clean Si(100) at low deposition rates and elevated temperature. This technique of silicidation may be of particular interest in the fabrication of advanced devices incorporating multilayer oxide/nitride gate stacks. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1555708]

As ultralarge scale integration design rules move into the deep submicron size regime, the fabrication of integrated circuits places increasingly stringent demands upon the performance of materials and processing technologies. The need to form ultrashallow junctions at the source, drain and gate electrodes of the metal–oxide–semiconductor field effect transistor device is an established challenge, and single-crystal epitaxial silicide contacts are an attractive potential solution. Epitaxial silicides are preferred over their polycrystalline counterparts because of their smoother interfaces, excellent layer uniformity and superior thermal stability.[1,2] In particular, $CoSi_2$ is superior to $TiSi_2$ since its formation is not linewidth dependent.[3] Additionally, $CoSi_2$ exhibits low resistivity (14 $\mu\Omega$ cm), low lattice mismatch with Si (−1.2%), and good process compatibility with very large scale integration technology.[4,5] However, a simple postjunction silicidation, involving room temperature Co deposition followed by a high temperature anneal, does not lead to the formation of epitaxial $CoSi_2$ except in the case of Si(111),[6] an orientation which is not widely used in the semiconductor industry.

To form an epitaxial $CoSi_2$ on Si(001), several methods have been developed including titanium-interlayer-mediated epitaxy,[7] oxide-meditated epitaxy (OME),[8] high-temperature sputtering,[9] molecular beam epitaxy on clean Si surfaces under UHV conditions,[1,10] the template method,[11] allotaxy[12] and fabrication by mesotaxy, using high-energy, high-dose, Co implantations.[13]

In this letter we report the synthesis of epitaxial $CoSi_2$ layers on Si(001) by first depositing an ultrathin layer of silicon nitride. A layer of Co ~20 Å in thickness was subsequently deposited over the nitride layer and the sample annealed at a temperature of 600 °C. The formation of epitaxial $CoSi_2$ (with cube on cube orientation) was observed during the annealing process. No evidence of the formation of any intermediate or second phases could be found during annealing, which was monitored *in situ* using transmission electron diffraction. The technique of nitride-mediated epitaxy may be of particular interest in advanced complementary metal–oxide–semiconductor (CMOS) front-end-process technology for the fabrication of devices incorporating multilayer oxide/nitride gate stacks.

Our experiments, involving the use of ultrathin nitride layers, were performed in the polepiece of a modified transmission electron microscope to enable us to monitor the growth and microstructural evolution *in situ*. The system is equipped with electron beam evaporation, gas injection, and sample heating capability (1400 °C) with a base pressure of 1.5×10^{-10} Torr (JEOL JEM 2000V). Boron-doped, *p*-type silicon on insulator wafers (resistivity 6–9 Ω cm) with ⟨001⟩ orientation were used as starting substrates. The silicon layer was ~1500 Å in thickness, and the oxide layer ~3000 Å. Electron-transparent samples were prepared by dimpling and

[a)]Author to whom correspondence should be addressed; electronic mail: m-yeadon@imre.a-star.edu.sg

 © 2003 American Institute of Physics
Downloaded 20 Mar 2003 to 137.132.3.10. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

chemical etching from the backside of the substrate. The samples were cleaned according to the Shiraki method,[9] with a layer of Shiraki oxide formed on the Si surface prior to insertion into the growth chamber, which is built around the polepiece of the objective lens.

The samples were heated *in situ* to $\sim 1100\,^{\circ}\mathrm{C}$ to remove surface oxide, before being cooled to room temperature to confirm the formation of a clean Si surface. Electron diffraction and imaging were used to confirm the absence of SiC islands, which are observed to form on samples either contaminated during preparation, or poorly outgassed prior to heating to $1100\,^{\circ}\mathrm{C}$.

Ammonia gas (99.95%) was then injected into the chamber and a partial pressure of 5×10^{-6} Torr was stabilized. The sample was heated to a temperature of $900\,^{\circ}\mathrm{C}$ in the ammonia ambient, for a period of 2 h, before being cooled to room temperature and the ammonia flow terminated. High-resolution phase contrast imaging, in combination with selected area electron diffraction, was used to confirm the formation of a uniform film of amorphous silicon nitride over the Si surface (image not shown). The thickness of the amorphous layer was estimated from high resolution images recorded from the very edge of the sample to be ~ 10 Å. Electron energy-loss spectroscopy analysis confirmed the incorporation of nitrogen into the sample, with no detectable carbon contamination (due, for example, to ammonia exposure).

