Empirical Cluster Modeling Revisited

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Abstract—**Impurities being present in a semiconductor in high concentrations may form agglomerates. Agglomeration usually demobilizes the impurities and, in case of dopants, also renders them electrically inactive. A standard approach in continuum process simulation assumes the formation of energetically favorable small clusters of size *m*. High numbers of *m* are used to mimic an often desired saturation of the concentration of unclustered impurity atoms with increasing total concentration. However, for systems far from equilibrium, potentiated high concentrations may lead to numerical problems. In this work, an alternative formulation is presented which features a saturation of the unclustered impurity concentration while introducing only one equation derived from Waite's theory of diffusion-limited reactions.**

Keywords—impurity clustering; empirical models; arsenic; silicon; solubility; process simulation; TCAD

I. INTRODUCTION

With increasing impurity concentration, a significant fraction of the impurities is often found to be immobile during annealing processes or electrically inactive thereafter. The phenomena responsible may range from the formation of clusters comprising only few impurity atoms up to the formation of precipitates incorporating hundreds to thousands of atoms and more. For some impurities like boron [1], arsenic and phosphorus [2], or oxygen [3], detailed models are available which explain at least a large part of the relevant experiments. For most of the other impurities, no detailed information is available about the energetics and formation kinetics of possible complexes.

In continuum process simulation, the base line of modeling immobile or electrically inactive impurities is to postulate the preferential formation of small clusters. Inspired by the early work of Hu [4], the rate of formation of such clusters is usually assumed to be proportional to the concentration of unclustered impurity atoms to the power of the number of impurity atoms in the cluster. In most publications, clusters comprising two to four impurity atoms are assumed. However, to mimic impurity precipitation with its saturation of the concentration of unclustered impurity atoms, the number of impurities in the cluster can be increased towards ten or more.

Particularly after ion implantation, impurities with a low solubility may be present in the host matrix with an oversaturation of several orders of magnitude. For such systems, numerical problems may arise from the power law. To avoid them, an alternative formulation of an empirical cluster law has been developed on the basis of the classical nucleation theory. In the following, after discussing the empirical cluster models, the new model will be motivated and its properties and potential applications will be outlined.

II. EMPIRICAL CLUSTER MODELING

In the early 1970s (e.g. [5]), researchers started to explain experimental evidence for an incomplete activation of arsenic by assuming that energetically particularly favorable clusters X_m comprising m monomers X form via the quasi-chemical reaction

$$m\, X \rightarrow X_m . \tag{1}$$

The first dynamic description of such a cluster formation was formulated by Hu [4] in analogy to the model of Kaiser et al. [10] for the formation of thermal donors. Hu assumed that X_4 clusters would form preferentially, with the reaction of arsenic monomers with X_3 clusters being the rate-limiting step. The X_2 and X_3 clusters were assumed to be in steady state with the monomer concentration on a much shorter timescale. Generalized to m impurities in a cluster, the change of the cluster concentration C_{X_m} and the monomer concentration C_X with time due to cluster formation was obtained as being proportional to the monomer concentration to the power of m

$$\left.\frac{dC_{X_m}}{dt}\right|_{\text{form}} = -\frac{1}{m}\left.\frac{dC_X}{dt}\right|_{\text{form}} = k_f C_X{}^m \tag{2}$$

with k_f denoting the forward reaction constant. A similar result would have been obtained from the kinetic law of mass action developed by Brönsted [6], [7] and Haase [8], [9]. It should be noted, however, that the substitutional arsenic atoms referred to in (2) are immobile per se and can move only by forming mobile complexes with self-interstitials or vacancies. Accordingly, no direct atomistic interpretation exists for the forward reaction rate k_f so that the cluster equation remains rather empirical. Simultaneous to the formation of clusters, already formed ones may dissolve. This leads to a change in the cluster and monomer concentrations of

$$\left.\frac{dC_{X_m}}{dt}\right|_{\text{diss.}} = -\frac{1}{m}\left.\frac{dC_X}{dt}\right|_{\text{diss.}} = -k_b\, C_{X_m} , \tag{3}$$

