Phosphorous-diffusion gettering in the presence of a nonequilibrium concentration of silicon interstitials: A quantitative model

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A quantitative model of phosphorous-diffusion gettering in silicon is presented, which combines the effects of segregation and self-interstitial injection on the distribution of dissolved metallic impurities. The model describes metal diffusion both in the bulk and in the highly phosphorous-doped layer and makes it possible to include phosphorous-diffusion models. By analyzing an approximate solution for the quasi-steady-state metal distribution, we show that for impurities like gold and platinum self-interstitial injection enhances the gettering efficiency compared to pure segregation. We apply the results to phosphorous-diffusion gettering of gold and demonstrate that all relevant features of recently measured gold distributions can be interpreted consistently. For $3d$ metals, which are predominantly dissolved on interstitial sites in intrinsic silicon, the model allows us to include the formation of precipitates resulting from self-interstitial injection as proposed earlier. [S0163-1829(97)08404-X]

I. INTRODUCTION

Phosphorous-diffusion gettering (PDG) in silicon is associated with phosphorous-diffusion leading to non-equilibrium concentrations of intrinsic point defects. It is widely used in silicon integrated circuit technology as a means to remove metallic impurities from the device-active area of the wafer. A new interest arises from solar cell technology, where PDG has to operate under the constraints of simultaneous pn-junction formation and is applied to multi- or polycrystalline silicon (Refs. 1–3). To reach improved solar cell efficiencies by this more complex application, a quantitative modeling of PDG is required. Although several qualitative features of the operative mechanisms are well established, a mathematical description of PDG necessary to simulate gettering is missing at present. In this work, we develop a model which combines the mechanisms induced by segregation and by self-interstitial injection and explicitly includes the gettering layer in the description. Using recent data for PDG of Au in silicon we demonstrate that our model reproduces all relevant features of dissolved metallic impurity distribution measured after PDG.

From the thermodynamic point of view, one mechanism which is expected to operate during PDG is segregation.[4] It leads to a redistribution of metallic impurities (M) between the wafer and the highly P-doped layer due to the effect of P doping on the solubility of M (Fermi level effect), the pairing probability of M with P yielding MP, and possibly due to the stabilization of a $Si_xP_yM_z$ phase which, however, has not been observed up to now. The first two effects have been carefully studied for gold and several 3d elements in homogeneously doped silicon (Refs. 5–8). For gold the concentration of the substitutional component Au_s, which is the dominant one in intrinsic silicon, increases with P doping as well as that of Au_sP. The 3d elements are dissolved as interstitial species (M_i) in intrinsic silicon, but—as has been shown for Mn, Fe, Co,[7] and Cu (Ref. 8)—become predominantly substitutional (M_s) at high P concentrations and form M_sP pairs. Quantitative evaluations of the maximum segregation effect in comparison with PDG data have shown that PDG of Co and Au yields concentrations within the gettering layer, which exceed the values expected from segregation by about two orders of magnitude (Refs. 9,10). Furthermore, concentration profiles of metallic impurities under PDG conditions are too steep to be described exclusively in terms of segregation.[10] Finally, it has been found that PDG of Ni, Fe, and Pt might lead to silicide formation inside the gettering layer (Refs. 11–13). These findings have been taken as strong evidence that besides segregation an additional very effective gettering mechanism must be operative. This mechanism has been attributed to various fluxes of self-interstitials occuring during phosphorous diffusion.

Despite sustained theoretical and experimental effort (for a review cf. Ref. 14) P diffusion at high concentrations is still a matter of active research.[15] Especially, the origin of electrically inactive P in the near surface part of diffusion profiles is still controversial. It is well established, however, that P diffusion leads to a supersaturation of self-interstitials and undersaturation of vacancies (Refs. 14,16). Several processes have been identified as possible sources of self-interstitials,[17] i.e., oxidation of the silicon due to phosphor-silica-glass formation, incorporation of P on substitutional sites, formation of different types of SiP precipitates,[18] and the phosphorous-diffusion process itself. A consistent description of buried layer experiments and the well-known kink-and-tail form of P concentration profiles is given by current models (Refs. 19–21) proposing P transport to be governed by phosphorous-self-interstitial pairs (PI). These models assume drift and diffusion of PI from the surface to the kink where they dissociate and thereby induce I injection. Owing to the fact that the substitutional species M_s of metallic impurities dominates at high P concentrations, a strong *injection-induced gettering* effect is expected if these fluxes of self-interstitials couple to M_s via the kick-

out reaction generating a drift of M from the source to the sink of I (Refs. 22–24).

