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In-diffusion of Pt in Si from the PtSi/Si interface

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The in-diffusion of platinum in *n*-type silicon from a platinum silicide source was investigated using mainly deep-level transient spectroscopy and *C-V* measurements. MeV helium backscattering, electron Auger spectroscopy, x-ray diffraction, and scanning electron microscopy observations were also used to obtain a metallurgical characterization of the samples. The Si samples were Pt diffused in a 2×10^{-7}-Torr vacuum furnace. The profiles of the platinum in silicon measured between 973 and 1123 K and for times ranging from a few tens of minutes to several days show a behavior that cannot be described with a complementary error function characteristic of dissociative diffusion via vacancies. The results can be interpreted by using the mechanism of kick-out diffusion via self-interstitials into a dislocation-free semi-infinite solid. From the model it was possible to estimate (1) the solid solubility of the electrically active platinum, 1.95×10^{14} cm^{-3} at 973 K and 1.6×10^{16} cm^{-3} at 1123 K, (2) the concentration of self-interstitials, 3.5×10^{10} cm^{-3} at 1123 K, and (3) the activation energy of the silicon self-interstitial diffusion coefficient, 5.01 eV.

I. INTRODUCTION

A large number of heavy transition metals form deep electronic levels in silicon and consequently affect the electron and hole lifetimes. For this reason they are widely used as lifetime controllers in fast switching diodes and thyristors; moreover, the position of energy levels near the middle of the silicon forbidden gap suggests their use as infrared detectors. Among these metals, gold and platinum impurities can be rapidly introduced into Si by diffusion from the surface at moderate temperatures. For this reason Au is largely used in the manufacture of commercial devices and recently Pt has received considerable attention as a possible substitute although it is less known.

Transition-metal silicides and among these platinum silicide, are widely used in a number of silicon integrated devices for ohmic and Schottky contacts. The thermal stability of the metal-silicide—silicon contacts suggests their application in very-large-scale integration. Since the junction depths are reduced to a few thousand angstroms, it is possible in these applications to degrade device performance by poisoning silicon with the transition metal during processing. In fact, electrical degradation of the platinum-silicide—silicon diodes during heat treatment due to the lowering of the barrier height and the increase of the ideality factor *n* have already been reported.[1]

Knowledge of the metallurgical and kinetic properties of Pt in silicon is interesting not only for technological applications but also for a better understanding of the diffusion processes in silicon. There exists a long-standing controversy on which type of point defects, vacancies or self-interstitials, dominate self-diffusion and impurity diffusion in Si under thermal equilibrium conditions. This question cannot be solved by measuring the diffusivity and equilibrium concentration of intrinsic point defects separately versus temperature since these concentrations are extremely small but must rather be approached less directly, particularly by carefully analyzing data on the diffusion of foreign atoms. In fact, observation of the specific features of Au diffusion in Si at high temperatures, together with other experiments, has found a possible theoretical explanation in the kick-out mechanism involving Si self-interstitials.[2] In this respect some of our preliminary results on diffusion of Pt in Si (Ref. 3) seem to indicate that at high temperatures Pt behaves very similarly to Au.

In this paper we present a complete set of data showing that the kick-out mechanism is responsible for the in-diffusion of Pt in silicon and that even at temperatures as low as 973 K silicon self-interstitials are important.

II. PREVIOUS RESULTS

A. Electrical behavior

Platinum acts as an acceptor in *n*-type Si and as a donor in *p*-type Si. In fact it compensates the original dopant and at high concentration can turn *n*-type Si into *p*-type. Figure 1 summarizes the most recent values of the energy levels of Pt in Si, found by various techniques by a number of workers.[3-18] Among this variety one common feature may be noted: namely an acceptor level between 0.23 and 0.26 eV from the conduction-band edge found in *n*-type Si and a donor level between 0.32 and 0.36 eV from the valence band edge found in *p*-type Si. The additional energy levels reported seem to originate from process-dependent metallurgical defects. The picture which emerges is that, as Au in Si, Pt is characterized by two dominant levels and has amphoteric features. By paramagnetic resonance experiments on *n*- and *p*-type Si containing Pt Woodbury and Ludwig[19] have determined the existence of two different lattice sites of Pt in *n*-type Si; no spectra were observed in *p*-type Si. Using evidence on the symmetry of the two sites, they concluded that one site, (Pt I)$^-$, is a single substitutional site which acts as acceptor impurity, the other, Pt II, present in lower concen-