characterized by the backward reaction constant k_b which can be seen as an inverse time constant of the cluster dissolution. The total change in the cluster and monomer concentrations is given as the sum of the both. In steady state, the total concentration C_X^{tot} is given by

$$C_X^{tot} = C_X + m\, C_{X_m} = C_X + m\frac{k_f}{k_b}C_X{}^m. \qquad (4)$$

Experiments at that time indicated a saturation of the electrically active dopant concentration with an increasing total concentration. However, on the basis of (4), one would just expect a flattening and not a saturation. Including charge carriers in the reaction so that a neutral cluster results from the reaction of m ionized impurities and m compensating charge carriers would just lead to a doubling of the exponent in (2) and not to the desired saturation. As a loophole, it was proposed by Tsai et al. [11] and Guerrero et al. [12] that a saturation of the concentration of unclustered arsenic atoms can be obtained when m arsenic atoms are assumed to form a (m-1)-positively-charged cluster at diffusion temperature. However, since charged clusters would also act as donors, it is necessary to assume that they are electrically inactive at room temperature.

III. CLUSTER FORMATION IN LIGHT OF THE CLASSICAL NUCLEATION THEORY

The empirical cluster model outlined above has been used successfully in many investigations of dopant diffusion and activation. Dopants in semiconductors are usually characterized by a high solubility so that the ratio of dopant concentration and solubility is rather limited. This is not necessarily the same for other systems. Platinum, as an example, diffuses in silicon as interstitial with a rather low solubility while high concentrations can be introduced by ion implantation [13]. Raised to a high power, such concentrations may lead to a cluster formation rate which requires inadmissibly small time steps for a sufficiently accurate solution. To overcome this problem, an alternative cluster model was derived on the basis of the classical nucleation theory of Turnbull and Fisher [14].

Within the classical nucleation theory, clustering of mobile monomers X proceeds via a chain of binary reactions

$$\begin{array}{c} X + X \rightleftharpoons X_2 \\ X + X_2 \rightleftharpoons X_3 \\ \cdots \\ X + \rightleftharpoons X_m \end{array} \qquad (5)$$

between the monomers and already formed clusters. Being interested at first in systems far from equilibrium, the backward reactions are ignored. One then obtains a system of equations in the form

$$\frac{dC_X}{dt} = -2\,k_2\,C_X{}^2 - k_3 C_X C_{X_2} - \cdots - k_m C_X C_{X_{m-1}}$$

$$\frac{dC_{X_2}}{dt} = k_2\,C_X{}^2 - k_3 C_X C_{X_2}$$

$$\frac{dC_{X_n}}{dt} = k_n\,C_X\,C_{X_{n-1}} - k_{n+1}C_X C_n;\ 2 < n < m \qquad (6)$$

$$\frac{dC_{X_m}}{dt} = k_m\,C_X\,C_{X_{m-1}}$$

The forward reaction rates k_n can be obtained from Waite's theory of diffusion-limited reactions [15]. For the reaction leading to the formation of X_n clusters, one then obtains a forward reaction rate of

$$k_n = 4\,\pi\,D_X\,a_{n-1} \qquad (7)$$
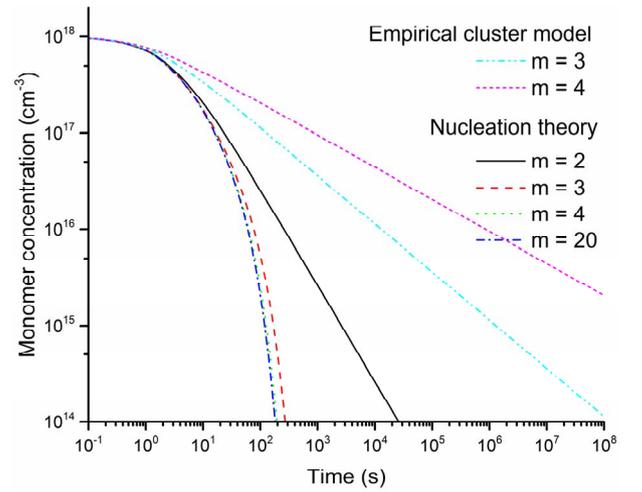
Fig. 1. Comparison of the monomer concentration resulting from the empirical cluster model (1) and the nucleation theory (6) for different dominating and maximum cluster sizes m, respectively.

with D_X denoting the diffusion coefficient of the monomers and a_{n-1} the capture radius of the X_{n-1} clusters. When we assume for the sake of demonstration that the immobile clusters have similar properties, all reaction constants k_n can be assumed equal for $n > 2$. Only the reaction constant k_2 between two monomers should be twice as large.