Let us first consider metallic impurities which predominantly occupy interstitial sites in intrinisic silicon like the $3d$-transition elements. Since a dominating substitutional species must be present for the above coupling to be effective, *injection-induced gettering* can only work in combination with segregation, which builds up a substitutional component M_s inside the gettering layer. Furthermore, to surmount the segregation effect significantly, precipitation of $3d$ elements inside the gettering layer has to occur.[22] It has been argued that as soon as the I-induced drift of M leads to a supersaturation of M at the sinks of I silicide formation should occur in agreement with available experimental evidence obtained by TEM (Refs. 11,12) and Mössbauer spectroscopy (Refs. 25,26). Self-interstitial supersaturation in the highly P-doped gettering layer also leads to diffusion of I into the bulk and to a I supersaturation there destabilizing metal silicide precipitates whose formation is accompanied by a volume expansion (cf. Ref. 27).

The situation is considerably different for metallic impurities which predominantly occupy substitutional sites in intrinisic silicon like Au, Pt, or Zn. The obvious effect of I supersaturation in the bulk is the increase of the highly mobile interstitial component which affects the kinetics of PDG. This effect has been observed by Lescronier *et al.*[28] and modeled by Bronner and Plummer[29] under the assumption, that the silicon surface is an infinite sink for Au. Going a step further, Chen and Schroder[30] model the sink action of the highly P-doped layer by a phenomenological parameter g in the surface boundary condition, which they integrate in the segregation model of Baldi *et al.*[4] A different modification of Baldi's model has been proposed by Sveinbjörnsson *et al.*[10] in order to explain their data for Au in Si. They correct the segregation coefficient by a solubility decrease of gold because of the self-interstitial supersaturation, which they obtain assuming that everywhere the concentration of interstitial gold is equal to the solubility in intrinsic silicon.

Hence, there is a qualitative picture of how PDG may work and there is a model of its effect on the outdiffusion of Au. However, a quantitative description of the general action of PDG, especially of its operation inside the gettering layer, is a longstanding open problem of semiconductor physics. In this work, we present a mathematical model whose keypoint is the description of the *combined action of segregation and injection-induced gettering* on the distribution of a dissolved metallic impurity and which can be easily extended to the case that silicide formation occurs inside the gettering layer.

II. MODELING

In a microscopic picture *injection-induced gettering* arises from the reaction by which the immobile substitutional metal species M_s is converted into the interstitial one, M_i, with the assistance of intrinsic point defects. In the case of gold and platinum it is well confirmed that this conversion takes place through the kick-out reaction,

$$M_s + I \rightleftharpoons M_i, \qquad (2.1)$$

in the temperature range of $850-1000\,^\circ$C typical for PDG.[16]

The kick-out diffusion in intrinsic, dislocation-free silicon is described by the following equations:[31]

$$\frac{\partial c_I}{\partial t} = D_I \frac{\partial^2 c_I}{\partial x^2} + \frac{\partial c_{M_s}}{\partial t}, \qquad (2.2)$$

$$\frac{\partial c_{M_i}}{\partial t} = D_i \frac{\partial^2 c_{M_i}}{\partial x^2} - \frac{\partial c_{M_s}}{\partial t}, \qquad (2.3)$$

$$\frac{c_{M_i}}{c_I c_{M_s}} = \frac{c_{M_i}^{\mathrm{eq}}}{c_I^{\mathrm{eq}} c_{M_s}^{\mathrm{eq}}}. \qquad (2.4)$$

Here x is the space coordinate in the diffusion direction considered, t the diffusion time, c_I, c_{M_i}, and c_{M_s} are the concentrations of self-interstitials, interstitial metal atoms, and substitutional metal atoms, c_I^{eq}, $c_{M_i}^{\mathrm{eq}}$, and $c_{M_s}^{\mathrm{eq}}$ are the corresponding equilibrium concentrations, and D_I, D_i are the diffusivities of self-interstitials and interstitial metal atoms, respectively. Equation (2.4) states that local equilibrium between I, M_s, and M_i is established everywhere at any time via the kick-out reaction (2.1). Equations (2.2)–(2.4) have been sucessfully used to describe gold diffusion into silicon from the corresponding equilibrium phase.[32]

It is our aim to fully adjust Eqs. (2.2)–(2.4) to the requirements of PDG, i.e., to describe the metal diffusion in the bulk as well as in the gettering layer. Several changes have to be made.

