New Insight into Silicide Formation: The Creation of Silicon Self-Interstitials

Maria Ronay and R. G. Schad
IBM T.J. Watson Research Center, Yorktown Heights, New York 10598
(Received 14 November 1989)

Diffusion studies of Cu+Re and Re+Cu films on silicon showed that the formation of a Cu_3Si percursor lowers the formation temperature of $ReSi_2$ from over 900 to 550 °C. The results are explained and generalized to all metal-rich silicides by the specific volume of silicon being much larger in these compounds than in elementary silicon. In forming metal-rich silicides, silicon atoms are forced out of their original planes and are free to form silicon-rich silicides with adjacent metals, or to form silicon self-interstitials at the metal-rich-silicide–silicon interface.

PACS numbers: 61.70.Bv, 66.30.Lw, 68.35.Fx

Among the most important questions concerning silicide contacts is their formation temperature and the nature of the moving species. While it is known that transition-metal disilicides form by silicon diffusion[1] in a temperature range between 450 °C and 750 °C, such relatively low formation temperatures are difficult to reconcile with the large activation energy for silicon self-diffusion[2] (4.1–5.1 eV). We observed that the formation temperature of disilicides correlates with the size of the transition-metal atom, suggesting that transition-metal diffusion may be a precursor to silicon diffusion, and may lower the formation enthalpy of mobile defects in silicon. Transition metals diffuse interstitially in silicon with an activation energy as low as 0.43 eV for the small copper ion and as high as 1.5 eV for the large titanium atom.[3] If a fast-diffusing transition metal lowers the formation enthalpy of a silicon defect, then this should decrease the formation temperature of a subsequently forming silicide of a slow-diffusing transition metal.

In order to investigate this suggestion we chose rhenium as an example for a slow-diffusing transition metal, which in thin-film reactions forms only $ReSi_2$ (Ref. 4). For a fast-diffusing transition metal we chose copper, which in thin-film reactions forms only Cu_3Si. What we want to find out is whether the formation of Cu_3Si will introduce mobile silicon defects in silicon and thereby lower the formation temperature of $ReSi_2$.

Thin films of rhenium and copper were evaporated on [100] n-type silicon wafers with an electron gun. The annealings of the samples took place in inert gas for 30 min. The elemental composition of the samples was determined with Auger-electron spectroscopy combined with Ar-ion etching for depth profiling. Because of preferential sputtering, Auger sputter profiles are not suitable to determine exact stoichiometry. The silicide phases formed were identified by x-ray diffraction. For experimental details see Ref. 5.

First, we studied the formation of $ReSi_2$ without any copper being present. A 2000-Å-thick rhenium film was deposited on a silicon wafer at 250 °C substrate temperature. Figure 1 shows the composition profile of the rhenium film on silicon after an anneal at 850 °C. We see no interdiffusion and no silicide formation. The profile looks the same after an anneal at 900 °C and no silicide formation is indicated by x-ray diffraction. After an anneal at 950 °C almost all of the rhenium transformed into $ReSi_2$, as evidenced by x-ray diffraction.

Next we deposited, at room temperature, on silicon substrates, 1000 Å copper, and on top of it, 1000 Å rhenium. After an anneal at 200 °C the composition profile in Fig. 2(a) shows that copper diffuses into silicon but according to x-ray analysis no new phases are formed. There is a dramatic change after an anneal at 550 °C as shown in Fig. 2(b). The copper film diffused completely into the silicon while seemingly no copper diffused into the rhenium. As evidenced by x-ray analysis, large amounts of the η'-Cu_3Si phase forms,[6] and, most importantly, *silicon diffuses into the rhenium,* way beyond the original interface [compare with Fig. 2(a)], and way beyond the copper front characterizing the η'-Cu_3Si phase. The composition profile after an anneal at 600 °C is shown in Fig. 2(c). We see that the

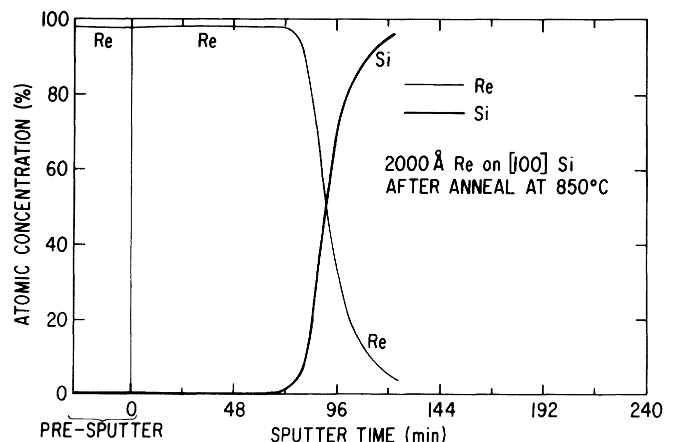

FIG. 1. The composition profile of a rhenium film on silicon after an anneal at 850 °C.

