Silicide Formation and the Generation of Point Defects in Silicon

B. G. Svensson and M. O. Aboelfotoh[a]
The Royal Institute of Technology, Solid State Electronics, P.O. Box 1298, S-164 28 Kista-Stockholm, Sweden

J. L. Lindström
National Defense Research Institute, P.O. Box 1165, S-581 11 Linköping, Sweden

(Received 5 February 1991)

The annealing behavior of the divacancy (V_2) acceptor levels in silicon is investigated with the use of Schottky-barrier structures formed by the deposition of copper on *n*-type silicon irradiated with 2-MeV electrons. At temperatures below ~150 °C an anomalously high annealing rate of the V_2 centers is observed, and we believe that the fast-diffusing interstitial Cu^+ passivates their electrical activity and forms neutral complexes. In the temperature range 150–200 °C, where the metal-rich silicide η'-Cu_3Si forms, the concentration of V_2 remains almost constant, and we find no evidence for the injection of silicon self-interstitials during the formation of η'-Cu_3Si, in contrast to recent experiments.

PACS numbers: 61.70.At, 61.70.Bv, 61.80.Fe, 71.55.Ht

In shallow p^+n junctions formed on single-crystal silicon preamorphized by Ge^+-ion implantation a substantial annihilation of the end-of-range defects was found during Ti silicidation.[1] The annihilation of these interstitial dislocation loops was attributed to the injection of vacancies during the silicide growth, and the type of point defect diffusing into the silicon was related to the dominant moving species during silicidations. Silicide formation limited by silicon diffusion (as for $TiSi_2$) leads to the injection of vacancies, while silicide formation limited by metal diffusion results in the injection of Si self-interstitials. Recently, Ronay and Schad[2] studied Cu+Re and Re+Cu films on Si and reported that the formation of a η'-Cu_3Si precursor lowers the formation temperature of $ReSi_2$ from over 900 to 550 °C. The results were interpreted in terms of a model where Si self-interstitials are generated during the formation of the metal-rich silicide η'-Cu_3Si (here Cu is the dominant moving species[3]), and, as a result, the formation enthalphy of interstitials in silicon is lowered and thereby also the formation temperature of $ReSi_2$.

Vacancies and self-interstitials in silicon are extremely mobile with diffusion coefficients of $\sim 10^{-8}$ and $\sim 10^{-4}$ cm^2/s, respectively, at room temperature,[4,5] and they are, therefore, rapidly distributed over large distances (≥ 100 μm) provided that the concentration of traps is sufficiently low. Thus effects caused by interstitials and vacancies generated in a thin surface layer can be observed at large depths, and here we study the diffusion of defects at depths between 0.5 and 3.0 μm below the surface. As a result, the influence of the silicide/silicon interface, e.g., stress and precipitation effects, is diminished, and the "pure" defect interaction is emphasized.

In this Letter a new approach is taken to examine the suggestion that the formation of metal-rich silicides generates self-interstitials in silicon. We deposit Cu on *n*-type silicon irradiated with 2-MeV electrons and investigate the annealing behavior of the divacancy (V_2) acceptor levels during the growth of η'-Cu_3Si. High-energy electrons generate "simple" point defects, and one of the most prominent intrinsic defects is the V_2 center. V_2 appears in both Czochralski and float-zone materials, irrespective of dopant type, and introduces three levels in the forbidden band gap, corresponding to four different charge states (singly positive, neutral, singly negative, and doubly negative).[6,7] The V_2 centers are normally stable up to temperatures above 200 °C, and this allows us to monitor their concentration during copper silicidation. A well-established annihilation reaction of V_2 is the recombination with Si self-interstitials ($V_2 + I \rightarrow V$),[8] and here we compare the annealing rate of V_2 during the growth of η'-Cu_3Si with that in samples prepared with Pt Schottky barriers to investigate the generation of Si self-interstitials during copper silicidation.

Samples were cut from Czochralski (Cz) silicon wafers grown in the ⟨100⟩ direction and doped with phosphorus to a concentration of $\sim 1\times10^{16}$ cm^{-3}. The concentrations of interstitial oxygen and substitutional carbon were measured by infrared-absorption spectroscopy and found to be 5.5×10^{17} and below 1×10^{16} $atoms/cm^3$, respectively. The samples were irradiated by 2.0-MeV electrons at nominal room temperature (≤ 30 °C) to doses in the range of 1×10^{15} to 1×10^{17} cm^{-2}. The sample surfaces were then cleaned using a standard chemical procedure which included a final dip in diluted hydrofluoric acid immediately before Schottky-barrier structures were prepared by deposition of ~1000-Å-thick Cu films on the samples. Annealing of the samples were performed in an inert atmosphere for 30 min at temperatures between 100 and 200 °C. For sample analysis, deep-level transient spectroscopy (DLTS) and capacitance-voltage (C-V) measurements were undertaken at temperatures between 80 and 290 K. The measurements were performed under reverse-bias conditions, and no forward injection was applied. The experimental setup has been described in detail elsewhere.[9] X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) were used to monitor the interfacial reaction between Cu and Si upon annealing, and the silicide phase formed was identified by electron diffraction.

