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Defect reactions in copper-diffused and quenched *p*-type silicon

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Electrical measurements carried out on copper-diffused and quenched *p*-type silicon indicate that a large acceptor deactivation occurs throughout the material. The passivation stability, limited to subambient temperatures, is shown to be dopant dependent, thus confirming previous results. The measurements also provide information on the generation of Cu-related defects and copper behavior. One of the observed defects, labeled an *M* center, exhibits metastability. It is shown that this can be understood as a pairing mechanism between the *M* defect and free Cu atoms, with the pair being electrically inactive. Kinetic studies reveal a correlation between the dopant-copper binding energy and the *M*-Cu reaction. The available mobile copper ions result from dissociation of acceptor-copper pairs leading to a dopant-dependent association frequency of the $M\mathrm{Cu}_i$ complex. On the basis of these results, certain recent data related to copper-defect reactions in silicon are reanalyzed. In particular, the so-called *X*-defect diffusion coefficient is reconsidered, taking into account the internal built-in electric field. The results support identification of the *X* defect as interstitial copper.

I. INTRODUCTION

Recently, the passivation of acceptors has been observed[1] in silicon following chemomechanical polishing at room temperature, using alkaline slurry containing small concentrations of ethylendiamine, or ammonia and copper. This has been explained by a pairing mechanism involving the dopant and a fast diffusing defect labeled *X* by Zundel, Weber, and Benson.[1] The extrapolation to high temperature of the diffusion coefficient of this *X* defect was shown to be higher than all known impurity diffusion coefficients in silicon including copper.[2] Prescha, Zundel, and Weber[3] and Keller *et al.*[4] found a strong correlation between the presence of copper and the *X* defect. However, the difference in diffusivities led Prescha, Zundel, and Weber[3] to suggest that copper acts as a catalyst for the creation of the unknown *X* defect.

Prigge *et al.*[5] have found that Cu is indeed incorporated uniformly into the bulk during chemomechanical polishing. Moreover, after long-term storage at room temperature, they measured an accumulation of Cu near the sample surface together with a decreasing bulk concentration and acceptor neutralization. These results strongly suggest that Cu is directly involved in the pairing mechanism. From infrared investigations, Hage, Prigge, and Wagner[6] concluded that Cu must be located near the acceptor atom and this interpretation was later supported by theoretical calculations.[7] The identification of the *X* defect as interstitial copper therefore seems very likely. This identification is strengthened in this work by taking into account both the pairing and the internal built-in electric-field effects, which greatly influence the diffusivity of the charged *X* defect. Therefore, the mobile species will be referred to as Cu_i^+.

Owing to its high diffusivity, copper is unstable at room temperature and is expected to be involved in numerous defect reactions. In this paper we report observations of a Cu-related complex revealing a metastable behavior. It will be referred to as an *M* center.[8] Its complete electrical characterization led us to understand the mechanism underlying its metastability and increased our knowledge of the behavior of copper in silicon at low temperature.

The organization of the paper is as follows. Details on sample preparation are given in Sec. II. The capacitance-voltage data on acceptor-copper pairing reactions and the capacitance spectroscopic results on the *M* center are presented in Sec. III. In Sec. IV, we emphasize the role of the dopant on the reaction kinetics of the *M* center with Cu_i. In Sec. V, a general discussion is presented and conflicting results are discussed. Finally, we have attempted to identify the observed defects and the paper is summarized in Sec. VI.

II. EXPERIMENTAL CONDITIONS

The samples used in this study were prepared from boron-doped floating zone (FZ) and gallium-doped Czochralski-grown (CZ) *p*-type ⟨100⟩-oriented silicon wafers from Wacker Chemitronic. Capacitance-voltage (*C*-*V*) profiling revealed uniform free-hole density in the range $3.7\times10^{14}-1.5\times10^{15}$ cm^{-3} for boron-doped material and 1.5×10^{15} cm^{-3} for gallium-doped silicon. A third batch of silicon was phosphorus-doped CZ-grown material, ⟨100⟩ oriented, with a doping level of 2×10^{15} cm^{-3}. In all samples, no deep levels were found at concentrations higher than 10^{11} cm^{-3} during preliminary deep-level transient spectroscopy (DLTS) characterization.

After cleaning and etching the silicon substrates, 200 nm of high-purity (99.9999%) copper was evaporated on both sides of the wafers. Thermal diffusion was then performed in an argon atmosphere at 1335 K for 30 min, followed by quenching in liquid nitrogen (LN2). 50 μm was removed by reactive chemical etching and the samples were restored in LN2 before and after Schottky-barrier realization.

The electronic properties of the *M* center in each unstable configuration and its transformation kinetics were studied using capacitance-voltage and deep-level transient spectroscopy. Possible nonuniformity of the dopant is taken into account.[9]

III. EXPERIMENTAL RESULTS

A. Acceptor-copper reactions

The *C-V* measurements show a large neutralization of the boron and gallium throughout the material, as illustrated in Fig. 1. The electrical inactivity begins to disappear above 200 K under reverse bias. Figure 1 shows that, whereas a 5-min anneal at 200 K is sufficient to completely reactivate the boron in the high electric-field region, 240 K is needed to achieve the same result in Ga-doped silicon. This is due to higher binding energy of Ga_sCu_i as compared to B_sCu_i and is expected from the data obtained after chemomechanical polishing.[1] The passivation is reversible below 300 K if the diode is shortened.