© 1990 The American Physical Society

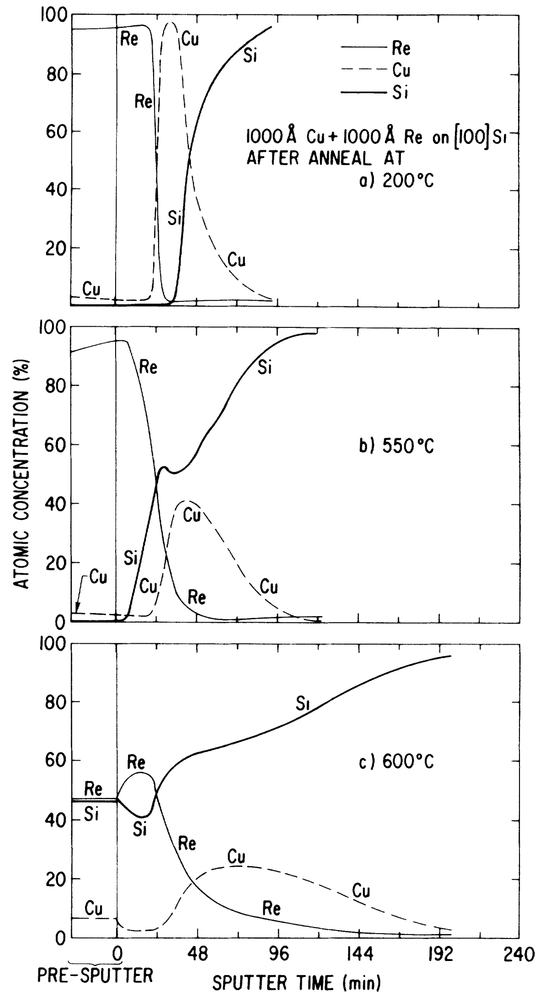

FIG. 2. The composition profile of copper and, on top of it, rhenium films on silicon after an anneal at (a) 200 °C, (b) 550 °C, and (c) 600 °C.

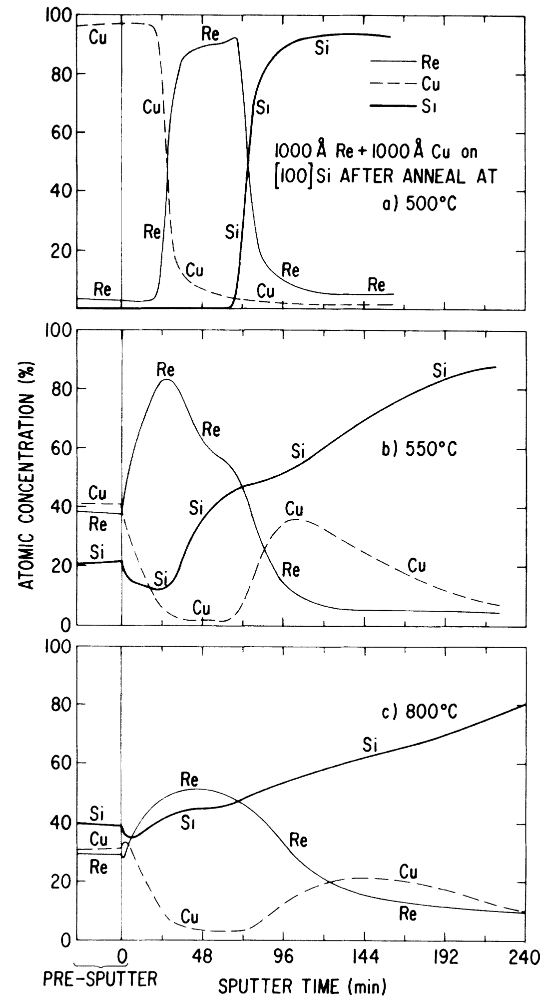

FIG. 3. The composition profile of rhenium and, on top of it, copper films on silicon after an anneal at (a) 500 °C, (b) 550 °C, and (c) 800 °C.

copper diffuses further into the silicon, while the silicon diffusion front reaches the surface. Both silicon and rhenium have a nearly constant concentration in the better part of the original rhenium layer indicating the formation of substantial amounts of $ReSi_2$ in agreement with x-ray analysis. There is an increased amount of rhenium diffusion into the silicon as compared to Fig. 2(b).

