

Copper passivation of boron in silicon and boron reactivation kinetics

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Copper passivation of substitutional boron in single-crystal silicon and the reactivation kinetics of the passivated boron have been investigated with the use of Schottky-barrier structures formed by the deposition of copper on boron-doped silicon at room temperature. It is found that passivation of the boron acceptors occurs after copper deposition. The results suggest that the fast-diffusing interstitial Cu^+ passivates the boron acceptors by forming neutral B-Cu complexes, rather than by direct compensation. No compensating donor levels associated with Cu are observed. These results are consistent with recent theoretical predictions. The reactivation kinetics are first order with an activation energy of 0.89 eV, and the annealing process is found to be controlled by long-range diffusion, rather than by pure dissociation. The thermal dissociation of the B-Cu complexes is driven by the formation of the copper silicide η' - Cu_3Si , indicating the importance of silicide formation in the reactivation of the boron acceptors.

I. INTRODUCTION

The passivation of a variety of shallow acceptors and donors by hydrogen in single-crystal silicon has been intensively investigated both experimentally¹⁻⁴ and theoretically.^{5,6} Total-energy calculations⁵⁻⁹ have shown that in the case of hydrogen-passivated substitutional boron, the lowest-energy configuration is realized when H is located near a bond-centered site. Hydrogen forms a strong bond with one of the four Si nearest neighbors to the boron atom, leaving the latter threefold coordinated while saturating the fourth Si dangling bond. A number of experimental data¹⁰⁻¹² support the bond-centered site as the lowest-energy configuration.

However, hydrogen is not the only interstitial which passivates shallow acceptors in silicon. The formation of {Li,B} and {Li,In} pairs has been observed by infrared¹³ and Raman¹⁴ spectroscopy and by the perturbed-angular-correlation technique.^{15,16} More recently, an ultrafast diffusing defect or impurity labeled X has also been shown to passivate shallow acceptors in silicon.¹⁶⁻¹⁹ This species X is speculated¹⁹ to be positively charged interstitial copper, and recent theoretical studies²⁰ have shown that Cu is a viable candidate for passivation of boron in silicon. These theoretical studies have also established that passivation results from the formation of a covalent bond between Cu and substitutional boron with the lowest-energy configuration corresponding to Cu at the antibonding site to the boron atom. The nature of the defect X is still, however, in debate, and it is unclear whether in previous studies¹⁹ X is indeed interstitial Cu. Furthermore, there have been no studies of the reactivation kinetics of Cu-passivated boron in silicon. Understanding the electrical behavior of Cu and Cu-related complexes in Si is of crucial importance to its applications in Si devices.²¹

In this work we investigate Cu passivation of substitutional boron in Si and present data on the annealing kinetics of the passivated boron. Unlike previous studies¹⁶⁻¹⁹ in which X was introduced by chemomechanical polishing of p -type Si wafers or by diffusion of Cu at a high temperature followed by rapid quenching, in our study we used Schottky-barrier (SB) structures formed by the deposition of Cu on boron-doped Si(100) at room temperature. We find that passivation of the boron acceptors occurs after Cu deposition, and suggest that the fast-diffusing interstitial Cu^+ passivates their electrical activity by a reaction where neutral complexes are formed, rather than by direct compensation. We also show that the reactivation kinetics are first order and that the annealing process is controlled by long-range diffusion, rather than by pure dissociation. Furthermore, our investigation gives additional insight into the role of copper silicide formation in the reactivation of the boron acceptors.

II. EXPERIMENTAL PROCEDURE

SB structures were prepared by depositing 1000-Å Cu films on Czochralski (Cz) silicon wafers grown in the $\langle 100 \rangle$ direction and doped with boron to a concentration of 1×10^{15} to $1 \times 10^{16} \text{ cm}^{-3}$. The concentrations of interstitial oxygen and substitutional carbon were measured by infrared absorption spectroscopy and found to be $5.5 \times 10^{17} \text{ atoms/cm}^3$ and below $1 \times 10^{16} \text{ atoms/cm}^3$, respectively. Before Cu deposition, the Si wafers were chemically prepared using a standard chemical cleaning procedure which included a final dip in diluted hydrofluoric acid.²² Auger spectra from the Si surfaces showed that such a chemical cleaning procedure leaves less than a monolayer of oxygen and carbon on the surfaces.²³ The Si wafers were inserted into the deposition

