The mobile silicon di-interstitial: Surface, self-interstitial clustering, and transient enhanced diffusion phenomena

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In the light of recent theoretical calculations predicting the mobile silicon di-interstitial (I_2) we have carried out a thorough analysis of its implications within a self-consistent, comprehensive modeling framework using atomistic Monte Carlo. In the study presented here we investigate its role in surface recombination and self-interstitial clustering processes, including boron transient enhanced diffusion (TED) under conditions where no boron clustering occurs. We conclude that, under such conditions, the mobile I_2 does not play a critical role and the single self-interstitial can be made to account for the missing mobile I_2. The main requirement for introducing the mobile I_2 is a bottleneck of two consecutive, relatively unstable, self-interstitial cluster sizes. We demonstrate that the different surface recombination lengths measured under oxidation/implantation conditions cannot be attributed to different recombination lengths for single interstitial and di-interstitial.

I. INTRODUCTION

During the last few years it has been extensively proven that the diffusion of conventional dopants in silicon is regulated by intrinsic point defects. Current technology uses ion implantation as the main process to introduce dopants in silicon. Inherent to this process is the creation of a high amount of intrinsic point defects, leading to the formation of different defect agglomerates. Their subsequent dissolution during annealing generates a point defect supersaturation that affects the diffusion of the implanted dopants. A thorough understanding of the dissolution kinetics of these defects is needed in order to correctly predict and control the final dopant profile in the deep submicron regime. In particular, extra self-interstitials (I) released both from big {311} rod like defects[1] and small clusters[2] bring about the Transient Enhanced Diffusion (TED) of commonly used dopants.

Recently, several theoretical calculations have predicted that besides the self-interstitial, the di-interstitial (I_2) is also highly mobile. The calculated migration energy value depends on the technique employed: empirical molecular dynamics (MD),[3,4] tight-binding molecular dynamics (TBMD)[5] or ab-initio local density approximation (LDA),[6–8] but ranges from 0.2 to 1 eV. Generally the calculated diffusivity of I_2 is higher than that of the single self-interstitial.

On the other hand, to our knowledge, there is no theoretical or experimental evidence against a high I_2 mobility. In spite of this, until to date all TED and cluster dissolution simulation studies have implicitly assumed that I_2 is immobile. One reason for such reluctance is that modeling advanced device processing is already burdened with too many differential equations, due to the complexity of the mechanisms that need to be taken into account. However, complexity is not a problem for atom-

istic kinetic Monte Carlo (kMC) process simulators,[9,10] their main limitation being that they can only handle deep submicron device sizes. Another attractive feature of kMC process simulators is that they can directly implement elementary mechanisms and use parameters derived from ab initio calculations as input, to simulate actual device processing. Thus, they can serve as a powerful workbench for testing out complex models and investigate possible simplifying assumptions.

For the reasons mentioned above, previous work[5,11] to include the mobile I_2, has mainly focused on the role of the surface in the presence of I and I_2 but has not considered the possible interactions of I_2 with I clusters and dopants and their subsequent implications. In the work presented here, we have analyzed some possible models and we have used an atomistic kinetic Monte Carlo process simulator[10,12] to elucidate possible interaction models to fulfill as many experimental and theoretical constraints as possible. Among other conclusions, we find that it is not possible to explain the different surface recombination lengths measured under oxidation/implantation conditions as being due to different recombination lengths for I and I_2. But still, we find that the mobile I_2 can be included with the parameters predicted by theoretical calculations to interact with small I clusters and with the surface in a comprehensive, physically based modeling scenario.

II. TESTING OUT POSSIBLE MODELS

In the following we have assumed that both I and I_2 are mobile, with migration energies $E_m(I) = 1$ eV and $E_m(I_2) = 0.5$ eV, respectively. For their interaction with the surface we first try to test out the suggestion[5,11] that the I_2 recombination length is small in comparison to the
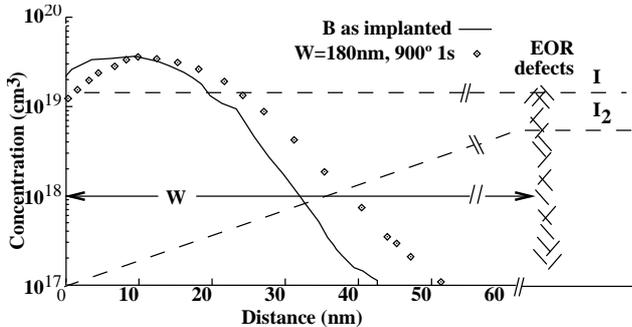
FIG. 1: Depth profiles of boron before and after annealing of a shallow boron implant in Ge-preamorphized layers (from Ref. 14). Thin solid curve: 3 keV boron implant profile. Symbols: SIMS profile after 1s, 900°C annealing. Dashed lines, simulated interstitial (assuming no surface recombination) and di-interstitial profiles from this work, (linear scale, arbitrary units).