Figure 1 shows DLTS spectra of samples irradiated to a dose of 1×10^{17} cm^{-2} and subsequently annealed at 100 and 200 °C. The spectra are dominated by a level $\sim$0.43 eV below the conduction-band edge (E_c) with a capture cross section of $\sim2\times10^{-15}$ cm^2. In moderately n-doped Cz silicon this peak originates predominantly from the singly-negative-charge state of V_2, while in more highly doped Cz material (resistivity $\ll 1$ Ω cm) and in float-zone material the overlapping signal from the E center (the vacancy phosphorus pair) becomes of major importance.[10] Moreover, in float-zone samples with high enough concentrations of phosphorus and carbon a third overlapping level has been reported; it is caused by a defect exhibiting configurational metastability and is tentatively attributed to a phosphorus-carbon pair (PC).[11,12] The contribution of V_2 to the level at $E_c-0.43$ eV in the present samples was determined by a comparison with the level at $\sim E_c-0.23$ eV originating from the doubly-negative-charge state of V_2, shown for the as-irradiated sample in Fig. 1; these two levels exhibit a close one-to-one proportionality in moderately doped Cz samples and low-doped float-zone samples irradiated with MeV electrons.[10,13] It is found that the relative contribution of V_2 to [$E_c-0.43$ eV] (brackets denote concentration values) is $\sim$80% directly after irradiation and $\sim$95% after annealing at 200 °C. Thus the level at $E_c-0.43$ eV is clearly dominated by V_2, and, in particular, at the temperatures where copper silicidation takes place ($\sim$200 °C) the influence of the E center and the PC pair is $\sim$5%. This is consistent with the results in Ref. 10 showing that the E center anneals out completely at 150 °C (20 min) in Cz silicon, and it is, therefore, not stable enough to play any significant role as a monitor for injection of Si self-interstitials during copper silicidation. In a first approximation, the contributions from the E center and the PC pair are neglected, and in the following, the level at $E_c-0.43$ eV is attributed to V_2.

A relatively weak peak appears at $\sim$255 K in Fig. 1, and its position and capture cross section are $\sim E_c-0.48$ eV and $\sim1\times10^{-16}$ cm^2, respectively. This level is normally observed in irradiated n-type Cz silicon,[10] but no firm identification exists. However, preliminary results of depth concentration profiles and of dose dependence indicate that it may originate from a higher-order vacancy-related defect.[14]

The amplitude of the level at $E_c-0.48$ eV remains essentially constant for annealing temperatures up to 200 °C, while [V_2] decreases drastically at 100 °C. However, a substantial concentration of V_2 still persists after an anneal at 200 °C where the copper film has fully reacted with Si to form η'-Cu$_3$Si, and in Fig. 2 we compare the isochronal annealing of V_2 in samples prepared with Cu contacts with that in samples prepared with Pt contacts. A rapid decrease of [V_2] is observed below

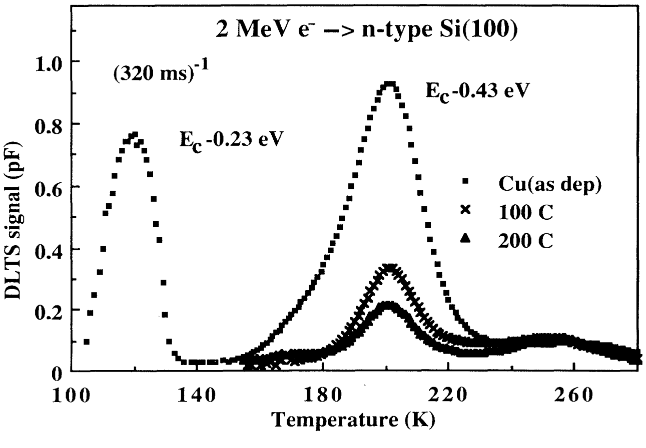

FIG. 1. DLTS spectra of electron-irradiated n-type Si samples obtained with Cu Schottky-barrier contacts in the as-deposited state and after a 30-min anneal at 100 and 200 °C. [Rate window = (320 ms)$^{-1}$.]