(1) Within the gettering layer phosphorous is present at high concentrations making the silicon strongly extrinsic. In order to include the resulting segregation, charged metal species and self-interstitials have to be taken into account. Besides, pairs of metal atoms and phosphorous atoms may form. For simplicity we introduce the following notation: c_{M_s}, c_{M_i}, and c_I, and the corresponding equilibrium concentrations include all respective charged species; in addition to the substitutional gold concentration, c_{M_s} further includes metal atoms that exist in pairs with phosphorous atoms. It can be shown (see the Appendix) that — with this meaning of the concentrations—Eq. (2.4) remains valid even in the strongly extrinsic gettering layer, if local equilibrium of electronic exchange reactions and pairing reaction is established.

(2) Equation (2.3) has to be changed if charged interstitial metal species diffuse. However, it has been shown by measuring the dependence of solubilities and diffusivities of several metals (Mn, Fe, Co) on the doping level,[7] that the interstitial species, in general, are neutral in intrinsic silicon and do not introduce acceptor levels into the band gap (for copper see Ref. 33). Therefore, only the neutral interstitial metal species has to be taken into account for PDG and Eq. (2.3) remains valid.

(3) The diffusion equation (2.2) for the self-interstitials has to be changed, because the self-interstitials are as well involved in the phosphorous diffusion. This is done by modifying the corresponding diffusion equation in the phosphorous-diffusion model by adding the term $\partial c_{M_s}/\partial t$ that accounts for creation/annihilation due to the kick-out reaction:

$$\frac{\partial c_I}{\partial t} = \left(\frac{\partial c_I}{\partial t}\right)_{\text{PD}} + \frac{\partial c_{M_s}}{\partial t}. \qquad (2.5)$$

For example, the term $(\partial c_I/\partial t)_{\text{PD}}$ represents the right-hand sides of the diffusion equations for the self-interstitials occuring in the model of Mulvaney and Richardson[20] or in the one of Orlowski.[21]

Equations (2.3), (2.4), and (2.5), and the remaining diffusion equations for phosphorous and vacancies in the respective phosphorous-diffusion model consistently describe the whole PDG process, if no precipitates occur in the course of the process, and may be used as a starting point for simulations. It should be noted that the treatments of both, the metal diffusion and the phosphorous diffusion, are based on the assumption of local equilibria of atomic reactions (kick-out reaction, PI pairing) and electronic exchanges. The equations are easily generalized by introducing reaction constants.

For comparison with experimental results the quantity of interest is the total metal concentration $c_M = c_{M_i} + c_{M_s}$. Introduced in Eqs. (2.3)–(2.5), one obtains

$$\frac{\partial c_M}{\partial t} = D_i \frac{\partial^2}{\partial x^2} \left\{ \frac{c_M}{1 + (c_{M_s}^{\text{eq}}/c_{M_i}^{\text{eq}})(c_I^{\text{eq}}/c_I)} \right\}, \qquad (2.6)$$

$$\frac{\partial c_I}{\partial t} = \left(\frac{\partial c_I}{\partial t}\right)_{\text{PD}} + \frac{\partial}{\partial t} \left\{ \frac{c_M}{1 + (c_{M_i}^{\text{eq}}/c_{M_s}^{\text{eq}})(c_I/c_I^{\text{eq}})} \right\}. \qquad (2.7)$$

It should be noted that the equilibrium concentrations $c_{M_s}^{\text{eq}}$ and c_I^{eq} cannot be treated as constants in Eqs. (2.6) and (2.7), because they do not only depend on temperature T but also on the phosphorous concentration c_P, which is a function of x and t. Since we assume that the interstitial metal species is neutral its equilibrium concentration does not depend on c_P.

