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Stability of NiSi₂ and CoSi₂ in contact with their free metal

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Rutherford backscattering has been used to study metal/disilicide thin-film interactions for Ni and Co. Upon heating, the metal reacted with disilicide to produce the phase M₂Si in both cases. On further heating the M₂Si itself reacted with the disilicide to form MSi. In the case of Co it was found that after all the metal had been converted to CoSi in this way, the reaction stopped. However, with Ni the disilicide substrate continued to dissociate into NiSi and Si even after all the original Ni had reacted to form NiSi. The stability of NiSi₂ under various conditions was investigated and it appears that twin requirements of a crystalline silicon substrate on which the excess Si can regrow and nucleation sites in the form of NiSi are necessary in order to induce dissociation.

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It has been reported that the monosilicides of Ni and Co are unstable in the presence of unreacted metal.^{1,2} When the silicon/monosilicide/metal system is annealed at temperatures below the formation temperature of the monosilicide, the metal-rich silicides Ni₂Si and Co₂Si grow at the expense of the monosilicide. A similar metal/monosilicide interaction has been reported in lateral diffusion studies.³ To date, though, studies of metal/disilicide interactions have largely been ignored. The object of this study is to determine the stability of the disilicides, particularly when in contact with unreacted metal.

Silicon/disilicide/metal thin-film structures were prepared in the following manner. Single crystal (100) Si substrates were organically cleaned and thereafter etched in dilute HF immediately prior to loading. Films of Ni and Co were then deposited on the substrates at pressures of about 5×10^{-7} Torr. After annealing in a vacuum quartz-tube furnace to form the disilicide, the final metal layer was deposited. The thickness of this metal layer was chosen so that it would be insufficient to consume all the disilicide on interaction. Subsequent annealing was done at temperatures below the formation temperature of the disilicide; i.e., where the disilicide should be stable. Silicon/disilicide/metal structures were also prepared in situ by depositing alternate layers of metal and silicon (in the correct proportion to produce MSi₂) on heated silicon substrates and then cooled to room temperature before the final metal layer was deposited. Apart from slight differences in rate no difference in reaction was observed between samples prepared by either method.

Rutherford backscattering spectra of the results for Ni and Co are given in Figs. 1 and 2, respectively. Figures 1(a) and 2(a) show the silicon/disilicide/metal structures prior to annealing. Upon annealing the Si/NiSi₂/Ni system, Ni metal reacts with the NiSi₂ to form Ni₂Si [Fig. 1(b)]. Only after the deposited Ni is entirely consumed does the monosilicide proceed to nucleate and grow at the NiSi₂/Ni₂Si interface [Fig. 1(c)]. Similar behavior is observed for the Co/Si system [Figs. 2(b), 2(c)]. The deposited Co reacts with the CoSi₂ to



form Co_2Si , and then CoSi proceeds to grow at the interface between the two silicide phases. Subsequent heating resulted in all the metal-rich (M_2Si) silicide being converted to monosilicide for both the Ni and Co structures. In the case of



FIG. 1. Rutherford backscattering spectra ($E_{ie} = 2.0 \text{ MeV}$, $\theta = 165^{\circ}$) showing the interaction of Ni with NiSi₂: (a) prior to annealing, (b) formation of the first phase, Ni₂Si, (c) reaction between NiSi₂ and Ni₃Si to form NiSi at their interface, and (d) dissociation of the remaining NiSi₂ into NiSi. (The arrows show the surface energies for Ni and Si.)

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FIG. 2. Rutherford backscattering spectra ($E_a = 2.0 \text{ MeV}$, $\theta = 165^\circ$) showing the interaction of Co with CoSi₂: (a) prior to annealing, (b) formation of Co₂Si as the first phase, (c) growth of CoSi as a result of the reaction of CoSi₂ with Co₂Si, and (d) unlike Ni, the stopping of the reaction once the original Co₂Si has been entirely converted to CoSi.

cobalt, the reaction stops at this stage, but for nickel the remaining $NiSi_2$ converts to NiSi [see Figs. 1(d) and 2(d)]. This interesting phenomenon will be discussed in greater detail later.

From the amount of metal and disilicide consumed, it can be concluded that the growth of Ni_2Si proceeds at the metal/disilicide interface according to the reaction

 $3Ni + NiSi_2 \rightarrow 2Ni_2Si$.

 Co_2Si growth on $CoSi_2$ appears to proceed in an identical manner. In accordance with Tu's argument⁴ that interstitial metal diffusion into the Si lattice is necessary for low-temperature breaking of Si–Si covalent bonds, one would expect the substrate to remain inactive as long as the metal is consumed at the silicide/metal interface. This is also true for metal/monosilicide studies of Ni and $Co^{1,2}$ and it is thus not surprising to find similar behavior in the metal/disilicide system.

This present metal/disilicide investigation, together with the work on metal/monosilicide systems,^{1,2} thus indicates that silicon-rich phases and unreacted transition metals cannot coexist simultaneously in thin-film structures and that the first phase to form is always the metal-rich phase M_2Si , regardless of whether the source of silicon is the disilicide, the monosilicide, or the silicon substrate. It is interesting that this should always be the first phase to be formed. Nucleation and surface energy considerations cannot account for this as the MSi and MSi₂ phases were already present in the metal/monosilicide and metal/disilicide systems, respectively, and in addition the growth of the M_2Si phase creates two new interfaces which should result in greater surface energy.