The properties of Cu_i can be explored by monitoring the dissociation-association kinetics of the pairing reaction given by

$$A_s\text{Cu}_i \Longleftrightarrow A_s^- + \text{Cu}_i^+ \ , \tag{1}$$

where A_s^- represents the substitutional dopant atom. At long distances at least, this reaction should be governed by a Coulombic attraction between two oppositely charged ions whereby the acceptor is immobile. When a high electric field is applied, reaction (1) is driven to the right as free Cu_i^+ drifts out of the space-charge layer toward the bulk, leading to an increased acceptor neutralization in the neutral region. The Cu_i^+ distribution is nonuniform (Fig. 1). When reaction (1) is reversed (zero bias), a long-range diffusion process toward the surface must be considered. The pairing reaction is thus described by a coupled system of equations

$$\frac{\partial[\text{Cu}_i]}{\partial t} = D_f \frac{\partial^2[\text{Cu}_i]}{\partial x^2} - \frac{d[A_s\text{Cu}_i]}{dt} \ , \tag{2}$$

$$\frac{d[A_s\text{Cu}_i]}{dt} = c_a([A_s]_0 - [A_s\text{Cu}_i]) - \frac{[A_s\text{Cu}_i]}{\tau_a} \ , \tag{3}$$

where the association rate $c_a = 4\pi R_a D_f[\text{Cu}_i]$. $[A_s]_0$ represents the total concentration of acceptors, R_a is the capture radius for Cu_i^+ by A_s^-, and $1/\tau_a$ is the dissociation rate of the complex $A_s^-\text{Cu}_i^+$; the subscript *a* stands for acceptor. D_f is the diffusion coefficient of Cu_i^+ and the brackets indicate concentration. Using appropriate boundary conditions and numerical calculations for the case in which reaction (1) was driven to the left, the system of Eq. (2) and (3) allowed Zundel, Weber, and Benson[1] to determine the diffusion coefficient of Cu_i^+ (called an *X* defect in their work) at low temperature. Their results will be discussed later.

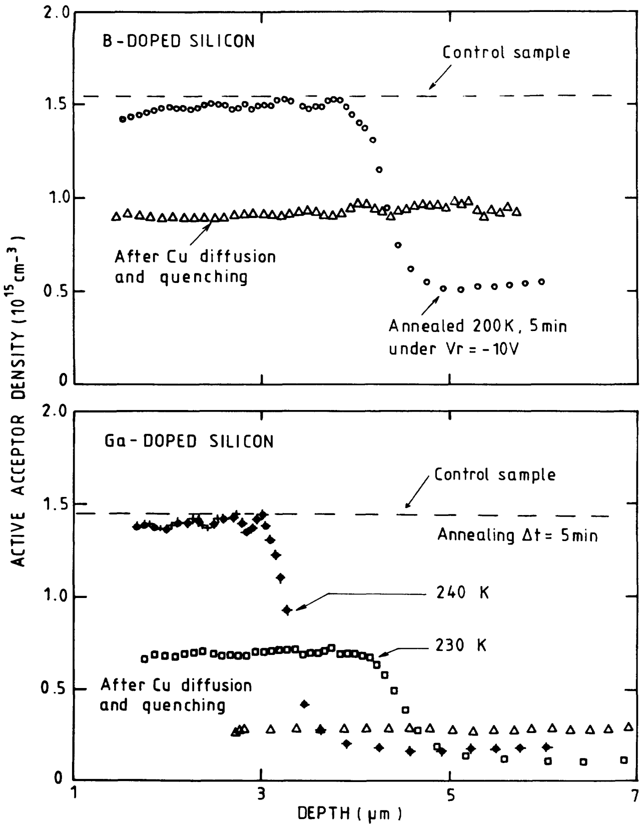

FIG. 1. Electrically active acceptor densities as a function of annealing conditions. 10-V reverse bias was applied to both samples.

Under a high electric field, the investigated region is depleted from Cu_i^+, so that the association rate c_a is neglected,[10] leading to a first-order dissociation reaction. Figure 2 shows the dissociation frequency of the Ga_sCu_i pair as a function of temperature. In the same figure we present the data obtained by Prescha, Zundel, and Weber[3] for boron- and gallium-doped silicon, which are copper-contaminated and chemomechanically polished,

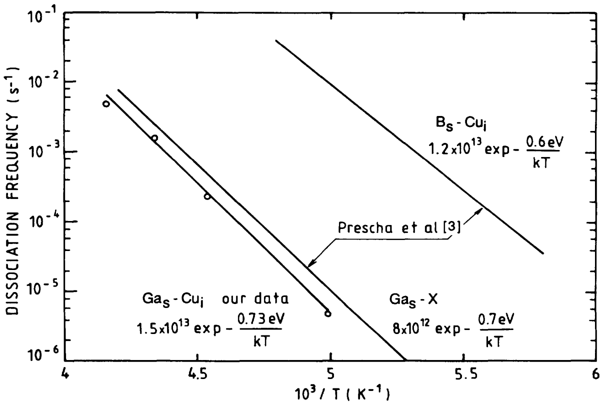

FIG. 2. Dissociation frequencies of the electrically inactive acceptor-copper complexes. Our data on Ga_s-Cu_i and those on Ga_s-*X* of Prescha, Zundel, and Weber (Ref. 3) are within the experimental errors.

respectively. These results confirm that the dopant-dependent binding energy of the $A_s\text{Cu}_i$ pair is as predicted in Fig. 1. The acceptor-copper pair belongs to the more general class of dipoles formed between transition metals and acceptors, of which the most frequently investigated system is the $A_s\text{Fe}_i$ pair. However, in the case of $A_s\text{Cu}_i$, the binding energy (characteristic for short-range interactions) seems to be dopant dependent, thus contradicting the Coulomb model. This effect will be discussed later; it is probably due to additional strain forces acting at short distances. Moreover, the $A_s\text{Cu}_i$ complex is electrically inactive and Cu_i^+ cannot be stabilized in interstitial site. Accordingly, no corresponding deep level has yet been observed.

Equations (2) and (3) assume that the irreversible loss or precipitation of copper is negligible. This assumption is no longer valid if the sample are stored at 300 K for a relatively long time. Within a few days for boron-doped silicon, and after several days for gallium-doped material, a complete and irreversible depassivation is reached at 300 K. It will be seen below that this property explains various conflicting experimental results.

B. Defect-copper reactions

In order to study the possible role of additional defects, DLTS measurements were performed. Figure 3 shows typical spectra observed for both boron- and gallium-doped silicon samples. Two hole traps, *Ha* ($E_v+0.085$ eV) and *Hb* ($E_v+0.210$ eV), are observed; the latter is the *M* center. Their position in the gap does not change with dopant nature. Control samples quenched under the same conditions but without intentional copper contamination do not show these centers. This establishes their copper-related nature and dopant independence. Other characteristics of these defects will confirm this assertion. Moreover, as both materials have different oxygen contents, oxygen does not seem to play a role in the formation of these defects. The first level has previously been seen by Graff and Pieper[11] and later identified by Weber, Bauch, and Sauer[12], by photoluminescence, as the Cu-Cu pair. This level has a donorlike character with a constant-capture cross section of 3.5×10^{-15} cm^2 and is annealed out above 423 K.