For the purpose of illustrating the interplay of *segregation- and injection-induced gettering*, we consider the metal flux $j_M = -D_i \partial c_{M_i}/\partial x$ and decompose it into three contributions:

$$j_M = j_M^{\text{(diff.)}} + j_M^{\text{(segr.)}} + j_M^{\text{(drift)}} \qquad (2.8)$$

with

$$j_M^{\text{(diff.)}} = -\frac{D_i c_I/c_I^{\text{eq}}}{c_{M_s}^{\text{eq}}/c_{M_i}^{\text{eq}} + c_I/c_I^{\text{eq}}} \frac{\partial c_M}{\partial x}, \qquad (2.9)$$

$$j_M^{\text{(segr.)}} = \frac{D_i c_I/c_I^{\text{eq}}}{(c_{M_s}^{\text{eq}}/c_{M_i}^{\text{eq}} + c_I/c_I^{\text{eq}})^2} \left(\frac{c_M^{\text{eq}}}{c_{M_i}^{\text{eq}}}\right)_{\text{intr.}} c_M \frac{\partial S}{\partial x}, \qquad (2.10)$$

$$j_M^{\text{(drift)}} = -\frac{D_i c_{M_s}^{\text{eq}}/c_{M_i}^{\text{eq}}}{(c_{M_s}^{\text{eq}}/c_{M_i}^{\text{eq}} + c_I/c_I^{\text{eq}})^2} c_M \frac{\partial}{\partial x}\left(\frac{c_I}{c_I^{\text{eq}}}\right). \qquad (2.11)$$

Here the segregation coefficient $S(c_P, T) \doteq c_M^{\text{eq}}/(c_M^{\text{eq}})_{\text{intr.}}$ has been introduced,[4] and the subscript ''intr.'' indicates that the respective quantity refers to intrinsic conditions. The diffusionlike metal flux $j_M^{\text{(diff.)}}$ tends to equalize the metal concentration throughout the specimen. The flux $j_M^{\text{(segr.)}}$ only occurs within the region of high phosphorous concentrations and is
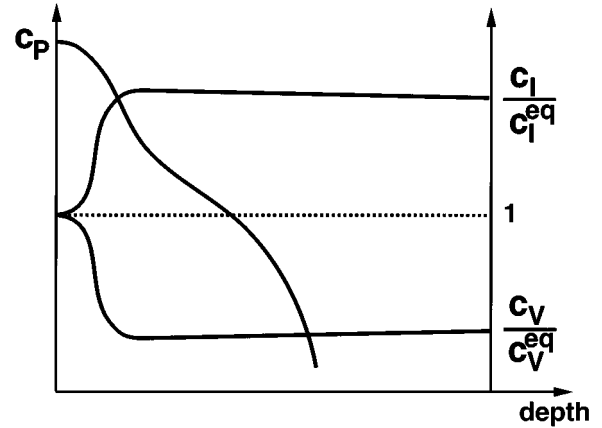

FIG. 1. Schematic presentation of an anomalous phosphorous-concentration profile c_P and of the normalized intrinsic point defect concentrations c_I/c_I^{eq} and c_V/c_V^{eq}. The dashed line indicates the equilibrium situation of the intrinsic point defects. (Ordinates are logarithmically scaled.)

due to segregation. The flux $j_M^{\text{(drift)}}$ finally is due to non-equilibrium self-interstitials and is directed towards decreasing I supersaturation.[34]

For interpretation of the individual metal fluxes occurring in Eq. (2.8) we consider P diffusion at not too high surface concentrations where almost all the phosphorous remains electrically active [e.g., below 3×10^{20} cm^{-3} at 900 °C (Ref. 36)]. For this regime, recent models of P diffusion (Refs. 19–21) assume that I injection is predominantly due to PI-pair dissociation in the kink region. Figure 1 schematically presents a phosphorous concentration profile with the associated distributions of self-interstitials and vacancies. The charactistic features of the self-interstitial concentration profile can be summarized as follows: it starts with the equilibrium value at the surface, shows a steep increase in the region of high phosphorous concentrations, and reaches near to the kink a maximum value, which spreads gradually with time into the bulk. It is obvious that once the supersaturation in the bulk has been established, large gradients of the I supersaturation only occur in the near surface region of the phosphorous profile.

From this the combined gettering action due to segregation and self-interstitial injection becomes obvious: $j_M^{\text{(segr.)}}$ and $j_M^{\text{(drift)}}$ are both directed towards the surface due to increasing P concentration and decreasing I supersaturation, respectively. The accumulation of metal atoms due to these fluxes, however, is accompanied by an increase of the oppositely directed metal flux $j_M^{\text{(diff.)}}$. Finally, in a quasi-steady-state (to be discussed below) the three fluxes are balanced. Figure 2 gives a schematic presentation of the fluxes occurring inside the gettering layer and of the reactions by which they are coupled.