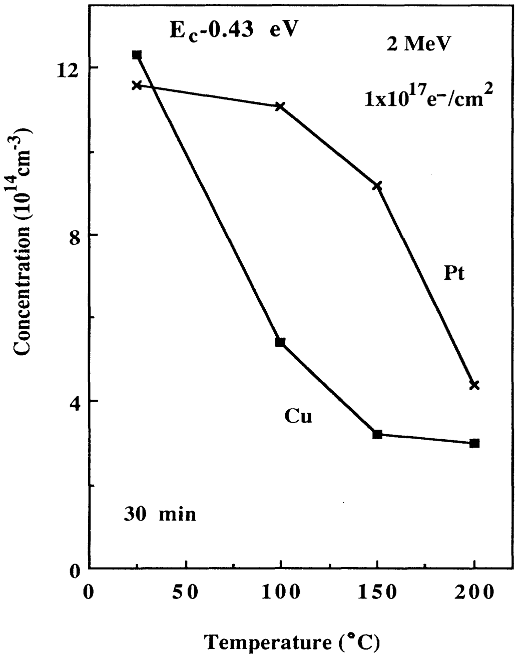

FIG. 2. Isochronal annealing (30 min) of the level at $E_c-0.43$ eV in n-type Si samples irradiated with 2-MeV electrons to a dose of 1×10^{17} cm^{-2} before deposition of Cu or Pt contacts to form Schottky-barrier structures.

150 °C in the Cu samples, but the annealing rate decreases at higher temperatures; the anneal is not a first-order (exponential) process, and at 200 °C, where η'-Cu_3Si is formed, $[V_2]$ is only 30% lower than in the Pt samples.

However, for the Pt samples a first-order process may be assumed, and an activation energy of ~ 1.2 eV and a frequency factor of $\sim 3\times10^9$ s^{-1} are obtained. Keeping in mind that no correction has been made for the initial contribution of $\sim 20\%$ from the E center and the PC pair to $[E_c-0.43$ eV], these values are in reasonable agreement with those previously reported for the annealing behavior of V_2 in Cz silicon.[7,10,15] The values indicate that the dominant annealing mechanism is long-range diffusion of V_2 and subsequent annihilation through reactions with impurities and defects in the silicon lattice.[15] In this context it may be emphasized that the annealing rate of V_2 in Cz silicon is substantially larger than in high-purity float-zone samples where V_2 is stable up to temperatures above 300 °C.[7,10] This difference is presumably due to the fact that the concentration of annihilation centers (impurities and defects) is several orders of magnitude higher in the Cz silicon. It should also be mentioned that the Pt contacts are expected to be stable in the temperature range studied since the formation rate of Pt_2Si is of the order of 10^{-17} cm^2/s or smaller at and below 200 °C.[16]

The SIMS profiles in Fig. 3 show that within a depth resolution of $\sim$20–30 Å and a dynamic range of $\sim 10^3$ no silicide formation takes place at and below 150 °C. However, XPS measurements show that a metal-rich (η'-Cu_3Si)-like phase forms in the initial stage of interfacial reaction during Cu deposition at room temperature, but a temperature of $\sim$200 °C is required for 1000 Å of Cu to fully react and form a uniform layer of η'-Cu_3Si.[17] The annealing rate of V_2, however, decreases between 150 and 200 °C, and thus provides strong evidence that Si self-interstitials are not injected into the silicon during the growth of η'-Cu_3Si. If it is assumed that every Cu atom generates one Si interstitial during the silicidation process, a *uniform* interstitial concentration of the order of 10^{19} cm^{-3} is obtained in an underlaying silicon substrate with negligible concentration of traps and recombination centers. This is $\sim$4 orders of magnitude higher than $[V_2]$ in the present samples, and a rapid annihilation of V_2 through the reactions $V_2+I\rightarrow V$ and $V+I\rightarrow\emptyset$ is expected. Furthermore, these annihilation processes have a high efficiency, e.g., only 10% of the vacancies and interstitials generated by high-energy electrons are estimated to escape direct recombination.[18]