Approximately 20 Å of Co was subsequently deposited (at room temperature) over the anorphous nitride layer, again *in situ*, by electron-beam evaporation at a rate of ~ 10 Å per hour. The pressure in the chamber was maintained below 5×10^{-10} Torr throughout the Co deposition sequence. Growth of the Co layer was monitored periodically under the electron beam, and the film was observed to nucleate and grow as three-dimensional islands of random orientation, as determined by electron diffraction.

Following Co deposition, the samples were heated to a temperature of $600\,^{\circ}\mathrm{C}$. As the temperature was increased from room temperature, a significant coarsening of the Co layer was observed, with the film breaking up into isolated islands of Co with no continuity between islands. The Debye–Scherrer diffraction rings from the Co film became less broad as island size increased, as expected. No evidence of any reaction was observed until the annealing temperature of $600\,^{\circ}\mathrm{C}$ was attained, approximately 5 min from the start of heating. At this stage, the first signs of reaction were indicated by the gradual formation of elongated islands in the bright-field images, emanating from the Co islands. Diffraction patterns recorded at this stage revealed the emergence of a set of reflections, which correspond to the $CoSi_2$ (200) planes, in addition to the existing Debye–Scherrer Co rings. The long axes of the $CoSi_2$ islands formed parallel to the two in-plane Si$\langle 110\rangle$ directions, with no apparent preference for either direction. In Fig. 1(a) we present a bright-field image recorded at short exposure time (0.1 s) due to the presence of sample drift following the ramp to $600\,^{\circ}\mathrm{C}$. The presence of both Co islands and $CoSi_2$ islands (arrowed) may be seen. As the $CoSi_2$ islands gradually increased in size, the Co islands decreased in number density and diameter [Fig. 1(b)] until they were no longer discernible [Fig. 2(a)]. Diffraction patterns recorded at this stage show no evidence of the presence of any remaining Co, and a representative example is presented in Fig. 2(b).

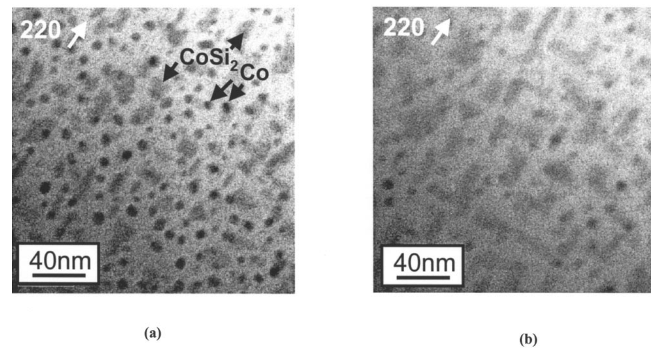

FIG. 1. Bright-field images recording after (a) 1 and (b) 2 min annealing at 600 °C.

The observed $CoSi_2$ exhibits the cube-on-cube epitaxial orientation, with Si(100)//$CoSi_2$(100) and Si[110]//$CoSi_2$[110]. With the reaction apparently complete (after ~ 15 min at $600\,^{\circ}\mathrm{C}$), the sample was cooled to room temperature and the thermal drift allowed to stabilize. Electron energy loss spectroscopy analysis at this stage revealed that the N K edge was still detectable, indicating that the silicon nitride layer was most likely still present at the sample surface. This is consistent with previous observations of oxide-mediated epitaxy of $CoSi_2$ on Si(001), where the amorphous silicon oxide layer remains after silicidation.[1]

Analysis of video recordings made during *in situ* annealing suggests that silicidation proceeds by vertical diffusion of Co through the interlayer, beneath the Co island. We observe the growth of epitaxial cobalt disilicide laterally, along the Si surface, the growth front moving away from the shrinking Co island along one of the two in-plane $\langle 110\rangle$ directions. Whilst it might be assumed that Co is diffusing primarily along the silicon: silicon nitride interface, subsurface diffusion of Co in Si can be substantial[14] and this may also play a role at this annealing temperature. The presence of nanoscale islands elongated along the in-plane Si $\langle 110\rangle$ directions suggests the early stages of growth may be dominated by a balance between interfacial energies in competition with heteroepitaxial strain relaxation.[15,16] From bright-field images