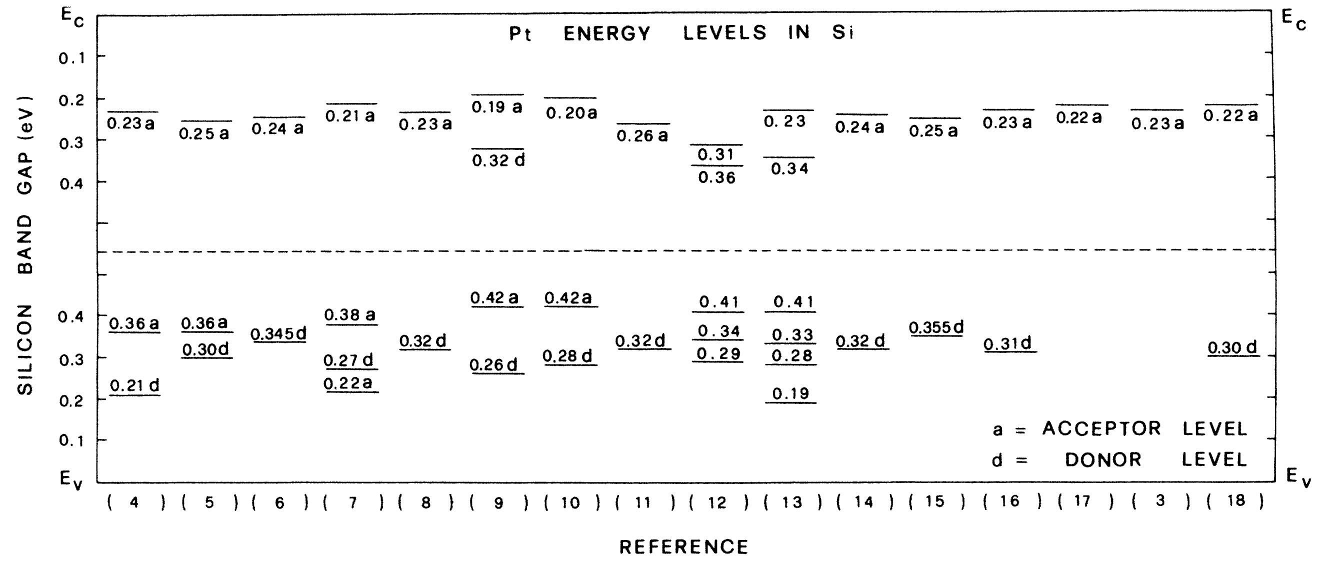

FIG. 1. Recent published data on the energy position of the platinum levels in silicon.

tration, may represent a defect pair on adjoining sites or some complex of Pt associated with oxygen and acts as a double acceptor. Because the resonance parameters indicate that the PT ion in the (PT I)$^-$ center is distorted from the normal substitutional position, they suggest a model in which the Pt atom forms bonds with two of its four silicon nearest neighbors, as does oxygen in the Si-*A* center, and the other two silicon nearest neighbors bond to each other. A recent cluster calculation by Lowther[20] based on a model which follows the suggestions of Woodbury and Ludwig[19] can readily account for electrical features associated with the (Pt I)$^-$ amphoteric center and also for the experimental data of capture cross section and emission rates of Pt in Si. In this model the incorporation of Pt in the silicon lattice site leads to a local lattice reconstruction, in the sense that Pt binds to only two nearest-neighbor Si atoms. The remaining two silicon atoms bind together. This reconstructed Si—Si bond gives rise to a bonding level and to an antibonding level, both lying in the forbidden gap. There is another orbital $m(s)$, which plays a role and which is associated with the 6*s* orbital of Pt. The position of $m(s)$ depends on the occupation of the levels. In the charge state (Pt I)$^-$ two electrons are in the Si—Si bonding orbital and one electron is in the antibonding orbital; $m(s)$ lies in the conduction band. If the number of electrons is reduced, the level $m(s)$ descends rapidly into the gap and becomes the lowest level in the charge state (Pt I)$^+$, when we are left with one electron. The orbital corresponding to $m(s)$ is highly delocalized and ESR lines due to such centers will be rather broad. Moreover, the position of $m(s)$ is very sensitive to strain and a strongly strain-dependent Zeeman splitting of this level must be expected. Strain-modulated ESR experiments recently performed[21] on *p*-type Si doped with Pt reveal a spectrum characteristic of a triplet state and facts that are in qualitative agreement with the Lowther model.

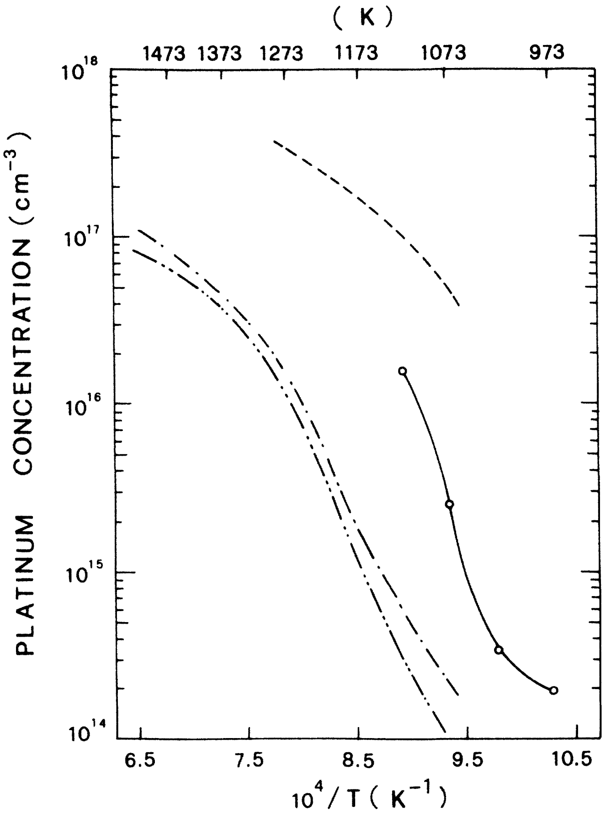

FIG. 2. Platinum concentration in silicon versus reciprocal diffusion temperature. Data of Bailey and Mills (Ref. 23) obtained by neutron irradiation (dashed line) and of Lisiak and Milnes (Ref. 10) obtained by neutron irradiation (dashed-dotted) and Hall measurements (double-dashed—dotted) on the same samples; the solid line is inferred from the solubility of the electrically active Pt (open circle) as derived from the present work.