Simulations of the monomer concentration C_X resulting from the empirical cluster model and the nucleation theory are compared in Fig. 1 for different assumptions about the dominating and maximum cluster size m, respectively. For the nucleation theory, forward reaction rates k_n of 10^{-19} cm^{-3}s^{-1} have been assumed while the parameters of the empirical cluster model were adjusted to give the same dC_X/dt for $t = 0$. For a cluster size of two, the two models are identical and lead to the same result. For larger clusters ($m > 2$), an increasingly slower reduction of the monomer concentration is predicted by the empirical cluster model. This is because $C_X{}^m$ decreases faster than $C_X{}^2$ with decreasing monomer concentration. In contrast, a faster decrease of the monomer concentration is predicted by the nucleation theory when m is increased. The faster decrease at lower monomer concentrations results from the additional reactions between monomers and clusters already formed. Since the concentration of clusters decreases rapidly with size, reactions with clusters of size m equal to two and three will dominate so that only marginal changes can be seen when larger clusters are considered in addition.

IV. THE NEW MODEL

In order to become a viable alternative to the empirical cluster model, any reformulation should better not increase the number of equations. This then comes down again to postulating a cluster X_m of size m for which only one equation is required. However, in contrast to the previous assumption of a dominant cluster size, we consider here a cluster which represents the entirety of the formed clusters in the sense of a one-moment model [16]. For the reaction scheme of mobile monomers formulated in (6), the rate-limiting clustering reactions are the reaction of two monomers

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$$X + X \xrightarrow{k_2} \frac{2}{m} X_m . \tag{8}$$
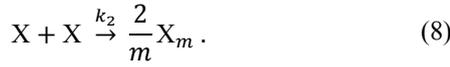
and the reaction of a monomer with the cluster

$$X + X_m \xrightarrow{k_m} \frac{m+1}{m} X_m . \tag{9}$$
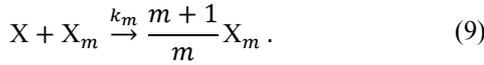
The factors $2/m$ and $(m+1)/m$ therein result from mass conservation. From (8) and (9), the formation rate of the clusters is obtained as

$$\left. \frac{dC_{X_m}}{dt} \right|_{\text{form}} = -\frac{1}{m} \left. \frac{dC_X}{dt} \right|_{\text{form}} \tag{10}$$
$$= \frac{2}{m} k_2 \, C_X^2 + \frac{1}{m} \, k_m \, C_X \, C_{X_m}$$

In order not to overload the figure, only few points of the resulting curves are shown in Fig. 2 in comparison to the predictions of the nucleation theory. For both values of m, a close agreement with the nucleation theory is observed for identical parameters k_2 and k_m. With increasing m, the monomer concentration decreases slower. This is owed to the fact that the concentration of the X_m cluster decreases with m due to mass conservation so that reaction (9) becomes slower. To complete the system, one can adopt the same assumption as for the empirical cluster model (3), namely that the X_m clusters dissolve with a rate k_b to m monomers each.

V. EXTENSIONS TO INCLUDE CHARGE CARRIERS AND INTRINSIC POINT DEFECTS

Within Waite's theory of diffusion-limited reactions, charge states of the reactants do not change the structure of the equations. As shown by Debye [17], one just obtains an enlarged capture radius in case of Coulombic attraction and a reduced capture radius in case of Coulombic repulsion.