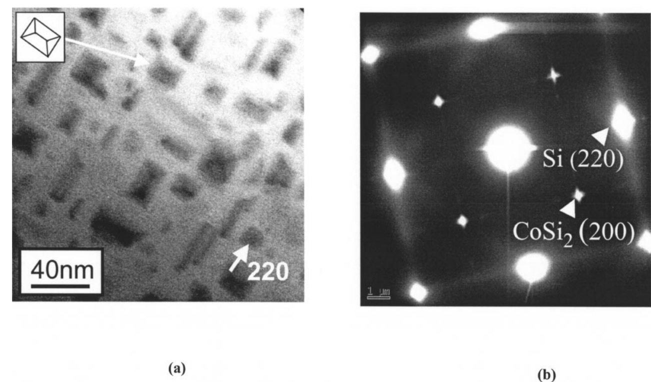

FIG. 2. (a) Bright-field image reccorded post-silicidation with (inset) a trace of the facets of one $CoSi_2$ island. (b) Corresponding selected area diffraction pattern.

Downloaded 20 Mar 2003 to 137.132.3.10. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

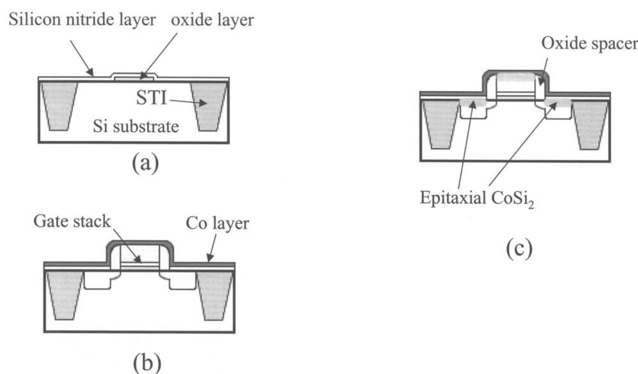

FIG. 3. Fabrication of epitaxial source and drain regions by (a) silicon nitride deposition, (b) Co deposition, and (c) final anneal.

such as that presented in Fig. 2(b), facets in some of the larger islands can be clearly distinguished (see inset) by a mass-thickness image contrast mechanism.

From the electron diffraction evidence, it is apparent that, upon reaching the Si surface, the Si-rich phase $CoSi_2$ is formed directly, with no evidence of any intermediate Co_2Si or CoSi phase formation being detectable. This is consistent with previous studies of the growth of epitaxial $CoSi_2$ on Si(100) by oxide-mediated epitaxy by Kleinschmit *et al.*[17] The absence of silicon-rich phases during the annealing process is key to the success of the oxide-mediated epitaxy technique, since full reorientation of nonepitaxial grains by a mechanism such as grain growth is unlikely once such regions have nucleated.

In the case of molecular beam epitaxy deposition of Co on Si(100) under UHV conditions, Vantomme *et al.*[10] showed that epitaxial $CoSi_2$ could be formed on Si(100) by directly depositing Co at substrate temperatures of $\sim 600\,^\circ C$ and with deposition rates below $0.1\ \text{Å}\ s^{-1}$. The arrival rate of Co atoms at the Si surface was found to be critical to the formation of an epitaxial layer. In the case of OME, only the Shiraki oxide has been found to be successful in mediating the epitaxial growth of $CoSi_2$, and neither the native nor thermally grown oxides can be used successfully without the use of reducing layers such as Ti.[7,18] The Shiraki oxide is known to be a highly defective oxide, and it is likely that the discontinuities in the oxide provide rapid-diffusion paths for Co through the layer.

Amorphous silicon nitride is known to exhibit a porous structure, with a range of densities depending upon the stoichiometric composition.[19] Recent structural models suggest extensive internal open pore structures;[20] these could provide excellent pathways for Co diffusion and be consistent with the low values reported for the activation energy for diffusion of Co and related metals in Si_3N_4.[21] Both the oxide and nitride interlayers are therefore apparently acting as purely physical barriers in their mediation of the silicidation reaction, limiting the Co flux to the silicon surface and maintaining the Si rich enviroment conducive to the formation of an epitaxial $CoSi_2$.