B. Metallurgical behavior (solubility and diffusion of Pt in Si)

In silicon, Pt has a finite solid solubility. However, the values reported in the literature in the (1073–1523)-K temperature range span 2 or 3 orders of magnitude, as is shown in Fig. 2. Various reasons may be adduced for such large discrepancies; some of them lie in sample preparation and some in the experimental technique used for analysis. It is always possible that in some cases the diffusions were not done for a long enough time to saturate the crystal. It is also necessary to distinguish between the data obtained by electrical measurements, such as the Hall effect and resistivity,[4–6,10,22] which give the solubility of electrically active platinum, and those obtained by metallurgical techniques such as neutron activation analysis,[10,23–25] which give the total platinum present. Moreover, the values obtained by electrical measurements can be affected by the model assumed for calculating the electrical activity, by the cooling rate, and by the quenched-in processing defects, and sometimes by the measurement technique which integrates over large distance. Only Lisiak and Milnes[10] have performed Hall-effect measurements and neutron activation analysis on the same samples. The data, obtained with the two techniques and reported in Fig. 2, are quite similar indicating that, in their samples, most of the platinum is electrically active. The kinetic processes of the thermal diffusion of Pt in Si have been poorly investigated. The only data available are from Bailey and Mills;[23] they conclude that Pt diffusion in Si is similar to that of Au. Recent experimental data on Au (Refs. 26 and 27) and preliminary on Pt (Refs. 3 and 17) suggest a process for the diffusion of these heavy atoms more complicated than the one indicated by Bailey and Mills.

C. Substitutional impurity diffusion in Si

Self-diffusion and substitutional impurity diffusion in silicon are believed to be mediated by thermally created intrinsic lattice defects such as vacancies and/or self-interstitials, etc., but no consensus has been achieved so far about either the nature of these defects or the details of diffusion mechanisms. Regarding their diffusivities in Si, the heavy atoms such as gold and platinum occupy an intermediate position between the slow-diffusing group-III and group-V substitutional dopants on the one hand, and the fast-diffusing transition metals which are mainly interstitially dissolved on the other hand. This makes it likely that, although the overwhelming fraction of the Au (Refs. 26 and 28) and Pt (Ref. 10) atoms is dissolved substitutionally, the long-range transport is almost exclusively carried on by the minute portion of the highly mobile atoms in the interstices. Therefore, in general, the diffusion of such impurities should involve an interchange between substitutional and interstitial sites. The basic mechanisms suggested[2] for such interchanges are the kick-out mechanism, the dissociative mechanism, or a combination of these two mechanisms. The kick-out mechanism involves the interchange of the foreign diffusing atoms (A) between substitutional (A_s) and interstitial sites (A_i) with the aid of self-interstitials (I) according to the reaction

$$A_i \leftrightarrows A_s + I \ . \tag{1}$$

The dissociative mechanism or the Frank-Turnbull mechanism involves the interchange of the diffusing foreign atoms between substitutional and interstitial sites with the aid of vacancies (V) according to the reaction

$$A_i + V \leftrightarrows A_s \ . \tag{2}$$

If only (1) or (2) are effective, since these equations are not symmetrical in the exchange of I and V, the theoretical predictions may differ widely.

The effective A_s diffusion via a substitutional-interstitial mechanism in a dislocation-free specimen may be described by the diffusion equation

$$\frac{\partial C_s}{\partial t} = \frac{\partial}{\partial x} \left[D_{\text{eff}} \frac{\partial C_s}{\partial x} \right] , \tag{3}$$

where C_s is the concentration of A_s, x the space coordinate in the diffusion direction, and t the diffusion time.

For the dissociative or Frank-Turnbull mechanism (assuming local equilibrium between A_i, A_s, and V, $C_i = C_i^{\text{eq}}$), after a short time owing to the high mobility of A_i, where C_i^{eq} is the equilibrium concentration of A_i, and $C_v^{\text{eq}} \ll C_s^{\text{eq}}$, and C_v^{eq} and C_s^{eq} are, respectively, the equilibrium concentrations of vacancies and substitutional impurity atoms, one obtains

$$D_{\text{eff}} = D_{\text{eff}}^{v} = \frac{D_v C_v^{\text{eq}}}{C_s^{\text{eq}}} , \tag{4}$$

where D_v is the diffusion coefficient of vacancies. In this case because the effective diffusivity D_{eff}^{v} is independent of C_s, Eq. (4) possesses the well-known solution for in-diffusion from the surface into the semi-infinite solid (thick specimen) given by

$$C = C_s / C_s^{\text{eq}} = \text{erfc}[x / 2 (D_{\text{eff}}^{v} t)^{1/2}] \tag{5}$$

For the kick-out mechanism [assuming local equilibrium between A_i, A_s, and I, $C_i = C_i^{\text{eq}}$ and $C_s \geq (C_I^{\text{eq}} C_s^{\text{eq}})^{1/2}$] one obtains

$$D_{\text{eff}} = D_{\text{eff}}^{I} = \left[\frac{D_I C_I^{\text{eq}}}{C_s^{\text{eq}}} \right] \frac{1}{C^2} , \tag{6}$$

where D_I is the diffusion coefficient for Si self-interstitials. In this case D_{eff}^{I} is an effective diffusivity strongly dependent on concentration C. For a dislocation-free crystal the in-diffusion of foreign atoms from the surface into a semi-infinite solid or into a wafer of thickness d (thick specimen) is mathematically described by Eqs. (3) and (6) and by the boundary and initial conditions

$$C_s(x=0,t) = C_s^{\text{eq}} , \tag{7}$$

$$C_s(0 < x < \infty \text{ or } d; t=0) = C_s^{0} , \tag{8}$$

where C_s^0 is the starting value of C_s due to local equilibrium usually taken as $C_s^0 = (C_s^{\text{eq}} C_I^{\text{eq}})^{1/2}$. For $C_s^0 \neq 0$ and $\ll C_s^{\text{eq}}$ Seeger[29] has derived an approximate parametric solution of the form

$$C=1/[1+x/(Gt)^{1/2}]\ , \tag{9}$$

where G is a temperature-dependent parameter,

$$G=D_I C_I^{\rm eq}/[C_s^{\rm eq}(a^0)^2]\ , \tag{10}$$

and a^0 is

$$|\,a^0\,|\exp[(a^0)^2]=C_s^{\rm eq}/(2\pi^{1/2}C_s^0)\ . \tag{11}$$

If vacancies and self-interstitials are present simultaneously and the reaction

$$I+V\leftrightarrows 0 \tag{12}$$

(where 0 denotes the ideal silicon lattice) is not hampered, then mechanisms (1) and (2) have to be taken into account in addition to (12). In this case in a dislocation-free silicon lattice if the local dynamical equilibrium between A_i, A_s, V, and I is established and if $C_i=C_i^{\rm eq}$, $C_s^{\rm eq}\geq C_v^{\rm eq}$, and $C_s>(C_I^{\rm eq}C_s^{\rm eq})^{1/2}$ one has

$$D_{\rm eff}=D_{\rm eff}^I+D_{\rm eff}^v=\left[\frac{D_I C_I^{\rm eq}}{C_s^{\rm eq}}\right]\left[\frac{1}{C^2}+\frac{D_v C_v^{\rm eq}}{D_i C_I^{\rm eq}}\right]\ . \tag{13}$$

If $D_I C_I^{\rm eq}$ and $D_v C_v^{\rm eq}$ are of the same order of magnitude then in the in-diffusion experiments where $C<1$, the term with $D_{\rm eff}^I$ becomes larger than the term with $D_{\rm eff}^v$ and the kick-out mechanism determines the features of diffusion. The reverse is true in precipitation experiments where $C>1$. To observe combined kick-out and dissociative diffusion and to get dynamical equilibrium between V and I, it is sufficient that two of the three reactions (1), (2), and (12) be active and $D_I C_I^{\rm eq}$ and $D_v C_v^{\rm eq}$ are different from zero. The tracer self-diffusion coefficient, i.e., the diffusivity D^T of radioactive tracer atoms under thermal equilibrium conditions can be correlated with the terms in Eq. (13) by

$$D^T=f_I D_I C_I^{\rm eq}+f_v D_v C_v^{\rm eq}\ , \tag{14}$$

where f_I and f_v are the correlation factors of self-interstitials and vacancies, respectively. In the diamond structure $f_v=0.5$, whereas f_I at high temperatures is unknown but of the same order of magnitude.

III. EXPERIMENTAL

The {111} Si wafers about 300 μm thick used in the experiments were n-type epitaxially grown on n^+ substrates. The n-type material had a thickness of 20–30 μm and was P doped at a concentration of about 1×10^{15} cm^{-3}. The substrate was As doped at a concentration of 5×10^{19} cm^{-3}. The cleaning procedure was done by growing 2000 Å of thermal silicon oxide on wafers degreased by trichloroethelene, acetone, and alcohol. Before loading into the vacuum chamber, the silicon oxide was removed by dipping the sample in a HF:H$_2$O solution. A 1000-Å Pt layer was electron-gun deposited at a vacuum of 2×10^{-7} Torr through a metal mask onto diode openings of 3.4×10^{-2} cm^2 in area; the deposition rate was 600 Å/min. At the same time, Pt was deposited on a blank wafer for metallurgical analysis. Thus prepared, the samples were diced in order to separate the diodes. The heatings were performed in a 2×10^{-7}-Torr vacuum furnace at temperatures ranging from 573 to 1123 K for times ranging from 30 min to two weeks. For each temperature and time a new sample was used. The specimens were rapidly cooled down from the diffusion temperature by moving them away from the furnace. Some heating was performed by adding a piece of blank wafer to the diodes. The metallurgical analyses were performed on some samples using 2-MeV He$^+$ Rutherford backscattering and x-ray diffraction. The energy levels were measured by a deep-level transient spectroscopy (DLTS) technique in the (77–350)-K temperature range using the correlator described by Miller.[30] The profiles of deep impurity centers were obtained by using predominantly a method based on high-frequency C-V measurements.[31] An example of a typical result is shown in Fig. 3. A diode, Pt diffused at 1073 K for 720 min and reverse biased at 35 V at room temperature was cooled to 80 K. At this temperature the decrease and the subsequent increase of the reverse applied voltage produces a hysteresis in the C-V characteristic. The inset shows an expanded view and illustrates the sensitivity of the technique. The large reverse bias V_r given at room temperature when the Fermi level is below the Pt level, together with the subsequent cooling, enable the traps in the space-charge region of width W to be in a steady state at 80 K. Furthermore, the low temperature makes the time constant for thermal emission of the charge carriers trapped in the deep level for very long, thus enabling their concentration to be assumed as constant during measurement; as a result, during the decrease of the bias ($V_r\rightarrow0$) the deep level is empty of electrons, in the space-charge region from $x=0$ at the interface, to $x=W-Y$. In $W-Y$ the quasi-Fermi level intersects the trap level. Decreasing the bias collapses the space-charge region and causes the deep-level

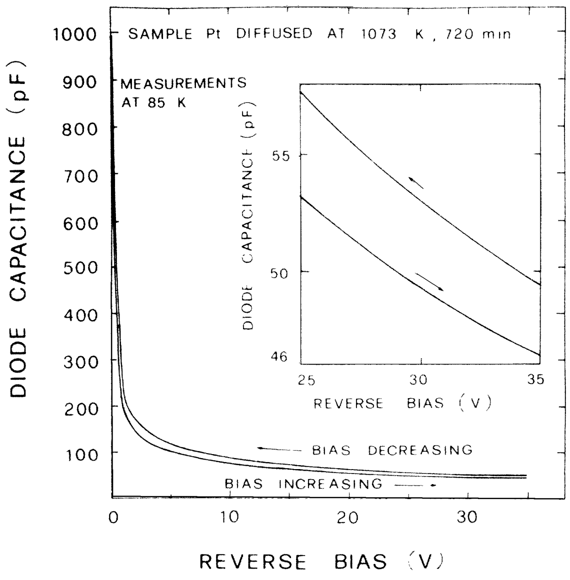

FIG. 3. Capacitance versus reverse bias at 85 K for a silicon diode Pt diffused at 1073 K for 720 min. The inset shows an expanded view to illustrate the sensitivity of the technique.

centers to become occupied at their equilibrium concentration at 80 K (at this temperature the Fermi level is above the deep level) and remain in this state during the successive biasing ($0 \rightarrow V_r$). Therefore the C-V curves obtained in the two biasing conditions must be different, if traps are present, because of the different net space-charge concentration. From these data by solving Poisson's equation by numerical iteration one can determine Y and the profile of deep-level centers. Some measurements have also been performed by using the constant-capacitance deep-level transient spectroscopy (CC-DLTS) method.[32] With both methods the results are equal within an experimental error of about 10%. The sensitivity is estimated to be of the order of 10^{-4} and is limited by the signal-to-noise ratio and by the magnitude of the leakage currents of the diodes. Since the starting shallow doping concentration is 10^{15} cm^{-3}, we can detect impurity concentrations down to 10^{11} cm^{-3}. The spatially obtainable resolution is naturally limited by the Debye length which, in the worst cases, reaches the value of 0.1 μm.

IV. RESULTS

A. Metallurgical characterization

Two thousand angstroms of platinum deposited on silicon reacts around 473 K to form Pt_2Si. Subsequent annealing produces the formation of 3500 Å of PtSi and no other phases are formed independently of the heat treatment performed. In the backscattering spectra of the samples heated at high temperatures, the back edge of the Pt signal is not very sharp and we believe that this is due more to a nonuniformity of the PtSi layer rather than to a Pt diffusion in silicon. Thinner Pt-deposited layers give substantially the same results. The backscattering technique does not enable impurity concentrations down to 1% of the host material to be detected. X-ray diffraction demonstrates the presence of only PtSi, as expected. One sample was also checked for impurities using Auger-electron spectroscopy with ion sputtering. Traces of oxygen were detected at the outermost PtSi surface. The scanning electron microscopy pictures show quite uniform Pt silicide layers.

B. Electrical measurements

The I-V characteristic of the Schottky diodes of samples Pt diffused at temperatures ranging from 573 and 1123 K were analyzed by the Norde method.[33] A mean barrier height of 0.86±0.02 eV was found, in good agreement with the data reported in literature for PtSi—n-type Si contacts.[1] For diodes diffused at temperatures higher than 1073 K the I-V characteristics tended to degrade, due to the increase of leakage current in the reverse-bias condition, and the ideality factor also increased. From DLTS scans, within the sensitivity of the apparatus only one level was detected in n-type Si samples diffused from 973 and 1123 K. The energy value found, $E_c - E_t = 0.23 \pm 0.02$ eV, agrees very well with recent data for the Pt dominant acceptor level (Fig. 1). Figures 4–6 report the representative profiles, obtained by this method and by CC-DLTS, of electrically active platinum Pt$^-$ found in Si after Pt diffusion at different temperatures and times. Figure 4 reports the Pt$^-$ profiles for 30 min diffusion for temperatures ranging from 973 and 1123 K. Figures 5 and 6 report the Pt$^-$ profiles for times ranging from 30 min to days for diffusion performed at 1023 and 1073 K, respectively. We note that (1), at a fixed depth

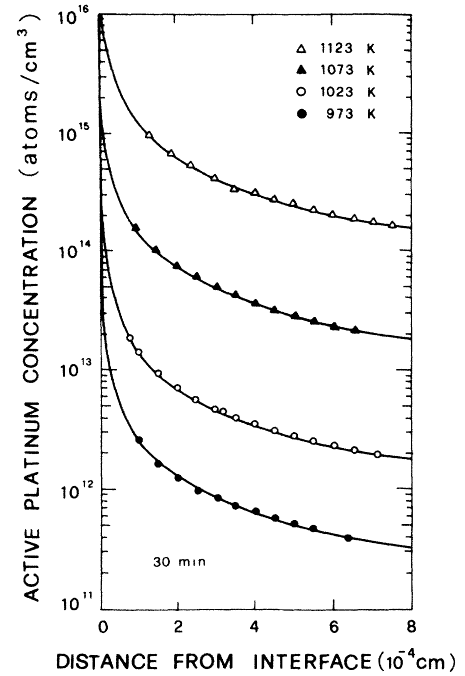

FIG. 4. Experimental concentration profiles of electrically active Pt in Si after diffusion at different temperatures for 30 min. The continuous lines represent the theoretical best fits obtained with the kick-out diffusion model described in the text.

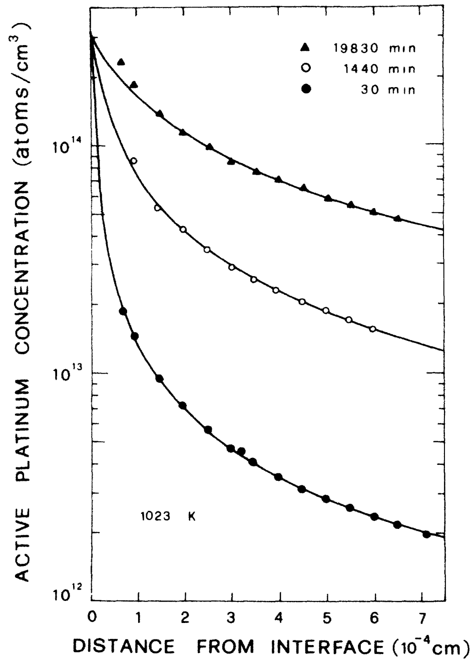

FIG. 5. Experimental Pt profiles in Si after diffusion at 1023 K for different times. The continuous lines represent the theoretical best fits obtained with the kick-out diffusion model described in the text.

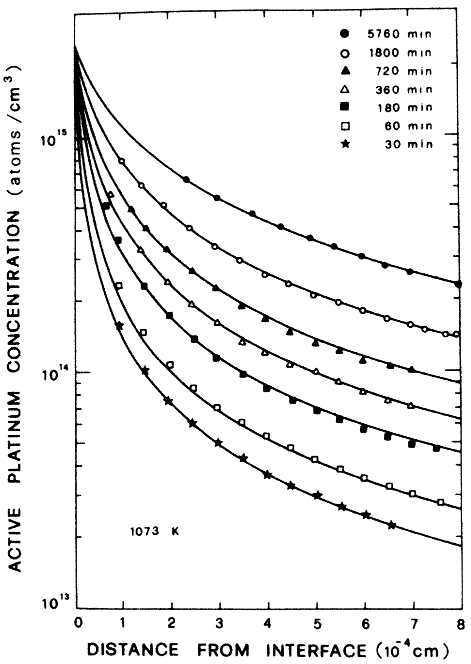

FIG. 6. Experimental Pt profiles in Si after diffusion at 1073 K for different times. The continuous lines represent the theoretical best fits obtained with the kick-out diffusion model described in the text.

from the interface, on increasing temperature or time the Pt^- concentration increases and (2) even after 4 days of diffusion at a temperature of 1073 K the Pt^- concentration had not reached the solubility value. Diodes diffused for 10 days at 1073 K lost their rectifying characteristics. The loss could be due to the heavy compensation of the silicon over layer. This enables a lower limit to be given to the Pt solid solubility at 1073 K, of the order of the P concentration, 10^{15} cm^{-3}. All the profiles, even those obtained in diodes heavily Pt compensated, deviate strongly from the complementary error function. This shape has been reported by Mantovani *et al.*[3] and by Prabhakar *et al.*,[17] and in Fig. 7 the results are compared. This means that the diffusion of Pt in Si in the range of temperatures investigated cannot be described by a Frank-Turnbull mechanism involving vacancies which would lead to a constant effective Pt diffusivity. The shape of these profiles is also very similar to the reported diffusion of Au profiles in Si between 1073 and 1473 K.[26,27] This similar behavior, the recent results of dual diffusion of Au and Pt in Si between 873 and 1173 K,[18] which indicate that Au and Pt atoms occupy the same kinds of substitutional sites in silicon, the fact that Au like Pt is amphoteric in silicon, and that the related similar electrical properties which can be explained by the same lattice reconstruction suggested for Pt,[20] all seem to indicate a similar mechanism for diffusion.

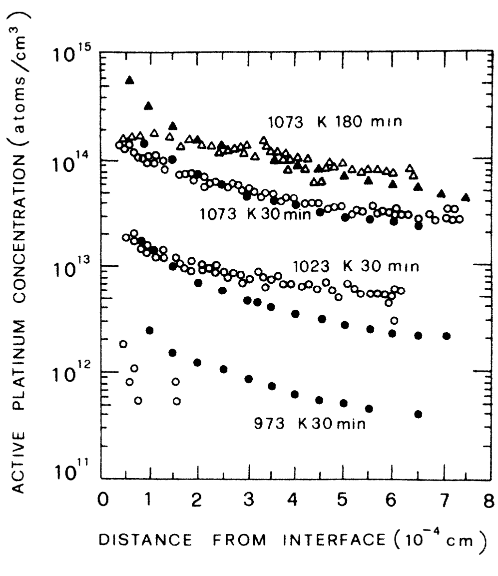

FIG. 7. Comparison between the Pt electron trap concentration profiles in Si obtained by Prabhakar *et al.* (Ref. 17) (open circles or triangles) and those of the present work (solid circles or triangles) for diffusions at the same times and temperatures.

V. DISCUSSION

From the results it is evident that even with heavy platinum diffusion the platinum profiles in silicon could not be described in terms of a constant diffusivity. Therefore it seems appropriate to try to account for the data in terms of the kick-out mechanism alone, as the most effective. Assuming that the measured electrically active platinum concentration $N_s^-(x,t)$ at time t and distance x from the source is proportional to the substitutional platinum concentration $N_s(x,t)$, $N_s^-(x,t)=BN_s(x,t)$, one has

$$N_s(x,t)/N_s^{\mathrm{eq}}=N_s-(x,t)/(N_s^-)^{\mathrm{eq}} \; .$$

This ratio is equal to C_s/C_s^{eq}, generally used in the theory, where C_s and C_s^{eq} are, respectively, the platinum substitutional concentration and platinum substitutional solubility at the diffusion temperature T expressed in atomic fractions. B is a constant at a given temperature and ≤ 1, since during cooling a number of substitutional platinum atoms could precipitate or form complexes. We have used expression (9) to fit our data with G and $(N_s^-)^{\mathrm{eq}}$ as free parameters. The continuous lines in Figs. 4–6 represent the best fit, where at the same temperature (Figs. 5 and 6), for different times, G and $(N_s^-)^{\mathrm{eq}}$ are taken the same. The best-fit curves extrapolated at $x=0$, i.e., at the PtSi/n-type Si interface give the $(N_s^-)^{\mathrm{eq}}$ values used at each temperature. Evaluation of B at different temperatures is not possible since N_s^{eq} for Pt in Si versus T is not well defined in the literature; in fact, no data are available for $T \leq 1073$ K and only very scattered data are given for $T > 1073$ K. As can be seen, expression (9) fits the experimental data, for values of the ratio $(1/C)^2 \geq 4$ at 1023 K (excluding only the two higher active Pt concentrations in Fig. 5, which do not match the theoretical curve) and ≥ 10 at 1073 K, very well. These results indicate that in the more general equation [(13)], the first term prevails, i.e., $D_v C_v^{\mathrm{eq}} < 4 D_I C_I^{\mathrm{eq}}$ at 1023 K and $D_v C_v \ll 10 D_I C_I^{\mathrm{eq}}$ at 1073 K. The trends with T of $D_v C_v$ and $D_I C_I^{\mathrm{eq}}$ inferred from Au diffusion profiles in Si have been reported in Ref. 2. These trends match each other at 1270 K and show that at temperatures higher than 1270 K the term $D_I C_I^{\mathrm{eq}}$ prevails with respect to $D_v C_v^{\mathrm{eq}}$, while at lower temperatures $D_v C_v^{\mathrm{eq}}$ prevails. If we compare our data with those of Ref. 2 we must deduce that their $D_v C_v^{\mathrm{eq}}$ has been overestimated by a factor of almost 2 compared to $D_I C_I^{\mathrm{eq}}$ at 1023 K. Assuming their dependence on T of $D_v C_v^{\mathrm{eq}}$ and $D_I C_I^{\mathrm{eq}}$ to be the same, the point where $D_I C_I^{\mathrm{eq}} = D_v C_v^{\mathrm{eq}}$ must lie not above 1170 K, or by fixing this point at 1270 K, the two activation energies must differ less. The $(N_s^-)^{\mathrm{eq}}$ found as a best-fit parameter between 973 and 1123 K and which must be $\leq N_s^{\mathrm{eq}} \leq N(\mathrm{Pt})^{\mathrm{eq}}$, where $N(\mathrm{Pt})^{\mathrm{eq}}$ is the total platinum solubility, are reported in Fig. 2 as open circles connected by a solid line where for comparison the total Pt concentration is also reported; the data obtained by neutron activation methods by Bailey and Mills[23] are shown as a dashed line and the data by Lisiak[10] as a dotted-dashed line. From Lisiak are also reported, as the double-dotted—dashed line in Fig. 2, the $(N_s^-)^{\mathrm{eq}}$ data obtained by Hall-effect measurements. Our inferred $(N_s^-)^{\mathrm{eq}}$ values seem reasonable, because where comparison is possible for the temperatures of 1073 and 1123 K, they are lower than the neutron activation data of Bailey and Mills[23] an are comparable with the solubility data of Au (Ref. 27) which seems to occupy the same kind of substitutional sites (Ref. 18). Even if our inferred values are higher than many published data, it must be noted that at these low-diffusion temperatures, the data in the literature have been obtained at too short times for them to reach equilibrium. From the values of G found at various temperatures and $C_s^{\mathrm{eq}} = 2\times10^{-23}(N^-)^{\mathrm{eq}}/B$ (at. %), we can estimate the interstitial component of the Si self-diffusion $D_I^{\mathrm{SD}} = f_I D_I C_I^{\mathrm{eq}}$. In fact, according to Eq. (10),

$$D_I^{\mathrm{SD}} = G C_s^{\mathrm{eq}} f_I (a^0)^2 = G(2\times10^{-23}) f_I (N^-)^{\mathrm{eq}} (a^0)^2/B ,$$

where f_I is a correlation factor. The values of

$$\ln\{D_I^{\mathrm{SD}} B/[f_I(a^0)^2]\} ,$$

so found versus kT, lie on a straight line with a correlation coefficient of 0.999 99 and can be well fitted by

$$\{B/[f_I(a^0)^2]\} D_I^{\mathrm{SD}} = [309\exp(-5.01/kT)] \ \mathrm{cm}^{-2}\,\mathrm{sec}^{-1} .$$

Assuming very reasonably that in the range of temperatures investigated, the ratio $B/[f_I(a^0)^2]$ is almost independent of T; we found an activation energy for D_I^{SD}, $E_a = 5.01$ eV. The same activation energy for Si self-diffusion (5.02 eV) has been obtained by ^{31}Si radioactive trace measurements at temperatures higher than 1320 K.[34] A similar energy for Si self-intersitital diffusion (4.84 eV) has been inferred by analyzing in- and out-diffusion of Au in Si for temperatures between 1073 and 1373 K.[2] Figure 8 reports the tracer self-diffusion coefficient determined by ^{31}Si radioactive tracer measurements (Ref. 31) (open circles) and by means of secondary-ion mass spectroscopy using ^{30}Si (Ref. 35) (open squares), and the self-diffusion interstitial coefficient derived from Au diffusion and solubility data (Ref. 27) (solid circles) and from our Pt diffusion data (triangles). The quantity $[f_I(a^0)^2]/B$ has been taken as equal to 4.5, in such a way that our data have values consistent with the data of other authors. Taking $f_I/B = 1$ we can infer a value for $|a^0| = 2.12$ very near to that of 2.01 used by Seeger[29] to fit the Au in-diffusion data in Si of Wilcox and LaChapelle[26] between 1073 and 1373 K. In Eq. (11), a value of the ratio C_s^0/C_s^{eq} of about 1.5×10^{-3} is found, very similar to that used for Au by Seeger[29] of 2.5×10^{-3} and to that of 5.5×10^{-3} used by Stolwijk *et al.*[27] at 1323 K. The C_s^0/C_s^{eq} value found is also self-consistent with the hypothesis that $C_s^0 \ll C_s^{\mathrm{eq}}$ necessary to use the approximate solution (9). If we assume that the usual approximation $C_s = (C_s^{\mathrm{eq}} C_I^{\mathrm{eq}})^{1/2}$ is valid, we find a value of the ratio $(C_I^{\mathrm{eq}}/C_s^{\mathrm{eq}}) = 2.2\times10^{-6}$, i.e., a concentration of self-interstitials of 4.3×10^{8} cm^{-3} at 973 K and 3.5×10^{10} cm^{-3} at 1123 K comparable, as a trend, with the value of about 1×10^{12} cm^{-3} at 1273 K obtained by optimizing the fit of Au in-diffusion data in Si.[36]