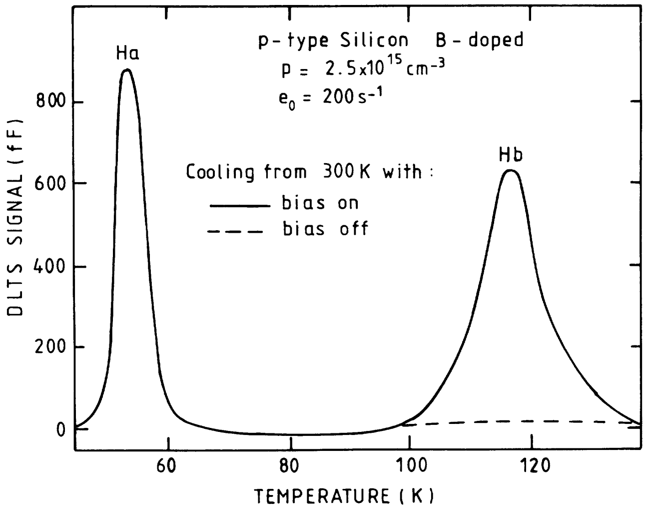

FIG. 3. DLTS spectra showing the Cu-related defects observed after Cu diffusion and fast quenching. The *Hb* level corresponds to the *M* center.

The *M* center, which will retain our attention below, has a concentration of 5×10^{13} cm^{-3} in all boron-doped samples. Its density is roughly twice as much in the gallium-doped material. It exhibits a junction electric-field-enhanced emission effect. The apparent activation energy of this level is proportional to $E^{1/2}$, where E is the average junction electric field over the depletion region. This behavior is consistent with the Poole-Frenkel effect.[13] The proportionality constant was found to be 1.8×10^{-4}, which is in good agreement with the calculated value[13] of 2.2×10^{-4}. Thus, the *M* center is a singly charged acceptor ($-/0$). Its hole-capture cross-section is found to be 1.5×10^{-15} cm^2 as measured by the pulse-width variation method.[9,14]

The peculiarity of the *M* center is its metastable behavior. A DLTS signal is observed only if the sample is cooled with applied reverse bias (full curve in Fig. 3); when cooled without bias (dashed curve) the *M* center cannot be detected. It is tempting to relate this observation to a classical configurational bistability, since the reversible behavior is phenomenologically close to the results obtained for thermal donors reported by Chantre.[15] However, such a model cannot explain all the observations and should be rejected for two reasons.

(i) In gallium-doped silicon, the level appears (cooling with reverse voltage) and disappears (cooling at zero volts) in a temperature range (260–290 K) where it lies below the Fermi level. The resulting invariant charge state would thus forbid classical metastability.

(ii) The metastable behavior is no longer observed when the samples are kept at room temperature for several days. In the intermediate time, the resultant DLTS signal (after cooling under zero bias) height increases monotonically until it is present independent of the cooling mode.

The above results suggest the alternative mechanism of a simple pairing reaction between an unknown *M* defect and the Cu_i^+ ion. According to this model and the observations described above, copper is involved simultaneously in the defect generation of the *M* center and in the formation of both $A_s\text{Cu}_i$ and $M\text{Cu}_i$ pairs. In this respect, the role of the electric field is only to drift the free mobile Cu_i out of the space-charge region. Therefore, the same reasoning as for acceptor-Cu can be applied, i.e., a thermal dissociation-association reaction limited by a Coulombic interaction between two oppositely charged species:

$$M^-\text{Cu}_i^+ \Longleftrightarrow M^- + \text{Cu}_i^+ \ . \tag{4}$$

The equation describing the pairing kinetics is as follows:

$$\frac{d[M\text{Cu}_i]}{dt} = c_d([M]_0 - [M\text{Cu}]) - \frac{[M\text{Cu}_i]}{\tau_d} \ , \tag{5}$$

with $c_d = 4\pi R_d D_f[\text{Cu}_i]$. R_d is the capture radius for Cu_i

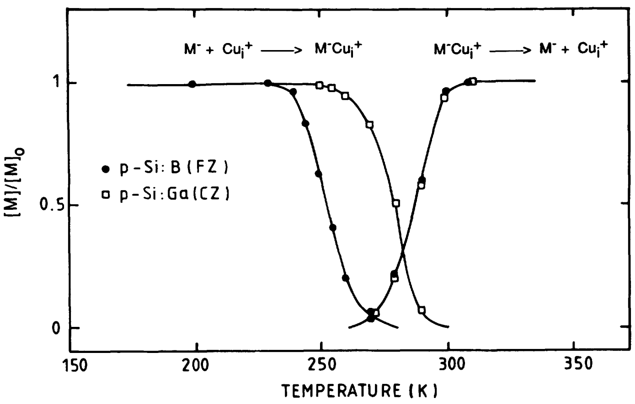

FIG. 4. Isochronal annealing ($\Delta t = 10$ min) data for the transformations $M^- + \mathrm{Cu}_i^+ \rightarrow M\mathrm{Cu}_i$ and its reverse reaction.

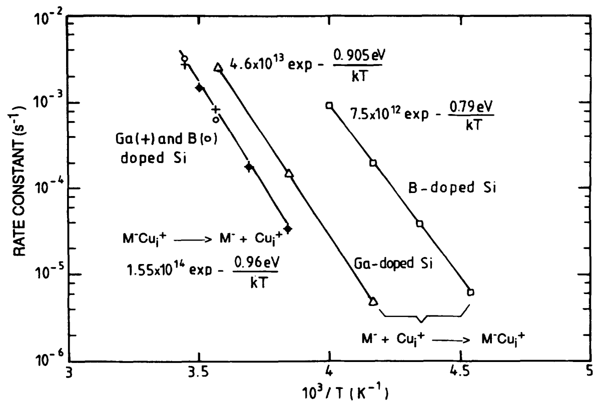

FIG. 6. Dissociation and association rates of $M^-\mathrm{Cu}_i^+$ in both boron- and gallium-doped silicon.

by the M center and $1/\tau_d$ the dissociation rate of the $M^-\mathrm{Cu}_i^+$ complex, where the subscript d corresponds to the defect M.