chamber immediately after chemical cleaning, and the Cu was deposited using electron-beam evaporation in a pressure of $\sim 1 \times 10^{-7}$ Torr at a rate of 10 \AA/sec , with the Si wafers kept at room temperature. The resistivity of the Cu films was $2.0\text{--}2.5 \mu\Omega\text{cm}$ at 300 K. SB structures were also prepared by sequentially depositing a Ge film first, followed by a Cu film on the same *p*-type Si wafers. The sequential deposition of the Ge and Cu films was accomplished in the same vacuum, with the Si wafers kept at room temperature. This was followed by a 30-min. in situ anneal at temperatures between 175 and 400°C in the deposition chamber in a pressure of $\sim 5 \times 10^{-7}$ Torr to form the metal-rich germanide Cu_3Ge . We have recently discovered that the $\epsilon\text{-Cu}_3\text{Ge}$ phase (which forms at temperatures below 200°C and has a monoclinic crystal structure) exhibits a remarkably low room temperature and metallic resistivity.²⁴ The room-temperature resistivity of the Cu_3Ge films ($1000\text{--}2000 \text{ \AA}$ thick) was as low as $\sim 5 \mu\Omega\text{-cm}$. During the same deposition, two types of samples were made: bare Si samples for secondary-ion mass spectrometry (SIMS) measurements, and bare Si samples held under a metal mask defining two rows of diodes of 0.75 and 1 mm in diameter for capacitance-voltage (*C-V*) and deep-level transient spectroscopy (DLTS) measurements. The Si wafers were then cut into separate diodes, and the diodes were subsequently annealed at temperatures between 90°C and 200°C in a pressure of $\sim 5 \times 10^{-7}$ Torr or in an atmosphere of pure nitrogen.

C-V measurements were carried out at a frequency of 1 MHz and with the samples held at temperatures in the range $80\text{--}250 \text{ K}$. DLTS measurements were performed as the sample temperature was scanned between 80 and 295 K. Eight different DLTS spectra with rate windows in the range of $(20 \text{ ms})^{-1}$ to $(2560 \text{ ms})^{-1}$ were obtained from a single temperature scan. The entire procedure has been described in detail elsewhere.²⁵

III. RESULTS

In Fig. 1 we show boron-acceptor concentration depth profiles obtained by *C-V* measurements at 250 K for as-deposited Cu/[*p*-type Si(100)] samples formed on Si(100) wafers with different initial boron concentrations ($N_A = 1 \times 10^{15}$, 2.3×10^{15} , and $1 \times 10^{16} \text{ cm}^{-3}$). The depth profiles were obtained by use of the relation²⁶ $\partial C^{-2}/\partial V = 2/[qa^2\epsilon_s N_A(x)]$, where q is the elementary charge, a is the diode area, ϵ_s is the permittivity of silicon, and $N_A(x)$ is the electrically active acceptor concentration at a depth x . A pronounced decrease of the electrically active acceptor concentration is observed towards the surface. Such an effect is not seen in control samples formed by deposition of Ti on the same *p*-type Si(100) wafers or in samples formed by deposition of Cu on *n*-type [phosphorus- or arsenic-doped to $(1\text{--}10) \times 10^{15} \text{ cm}^{-3}$] Cz Si(100) wafers. The depth profiles measured at 77, 150, and 200 K are identical to those shown in Fig. 1. This shows that the passivation of the boron acceptors does not exhibit a temperature dependence. The results in Fig. 1 further reveal that the depth of passivation increases (from ~ 0.65 to $2 \mu\text{m}$ at half-boron concentra-

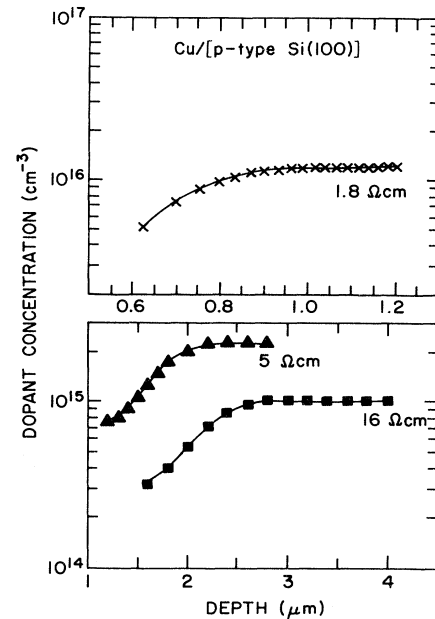


FIG. 1. Active boron concentration depth profiles obtained by *C-V* measurements at 250 K for as-deposited Cu/[*p*-type Si(100)] samples with $N_A = 1 \times 10^{15}$, 2.3×10^{15} , and $1 \times 10^{16} \text{ cm}^{-3}$.