Some may argue that the formation temperature of $ReSi_2$ in our first experiment was found to be high because rhenium or silicon oxides form at the interface preventing the diffusion of silicon into rhenium, but when there is copper between silicon and rhenium, copper oxide forms, which does not present a barrier to silicon and silicon can diffuse into rhenium at a much lower temperature, as found in our second experiment. To prove that this is not the case, we deposited at 250 °C substrate temperature 1000 Å rhenium and, on top of it, at room temperature, 1000 Å copper, so as to preserve the Re-Si interface and study the influence of copper on rhenium silicide formation this way. The composition profile of this bilayer on silicon is shown after an anneal at 500 °C in Fig. 3(a). The profile is the same as the profile in the as-deposited state (not shown). After an anneal at 550 °C [Fig. 3(b)] we see that a large amount of copper diffused into the silicon forming η'-Cu_3Si, as evidenced by x-ray diffraction, and the silicon diffuses deeply into the rhenium film, way beyond the copper front that represents the Cu_3Si phase [compare with Fig. 3(a)], and the outdiffusing silicon reaches the surface. The rhenium hardly diffuses into the silicon; however, it does diffuse into the copper film that is on the surface. The formation of $ReSi_2$ just begins. After an anneal at 600 °C x-ray analysis shows the formation of large amounts of $ReSi_2$. After an anneal at 800 °C the composition profile is shown in Fig. 3(c). The copper diffused deeply into the silicon except the part which remains at the surface; silicon diffused completely into the rhenium

and reached the surface. There are probably Cu_3Si precipitates at the surface. The profile of rhenium is almost symmetric, showing rhenium diffusion both into silicon and towards the surface copper film. It seems then that the copper-silicide–induced silicon diffusion into rhenium is independent of the sequence of the copper and rhenium films and is not due to the removal of an interface impurity.

What we found is that the formation temperature of $ReSi_2$, which is over 900 °C, got reduced to 550 °C when $ReSi_2$ formation was preceded by η'-Cu_3Si. How does this happen? Silicon atoms in pure crystalline silicon occupy a 20-$Å^3$ volume. This we call the specific volume of silicon in silicon. The specific volume of silicon in a metal-rich silicide such as Pd_2Si is much larger, 42.26 $Å^3$. We obtain this number by dividing the unit-cell volume by Z, which is the number of chemical formula units in the unit cell. We ignore the fact that there are Pd atoms in this volume. Buckley and Moss[7] have shown that when Pd_2Si forms epitaxially on the (111) plane of silicon, the Pd atoms drop into the three interstitial positions around a silicon atom and force the central silicon atom out of the way, moving it up between them so that it nests on top of them to form the second plane of the silicide; *thus one original silicon plane forms two planes of the silicide.* Unfortunately, the structure of Cu_3Si is not known in detail, but due to the similarity of the specific volumes of silicon in Pd_2Si and Cu_3Si, and, as a matter of fact, in Fe_3Si, and Pt_2Si as well, we believe that all of their formations force silicon atoms out of their original planes.

Table I gives the crystal structure and the lattice constants of some metal-rich silicides, monosilicides, and disilicides. All this information was taken from data by the Joint Committee on Powder Diffraction Standards[8] (JCPDS). In some instances, where the structure is not known, we estimated the Z number and included this number in parentheses in the table. Estimation of the Z number for Cu_3Si is given in Ref. 9. The specific volume of silicon in disilicides is quite low, as low as, or even lower than, in silicon itself. Here one silicon plane forms one silicide plane and no silicon atoms are forced out of their original planes, and no unattached silicon atoms are created. The specific volume of silicon in the monosilicides is in between that of the metal-rich and the silicon-rich silicides and their formation may resemble either of the two. The formation of metal-rich silicides forces silicon atoms out of the original silicon planes. If there is more metal there, these extra silicon atoms form more silicides. If the Cu_3Si forms adjacent to the rhenium film, the silicon atom forced out by the copper atoms is free to form $ReSi_2$. What happens at the Cu_3Si-silicon interface? The silicon atoms forced out by the silicide formation process can only occupy interstitial positions in the silicon lattice. Interstitial-type dislocation loops containing extra silicon atoms were indeed observed around both Pd_2Si and Cu_3Si precipitates in silicon.[10] The copper concentration in Figs. 2 and 3 indicates that the Cu_3Si is clearly not a continuous phase, but forms precipitates in the silicon matrix. The silicon atoms

TABLE I. Specific volume of silicon atoms in some metal-rich silicides, monosilicides, and disilicides.