In semiconductors, many impurities reside preferentially on substitutional sites (X_s) and are immobile there. In order to diffuse, they have to form complexes with intrinsic point defects, i.e. vacancies (XV) or self-interstitials (XI). Since the concentrations of these mobile species are rather low in comparison to the substitutional concentration, one would expect that the rate-limiting reaction changes to

$$XI + X_s \rightarrow \frac{2}{m} X_m + I. \tag{11}$$
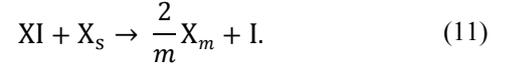
for the example of a species which diffuses preferentially via self-interstitials. The reaction with XM complexes can be written in analogy and added to give the total cluster formation rate. Similarly, in (9), the nascent intrinsic point defect needs to be included on the right-hand side when a mobile XV or XI defect reacts with a cluster. Point defects have to be considered also in the dissolution equation of the clusters. Assuming again a dominance of the diffusion via self-interstitials, dissolution of an X_m complex could be described, e.g., by the creation of impurity-self-interstitial complexes

$$X_m \rightarrow X_s + (m-1)\, XI + (m-1)\, V. \tag{12}$$
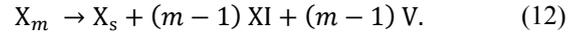
which leaves an appropriate number of vacancies behind.

VI. APPLICATION TO SYSTEMS IN OR CLOSE TO EQUILIBRIUM

While the model has been developed for systems strongly out of equilibrium, it might also be of interest for systems in or close to equilibrium. In equilibrium, the total concentration C_{X_T} of the impurities is related to the monomer concentration by

$$C_X^{tot} = C_X + m \, C_{X_m} = \frac{m \, k_b C_X + (2\, m\, k_2 - k_m) C_X^2}{m \, k_b - k_m C_X} . \tag{13}$$

From the denominator follows that the monomer concentration saturates for $C_X^{tot} \rightarrow \infty$ at $C_X = m \, k_b / k_m = C_{sol}$. As mentioned already in Section II, such a behavior was always desired for dopant clustering but could previously be achieved only on the basis of debatable assumptions. Based on the solubility concentration C_{sol}, (13) can be rewritten in the form

$$C_X^{tot}/C_{sol} = \frac{C_{X_T}/C_{sol} + \alpha \left(C_{X_T}/C_{sol} \right)^2}{1 - C_{X_T}/C_{sol}} \tag{14}$$

with the parameter $\alpha = 2\, m\, k_2 / k_m$. This relationship is shown in Fig. 3 for selected values of α. Assuming k_2 to be twice as large as k_m leads for $m = 4$ to a value of $\alpha = 16$ which gives a rather gradual approach of the solubility concentration. Decreasing α towards the limiting value of $\alpha = -1$ enables sharper approaches.

To demonstrate also the empirical capabilities of the model, experimental data on the electrical activation of arsenic from Guerrero et al. [12] and the references therein as well as from Bauer et al. [18] are compared in Fig. 4 to simulations with the new model. In equilibrium, the experiments are reproduced excellently with a shape parameter of $\alpha = 0.8$. As a further example, dynamic simulations for the data of Bauer et al. at 900 °C are shown in Fig. 5. Here, it is apparent that the experimental data shows a somewhat slower decrease with time than the simulations. This is in agreement with the general expectation that arsenic clustering is associated with a configuration comprising few arsenic atoms around a vacancy.
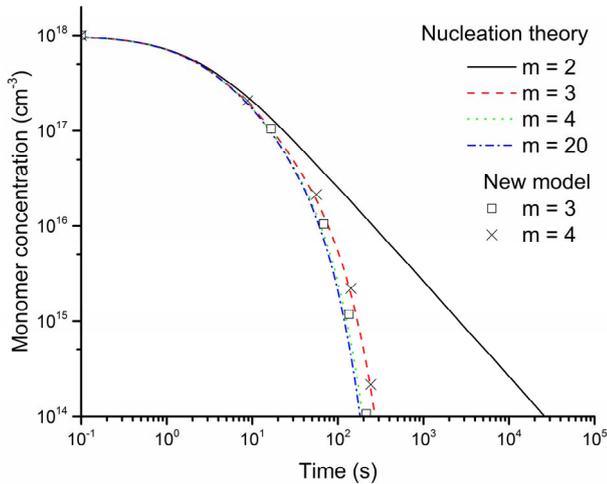
Fig. 2. Comparison of the monomer concentration resulting from the nucleation theory (6) and the new model (10) for different maximum and representative cluster sizes m, respectively.
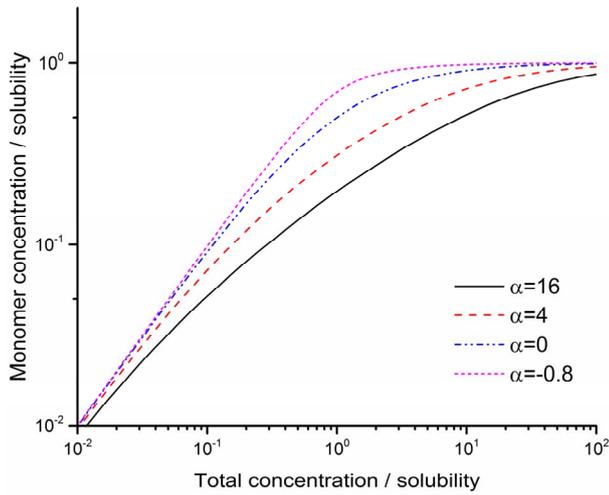
Fig. 3. Monomer concentration scaled by the solubility concentration as a function of the total concentration scaled by the solubility concentrations for different values of the parameter α.