The association and dissociation rates of reaction (4) were studied by means of low-temperature isochronal (10-min) anneals under either reverse or zero bias. The data shown in Fig. 4 reveal that both transformations occur in a single stage but at different temperatures. Reaction (4) conducted to the right takes place at higher temperatures (280 K) and is independent of the dopant nature, whereas the reverse reaction exhibits an apparent dopant dependence and takes place at lower temperatures: 250 K for boron-doped silicon and 280 K for gallium-doped material.

Under high electric field, thermal dissociation of the complex is followed by a drift toward the bulk of Cu_i^+ and disables significant reassociation of the $M\mathrm{Cu}_i$ pair. The first-order behavior is confirmed by the uniform increase of the M center concentration in the depletion region, as shown in Fig. 5. The extracted dissociation frequencies do not depend on the dopant nature, thus confirming the above assertion that dopants are not involved in the M center. The Arrhenius plot shown in Fig. 6 satisfies the relation

$$1/\tau_d = 1.55\times10^{14}\exp(-0.960\ \mathrm{eV}/kT)\ (\mathrm{s}^{-1}) \quad \text{(for both dopants)}\ . \qquad (6)$$

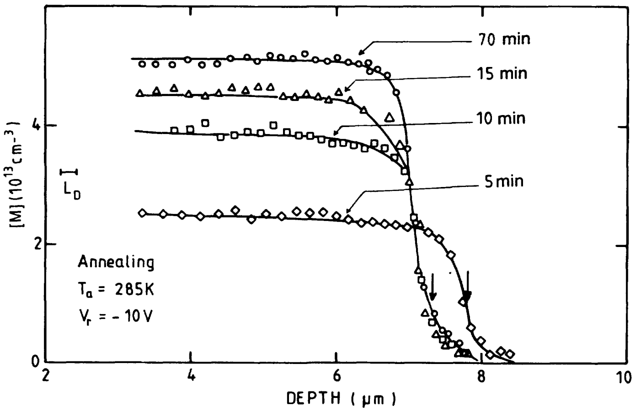

FIG. 5. M-center profiles under different annealing conditions. The arrows show the limits of the depletion region under annealing. We used high-resistive boron-doped material (45 Ωcm) to minimize the temperature shifts of the DLTS peak due to the Poole-Frenkel effect. Note that for the initial profile ($t_a = 5$ min), the depletion limit is slightly deeper owing to a larger fraction of neutralized dopant. The appearance of the defect is therefore a direct consequence of the electric field.

More surprising is the observed first-order decay of $[M]$ when reaction (4) is driven to the left (0 V). A careful analysis of the data shows below that the Cu_i^+ diffusion process is not the rate-limiting factor, and leads to the observed first-order behavior. The isothermal-annealing data shown in Fig. 6 are consistent with the following relations:

$$c_d = 7.50\times10^{12}\exp(-0.790\ \mathrm{eV}/kT)\ (\mathrm{s}^{-1}) \quad \text{(B-doped silicon)}\ . \qquad (7)$$

$$c_d = 4.60\times10^{13}\exp(-0.905\ \mathrm{eV}/kT)\ (\mathrm{s}^{-1}) \quad \text{(Ga-doped silicon)}\ . \qquad (8)$$

IV. ASSOCIATION KINETICS; DOPANT EFFECT

On the basis of the spectroscopic data described above and the unique dissociation frequency of the $M^-\mathrm{Cu}_i^+$ complex in both kinds of samples, we can expect that neither boron nor gallium is involved in the observed defect. However, examination of the deactivation frequencies given by relations (7) and (8) cannot exclude the role of the dopant in the association kinetics.

To account for this we must clearly define the role of the different reacting particles. They are of two types: (i) the fixed charges, boron, gallium, and the defect M, and (ii) the mobile species (Cu_i), which has a positive gradient from the surface to the bulk (see Fig. 1) before pairing takes place. The resulting reactions (3) and (5) may of course interfere because mobile Cu_i^+ participates in both reactions. The association kinetics $M^- + \mathrm{Cu}_i^+$ could be numerically solved by finding a solution to the three coupled equations (2), (3), and (5), with appropriate boundary conditions. This approach seems rather complicated and even useless. Indeed, the exponential increase of $[M\mathrm{Cu}]$ or decay of $[M]$, observed experimentally, indicates that reasonable simplifications can be made.

After cooling the sample under reverse bias from 285 K, the M center is not detected in the neutral region (Fig. 5). This indicates that, at this temperature, equilibrium of reaction (4) corresponds to a negligible amount of unpaired M defects. Consequently, when the bias is switched off, the dissociation of $M^{-}\mathrm{Cu}_i^{+}(1/\tau_d)$ is negligible and reaction (4) is driven only to the left. Moreover, to account for the exponential decay of the defect density, the association frequency c_d should be time invariant, which leads to a constant, or slowly varying, density of free Cu_i. This is indeed the case, as we shall see below. Finally, an experimental trend is observed between $A_s^{-}\mathrm{Cu}_i^{+}$ dissociation and the $M\mathrm{Cu}_i$ association barrier. The higher the binding energy of $A_s^{-}\mathrm{Cu}_i^{+}$ complex, the lower the $M^{-}\mathrm{Cu}_i^{+}$ association rate. This would suggest that the rate-limiting factor in the passivation of the defect is the availability of free Cu_i.

The following picture can account for all these requirements. Reaction (1), assumed at equilibrium in the neutral region, provides free Cu_i^{+} which, when the bias is turned off, diffuses toward the surface. Owing to the large diffusivity of Cu_i^{+}, reaction (1) very quickly reaches the equilibrium in the previously depleted zone. The available density of free Cu_i should thus constitute the limiting factor for reaction (4). Indeed, at the temperatures considered for $M^{-}\mathrm{Cu}_i^{+}$ association (240 K for boron-doped Si and 260 K for gallium-doped Si), the $A_s^{-}\mathrm{Cu}_i^{+}$ profiles (Fig. 1) are flat after 2–5 min at zero volts, which is very short compared to the time required for a complete $M^{-}\mathrm{Cu}_i^{+}$ association (a few hours). Thus, Cu_i^{+} diffusion as a limiting factor is excluded, and leads to the required uniform $[\mathrm{Cu}_i^{+}]$ distribution. Profiles of the M center during passivation at 285 K and $Vr=0$ (not shown here) exhibit a parallel decrease of the density with increasing annealing time. Therefore, we can write that $d[A_s\mathrm{Cu}_i]/dt=0$ during reaction (4), following a short transient. The substitution of $[\mathrm{Cu}_i]$, extracted form Eq. (3), in to Eq. (5), gives the $M^{-}\mathrm{Cu}_i^{+}$ complex association rate

$$c_d=\frac{R_d}{R_a}\frac{1}{\tau_a}\frac{[A_s\mathrm{Cu}_i]}{[A_s]_0-[A_s\mathrm{Cu}_i]}\,, \tag{9}$$

where $1/\tau_a$ is the acceptor-copper dissociation frequency. $[A_s\mathrm{Cu}_i]$ is extracted from the C-V profiles in the bulk. Relation (9) agrees with our experimental results. Indeed, a linear shape is obtained form the plot of c_d versus

$$[\mathrm{Ga}_s\mathrm{Cu}_i]/([\mathrm{Ga}_s]_0-[\mathrm{Ga}_s\mathrm{Cu}_i])$$

at constant temperature, as shown in Fig. 7. The slope, $3.7\times10^{-4}\ \mathrm{s}^{-1}$, compared to the value given by relation (8), $1.3\times10^{-4} T=260$ K, leads to a factor of 3 for the ratio R_d/R_a.

However, relations (7) and (8) give activation energies about 20% higher than the predicted values of 0.69 eV in boron- and 0.73 eV in gallium-doped silicon. We attri~~bute this deviation to an appreciable irreversible precipi~~tation of free Cu_i^{+} from one isothermal annealing experiment to the next. Indeed, the association kinetics data in Fig. 6 were plotted considering $[A_s\mathrm{Cu}]/([A_s]_0-[A_s\mathrm{Cu}_i])$ as constant. However, from C-V measurements, we have found that this quantity slightly decreases. The data of Fig. 6 were recorded in a specific order (280 K down to 240 K) for which the loss of available free copper follows roughly an exponential decrease as shown in the inset of Fig. 7. The extracted effective energy barrier for loss, stating for the equilibrium concentration of Cu_i is around 0.17 eV. This barrier is high enough to account for the deviation in activation energy given by relations (7) and (8). Normalizing the data of Fig. 6 by $\exp(-0.17\ \mathrm{eV}/kT)$ yields the expected dissociation energies for $A_s\mathrm{Cu}_i$ pairs. However, the narrow range of investigated temperatures leads to a nonnegligible uncertainty in the preexponential factor.

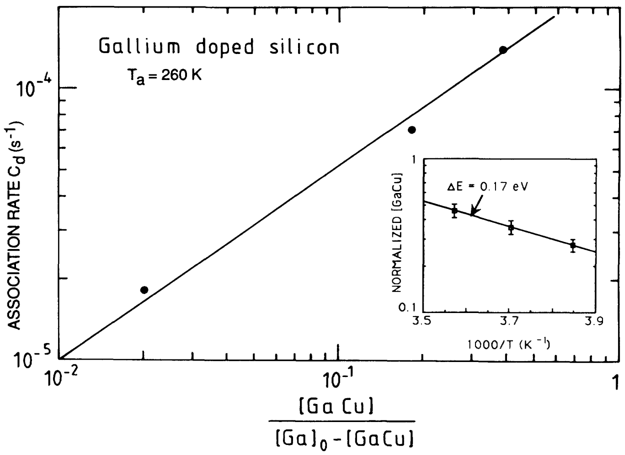

FIG. 7. $M^{-}\mathrm{Cu}_i^{+}$ association rate as a function of the residual fraction of $\mathrm{Ga}_s\mathrm{Cu}_i$. The inset shows the temperature dependence of the loss of free Cu_i in the course of studying the association kinetics $M+\mathrm{Cu}_i$.

With respect to the long-term behavior of the material stored at room temperature, it is seen that a complete and irreversible depassivation of acceptors occurs; the source of free Cu_i^{+} disappears and the defect loses its apparent reversible metastability, in accordance with the model proposed here. Moreover, when the annealing experiments are carried out at an intermediate time, the $[A_s\mathrm{Cu}_i]$ and, hence, $[\mathrm{Cu}_i^{+}]$ concentrations reach values comparable to $[M]$ so that the assumed simplifications do not hold. The kinetics deviate considerably from a first-order behavior since the Cu_i concentration can no longer be considered as constant during reaction (4).

V. DISCUSSION

A. Comparison of *M*Cu with other copper-related complexes

Table I summarizes the data of all complexes identified as involving the so-called X defect, or interstitial copper.

TABLE I. Dissociation energies and vibrational frequencies of *M*Cu pair determined in this work, and those reported in the literature for Pt*X*, Au*X*, and acceptors-$X(\mathrm{Cu}_i)$ pairs.

Defects-$X(\mathrm{Cu}_i)$ pairs	Dissociation energy E_a (eV)	Preexponential factor (s^{-1})	Ref.
$(\mathrm{Pt}X)^0$	0.85	7.6×10^{10}	17
$(\mathrm{Pt}X)^+$	0.86	2.4×10^{13}	
$(\mathrm{Au}X)^0$	0.67	2.3×10^{7}	
$(\mathrm{Au}X)^+$	0.94		17,18
$(M\mathrm{Cu})^0$	0.96	1.55×10^{14}	this work
Acceptor-$X(\mathrm{Cu}_i)$ pairs			
$(\mathrm{B}X)^0$	0.60	1.2×10^{13}	3
$(\mathrm{BCu})^0$	0.61	2.6×10^{13}	
$(\mathrm{Al}X)^0$	0.70	2.0×10^{12}	
$(\mathrm{Ga}X)^0$	0.71	8.0×10^{12}	
$(\mathrm{GaCu})^0$	0.73	1.5×10^{13}	this work
$(\mathrm{In}X)^0$	0.69	2.6×10^{12}	1

The dissociation of all pairs is a two-step process, corresponding to thermal separation of the species followed by a migration of Cu_i at long-range distance. Therefore, the activation energy E_a represents the sum of the binding energy E_b of the partners and the migration energy E_m of the mobile species ($E_a=E_b+E_m$). Comparison of $M\mathrm{Cu}_i$ and $A_s\mathrm{Cu}_i$ pairs shows a binding-energy difference in the range 0.27–0.37 eV, depending on the acceptor type. This is controversial since, if we assume both pairs to be controlled by Coulombic interaction, the difference mentioned above should be close to zero. It strongly suggests the presence of strain forces which are most effective at short distances and are dependent on the size of the involved species. However, the simple model remains valid for the association mechanism, since we consider that pairing occurs when both charges approach each other within a Thomson[16] capture radius (≈500 nm). This radius is large compared to the extension of strain forces, which should be of the order of only a few lattice constants.

The preexponential factor of $M\mathrm{Cu}_i$ dissociation ($1.55\times10^{14}\ \mathrm{s}^{-1}$) falls within the range of the lattice-phonon vibration frequency ($\approx10^{13}\ \mathrm{s}^{-1}$) required for a single jump from the paired to the unpaired state, where Cu_i becomes free to move. On the other hand, the preexponential factor of the dissociation rate of the Pt*X* system investigated by Prescha[17] was found to be much smaller than the lattice phonon vibration frequency. Careful analysis led to the introduction of a carrier emission-limited process for the dissociation of the $(\mathrm{Pt}X)^+$ and $(\mathrm{Pt}X)^0$ pairs. Another example is found in the work of Czaputa,[18] who discovered the $\mathrm{Au}_s\mathrm{Cu}_i$ pair by codiffusing these two metallic impurities. From an apparent charge-state dependence of the DLTS signal, they concluded for a classical bistability. This interpretation, later discussed by Prescha[17] should be reconsidered in the light of our own observations. In conclusion, all the defects shown in Table I belong to the same class of low-bounded pairs and do not exhibit any configurational metastability. Interstitial copper has the ability to form complexes, and thus all the reactions taking place in the silicon are not independent. Consequently, a specific pair formation, for instance, $M\mathrm{Cu}_i$, is necessarily limited by the reaction releasing free copper. In our case the source is the $A_s\mathrm{Cu}_i$ pair.

B. On the diffusion coefficients of Cu_i and *X* defect: Are both species identical?

In order to justify that the mobile species involved in the defect reactions described above is interstitial copper, it is necessary to reconsider related data found in the literature. Although many experimental results correlated the *X* defect to copper, the excessively high *X*-diffusion coefficient forbids its identification as Cu_i. This is shown in Table II, which compares the experimental data available on both species. The Cu diffusion coefficient given by Hall and Racette, when extrapolated to low temperature, deviates by a few orders of magnitude from the *X*-diffusion results. The question is, therefore, are the *X* defect and interstitial copper actually different and, if not, how can the data of Hall and Racette for copper be reconciled with those established by Reichel and Sevcik, more recently refined by Zundel, Weber, and Benson,[1] for the *X* defect? In the following, an attempt is made to settle this question.

The first data were published by Hall and Racette,[2] who proposed the expression $1.4\times10^{-3}\exp(-0.43\ \mathrm{eV}/kT)$ for $D_f(\mathrm{Cu}_i)$. They derived this expression in the temperature range 680–1179 K, which includes the value given by Struthers[19] at 1179 K obtained for intrinsic crystals. The only results of Hall and Racette[2] lead to a slightly different expression, and were obtained from solubility measurements in heavily doped silicon ($[B]=5\times10^{20}\ \mathrm{cm}^{-3}$), where the role of pairing was neglected. Pairing should, however, reduce the diffusion.

Later, Reichel and Sevcik[20] estimated the diffusion

TABLE II. Experimental diffusion coefficients of interstitial copper and X defect reported in the literature. The same data are also shown after consideration of the pairing and local electric-field effects.

Diffusion parameters					Extrapolated diffusion coefficients		
X defect		Interstitial Cu_i		Temperature range (K)			
D_0 (cm^2/s)	E_m (eV)	D_0 (cm^2/s)	E_m (eV)		295 K	1000 K	Ref.
		4.7×10^{-3}	0.47	900–1200	4.38×10^{-11}	2.01×10^{-5}	2
		$(1.4\times10^{-2})^{a}$	$(0.49)^{a}$		$(5.95\times10^{-11})^{a}$	$(4.75\times10^{-5})^{a}$	
				295	$\approx10^{-7}$		20
	20.0						
5×10^{4}	0.665			220–280	2.17×10^{-7}	22.2	1
$(10^{-1})^{b}$	$(0.3)^{b}$				$(7.50\times10^{-7})^{b}$	$(3.07\times10^{-3})^{b}$	
		3×10^{-3}	0.15	900–1200	8.02×10^{-6}	5.26×10^{-4}	4
		5×10^{-3}	0.40	295–1200	7.33×10^{-10}	4.82×10^{-5}	this work
					$(\approx10^{-10})^{c}$		
			0.30				28

[a] Values obtained from the sole data of Hall and Racette. The additional value of Struthers at 1179 K was removed.

[b] Estimated by Zundel *et al.* (Ref. 1) using the model of Koiwa (Ref. 24).

[c] The value of Reichel and Sevcik corrected by the pairing and local electric-field effect induced by the charged mobile species.

coefficient of the X defect at room temperature from boron depassivation and outdiffusion after chemomechanical polishing. They found $D_f(X)\approx10^{-7}$ cm^2/s at 295 K. More recently, Zundel, Weber, and Benson[1] determined a set of values in the temperature range 220–280 K in moderately doped silicon ($[B]\approx2\times10^{15}$ cm^{-3}). They gave the expression $5\times10^{4}\exp(-0.665\text{ eV}/kT)$. It will be seen below that the barrier energy for diffusion, 0.665 eV, is in conflict with the dissociation energy of the A_sX pairs. Nevertheless, from an extrapolation to high temperatures, it clearly appears that the X defect cannot be identified as interstitial copper.

Keller *et al.*[4] were the first to reconsider the data of Hall and Racette[2] according to the following arguments. Assuming a binding energy $E_b=0.5$ eV for the In_sCu_i pair, as expected from the Coulomb model, and taking the experimental dissociation energy $E_a=0.70$ eV, they concluded that the migration energy E_m of Cu_i should be 0.20 eV. This led them to add corrections to the expression derived by Hall and Racette,[2] since these authors had neglected pairing phenomena in their heavily doped samples. Following the model of Reiss, Fuller, and Morin,[21] the diffusion coefficient of free Cu_i, D_0, is given by

$$\frac{D_0}{D_f}=1+N_a\Omega\ . \tag{10}$$

N_a is the dopant concentration and Ω the equilibrium constant of reaction (1) given by:[21]

$$\Omega=4\pi\int_a^b r^2\exp[V(r)/kT]dr\ , \tag{11}$$

where $V(r)$ is the potential between the acceptor and the mobile donor species, a represents the nearest-neighbor equilibrium distance (2.35 Å for a tetrahedral site), and b depends on the shape of the potential. For purely Coulombic interactions, b is 0.5 aE_b/kT, where E_b is the binding energy of A_sCu_i. Introducing the concept of pairing via expressions (10) and (11), Keller *et al.*[4] found an expression for $D_f=3\times10^{-3}\exp(-0.15\text{ eV}/kT)$. Hence, they concluded that the pairing has a significant effect on the barrier energy and leads to a variation close to the value 0.2 eV which they expected above.

Owing to the high concentration of free carriers in Hall and Racette's samples, we believe that the introduction of pure Coulombic attraction considerably overestimates the pairing process because it does not take into account the screening effect by free carriers. In this case, $V(r)$ should be written as

$$V(r)=\frac{q^2}{4\pi\epsilon_0\epsilon_r}\frac{1}{r}\exp(-r/\lambda)\ , \tag{12}$$

where λ is the screening length[22] given by $\lambda=(\epsilon_0\epsilon_r kT/pq^2)^{1/2}$, p being the free-hole density and $\epsilon_0\epsilon_r$ the dielectric constant. Our calculations,[23] based on the three preceeding relations, give the expression $5\times10^{-3}\exp(-0.40\text{ eV}/kT)$ for D_f as shown in Table II. This leads us to the conclusion that the data of Hall and Racette[2] remains roughly valid. The migration energy $E_m=0.4$ eV and the dissociation energy of the A_sCu_i pair found in the range 0.6–0.7 eV (see Table I) suggest that the binding energy of the pairs is slightly lower than the Coulombic value of 0.5 eV. Strain forces at short distances are probably responsible for this deviation. Therefore, the Coulombic potential shape around the defect is only an approximation.

Concerning the results of Zundel, Weber, and Benson[1] on the X defect, several observations can be made. First, the importance of E_m ($=0.665$ eV) relative to E_a leads to an excessively low E_b, around 0.05 eV, depending on the dopant considered. In the case of boron, E_m is even higher than the dissociation energy E_a. This led Prescha[17] to suggest that 0.665 eV is an upper limit. Second, the preexponential diffusion coefficient of 5×10^{4} cm^2 s^{-1} deviates considerably form values expected for fast-diffusing interstitial species. To resolve this contradiction, Zundel, Weber, and Benson[1] proposed the influence of an additional trapping center. Following the model developed by Koiwa,[24] they estimated a lower limit of the diffusion coefficient as $D_f \approx 10^{-1}\exp(-0.3\text{eV}/kT)$ for a concentration of the additional trap of about 10^{17} cm^{-3}. Zundel, Weber, and Benson[1] suggested oxygen as a candidate for the trap. However, a similar high diffusion coefficient has been found in silicon samples with low oxygen content.[4] Our own studies[23] in FZ and CZ materials, via the dissociation kinetics of *M*Cu pairs, conclude that oxygen has no influence on the diffusivity of the mobile species. Moreover, this lower limit of Zundel, Weber, and Benson,[1] when extrapolated to high temperatures, is still four orders of magnitude higher than the result of Hall and Racette.

In the work cited above, no attention has been given to the consequences of the charged state of the impurity. Zaromb[25] and Smits[26] have pointed out that the diffusion of charged particles along a concentration gradient sets up a local electric field which actually enhances the diffusion rate. The case of a donor impurity diffusing in a *p*-type semiconductor has been described by Shaw.[27] This effect, although negligible in the experiments of Hall and Racette[2] because $[A] \gg [\text{donor}]$, is significant when $[A] \approx [\text{donor}]$. It is even more pronounced when both acceptors and donors have opposite concentration gradients. Therefore, to extract the true diffusion coefficient of the *X* defect we should consider, with the system of Eqs. (2) and (3), a third equation including the local electric field.[27] The resolution of these three coupled equations is currently under consideration. In Table II, however, we give our first estimation from the data of Reichel and Sevcik (10^{-7} cm^{-3} at 295 K), who neglected both the pairing and the local field. The calculation, based on the model developed by Reiss, Fuller, and Morin,[21] decreases the value of Reichel and Sevcik by three orders of magnitude (from 10^{-7} to 10^{-10} cm^2/s at 295 K). The calculations assume a concentration of donors (Cu_i^+) close to that of the dopant according to reaction (1) at equilibrium at 295 K. The value fits quite well with the low-temperature extrapolation of the data of Hall and Racette corrected for the screened pairing effect.

The concentration of free Cu_i available when reaction (1) is at thermal equilibrium, $(d[A_s\text{Cu}_i]/dt=0)$, strongly depends on the diffusion coefficient. The values of Zundel, Weber, and Benson[1] and those of Keller *et al.*[4] predict variations in the range 10^{10}–10^{12} cm^{-3} for $[\text{Cu}_i]$ at 295 K. These values cannot explain the first-order decay of $[M]$ when reaction (4) is driven to the left (0 V) since we assume that $[\text{Cu}_i] \gg [M]$. Our proposed diffusion coefficient leads to a value of 5×10^{14} cm^{-3}, which is higher than $[M](\leq 10^{14}\ \text{cm}^{-3})$.

In conclusion, we believe that the additional correction due to the local electric field is sufficient to remove the reported discrepancy between low- and high-temperature diffusion coefficients. Hence, the argument that the *X* defect and interstitial copper are different entities is weakened. At the end of Table II, we have reported the theoretical value on migration energy found very recently by Woon, Marynick, and Estreicher.[28] For a diffusion along the path tetrahedral-hexagonal-tetrahedral, the hexagonal site being the saddle point, they found $E_m = 0.30$ eV. This barrier is consistent with the fact that the filled 3*d* shell of Cu^+ does not interact significantly with the host lattice.

C. On the mechanism of defect formation

Suggestions on the origin of the electrically active defect observed in this work must be tentative since we rely solely on electrical characterization. A more complete description of the *M* center would require structural information, such as that obtained by EPR and which is difficult to perform for the relatively low density ($N_t = 5\times10^{12}$ cm^{-3}) of the defect present after quenching. However, using our observations described above, we can speculate on its formation mechanism.

It has been shown that neither acceptors nor oxygen are involved in the structure of the *M* center. It should therefore be present in copper-diffused *n*-type material. Figure 8 shows the minority carrier transient spectroscopy[9] signal. This spectrum, as well as the DLTS features (not reported here), are very similar to those already reported by Brotheton, Ayres, and Gill[29] and Kimerling, Benton, and Rubin.[30] Despite the close signatures of H_1 and the *M* center (*Hb* level in Fig. 3), the two defects differ because (i) H_1 is very stable and has a donor character,[29] whereas our center is negatively charged when empty of holes, and (ii) H_1 has been demonstrated [29,30] to be an amphoteric defect, coupled to the acceptorlike level H_2. Therefore, if *Hb* is present, it is hidden by H_1.

As a fast-diffusing impurity, isolated copper is known to vanish during cooling, mostly into precipitates, in agreement with the solubility data.[31] This statement should be reconsidered at low density. In our quenching procedure, a fraction of copper is trapped by acceptors and the remainder generates the observed defects. Therefore, the complexes could be of copper-cluster type, but such as copper-decorated dislocations, for instance, are unlikely since the hole-capture process at the *M* center does not exhibit logarithmic behavior.[32]

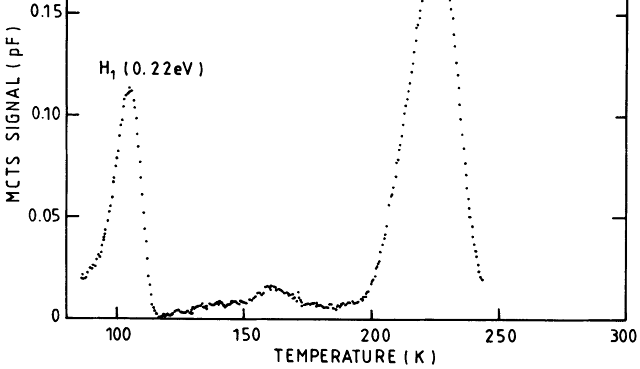

FIG. 8. MCTS spectrum of Cu-diffused and quenched *n* type silicon showing two amphoteric Cu-related levels.

The fact that the *M* center is only observed in *p*-type materials suggests that the dopant influences the defect formation. Acceptors prevent precipitation of interstitial copper during cooling. A small fraction of free copper ions, which decreases with temperature, serves to form the defect while the major part remains bound to acceptors.

Hence, it is possible to explain why the *Hb* level is difficult to detect in *n*-type silicon prepared in the same manner. Because of the absence of acceptors or their very low density in the compensated materials, precipitation is favored over pairing, leading to at most a very small concentration of the *M* center. In consequence, we would expect difficulty in detecting the *M* center even in *p*-type silicon of low acceptor concentration (less than or equal to 10^{14} cm^{-3}) unless the quenching rate is increased. The absence of the *M* center in the spectra obtained by Brotherton, Ayres, and Gill[29] in their resistive material ($[\mathrm{B}]=10^{14}$ cm^{-3}) support this idea. On the other hand, the *M* center density is increased roughly by one order of magnitude for a corresponding increase in dopant.[33]

This scenario is not so uncommon, since an experiment demonstrating this effect has been observed by Reiss and Fuller[34] for *p*-type germanium doped with lithium. Very recently, Marwick[35] also proposed a "pumping mechanism" to explain the crucial role played by acceptor-hydrogen pairs in the formation of hydrogen clusters during H-plasma treatment.

Finally, and until complementary measurements revealing the structural and chemical identity are available, it seems reasonable to consider that the *M* center could be an electrically active cluster of Cu atoms. A critical size is required to give rise to a deep level in the gap. In such a case, the question of how many copper atoms are involved in the *M* center remains to be answered, since the addition of one ion leads to an electrically inactive complex. The simplest cluster, formed by at least two atoms, is given by the level *Ha* ($E_v = 0.085$ eV) already attributed to the Cu-Cu pair (Fig. 3).

VI. CONCLUSION

We have shown in this study that numerous defect reactions can take place in copper-diffused and fast-quenched *p*-type silicon. Owing to its very high mobility, even below room temperature, interstitial copper forms pairs either with acceptors or with more complex defects such as the *M* center. The detailed kinetics in the latter case are due to the interference of several pairing reactions. In particular, the $A_s\mathrm{Cu}_i$ equilibrium concentration is the limiting factor for the *M*Cu association rate. Moreover, the possible role of the $A_s\mathrm{Cu}_i$ pairs in preventing precipitation was proposed as responsible for generation of the *M* center.

The excessively high diffusion coefficient of the mobile species in chemomechanical polishing treatment has led to a controversy about its copper-related nature. We have shown that the local electric field generated by the positively charged copper atoms, enhances considerably its effective diffusivity. Thus, the discrepancy between diffusion data can be explained. Diffusion is not the limiting factor in the defect reactions. The substitution of copper by other fast-diffusing elements such as nickel and cobalt is currently under study.

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