Silicide	Crystal structure	Lattice constants (Å)			Z	Volume/(Si atom) ($Å^3$)
Si	Cubic	5.4301			8	20.01
η'-Cu_3Si	Tetragonal	7.267		7.892	(9)	46.0
α-Fe_3Si	Cubic	5.655			4	45.21
Pt_2Si	Tetragonal	3.933		5.910	2	45.71
Pd_2Si	Hexagonal	13.055		27.490	96	42.26
Co_2Si	Orthorhombic	7.109	4.918	3.737	(4)	32.66
δ-Ni_2Si	Orthorhombic	7.39	9.90	7.03	16	32.14
HfSi	Orthorhombic	6.855	3.753	5.191	4	33.39
PtSi	Orthorhombic	5.932	5.595	3.603	4	29.89
TiSi	Orthorhombic	6.544	3.638	4.997	4	29.74
RhSi	Cubic	2.963			1	26.01
NiSi	Orthorhombic	5.657	5.238	3.240	(4)	24.00
FeSi	Cubic	4.46			4	22.18
CoSi	Cubic	4.43			(4)	21.73
$TaSi_2$	Hexagonal	4.7821		6.5693	3	21.68
$TiSi_2$	Orthorhombic	8.2687	8.5534	4.7983	8	21.21
$CoSi_2$	Cubic	5.43			4	20.01
VSi_2	Hexagonal	4.571		6.372	3	19.22
$ReSi_2$	Orthorhombic	3.1279	3.1442	7.677	2	18.87

created by the silicide formation process thousands of angstroms away from the rhenium film must diffuse through silicon in order to reach the rhenium. We see no other way but that this takes place by interstitial silicon diffusion.

The formation enthalpies of the self-interstitial in silicon were calculated by Car *et al.*[11] for various charge states as a function of the Fermi-level position in the gap and were found to be in excess of 5 eV. Baraff and Schlüter[12] find 4.7 eV for tetrahedral Si^{2+}, assuming that the two charge-compensating electrons are placed midgap. These formation enthalpies are very large and are clearly lowered by the silicide formation process. Unfortunately there are no total-energy calculations related to the microscopic mechanism of metal-rich silicide formation. The energetics involved in the formation of the silicide is also involved in creating the self-interstitials, but until we know something about the first, we cannot say anything about the latter. Once silicon self-interstitials are formed, however, the barriers to migration are small and can be overcome by carrier capture.[11-13] When the formation enthalpy of self-interstitals is lowered by some process such as silicide formation, diffusion of silicon can take place at as low a temperature as 550 °C.

In summary, the formation of metal-rich silicides creates extra silicon atoms, which lowers the formation temperature of a subsequently forming disilicide either by reacting *in situ* with the metal, or by forming interstitials in silicon and diffusing as such to the metal. All metal-rich silicides at the top of Table I are predicted to lower the formation temperatures of all silicon-rich silicides. The implication for silicide-enhanced dopant diffusion will be given elsewhere.[5]

[1]K. N. Tu and J. W. Mayer, in *Thin Films-Interdiffusion and Reactions,* edited by J. M. Poate, K. N. Tu, and J. W. Mayer (Wiley, New York, 1978), p. 359.

[2]W. Frank, U. Gösele, H. Mehrer, and A. Seeger, in *Diffusion in Crystalline Solids,* edited by G. E. Murch and A. S. Nowick, Materials Science and Technology Series (Academic, New York, 1984), p. 63.

[3]Eicke R. Weber, Appl. Phys. A **30**, 1 (1983).

[4]J. J. Chu, L. J. Chen, and K. N. Tu, J. Appl. Phys. **62**, 461 (1987).

[5]Maria Ronay and R. G. Schad, in *Impurities, Defects and Diffusion in Semiconductors: Bulk and Layered Structures,* edited by J. Bernhole, E. E. Haller, and D. J. Wolford, MRS Symposia Proceedings No. 163 (Materials Research Society, Pittsburgh, 1990).

[6]K. P. Mukherjee, J. Bandyopadhyaya, and K. P. Gupta, AIME Trans. **245**, 2335 (1969). There are three polymorphs of the Cu_3Si composition, referred to as η, η', and η''. The distinction between these superlattice-related structures is not resolved here, and we refer to the Cu_3Si phase as the η' phase.

[7]W. D. Buckley and S. C. Moss, Solid State Electron. **15**, 1331 (1972).

[8]Published by the International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081.

[9]Maria Ronay and R. G. Schad, IBM Research Report No. RC 15306, 1989 (unpublished).

[10]M. Seibt and K. Graff, J. Appl. Phys. **63**, 4444 (1988).

[11]Roberto Car, Paul J. Kelly, Atsushi Oshiyama, and Sokrates T. Pantelides, Phys. Rev. Lett. **52**, 1814 (1984).

[12]G. A. Baraff and M. Schlüter, Phys. Rev. B **30**, 3460 (1984).

[13]Y. Bar-Yam and J. D. Joannopoulos, Phys. Rev. Lett. **52**, 1129 (1984).