tion) with decreasing initial boron concentration (from 1×10^{16} to $1 \times 10^{15} \text{ cm}^{-3}$). This indicates that Cu diffusion is slowed by the presence of boron, which we attribute to the formation of neutral B-Cu complexes. On

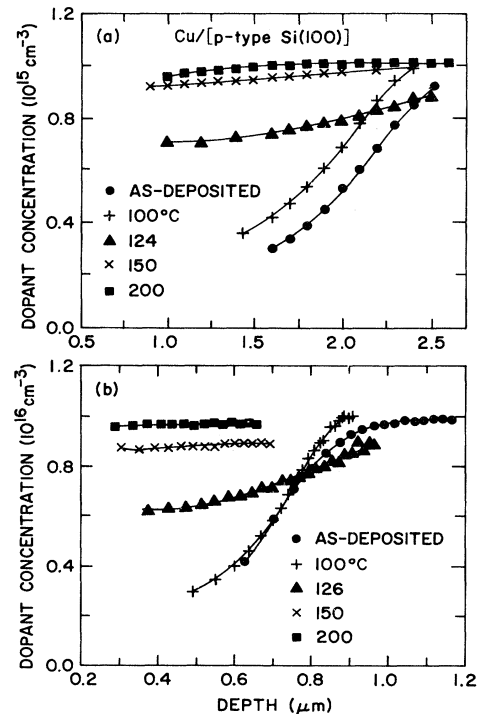


FIG. 2. Active boron concentration depth profiles for annealed Cu/[*p*-type Si(100)] samples with (a) $N_A = 1 \times 10^{15}$ and (b) $N_A = 1 \times 10^{16} \text{ cm}^{-3}$.

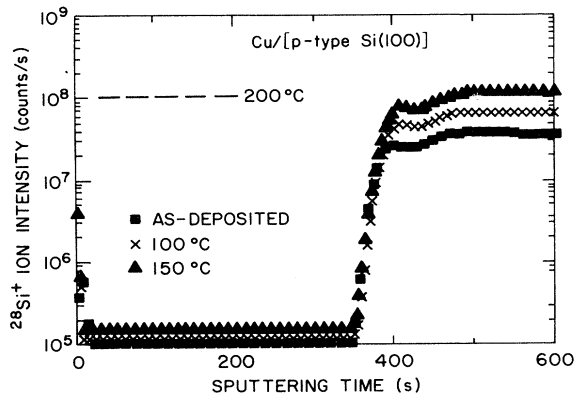


FIG. 3. SIMS spectra of the $^{28}\text{Si}^+$ ion intensity as a function of sputtering time from as-deposited and annealed Cu/[p-type Si(100)] samples. The levels of the curves are displaced in order to guide the eye, and the broken line indicates the signal intensity after a 30-min anneal at 200 °C where η' -Cu₃Si is formed. (The noise level of the Faraday cup detector is $\sim 10^5$ counts/sec.)

the other hand, the fact that no passivation of shallow donors is observed demonstrates that formation of neutral copper-donor complexes does not take place. It also rules out the possibility that Cu introduces acceptor levels in the band gap (see DLTS spectra in Sec. IV). This is in contrast to H which has been shown to passivate phosphorus donors in Si by a reaction where neutral P-H complexes are formed.³

Annealing the samples at temperatures up to 200 °C for 30 min causes a progressive reactivation of the boron acceptors in the surface region which extends from ~ 0.9 to $2.5 \mu\text{m}$ in unannealed samples with $N_A = 1 \times 10^{16}$ and $1 \times 10^{15} \text{ cm}^{-3}$, respectively, and after a 30-min anneal at 200 °C, the initial acceptor concentration is completely

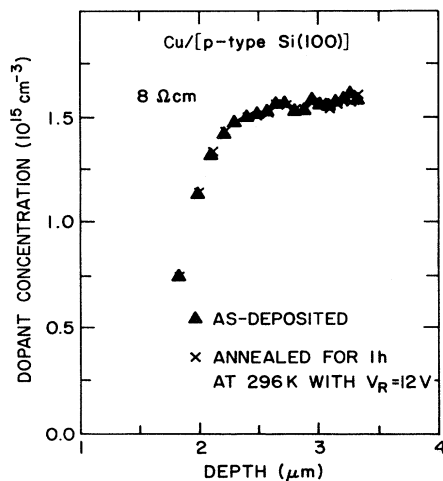


FIG. 4. Active boron concentration depth profiles for Cu/[p-type Si(100)] samples with $N_A = 1.5 \times 10^{15} \text{ cm}^{-3}$ in the as-deposited state (solid triangles) and after annealing at 296 K for 1 h under a reverse bias of 12 V (crosses).

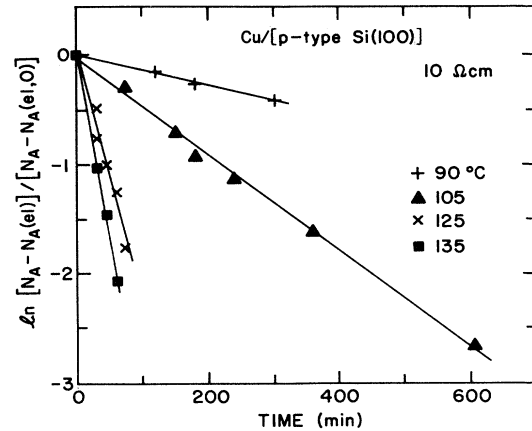


FIG. 5. The logarithm of the inactive boron concentration values at a depth $x = 1.6 \mu\text{m}$ as a function of annealing time for Cu/[p-type Si(100)] samples with $N_A = 1 \times 10^{15} \text{ cm}^{-3}$. The concentration values are normalized with respect to the values at $t = 0$. Solid line: least-square fit to the experimental data.

restored, as shown in Fig. 2. In this context it should be emphasized that copper silicide formation occurs at 200 °C, as shown by the SIMS spectra in Fig. 3. This is consistent with the results of recent Rutherford backscattering-spectrometry and x-ray photoemission-spectroscopy studies²⁷ of Cu on Si(100) which showed that a metal-rich silicide phase (which has been identified to be the η' -Cu₃Si phase with a tetragonal crystal structure) is formed after a 200 °C anneal.

In order to investigate the influence of an electric field on the deactivated boron, Cu/[p-type Si(100)] samples in the as-deposited state were annealed at 296 K for 1 h with a reverse bias of 12 V applied to the Schottky diodes. The sample temperature was then decreased to 250 K, where the depth profiles were measured. In Fig. 4 typical acceptor concentration profiles are shown. It is evident that annealing under reverse bias does not influence the electrically active acceptor profiles, in contrast to the results recently reported by Zundel *et al.*¹⁷ and Wagner *et al.*¹⁹ which showed that such an anneal even at temperatures below 295 K leads to complete reac-

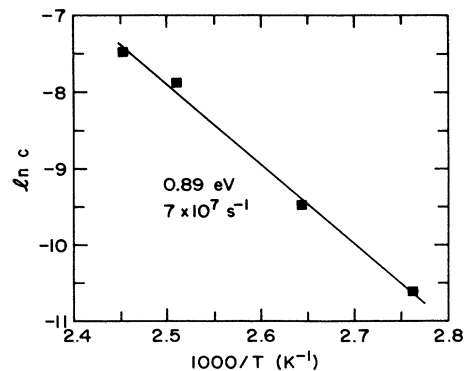


FIG. 6. Arrhenius plot of the rate constant for reactivation of the boron acceptors.

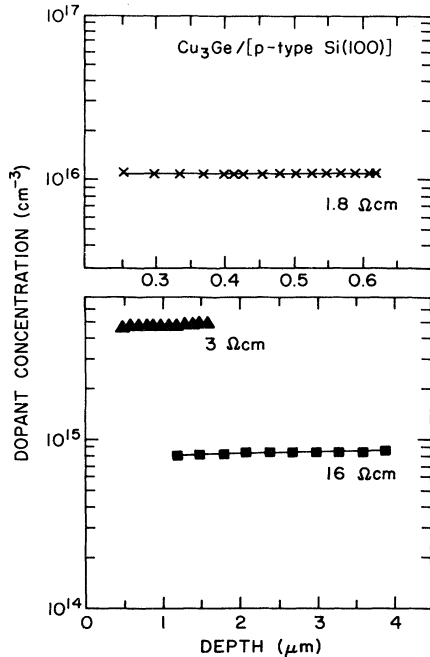


FIG. 7. Active boron concentration depth profiles for $\text{Cu}_3\text{Ge}/[p\text{-type Si}(100)]$ samples with $N_A = 1 \times 10^{15}$, 4.5×10^{15} , and $1 \times 10^{16} \text{ cm}^{-3}$.

tivation of the boron acceptors in the space-charge region due to thermal instability of the so-called B-X complex.

In Fig. 5 the logarithm of the inactive boron concentration values at a depth $x = 1.6 \mu\text{m}$ obtained by isothermal annealing at different temperatures is depicted versus annealing time for samples with $N_A = 1 \times 10^{15} \text{ cm}^{-3}$. The concentration values are normalized with respect to the values at $t = 0$ and within the experimental accuracy a linear dependence holds. Thus the annealing process follows first-order kinetics. Rate constants c were determined using least-square fits to the experimental data and in Fig. 6 the logarithm of c is plotted as a function of the reciprocal absolute temperature. The slope of the straight line through the data points gives an activation energy for the thermal reactivation of the boron acceptors of 0.89 eV and a frequency factor of $7 \times 10^7 \text{ sec}^{-1}$.

Figure 7 shows boron-concentration depth profiles obtained by C - V measurements at 250 K for $\text{Cu}_3\text{Ge}/[p\text{-type Si}(100)]$ samples formed on the same p -type Si(100) wafers as in Fig. 1. It is clear that these samples do not exhibit a decrease of the electrically active acceptor concentration. This contrasts markedly the behavior of the as-deposited $\text{Cu}/[p\text{-type Si}(100)]$ samples shown in Fig. 1. Furthermore, annealing the samples at temperatures up to 400° C for 30 min does not influence the electrically active acceptor profiles

IV. DISCUSSION

It is known that copper is the fastest interstitial-diffusing element in silicon. It diffuses as a positively charged Cu^+ species, as demonstrated by its drift in an

electric field,²⁸ and is likely to be captured by the negatively charged boron acceptors due to long-range Coulomb attraction, resulting in the formation of neutral B-Cu complexes. On the basis of theoretical calculations, Estreicher²⁰ showed that the lowest-energy configuration which results in passivation, involves the formation of a Cu-B covalent bond with Cu at the boron-antibonding site (here Cu is moved away from the tetrahedral interstitial site towards the substitutional boron). In this configuration, no deep levels appear in the band gap after passivation.²⁰ This can be seen from the DLTS spectra (a) and (b) in Fig. 8. On the other hand, if passivation is due to direct compensation (direct electron-hole annihilation), the interstitial-diffusing Cu must introduce a donor level in the band gap. However, no donor levels with a position between $\sim 0.1 \text{ eV}$ below the conduction-band edge and $\sim 0.1 \text{ eV}$ above the valence-band edge and with concentrations above 10^{11} cm^{-3} are observed (Fig. 8). Furthermore, results from infrared-absorption-spectroscopy and photoluminescence measurements at liquid-helium temperatures showed no existence of Cu-associated donor levels in the band gap. We therefore conclude that the passivation is not due to direct compensation, but rather a result of complex formation. Wagner *et al.*¹⁹ also concluded from infrared-absorption-spectroscopy and C - V measurements, that the passivation of shallow acceptors by the defect X results from the formation of neutral A - X complexes. The formation of $\epsilon\text{-Cu}_3\text{Ge}$, however, completely suppresses the passivation of the boron acceptors (Fig. 7), indicating that it impedes the diffusion of Cu into silicon.

We have shown that the annealing kinetics of the passivated boron are first order with an activation energy of 0.89 eV and a frequency factor of $7 \times 10^7 \text{ sec}^{-1}$. On the other hand, Prescha *et al.*¹⁸ and Wagner *et al.*¹⁹ reported an activation energy of 0.61 eV and a frequency factor of $\sim 10^{13} \text{ sec}^{-1}$ for the dissociation of the B-X complex. It should be emphasized that the passivation (the B-Cu complex) observed in our work is stable at room temperature (Fig. 4). This differs considerably from the results in Refs. 18 and 19 where the passivation was found to be very unstable at room temperature as manifested by the low dissociation energy of the B-X complex. The frequency factor of $7 \times 10^7 \text{ sec}^{-1}$ compared to $\sim 10^{13} \text{ sec}^{-1}$ also indicates that the annealing process is controlled by long-range diffusion, rather than by pure dissociation. In this context it should be pointed out that the formation of

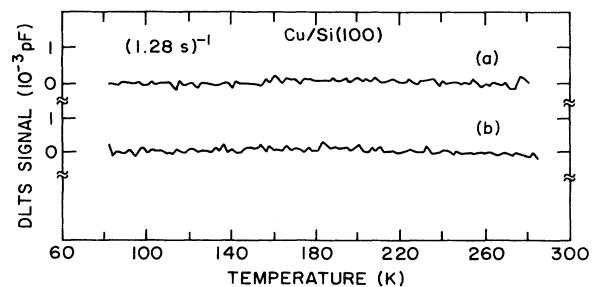


FIG. 8. DLTS spectra from (a) $\text{Cu}/[p\text{-type Si}(100)]$ and (b) $\text{Cu}/[n\text{-type Si}(100)]$ samples in the as-deposited state.

η' -Cu₃Si is limited by Cu diffusion,²⁹ and a strong chemical driving force is expected for Cu bound to the boron atoms to participate in the silicidation process. In other works, the thermal dissociation of the B-Cu complexes is driven by silicide formation, or the formation of the more energetically favorable Cu(*d*)-Si(*p*) bonding.²⁷ It therefore appears that in the aforementioned^{18,19} studies *X* is not interstitial Cu, but rather involves intrinsic defects (e.g., self-interstitials) as originally suggested by Reichel and Sevcik.³⁰

This raises an interesting question concerning possible injection of Si self-interstitials during η' -Cu₃Si formation.³¹ We have recently taken a new approach to examine the suggestion that the formation of metal-rich silicides generates self-interstitials in silicon.³² Copper was deposited on both boron- and phosphorus-doped Cz Si(100) wafers irradiated with 2 MeV electrons at room temperature, and the annealing behavior of the divacancy center (V_2) was monitored during the formation of η' -Cu₃Si. The V_2 center is one of the most prominent defect in electron-irradiated silicon and introduces three levels in the band gap located ~ 0.25 eV above the valence-band edge and ~ 0.42 and ~ 0.24 eV below the conduction-band edge, corresponding to four different charge states (singly positive, neutral, singly negative, and doubly negative)³³. 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,³⁴ and an abrupt decrease in the concentration of V_2 is expected if injection of Si self-interstitials takes place during the formation of η' -Cu₃Si. An anomalously high annealing rate of the three V_2 -related levels was observed below 150 °C and is attributed to passivation of the V_2 centers by interstitial-diffusing Cu⁺ through formation of neutral complexes.³² In addition, in *p*-type samples a substantial passivation of the boron acceptors was observed. However, in the temperature range 150 °C–200 °C, where η' -

Cu₃Si was formed, the concentration of the three V_2 -related levels remained almost constant, thus providing strong evidence that Si self-interstitials are not injected into the silicon substrate during the formation of η' -Cu₃Si. Simultaneously, complete reactivation of the boron acceptors occurred. The active boron concentration depth profiles are similar to those shown in Figs. 1 and 2 for the unirradiated *p*-type samples. These results thus favor a model where the silicide formation promotes thermal dissociation of the neutral B-Cu complexes without any influence by Si self-interstitials.

V. CONCLUSION

We have investigated Cu passivation of substitutional boron and the reactivation kinetics of the passivated boron using Schottky-barrier structures formed by the deposition of Cu on boron-doped Si(100) at room temperature. Passivation of the boron acceptors is observed after Cu deposition and is attributed to the formation of neutral B-Cu complexes, rather than to direct compensation, since no Cu-associated donor levels are observed. These results are consistent with recent theoretical predictions based on potential-energy surface calculations. The reactivation kinetics are first order with an activation energy of 0.89 eV, and the annealing process is controlled by long-range diffusion, rather than by pure dissociation. The thermal dissociation of the B-Cu complexes is driven by the formation of η' -Cu₃Si, indicating the importance of silicide formation in the reactivation of the boron acceptors.

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