The response of the bulk metal distribution is different for metals that are mainly dissolved on interstitial sites, e.g., the $3d$ metals, and those, which are dissolved predominantly on substitutional sites, e.g., Au and Pt. The former are not affected by the proceeding I supersaturation and therefore show normal out diffusion. For the latter the main effect of the I supersaturation is the increase of the highly mobile interstitial species. As a result the ''effective diffusion coef-
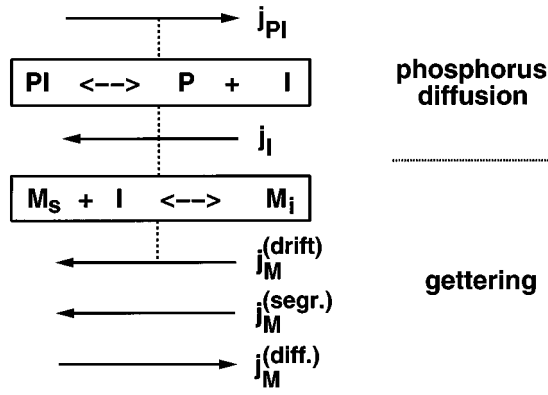
FIG. 2. Schematic presentation of the fluxes (arrows) and their coupling (dashed lines) by reactions (boxes) associated with phosphorous-diffusion (upper part) and with PDG (lower part). The segregation-induced flux of M, $j_M^{(\text{segr.})}$, is driven by the solubility enhancement of M near the surface due to phosphorous doping. The drift flux of M, $j_M^{(\text{drift})}$, is coupled to the self-interstitial flux j_I by the kick-out reaction. The diffusionlike flux of M, $j_M^{(\text{diff.})}$ counteracts the permanent gettering of M due to the former two fluxes.

ficient'' occuring in $j_M^{(\text{diff.})}$ is enhanced [cf. Eq. (2.9)], whereby this effect spreads gradually with time into the bulk. The characteristic metal concentration profiles measured after PDG of gold[37] had been mainly attributed to this effect.[29]

What can be said about the conditions required for *injection-induced gettering* to be present besides segregation? Following an argument due to Goesele and Tan[16] nonequilibrium of intrinsic point defects occurs when the effective flux of in-diffusing phosphorous exceeds the flux of host atoms trying to reestablish the intrinsic point defect equilibrium. This condition may be approximately written $D_P^{(s)} C_P^{(s)} > D_{SD}^{(s)}$, where $C_P^{(s)}$ denotes the phosphorous-surface concentration (in atomic fractions), and $D_P^{(s)}$ and $D_{SD}^{(s)}$ denote the effective phosphorous-diffusion coefficient and the silicon self-diffusion coefficient, respectively, at the surface. While $D_P^{(s)}$ strongly depends on the electron density $n^{(s)}$, the weak doping dependence of $D_{SD}^{(s)}$ may be neglected for our purpose. Taking the diffusion coefficients as summarized by Goesele and Tan,[16] one estimates for the critical P-surface concentration $c_P^{(\text{crit})}(900\,°\text{C}) \approx 5 \times 10^{19}\,\text{cm}^{-3}$. Indeed this phosphorous-surface concentration corresponds to the onset of enhanced tail diffusion and enhanced diffusion in buried layers (Refs. 38,39). Remarkably there is as well a correspondence to PDG of gold which starts working when the phosphorous-surface concentration exceeds this critical value.[40] Furthermore, at higher phosphorous-surface concentrations a strong correlation between diffusion enhancement data and gettering efficiencies has been found,[40] which supports the importance of the *injection-induced gettering mechanism* for PDG.

III. COMPARISON WITH EXPERIMENTAL RESULTS: PDG OF GOLD

Since the formation of precipitates is not yet included in our analysis, we consider in the following PDG of gold in silicon in some more detail where precipitation is not likely to occur.[41] We show that our model can account for the

following features of PDG of gold: (a) the very high gettering efficiencies, (b) the strong temperature dependence, (c) the steepness of the gold concentration profiles within the gettering layer, and (d) the ''reversibility.''