The use of silicon nitride as an interlayer may offer particular advantages in the fabrication of devices incorporating thin nitride layers as part of the heterostructure. For example, there is substantial interest in fabricating field effect transistor devices comprising alternating oxide and nitride layers as part of a multilayered stack for the gate dielectric.[22–24] As the gate dielectric typically adjoins the region in which epitaxial cobalt disilicide is desired, nitride-mediated epitaxy may be a viable technique compatible with this technology. During the fabrication of the oxide–nitride multilayered stack, the formation of the first nitride layer of the multilayer could be extended over the source and drain contact regions [Fig. 3(a)], followed by the addition of one or more other layers to the stack region. Subsequent deposition of a layer of Co [covering both the stack region as well as the nitride-coated source and drain contact regions, Fig. 3(b)] followed by annealing would result in the formation of an epitaxial cobalt disilicide at the source and drain contact regions [Fig. 3(c)]. Clearly, continuous $CoSi_2$ layers would be required for device fabrication; such layers could be formed either by deposition of a thicker layer of Co, or by the repeated deposition of Co followed by annealing.[25]

The authors thank the Singapore Agency for Science, Technology and Research (A*STAR), and the Ministry of Education (MOE) for funding this research. R.K.K.C acknowledges the support of Chartered Semiconductor Manufacturing Pte Ltd.; E.A.S acknowledges funding through the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

[1] R. T. Tung, Mater. Chem. Phys. **32**, 107 (1993).
[2] L. J. Chen and K. N. Tu, Mater. Sci. Rep. **6**, 53 (1991).
[3] L. M. Gignac, V. Svilan, L. A. Clevenger, C. Cabral, Jr., and C. Lavoie, Mater. Res. Soc. Symp. Proc. **441**, 255 (1997).
[4] S. P. Murarka, *Silicides for VLSI Applications* (Academic, New York, 1983).
[5] K. Maex, Mater. Sci. Eng., R. **11**, 53 (1993).
[6] R. T. Tung, J. C. Bean, J. M. Gibson, and D. C. Jacobson, Appl. Phys. Lett. **40**, 684 (1982).
[7] M. L. A. Dass, D. B. Fraser, and C. S. Wei, Appl. Phys. Lett. **58**, 1308 (1991).
[8] R. T. Tung, Appl. Phys. Lett. **68**, 3461 (1996).
[9] K. Ionue, K. Mikagi, H. Abiko, and T. Kikkawa, Tech. Dig. - Int. Electron Devices Meet. **1995**, 445 (1995).
[10] A. Vantomme, S. Degroote, J. Dekoster, and G. Langouche, Appl. Surf. Sci. **91**, 24 (1995).
[11] S. M. Yalisove, R. T. Tung, and D. Loretto, J. Vac. Sci. Technol. A **7**, 1472 (1989).
[12] S. Mantl and H. L. Bay, Appl. Phys. Lett. **61**, 267 (1992).
[13] A. E. White, K. T. Short, R. C. Dynes, J. P. Garno, and J. M. Gibson, Appl. Phys. Lett. **50**, 95 (1987).
[14] M. Y. Lee and P. A. Bennett, Phys. Rev. Lett. **75**, 4460 (1995).
[15] V. Scheuch, B. Voigtländer, and H. P. Bonzel, Surf. Sci. **372**, 71 (1997).
[16] J. Tersoff and R. M. Tromp, Phys. Rev. Lett. **70**, 2782 (1993).
[17] M. Kleinschmit, M. Yeadon, and J. M. Gibson, Appl. Phys. Lett. **75**, 3288 (1999).
[18] C. Detavernier, R. L. Van Meirhaeghe, F. Cardon, and K. Maex, Thin Solid Films **286**, 19 (2001).
[19] *Properties of Amorphous Silicon and Its Alloys*, edited by T. Searle (INSPEC, London, 1998).
[20] P. Kroll, J. Non-Cryst. Solids **293–295**, 238 (2001).
[21] F. Edelman, E. Y. Gutmas, and R. Brener, Vacuum **41**, 1268 (1990).
[22] H. Ikeda, D. Matsushita, S. Naito, K. Ohmori, A. Sakai, S. Zaima, and Y. Yasuda, Jpn. J. Appl. Phys., Part 1 **41**, 2463 (2002).
[23] Q. D. M. Khosru, A. Nakajima, T. Yoshimoto, and S. Yokoyama, IEEE Electron Device Lett. **23**, 179 (2002).
[24] H. Yu, Y.-T. Hou, M.-F. Li, and D.-L. Kwong, IEEE Trans. Electron Devices **49**, 1158 (2002).
[25] M. Yeadon and R. Nath (unpublished).

Downloaded 20 Mar 2003 to 137.132.3.10. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp