Intrinsic Diffusion Coefficient of Interstitial Copper in Silicon

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Transient ion drift experiments designed to obtain reliable values for the intrinsic copper diffusivity in silicon are reported. From these measurements, the diffusion barrier of Cu in Si is determined to be 0.18 ± 0.01 eV. It is shown that the commonly used expression of Hall and Racette [J. Appl. Phys. **35**, 379 (1964)] actually gives an effective diffusion coefficient for heavily boron-doped silicon and can neither be used for other doping levels nor extrapolated to lower temperatures. A model is developed which predicts the effective diffusion coefficient as a function of temperature, doping level, and the type of dopant. [S0031-9007(98)06824-0]

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Copper is one of the most prevalent and detrimental impurities in silicon device production [1]. The electrical and structural properties of copper in silicon are still poorly understood despite intensive research during the last 30 years (see [2] for a review). Even such a fundamental property of Cu in Si as its diffusion coefficient remains uncertain. Unlike most other $3d$ transition metals, copper diffuses in silicon in the positively charged state [3]. The theory of diffusion of donors in the presence of immobile acceptors was developed by Reiss *et al.* [4]. They showed that, due to acceptor-donor pairing, the effective (apparent) diffusivity D_{eff} of donors in p-type material is lower than their diffusivity in intrinsic material D_{int} and in the case of $N_D \ll N_a$ is given by

$$D_{\mathrm{eff}} = D_{\mathrm{int}}/[1 + \Omega N_a], \tag{1}$$

where N_a is the acceptor concentration, N_D is the concentration of mobile donors, and Ω is the pairing constant. The latter can be calculated as

$$\Omega = 4\pi \int_a^b r^2 \exp\left[\frac{V(r)}{k_B T}\right] dr, \tag{2}$$

where $V(r)$ is the potential energy of donor-acceptor interaction, k_B is the Boltzmann constant, T is the temperature, a is the nearest-neighbor equilibrium distance, and b is the capture radius of the potential $V(r)$ [4].

The first data point on copper diffusivity was obtained on intrinsic silicon by Struthers [5]. Later temperature-dependent measurements were done by Hall and Racette [6] on heavily boron doped p-type Si ($N_a = 5 \times 10^{20}$ cm^{-3}). Assuming negligible copper-acceptor pairing, Hall and Racette [6] suggested the expression $D = 4.7 \times 10^{-3} \exp(-0.43\ \mathrm{eV}/k_B T)$ cm^2 s^{-1}, which was then widely used as the intrinsic copper diffusion coefficient in silicon (see, e.g., [1]). Keller *et al.* [7] and Mesli *et al.* [8] attempted to make a correction for donor-acceptor pairing, using the data of Hall and Racette. Later Heiser *et al.* [9] measured the effective copper diffusivity in In- and Ga-doped p-Si around room temperature by the transient ion drift (TID) technique. Plotting the corrected data from [6,9] on the same plot, Mesli *et al.* [10] suggested the expression $D = 4.5 \times 10^{-3} \exp(-0.39\ \mathrm{eV}/k_B T)$ cm^2 s^{-1}. The model [Eqs. (1),(2)], used in Refs. [7–10], implies that the potential energy of donor-acceptor interaction $V(r)$ should depend only on the acceptor charge state and not on its chemical nature. Yet recent experimental studies of the copper-acceptor dissociation energy reported by Wagner *et al.* [11] revealed that the dissociation energy is different for different types of acceptors (0.61 eV for CuB, about 0.70 eV for CuAl, CuGa, and CuIn and 0.85 eV for CuPt), thus indicating that the binding in these pairs has a covalent component. This conclusion is in agreement with theoretical calculations done by Estreicher [12]. As follows from the results presented below, the assumption of a purely Coulomb interaction [8–10] underestimates the pairing constant Ω by more than an order of magnitude and the previously published "intrinsic" diffusion data need to be reconsidered.

In this Letter we report the first direct experimental measurements of the intrinsic diffusivity of copper in silicon in the temperature range between 240 and 380 K. The experimental procedure used to quench copper in the interstitial state and to prepare Schottky diodes is described elsewhere [9]. Measurements were done by TID [9], which analyzes the transient capacitance signals induced by Cu_i^+ drift and diffusion. The time constant of the capacitance transients τ_{TID} is determined by the Cu effective diffusion coefficient [9,13,14]:

$$\tau_{\mathrm{TID}} = \alpha \times \frac{\varepsilon\varepsilon_0 k_B T}{q^2 N_a D_{\mathrm{eff}}}, \tag{3}$$

$$D_{\mathrm{eff}} = \frac{D_{\mathrm{int}}}{1 + \beta\Omega N_a}, \tag{4}$$

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$$\Omega = \frac{\tau_c^{-1}}{N_a \tau_{\rm diss}^{-1}} = \frac{4\pi D_{\rm int} R_C}{\tau_{\rm diss}^{-1}}, \qquad (5)$$

where ε and ε_0 are the dielectric permittivity of silicon and vacuum, respectively, q is the elementary charge, τ_c and $\tau_{\rm diss}$ are, respectively, the temperature-dependent time constants of association and dissociation of ion pairs, and R_C is the capture radius of mobile ions by acceptors. These equations were obtained for $N_D \ll N_a$ and are identical to the ones previously discussed by Heiser *et al.* [9] and Zamouche *et al.* [15] with the only difference that two correction coefficients $\alpha = 2.85$ and $\beta = 1.95$ are introduced, as suggested by Heiser *et al.* [14]. They solved numerically a system of coupled differential equations, which accounted for drift, diffusion, and trapping of copper by shallow acceptors in the depletion region and showed that although an exact analytical solution for the TID kinetics does not exist, previously reported equations [9] are generally correct and, after α and β are introduced, Eqs. (3)–(5) can serve as an accurate approximation to evaluate TID data. It is also important to note that Eq. (2) is substituted in this treatment by Eq. (5), which does not depend on the shape of the attractive potential $V(r)$ and anticipates only that the trapping of ions is diffusion limited [13]. The process of trapping is characterized by a capture radius R_C, which is calculated from the condition that the average thermal energy $k_B T$ equals the attractive potential energy $V(r)$, i.e., $k_B T = V(R_C)$. Since in most cases R_C is as large as several nm, the covalent component of the ion interaction can be neglected and $V(R_C)$ can be approximated by a screened Coulomb potential:

$$k_B T = \frac{q^2}{4\pi\varepsilon\varepsilon_0 R_C} \exp\left[-R_C \Big/ \left(\frac{\varepsilon\varepsilon_0 k_B T}{q^2 p}\right)^{1/2}\right], \qquad (6)$$

where p is the free hole density. For the doping levels $N_A \leq 10^{17}\ \mathrm{cm}^{-3}$ and under extrinsic conditions the screened Coulomb potential can be approximated by a simple Coulomb potential, and the capture radius R_C can be obtained explicitly as $R_C = q^2/4\pi\varepsilon\varepsilon_0 k_B T$. Inserting Eqs. (4),(5) into Eq. (3), we obtain

$$\tau_{\rm TID} = \alpha \frac{\varepsilon\varepsilon_0 k_B T}{q^2 N_a D_{\rm int}} + \alpha\beta\tau_{\rm diss}. \qquad (7)$$

The first term on the right-hand side of Eq. (7) describes the average drift time of unpaired copper ions through the depletion region. The second term describes the dissociation of copper-acceptor pairs. If $\tau_{\rm TID} \gg \alpha\beta\tau_{\rm diss}$, the pairing is weak and the TID time constant is determined primarily by the intrinsic drift of copper ions through the depletion region. The intrinsic diffusivity $D_{\rm int}$ can in this case be determined directly from the experimental data as follows:

$$D_{\rm int} = \frac{\alpha\varepsilon\varepsilon_0 k_B T/q^2 N_a}{\tau_{\rm TID} - \alpha\beta\tau_{\rm diss}}. \qquad (8)$$

On the other hand, if $\tau_{\rm TID} \approx \alpha\beta\tau_{\rm diss}$, then the pairing is strong and the denominator in Eq. (8) becomes arbitrary close to zero. In this case the information on the intrinsic diffusion coefficient contained in the dependence $\tau_{\rm TID}(T)$ drops below the measurement errors and $D_{\rm int}$ cannot be extracted unambiguously from the experimental data.

The conditions of strong pairing, $\tau_{\rm TID} \approx \alpha\beta\tau_{\rm diss}$, and weak pairing, $\tau_{\rm TID} \gg \alpha\beta\tau_{\rm diss}$, can be distinguished by the slope of the temperature dependence of $\tau_{\rm TID}$. Figure 1 shows an example of such a dependence obtained from TID studies of Cu diffusivity in Ga-doped ($N_{\rm Ga} = 1.5 \times 10^{15}\ \mathrm{cm}^{-3}$) silicon. The experimental data points fall on a straight line with the slope of 0.68 ± 0.03 eV, which matches the dissociation energy of CuGa pairs [11]. This implies that $\tau_{\rm TID}(T)$ is proportional to $\tau_{\rm diss}(T)$ over the whole temperature range; i.e., all data points were obtained under strong pairing conditions. Equation (8) shows that the conditions of weak pairing can be achieved by increasing the temperature to a value which depends on the doping level N_a, on the dissociation rate of copper-acceptor pairs $\tau_{\rm diss}^{-1}$, and on the intrinsic copper diffusion coefficient $D_{\rm int}$. The influence of the last two parameters is illustrated in Fig. 1 by varying the diffusion barrier for Cu in Ga-doped (curves 1–3, solid lines) and B-doped (curves 1–3, dashed lines) Si. From a comparison between calculations (curves 1–3, solid lines) and the experimental data obtained on Si:Ga (triangles) it appears that no conclusion about the Cu diffusion barrier can be reached except for a lower estimate of approximately 0.35 eV. For diffusion barrier heights lower than this value (curves 2 and 3) a general agreement is obtained between experimental data and calculated curves. Because of the lower dissociation energy of CuB pairs,

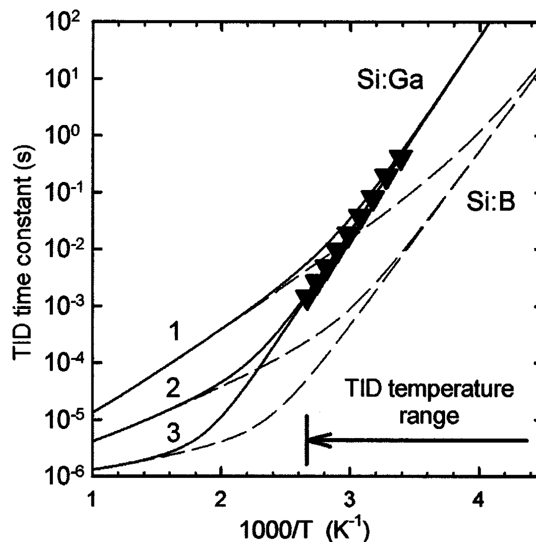

FIG. 1. Experimentally measured dependence of the TID time constant on temperature for gallium-doped silicon with the doping level of $1.5 \times 10^{15}\ \mathrm{cm}^{-3}$ (triangles). Curves 1–3 are simulated dependencies for gallium-doped (solid lines) and boron-doped (dashed lines) silicon for copper diffusion barriers of 0.35 eV (curve 1), 0.25 eV (curve 2), and 0.15 eV (curve 3). The diffusivity prefactor D_0 used in the simulations was set equal to that of Hall and Racette [6].

an experiment done on B-doped silicon with a similar resistivity would enable us to distinguish curves 2 and 3, if the experimental data were measured in the same temperature range (dashed lines in Fig. 1). The upper temperature limit where TID can be measured (about 380 K, denoted by an arrow in Fig. 1) is imposed by the leakage currents generated due to the relatively narrow Si band gap. The temperature range where TID measurements can be done under the conditions of weak pairing can be further extended to lower temperatures by reducing the boron doping level [see Eq. (7)].

Figure 2 presents the TID measurements done on boron-doped float zone (FZ) silicon with boron densities of 1.5×10^{14} cm^{-3} and 2×10^{15} cm^{-3}. Oxygen and carbon concentration in the samples was below 10^{16} cm^{-3} for both impurities. For the boron doping level of $N_a = 2 \times 10^{15}$ cm^{-3} the dependence $\tau_{\mathrm{TID}}(T)$ is determined by pairing with boron up to the temperature of about 320 K (Fig. 2, triangles). In the low-doped samples (Fig. 2, circles) the pairing of copper with boron is dominant only at $T < 255$ K. Equation (8) can be used to determine the time constant of CuB dissociation at temperatures where the pairing is strong, and the intrinsic copper diffusion coefficient at the higher temperatures. Using these two data sets between 240 and 320 K, the following expression for the CuB dissociation rate was obtained:

$$\tau_{\mathrm{diss}}^{-1}(T) = (2.05 \pm 0.80) \times 10^{13} \times \exp\left(-\frac{0.61 \pm 0.01\ \mathrm{eV}}{k_B T}\right). \quad (9)$$

This expression is very close to the one reported by Wagner *et al.* [11]. The intrinsic diffusivity of copper calculated using Eqs. (8),(9) for the samples with $N_a = 1.5 \times 10^{14}$ cm^{-3} is presented in Fig. 3 as an Arrhenius plot, built using our data and the data obtained on intrinsic silicon at 1173 K by Struthers [5]. This yields the following expression for the interstitial copper intrinsic diffusion coefficient:

$$D_{\mathrm{int}} = (3.0 \pm 0.3) \times 10^{-4} \times \exp\left(-\frac{0.18 \mp 0.01\ \mathrm{eV}}{k_B T}\right)(\mathrm{cm}^2/\mathrm{s}), \quad (10)$$

which is valid in the temperature range between 265 and 1173 K. The intrinsic diffusion barrier of 0.18 eV in Eq. (10) is close to the values recently predicted by Woon *et al.* [16].

We emphasize that Eq. (10) describes the copper diffusivity in the absence of copper-acceptor pairing and is valid only in intrinsic or n-type silicon, provided that no other trapping process exists. In p-type material, however, it is the effective diffusivity D_{eff} which describes copper diffusion and which is relevant for all practical applications. D_{eff} can be either determined experimentally, e.g., from TID measurements [Eq. (3)] or calculated using Eqs. (4),(5):

$$D_{\mathrm{eff}}(N_A, T) = D_{\mathrm{int}}/[1 + 4\pi\beta D_{\mathrm{int}} R_C N_a \tau_{\mathrm{diss}}], \quad (11)$$

where τ_{diss} and D_{int} are given by Eqs. (10) and (11). The capture radius R_C is determined by Eq. (6). As discussed in [14], the coefficient β reflects nonequilibrium capture conditions in the depletion region during TID measurements and should be set to unity for bulk measurements. Inserting the constants and Eqs. (6), (9), and (10) into Eq. (11), we obtain a convenient numerical equation for effective diffusion coefficient in moderately boron-doped ($N_a \leq 10^{17}$ cm^{-3}) silicon:

$$D_{\mathrm{eff}} = \frac{3 \times 10^{-4} \exp(-2090/T)}{1 + 2.584 \times 10^{-20} \exp(4990/T)(N_a/T)}. \quad (12)$$

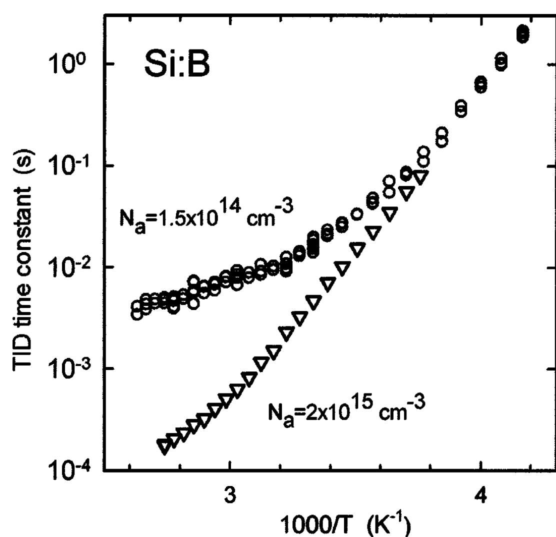

FIG. 2. Experimentally measured dependence of the TID time constant on temperature for boron-doped silicon with the doping levels of 1.5×10^{14} cm^{-3} (circles) and 2×10^{15} cm^{-3} (triangles).

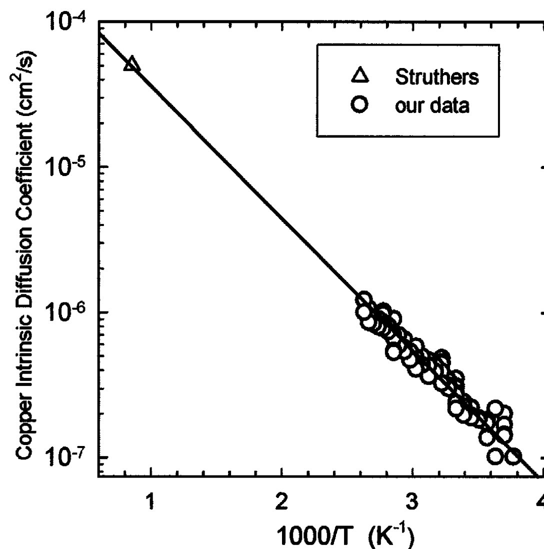

FIG. 3. Intrinsic diffusion coefficient of copper determined from our experimental data ($N_a = 1.5 \times 10^{14}$ cm^{-3}) in the temperature range 265 to 380 K (circles) and experimental data point reported by Struthers ([5], open triangle).

In Fig. 4 we present the effective Cu diffusivity, calculated for different doping levels using $\beta = 1$ (bulk diffusion). Also represented are the effective copper diffusivities determined from TID measurements using Eq. (3) with $\beta = 1.95$ (diffusion in a depletion region) and the data of Hall and Racette. The different values used for β lead to a slight deviation between curves 2 and 3 and the experimental points at temperatures where pairing is dominant. The calculations agree over the whole temperature range not only with the data used for the determination of D_{int} but also with the data measured in the medium doped material ($N_a = 2 \times 10^{15}$ cm^{-3}). This confirms the validity of Eq. (10) used for the intrinsic diffusion coefficient. The agreement also extends over the whole investigated doping level range (1.5×10^{14} to 5×10^{20} cm^{-3}) since Hall and Racette's data points are close to the calculated dependence (curve 5). This confirms that the Hall and Racette data represent the effective diffusion coefficient for $N_a = 5 \times 10^{20}$ cm^{-3} and explains their significant deviation from the intrinsic diffusivity curve. Furthermore, since the effective diffusion coefficient depends nonexponentially on temperature [see Eq. (12)], the exponential expression suggested by Hall and Racette can be used only as an approximation in the temperature range where the data points were taken and may result in significant errors if extrapolated outside of this range.

In this study we neglected interaction of interstitial copper with carbon and oxygen. There are indications that this pairing is weak in FZ silicon [10], although it may become non-negligible in Czochralski-grown silicon, where C and O concentrations are 2 to 3 orders of magnitude higher, and especially below room temperature.

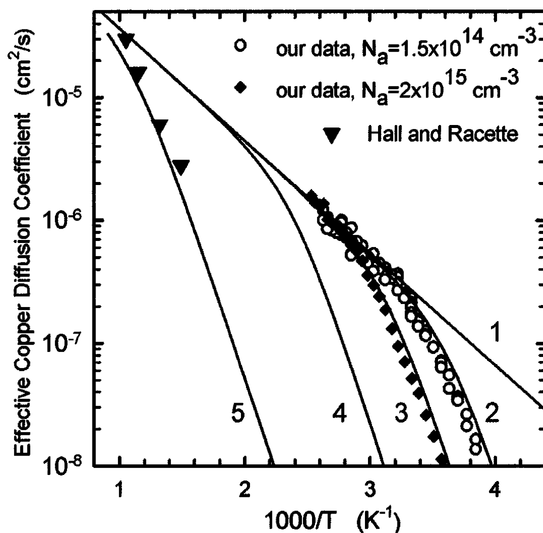

FIG. 4. Effective diffusion coefficient of copper in silicon calculated for different boron doping levels (lines) and experimental data obtained in this study (circles, $N_a = 1.5 \times 10^{14}$ cm^{-3} and diamonds, $N_a = 2 \times 10^{15}$ cm^{-3}) and by Hall and Racette [6] (triangles, $N_a = 5 \times 10^{20}$ cm^{-3}). Curve 1—intrinsic silicon; curve 2—$N_a = 1.5 \times 10^{14}$ cm^{-3}; curve 3—$N_a = 2 \times 10^{15}$ cm^{-3}; curve 4—$N_a = 1 \times 10^{17}$ cm^{-3}; curve 5—$N_a = 5 \times 10^{20}$ cm^{-3}.

In conclusion, the intrinsic diffusion coefficient of silicon was determined experimentally in a wide temperature range using the transient ion drift technique. The use of boron-doped FZ silicon with a low doping level enabled us to obtain, over a wide temperature range, the conditions where the diffusivity of copper is determined by intrinsic diffusion barrier rather than pairing with acceptors and can thus be determined directly. The obtained diffusion barrier of 0.18 eV agrees with the recent theoretical predictions. The corresponding intrinsic diffusion coefficient is consistent with all previously reported data on the diffusivity of Cu in silicon, provided that copper-acceptor pairing is properly taken into account. The final expression obtained for the effective copper diffusivity can be used to model diffusion of Cu in p-type silicon for various doping levels and temperatures.

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