Sveinbjörnsson *et al.*[10] have found that during PDG gold redistributes towards quasi-steady-states that depend on the phosphorous concentration profile and the temperature only. Once quasi-steady-state has reached, the further development of the metal distribution is therefore determined by the slow P diffusion. The quasi-steady-state itself is reached through transient states, which are as well governed by the much faster diffusion of Au$_i$ and I. For the quasi-steady-state an approximate solution for $c_M(x,t)$ is obtained from Eq. (2.8) with $j_M \approx 0$ and inserting S and c_I/c_I^{eq} from the phosphorous-diffusion model. Integration yields

$$c_M(x,t) = \kappa(t)\left\{ 1 + \frac{c_I^{\text{eq}}}{c_I}(x,t)\left[\left(\frac{c_M^{\text{eq}}}{c_{M_i}^{\text{eq}}} \right)_{\text{intr.}} S(x,t) - 1 \right] \right\},$$

(3.1)

where $\kappa(t)$ depends on the metal boundary condition. It has been found experimentally that during PDG gold remains in the specimen (Refs. 10,28,41); therefore, the constancy of metal amount contained in the specimen is the appropriate boundary condition in this case.

In the absence of self-interstitial nonequilibrium, where PDG is only due to segregation, Eq. (3.1) yields

$$c_M(x,t) = \kappa^*(t) S(x,t),$$

(3.2)

whereby $\kappa^* = (c_M^{\text{eq}}/c_{M_i}^{\text{eq}})_{\text{intr.}} \kappa$. Of course, Eq. (3.2) corresponds to the quasi-steady-state within the *segregation model* (Refs. 4,42).

Compared with the exclusive action of segregation, I injection strongly enhances the amount of gettered gold due to the additional metal drift towards the surface [cf. Eq. (2.8) and Fig. 2]. For the quasi-steady-state the effect is illustrated in Fig. 3. Figure 3(a) schematically shows profiles of the segregation coefficient and the I supersaturation that result from phosphorous in diffusion. In Fig. 3(b) the corresponding gold concentration profiles are sketched for the respective cases that only segregation-induced gettering and the combined action of segregation- and injection-induced gettering is taken into account (see also caption). The ratio G of the metal concentration at the surface, $c_M^{(s)}$, to that in the bulk, $c_M^{(b)}$, in the quasi-steady-state may serve as a measure for the gettering efficiency. According to Eq. (3.1) this ratio is given by

$$G = \frac{(c_I/c_I^{\text{eq}})^{(b)}(c_M^{\text{eq}}/c_{M_i}^{\text{eq}})_{\text{intr.}}}{(c_I/c_I^{\text{eq}})^{(b)} + (c_M^{\text{eq}}/c_{M_i}^{\text{eq}})_{\text{intr.}} - 1} S^{(s)},$$

(3.3)

whereas segregation alone predicts $G = S^{(s)}$. Here $S^{(s)}$ and $(c_I/c_I^{\text{eq}})^{(b)}$ denote the segregation coefficient at the surface and the I supersaturation in the bulk, respectively.

Sveinbjörnsson *et al.*[10] found that their experimental data of G exceed the segregation coefficient $S^{(s)}$ as predicted theoretically by Baldi *et al.*[4] by about two orders of magnitude depending on temperature and phosphorous-surface concentration. This experimental finding can now be dis-
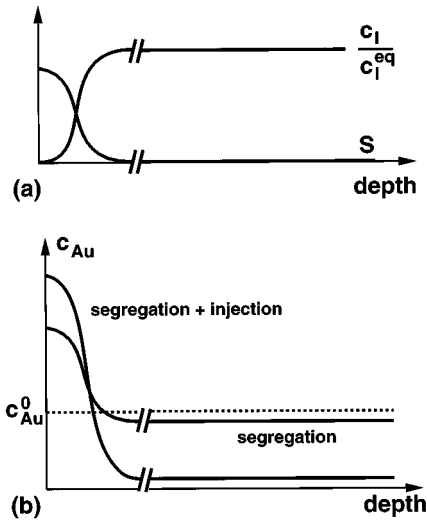
FIG. 3. (a) Profiles of the segregation coefficient S and the supersaturation of self-interstitials c_I/c_I^{eq} resulting from phosphorous in diffusion under PDG conditions (schematic); (b) corresponding quasi-steady-state gold distributions assuming that gettering is due to segregation only or assuming a combined action of segregation-induced gettering and injection-induced gettering. In the latter case a stronger redistribution of gold towards the gettering layer and a steeper gold profile within the gettering layer is predicted (see text). The initial gold level c_{Au}^0 is indicated by the dashed line. (Ordinates are logarithmically scaled.)