One may argue that the free energy of formation is the determining factor in the metal/disilicide reactions. It would appear more likely, however, that during the initial stages of silicide growth, both kinetic and thermodynamic factors will affect phase selection. If the supply of metal or silicon to the growth interface is not limited, the reaction should follow the thermodynamically favored path, i.e., the phase nucleated will be the one with the largest heat of reaction. However, bulk thermodynamic data do not reflect reaction barriers that exist at a growth interface. Although a phase may have a larger thermodynamic driving force, the kinetic barrier to its growth may prevent its formation.⁵ If the unreacted metal in the silicon/disilicide/metal system is to react with silicon from the substrate, then diffusion of silicon or metal through the disilicide layer must take place. The disilicide layer thus acts as a diffusion barrier, by limiting the supply of metal to the silicon/disilicide interface or the supply of silicon to the disilicide/metal interface. It is therefore more likely that the metal will prefer to react directly with the silicon in the disilicide layer and in the process preventing unreacted metal from diffusing through to the silicon substrate. The heats of reaction of Ni with NiSi₂ to form Ni₂Si and NiSi are - 21.2 and - 10.0 kcal/g mol product respectively and that of Co with CoSi2 to form Co2Si and CoSi are -15.3 and -11.7 kcal/g mol product, as calculated from published heats of formation.⁶ It can be seen



FIG. 3. Schematic showing the similarities and differences of the nickel and cobalt systems.

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that in both cases the formation of the metal-rich M_2Si is thermodynamically favored and thus it should proceed to nucleate and grow at the disilicide/metal interface until all the metal is consumed.

On extended heating of the silicon/disilicide/metal systems a significant difference in behavior between the two systems is observed (see Fig. 3). As referred to earlier, it is found that once the Co₂Si has been entirely converted to CoSi [Fig. 3(c)], no further phase change occurs [Fig. 3(d)]. On the other hand, in the Si/NiSi₂/Ni system the remaining NiSi₂ continued to dissociate in the presence of NiSi until only the monosilicide remained [Fig. 3(e)]. A nickel thickness of 300 Å will react with NiSi₂ to form approximately 1320 Å of NiSi and in doing so it will consume 1100 Å of NiSi₂. Thus about 700 Å of NiSi₂ must have dissociated into Ni and Si with the excess silicon regrowing on the silicon substrate. The complete dissociation to NiSi was found to be independent of the thickness of the nickel deposited onto the NiSi₃.

Recently it has been suggested^{7,8} that silicides, such as NiSi₂, which form by a nucleation process at elevated temperatures may be inherently unstable. It was proposed that because of their small heats of formation from the monosilicide ($\Delta H = -0.3$ kcal/g mol silicide for NiSi₂) it may be possible for stress-strain and surface effects to make the overall reaction enthalpy positive. If this were to occur then disilicide growth would only proceed above some critical temperature where the change in free energy of the reaction, given by

$$\Delta G = \Delta H - T \Delta S,$$

becomes negative (provided ΔS is positive). Since the driving force for the formation of the disilicide is the relatively high entropy term, annealing at temperatures below the critical temperature should result in the disilicide reverting back to the more stable monosilicides.

To eliminate the possibility that the observed $NiSi_2$ dissociation is due to the Si/NiSi₂ instability, we subjected Si/

NiSi, structures (grown at 850 °C) to extended anneals at temperatures ranging from 300 to 600 °C. In no instance was any dissociation of NiSi, observed thereby indicating that NiSi, is stable by itself at the temperatures used in this investigation. In addition, preliminary investigations involving NiSi₂/Ni films on amorphous Si and inert SiO₂ substrates showed no NiSi, dissociation after initial NiSi formation. It thus appears that twin requirements of a crystalline silicon substrate, on which the excess silicon can regrow, and nucleation sites in the form of NiSi are necessary in order to induce dissociation. Presumably surface energy considerations associated with epitaxial silicon regrowth on the silicon substrate and nucleation sites for monosilicide growth at the other interface are collectively sufficient for NiSi2 dissociation to become energetically favorable. One assumes that in the case of CoSi2 with its slightly larger heat of formation from CoSi ($\Delta H = -0.6$ kcal/g mol silicide) the surface energy and nucleation effects are insufficient to make the overall reaction enthalpy positive, with the result that CoSi, is stable under similar conditions. Thus, the normal sequence of silicide formation (progressing towards the most siliconrich phase) can be reversed in the case of nickel. The only other similar example is the conversion of PdSi to Pd₂Si.^{9,10}

- ¹G. Ottaviani, G. Majni, and C. Canali, Appl. Phys. 18, 285 (1979).
- ²K. N. Tu, G. Ottaviani, and R. B. Thompson, J. Appl. Phys. 53, 4406 (1982).
- ³L. R. Zheng, L. S. Hung, J. W. Mayer, G. Majni, and G. Ottaviani, Appl. Phys. Lett. **41**, 646 (1982).
- ⁴K. N. Tu, Appl. Phys. Lett. 27, 221 (1975).
- ⁵U. Gösele and K. N. Tu, J. Appl. Phys. 53, 3252 (1982).
- ⁶R. Pretorious, J. M. Harris, and M-A. Nicolet. Solid State Electron. 21, 667 (1978).
- ⁷R. Anderson, J. Baglin, J. Dempsey, W. Hammer, F. d'Heurle, and S. Petersson, Appl. Phys. Lett. **35**, 285 (1979).
- ⁸C. S. Petersson, J. E. E. Baglin, J. J. Dempsey, F. M. d'Heurle, and S. J. La Placa, J. Appl. Phys. **53**, 4868 (1982).
- ⁹B-Y. Tsaur and M-A. Nicolet, Appl. Phys. Lett. 37, 708 (1980).
- ¹⁰K. N. Tu, Appl. Phys. Lett. 53, 428 (1982).

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