FIG. 2: Energy diagram for the different emission and capture processes that can be involved in the formation of BI_2.

single interstitial. This means that single interstitials annihilate at the surface only rarely, whereas the surface is a perfect sink for di-interstitials. This assumption is made as an attempt to explain the fact that in OED, the surface recombination length is large (about $20\mu m$ in Ref. 13) whereas in TED this magnitude is small (< 10nm in Refs. 14,15). With such recombination lengths, in TED the surface is a sink for interstitials in the form of I_2 because the high interstitial concentration produces a high I_2 concentration. But in OED the dominant one would be the single interstitial concentration, which recombines very slowly at the surface.

However, the theoretical and experimental consequences of the assumption of a large I surface recombination length have not been discussed in depth yet. We now analyze some of these consequences.

As a testing case for this surface recombination model we will refer to the experiment described in Ref. 14 where the authors use an amorphizing Ge implant to produce a moderate density of end of range (EOR) defects (Fig. 1). They then vary the thickness (W) of the resulting amorphous layer by etching away the silicon without affecting the defect band. Subsequently boron is implanted in the remaining amorphous layer at low energy, and annealed at 900°C. The samples are measured to monitor the difference in the concentration of interstitials as a function of the distance W of the EOR defects that emit those interstitials to the surface. The conclusion is that the concentration of the species responsible for boron diffusion decreases towards the surface. In principle, those species could be I, I_2 or both. Our atomistic simulations, assuming that EOR defects emit and capture I and I_2 reveal that, the I and I_2 concentrations are not in local equilibrium towards the surface (a simplifying assumption used in previous work[11]), due to the high mobility of I_2, that reaches the surface before breaking up, and to the absence of clusters or other defects that could mediate the exchange of I and I_2. Because of this lack of
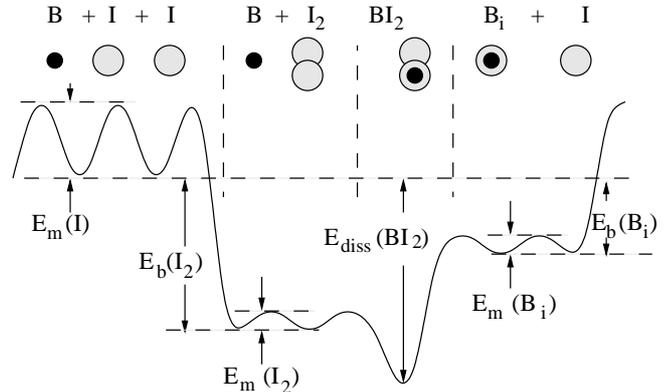
local equilibrium, the I concentration is uniform up to the surface (Fig. 1), and cannot explain the different boron broadening observed in the experiments as a function of W.[14] However, the I_2 concentration decreases linearly towards the surface. Therefore, one could try to explain the experimental data by assuming that I_2 interacts with B and controls its diffusivity. Now we analyze the possibilities and implications of such an assumption. As a first requirement, we realize that the equilibrium boron diffusion mechanism (through B_i) has to be maintained in order to explain B diffusion under such conditions (where there is a negligible I_2 concentration, as shown below).

One way by which mobile I_2 could contribute to B diffusion is by generating B_i through the reaction

$$I_2 + B \rightarrow BI_2 \rightarrow B_i + I,$$

(Fig. 2). Another is by assuming BI_2 itself to be mobile. Let us consider the first alternative. In order to have BI_2 break into B_i+I instead of returning to I_2+B we require (see Fig. 2)

$$E_b(B_i) - E_m(B_i) > E_b(I_2) - E_m(I_2),$$

where E_b represents the binding energy. Typical values are $E_b(B_i) = 0.9$ eV, $E_m(B_i) = 0.6$ eV,[16] $E_b(I_2) = 2$ eV, $E_m(I_2) = 0.5$ eV. Therefore, BI_2 is most likely expected to revert back to I_2+B rather than to B_i+I.

Next we discuss the second alternative, namely the assumption that BI_2 itself is mobile. To our knowledge, no study about the possible mobility of BI_2 or B_2I_2 has been reported to date. But, at least in principle one should consider them as suspect candidates to be immobile since I+I produce a mobile cluster (I_2) and the interstitial boron atom (B_i) is even more mobile than the interstitial silicon atom (I). The three of them (I_2, BI_2, B_2I_2) consist of two extra atoms (silicon or boron) within the silicon lattice. Coming back to the explanation through a mobile BI_2, to be able to explain the I-source depth dependence in TED experiments, the BI_2 flux has to be dominant over the B_i flux. This implies
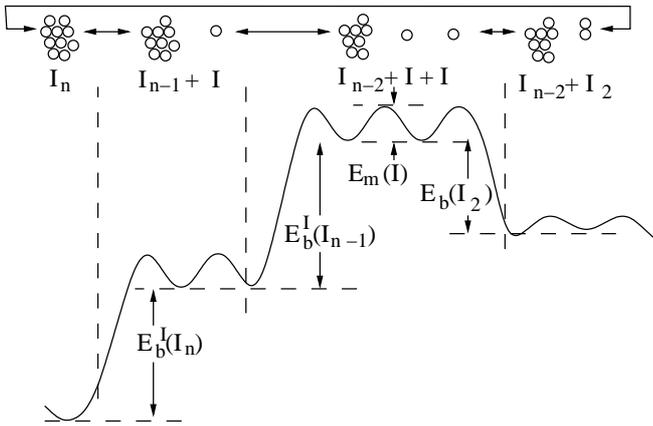
FIG. 3: Energy diagram that shows the energies involved in the emission and capture of I and I_2 from a cluster.