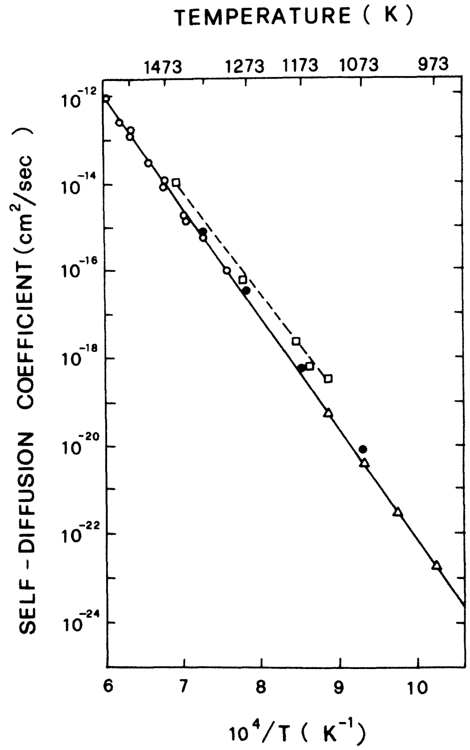

FIG. 8. Tracer self-diffusion coefficient in Si, D^T, and interstitial components of D^T, D_I^{SD}, as a function of the reciprocal temperature. D^T data of Mayer *et al.* (Ref. 34) (open circles); D^T data of Kalinowski and Seguin (Ref. 35) (open squares); D_I^{SD} calculated from the diffusion data of Au in Si (Ref. 27) (solid circles); D_I^{SD} calculated from the diffusion data of Pt in Si of the present work (open triangles). The solid line has the expression $[1400\exp(5.01/kT)]$ cm^{-2} sec^{-1}.

VI. CONCLUSIONS

Let us now synthetize and comment on the main results of our investigation.

(1) The Pt in-diffusion in Si between 973 and 1123 K is very similar to that of Au between 1073 and 1373 K,[26] i.e., (a) the penetration Pt profiles cannot be described

with a complementary error function characteristic of dissociative diffusion via vacancies; (b) instead these profiles can be well described by the analytical expression $N_s^- = (N_s^-)^{\text{eq}}[1+x(Gt)^{-1/2}]^{-1}$, which is of the form of the approximate solution derived for kick-out diffusion via self-interstitials into a dislocation-free semi-infinite solid.

(2) The Pt in-diffusion profiles which do not saturate even after 14 days of heating at 1023 K, 4 days of heating at 1073 K, and for distances from the supply lower than 10 μm indicate that the solubility of the electrically active Pt has not been reached with these times and temperatures, and casts some doubts on the literature data obtained at 1073 K with times of 3 or 4 days[10] or less.

(3) Because it is generally accepted that, as in the case of self-diffusion, a vacancy and an interstitial mechanism are both acting at the same time to mediate impurity diffusion,[37-40] we have analyzed our measurements in terms of dissociative and kick-out mechanisms as the dominant mechanisms of vacancies and self-interstitials respectively [see Eq. (13)]. The hypothesis is not only suggested by many and various experiments,[2] but also recently confirmed by theoretical calculations.[41] Our Pt data show that the predominance of the kick-out mechanism reaches as low as at least 973 K and heating at 1023 K for 14 days gives us the limiting condition $D_v C_v^{\text{eq}} < 4 D_I C_I^{\text{eq}}$. This seems to be different from the behavior of Au. In fact Au in-diffusion data[26] show the predominance of a dissociative mechanism in thick dislocation-free silicon samples at 970 K after several days of heating. Following the suggestion of Frank *et al.*,[2] indicating that below about 1170 K the reaction (12) is considerably hampered by an entropy barrier against self-interstitial vacancy recombination, the predominance of the kick-out mechanism between 1170 and 973 K, for Pt in-diffusion, may be taken as an indication that in this range of temperature the kick-out reaction (1) is operating effectively and not simulated by the reactions (2) and (12).

(4) Quantitative analysis in terms of the kick-out mechanism of the Pt$^-$ in-diffusion gives the following results. (a) The interstitial component of the self-diffusion coefficient in Si has an activation energy of 5.01 eV, i.e., almost the same as the 5.02 eV obtained by direct Si tracer diffusion measurements between 1658 and 1320 K (Ref. 34) and very similar to that of 4.84 eV inferred by the Au tracer diffusion in conjunction with other experiments (Ref. 2) between 1371 and 1073 K; it thus confirms that at high temperatures, i.e., in the range of temperatures of the direct tracer measurements, self-diffusion in Si occurs mainly via self-interstitials. (b) It was possible to evaluate the active platinum solubility in the range of temperatures between 973 and 1123 K and to estimate the very low solubility of the self-interstitials in the same range of temperatures which cannot be measured directly. (c) All the data derived are self-consistent with the model and in reasonable agreement with the existing data.

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