VII. CONCLUSIONS

In this work, a complementary formulation of a clustering model was developed. It was derived on the basis of the classical nucleation theory and uses only physically motivated binary reactions. Featuring a saturation of the monomer concentration, the sharpness of this saturation can be tuned via the model parameters. To demonstrate the empirical capabilities of the model, it was compared to arsenic clustering experiments.

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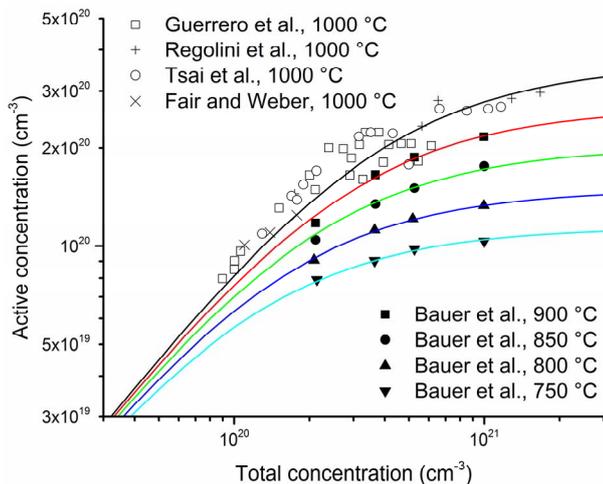
Fig. 4. Active vs. total arsenic concentration modeled with $\alpha = 0.8$, experimental data points from Guerrero et al. [12] and the references therein, and from Bauer et al.[18].
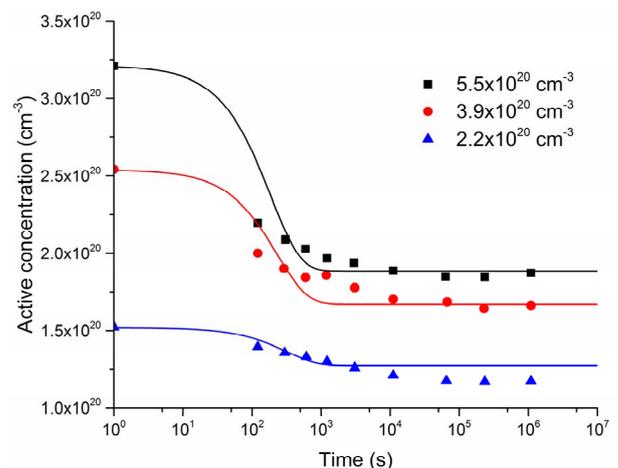
Fig. 5. Simulation of dynamic arsenic clustering at 900 °C, experimental data points from Bauer et al. [18].