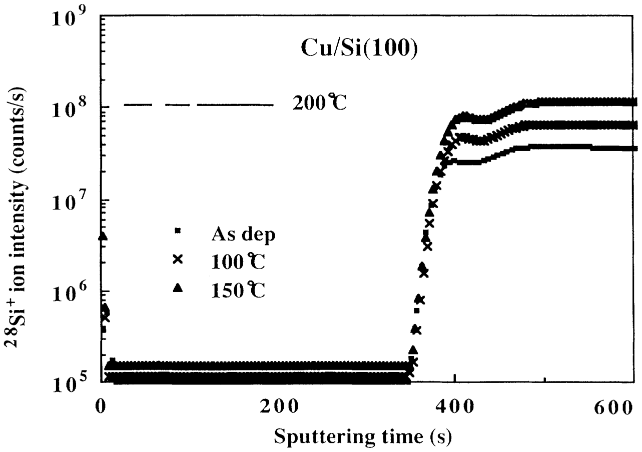

FIG. 3. SIMS spectra of the $^{28}Si^+$-ion intensity as a function of sputtering time in as-deposited and annealed Cu/Si structures. The levels of the curves are displaced in order to guide the eye, and the broken line indicates the signal intensity after a 30-min anneal at 200 °C where a uniform layer of η'-Cu_3Si is formed. (The noise level of the Faraday cup detector is $\sim 10^5$ counts/s.)

The absence of generation of Si self-interstitials during the growth of η'-Cu_3Si is in contradiction to the suggestion of Ronay and Schad[2] that the formation enthalphy of Si interstitials is drastically lowered by the formation of metal-rich silicides. The formation enthalphy of self-interstitials in silicon is normally in excess of 5 eV (Ref. 19), resulting in an almost vanishing equilibrium concentration at 200 °C. Furthermore, the model proposed by Wen *et al.*[1] on the basis of results showing defect annihilation during titanium silicidation at 1050 °C appears not to be generally applicable. The model suggests that the type of point defect injected into silicon is determined by the dominant moving species during silicidation; silicon diffusion leads to vacancy injection, while metal diffusion leads to injection of interstitials. We believe that the generation of point defects in silicon during silicide growth is strongly influenced by the experimental conditions, e.g., film thickness, annealing temperature, and time. The temperatures and annealing times used in Refs. 1 and 2 are significantly higher than required to form films with a stoichiometry of $TiSi_2$ and Cu_3Si. Moreover, Hu[20] performed high-temperature (950 °C) Ta silicidation and found an enhancement of *both* B and Sb diffusion in the Si bulk crystal. This is in contrast to what is observed during the oxidation of Si.[21] The formation of SiO_2 is generally agreed to cause injection of Si self-interstitials, and the diffusion of B is found to be enhanced while the opposite holds for Sb. Recently, Honeycutt and Rozgonyi[22] reported an enhanced Sb diffusion during growth of both $TiSi_2$ and $CoSi_2$ (Co dominant moving species).

Let us now consider the rapid decrease of $[V_2]$ at temperatures below $\sim$150 °C in samples with Cu contacts. Interstitial Cu diffuses very fast as a positively charged ion,[23] and a substantial interaction with negatively charged divacancy centers may be expected. Theoretical considerations by Estreicher[24] show that Cu, like hydrogen, passivates the boron acceptor in crystalline silicon.

However, in contrast to H, which bridges a B-Si bond and forms a stronger bond with Si than B, Cu is at the antibonding site to the boron atom and forms a Cu-B covalent bond. These potential-energy surface (PES) calculations[24] are supported by experiments showing passivation of shallow acceptors (B,In) in *p*-type silicon by diffusion of Cu or Cu-related impurities.[25,26] In analogy with hydrogen passivation of both shallow acceptors and irradiation-induced vacancy-type defects involving broken bonds,[27] we suggest that Cu also passivates the V_2 centers, and neutral complexes are formed. This is consistent with the annealing kinetics showing a rapid decrease in $[V_2]$ at temperatures below 150 °C followed by a reduction in the rate of loss at higher temperatures and not a first-order process as has been previously reported.[7,10,15] A similar annealing behavior is also found for V_2 in *p*-type samples,[14] and the kinetics may be interpreted as a sum of two competing processes; one "ordinary" annealing reaction and one "extraordinary," generating new V_2 centers. A candidate for the latter process is dissociation of Cu-passivated neutral V_2 complexes ($\mathrm{Cu}\,V_2 \rightarrow \mathrm{Cu} + V_2$), and as a result, electrically active V_2 centers reappear and give rise to an almost constant net concentration of levels at $E_c - 0.43$ eV at temperatures above 150 °C.

In summary, the annealing behavior of the divacancy acceptor levels is investigated during the formation of the metal-rich silicide η'-$\mathrm{Cu_3Si}$ on electron-irradiated silicon. An anomalously high annealing rate is observed at temperatures below ~150 °C and is attributed to passivation of the V_2 centers by the fast-diffusing interstitial Cu^+. However, in the temperature range between 150 and 200 °C where η'-$\mathrm{Cu_3Si}$ forms (here Cu is the dominant moving species) $[V_2]$ remains almost constant, and no evidence for injection of Si self-interstitials into the underlaying silicon substrate is found.