cussed in respect of Eq. (3.3). Reported data of $(c_M^{eq}/c_{M_i}^{eq})_{intr.}$ at 900 °C are 30 (Ref. 43) respective 130 (Ref. 44) with a temperature dependence $\propto \exp(\Delta E/kT)$, ΔE lying between 0.7 and 1 eV. The I supersaturation in the bulk $(c_I/c_I^{eq})^{(b)}$ depends on the detailed conditions of phosphorous in-diffusion: yet from studies on enhanced tail diffusion and dopant diffusion in buried layers (Refs. 38,39) it can be inferred that the I supersaturation is at least 10^2 if the phosphorous is diffused at 900 °C with a surface concentration of 2×10^{20} cm^{-3}; the temperature dependence of $(c_I/c_I^{eq})^{(b)}$ for this phosphorous surface concentration corresponds to an energy of $\Delta E \simeq 1.5$ eV. Within the uncertainty of the available data for $(c_M^{eq}/c_{M_i}^{eq})_{intr.}$, $(c_I/c_I^{eq})^{(b)}$, and $S^{(s)}$ the high values of G as measured by Sveinbjörnsson et al. and its strong temperature dependence can be interpreted on the basis of Eq. (3.3).

A further point concerns the shape of the gold concentration profile within the gettering layer. Sveinbjörnsson et al. found that c_{Au} is proportional to c_P^4 for phosphorous concentrations above $c_P = 4\times10^{19}$ cm^{-3}. This can hardly be explained by segregation because a fourfold charge state would have to be assumed; please note that a neutral gold-phosphorous pair[5] as well cannot account for this dependency regardless of the binding energy. However, if injection-induced gettering is taken into account, a steeper gold concentration profile results due to the decrease of the I supersaturation towards the surface (cf. Fig. 3).

The well established ''reversibility'' of PDG of gold has been regarded as strong evidence for the segregation approach (Refs. 4,10,28). However, injection-induced gettering as discussed above is fully consistent with the reversibility since a I-supersaturation characteristic for the phosphorous

profile and temperature builds up whenever the phosphorous diffuses. Therefore, the quasi-steady-state gold distribution basically is a function of temperature alone as long as the phosphorous profile is not considerably changed due to drive in [cf. Eq. (3.1)].

IV. SUMMARY AND DISCUSSION

We have modeled gettering of metallic impurities in silicon by considering the combined action of segregation and self-interstitial injection. For dissolved metallic impurities our model enables us to predict concentration profiles $c_M(x,t)$ also inside the gettering layer. Using phosphorous and associated self-interstitial profiles from the literature and comparing with recent results obtained for PDG of Au in Si by Sveinbjörnsson et al.,[10] we have demonstrated that our model correctly accounts for amplitude and shape of $c_{Au}(x)$ in the quasi-steady-state, its temperature dependence and its ''reversibility.''

In a previous treatment of PDG for Au in Si, Bronner und Plummer[29] propose that the gettering region acts as a source of self-interstitials, so that gold is driven in its interstitial form and can there easily diffuse and be trapped at the surface. However, the assumption in their model, that the surface is a perfect sink for gold, is not in agreement with the data of Sveinbjörnsson et al.[10] Chen and Schroder[30] take into account that the gettering region only is a finite sink for self-interstitials. Like in the model of Bronner and Plummer the gettering region is not explicitly included in the treatment, whereas its sink-behavior enters through boundary condition. The extension of Baldi's segregation model[4] proposed by Sveinbjörnsson et al.[10] to take into account self-interstitial supersaturation results in an expression for the gettering efficiency G, which agrees with Eq. (3.3) in the limiting case of $(c_M^{eq}/c_{M_i}^{eq})_{intr} \gg (c_I/c_I^{eq})^{(b)}$. Their assumption of a concentration of the interstitial species equal to its solubility in intrinsic silicon, however, is not sufficient to treat PDG of $3d$ transition elements in silicon.

A more quantitative examination of experimental data reported by Sveinbjörnsson et al.[10] shows that the gold concentration at the wafer surface exceeds the solubility as estimated from pure segregation[45] in some of their samples (e.g., sample b in Fig. 5 of Ref. 10). Due to the lack of microscopic investigations, however, there is no direct evidence for gold precipitation in the highly phosphorous-doped region as for PDG of platinum in silicon where PtSi precipitates have been observed recently by TEM.[13]

As has been described earlier (Refs. 22,23), the experimentally observed (Refs. 11,12,25,26) formation of metal silicide precipitates must be an integral part of effective PDG for $3d$ elements which are predominantly dissolved on interstitial sites in intrinsic silicon. High P doping in the gettering layer has been shown to lead to a strong increase of the substitutional solubility of these elements (Refs. 7,8). In the gettering layer, solute drift and diffusion fluxes are induced for these elements by self-interstitial fluxes. While the solute drift is directed towards the sink of self-interstitials the diffusion flux is directed away from the sink. The balance between these two establishes a concentration of c_M^{sink} at the sink. It has been argued that metal atoms precipitate as soon as $c_M^{sink} > c_M^{eq}$.[9] Incorporating this criterion into our model

would allow us to quantitatively describe PDG by silicide formation.

APPENDIX

The metal species and the self-interstitials, in general, exist in several charge states: M_s^σ, M_i^σ, I^σ. Apart from this (charged) pairs of metal atoms and phosphorous atoms may form: $(M_s P)^\sigma$. Since electronic exchanges between different charge states, e.g.,

$$M_s^\sigma + \sigma e^- \rightleftharpoons M_s^0, \tag{A1}$$

take place on a much shorter time scale than any diffusion process, local electronic equilibrium should always be established. While there is no direct evidence that the same is true for the pairing reaction,

$$M_s^0 + P^{+1} + e^- \rightleftharpoons (M_s P)^0, \tag{A2}$$

we assume local equilibrium as well in order to include $M_s P$ pairs quantitatively.

During PDG the electron density n and the phosphorous concentration c_P are much higher than the concentrations of metal and self-interstitials. Therefore, the considered electronic exchange reactions and the pairing reaction do not noticably affect their values. It should be noted that outside the high concentration region of the phosphorous profile, where c_P may be comparable with or smaller than the metal concentration, pairing does not play any role. Consequently, the electron density and the phosphorous concentration may be treated as constants in the respective laws of mass action.

By taking the laws of mass action of the electronic exchange reactions and the pairing reaction and summing up all respective charge states, the following relations are obtained:

$$\frac{c_{M_s}}{c_{M_s}^{eq}} = \frac{c_{M_s^0}}{c_{M_s^0}^{eq}}, \tag{A3}$$

$$\frac{c_{M_s P}}{c_{M_s P}^{eq}} = \frac{c_{(M_s P)^0}}{c_{(M_s P)^0}^{eq}} = \frac{c_{M_s^0}}{c_{M_s^0}^{eq}}, \tag{A4}$$

$$\frac{c_{M_i}}{c_{M_i}^{eq}} = \frac{c_{M_i^0}}{c_{M_i^0}^{eq}}, \tag{A5}$$

$$\frac{c_I}{c_I^{eq}} = \frac{c_{I^0}}{c_{I^0}^{eq}}. \tag{A6}$$

Here c_{M_s}, $c_{M_s P}$, c_{M_i}, and c_I denote total concentrations, i.e., sums over all charged species of the respective defect (c_{M_s} not yet includes the metal atoms existing in pairs with phosphorous, see below); $c_{M_s^0}$, $c_{(M_s P)^0}$, $c_{M_i^0}$, and c_{I^0} are the concentrations of the neutral species, and ''eq'' denotes equilibrium values.

If the kick-out reaction between the neutral species

$$M_s^0 + I^0 \rightleftharpoons M_i^0 \tag{A7}$$

obeys a law of mass action, Eqs. (A3)–(A6) give

$$\frac{c_{M_i}}{c_I (c_{M_s} + c_{M_s P})} = \frac{c_{M_i}^{eq}}{c_I^{eq} (c_{M_s}^{eq} + c_{M_s P}^{eq})}, \tag{A8}$$

which reduces to Eq. (2.4), if the concentration of $M_s P$ pairs is included in c_{M_s}.

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