We greatly appreciate the assistance of the Central Scientific Materials Laboratory at IBM, Yorktown Heights, NY, in preparing the samples. Financial support was received from the Swedish Board for Technical Development and the Swedish Natural Science Research Council.

---

[a] Permanent address: IBM Research Division, T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, NY 10598.

[1] D. S. Wen, P. L. Smith, C. M. Osburn, and G. A. Rozgonyi, Appl. Phys. Lett. **51**, 1182 (1987).

[2] M. Ronay and R. G. Schad, Phys. Rev. Lett. **64**, 2042 (1990).

[3] See, e.g., W. J. Ward and K. M. Carroll, J. Electrochem. Soc. **129**, 227 (1982).

[4] G. D. Watkins, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum, New York, 1968), p. 67.

[5] S. Mottet and A. Roizés, in *Defects and Radiation Effects in Semiconductors—1978*, IOP Conference Proceedings No. 46, edited by J. H. Albany (Institute of Physics, Bristol, 1979), p. 281.

[6] J. W. Corbett and G. D. Watkins, Phys. Rev. Lett. **7**, 314 (1961).

[7] G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).

[8] See, e.g., A. R. Bean, R. C. Newman, and R. S. Smith, J. Phys. Chem. Solids **31**, 739 (1970).

[9] B. G. Svensson, K.-H. Rydén, and B. M. S. Lewerentz, J. Appl. Phys. **66**, 1699 (1989).

[10] A. O. Evwaraye and E. Sun, J. Appl. Phys. **47**, 3776 (1976); L. C. Kimerling, in *Radiation Effects in Semiconductors—1976*, edited by N. B. Urli and J. W. Corbett, IOP Conference Proceedings No. 31 (Institute of Physics, Bristol, 1977), p. 221; B. G. Svensson and M. Willander, J. Appl. Phys. **62**, 2758 (1987).

[11] L. W. Song, B. W. Benson, and G. D. Watkins, Phys. Rev. B **33**, 1452 (1986).

[12] A. Chantre, J. L. Benton, M. T. Asom, and L. C. Kimerling, Mater. Sci. Forum **10-12**, 1111 (1986).

[13] B. G. Svensson, B. Mohadjeri, A. Hallén, J. H. Svensson, and J. W. Corbett, Phys. Rev. B **43**, 2292 (1991).

[14] B. G. Svensson and M. O. Aboelfotoh (unpublished).

[15] B. G. Svensson, K. Johnson, D-X. Xu, J. H. Svensson, and J. L. Lindström, Radiat. Eff. Defects Solids **111 & 112**, 439 (1989).

[16] M. A. Nicolet and S. S. Lau, in *VLSI Electronics*, edited by N. G. Einspruchand and G. B. Larrabee (Academic, New York, 1983), p. 329.

[17] A. Cros, M. O. Aboelfotoh, and K. N. Tu, J. Appl. Phys. **67**, 3328 (1990).

[18] G. S. Oehrlein, I. Krafcsik, J. L. Lindström, A. E. Jaworowski, and J. W. Corbett, J. Appl. Phys. **54**, 179 (1983).

[19] R. Car, P. J. Kelly, A. Oshiyama, and S. T. Pantelides, Phys. Rev. Lett. **52**, 1814 (1984).

[20] S. M. Hu, Appl. Phys. Lett. **51**, 308 (1987).

[21] See, e.g., P. M. Fahey, P. B. Griffin, and J. D. Plummer, Rev. Mod. Phys. **61**, 289 (1989).

[22] J. W. Honeycutt and G. A. Rozgonyi, Appl. Phys. Lett. **58**, 1302 (1991).

[23] C. S. Fuller and J. C. Severins, Phys. Rev. **96**, 21 (1954); C. J. Gallagher, J. Phys. Chem. Solids **3**, 82 (1982).

[24] S. K. Estreicher, Phys. Rev. B **41**, 5447 (1990).

[25] T. H. Prescha, T. Zundel, J. Weber, H. Progge, and P. Gerlach, Mater. Sci. Eng. B **4**, 79 (1989).

[26] B. G. Svensson and M. O. Aboelfotoh, Mater. Sci. Forum **65-66**, 253 (1990).

[27] S. J. Pearton, Phys. Status Solidi (a) **67**, K73 (1983).