that

$$E_f^{TED}(BI_2) + E_m(BI_2) < E_f^{TED}(B_i) + E_m(B_i)$$

where $E_f^{TED}(B_i) = E_b^I(\{311\}) - E_b(B_i)$ and $E_f^{TED}(BI_2) = 2E_b^{311}(I) - E_{diss}(BI_2)$. E_{diss} stands for dissociation energy and $E_b^I(\{311\})$ is the binding energy of one I to a {311} defect (see Fig. 3). Commonly accepted values are $E_b^I(\{311\}) = 2.7$ eV.[1] Even assuming $E_m(BI_2) = 0.2$ eV (minimum expected value) the $E_{diss}(BI_2)$ has to be greater than 3.1 eV (to be compared to the calculated 2-2.5 eV, Ref. 17). Besides, under equilibrium conditions (negligible presence of I_2) the boron flux has to result from the B_i component and this translates into

$$E_{diss}(BI_2) < E_f(I) + E_m(BI_2) + E_b(B_i) - E_m(B_i),$$

where $E_f(I)$ is the I formation energy from the surface. This implies $E_{diss}(BI_2) < 4$ eV. Therefore, to safely fulfill both conditions $E_{diss}(BI_2)$ is constrained to values between 3.4 and 3.7 eV, approximately. A further constraint evidenced by our simulations is the necessity to prevent very long B diffusion hops, which yield exponential rather than the typical Gaussian diffusion profiles (Fig. 1) observed in experiments.[14] With mobile BI_2 these long boron diffusion hops arise from a too slow $BI_2 \rightarrow B + I_2$ break up. This requirement, together with an $E_{diss}(BI_2)$ between 3.4 and 3.7 eV, defines an acceptable window for $E_b(I_2)$ from 2.7 to 2.8 eV, well outside the calculated allowed range of 1.8 to 2.2 eV. Also, $E_b(I_2) = 2.7$ to 2.8 eV corresponds to a {311} defect activation energy of (Fig. 3) $E_b(I_{n+2}) + E_b(I_{n+1}) - Eb(I_2) + E_m(I_2) \approx 2.9$ eV in contrast with the measured value of 3.6 eV.[1] Thus, even if BI_2 were mobile, the expected BI_2 flux towards the surface, much smaller than the expected B_i flux, would not account for the experimental observations.[14]

In summary, we are led to conclude that any attempt to attribute the different surface recombination length observed in OED and TED to different recombination lengths for I and for I_2, is incompatible with other theoretical and experimental constraints. In addition, there are indications that the OED recombination length is different depending on the oxidation technique (e.g. oxynitrides[18,19]). Thus, different chemical effects seem to influence the surface recombination behavior. In consequence, at present we cannot provide a comprehensive, physically based explanation for the apparently different self-interstitial recombination length under TED and OED conditions.

III. PROPOSED MODEL

Having discarded some alternative models we now propose a comprehensive model that complies with all of the above mentioned theoretical and experimental constraints.

The surface, as a conclusion from the preceding analysis, has to be a good sink for the single I (at least under TED conditions) as this is necessary to explain the observed boron broadening. Regarding the I_2 surface recombination length, we are not aware of any particular constraint up to date. However, we have done MD simulations using Tersoff[20] and Stillinger-Weber potentials and they reveal the same behavior for I and for I_2 interacting with the silicon free surface, namely, the surface behaves as a good sink (unlike the simple conceptual model suggested by Hu[21]). In our model the surface is allowed to emit I_2, to fulfill microscopic reversibility, but the activation energy is so high (as calculated below) that no I_2 emission is observed from the surface. Thus, the overall model becomes very simple: a mobile I_2 with the parameters predicted by theoretical calculations can be included, but under TED conditions the boron transport is still controlled mainly by the single I and the surface is a good I sink. We assume that I_2 can interact with small interstitial clusters, influencing their ripening process. The activation energy for I_2 emission from a cluster of size n can be calculated from the single I binding energy to the cluster, $E_b^I(I_n)$ as (see Fig. 3)

$$E_b^I(I_n) + E_b^I(I_{n-1}) - E_b(I_2) + E_m(I_2).$$

Using reversibility conditions it can be shown that the I_2 emission prefactor from the clusters is given by

$$\frac{2V_{cap}(I)D_{0,em}^I(I_n)D_{0,em}^I(I_{n-1})D_{0,m}(I_2)}{V_{cap}(I_{n-1})D_{0,m}(I)D_{0,break}(I_2)},$$

where $V_{cap}(I_n)$ is the cluster capture volume, $D_{0,em}^I(I_n)$ the I emission prefactor for size n, $D_{0,m}(I_2)$ the di-interstitial migration prefactor, $D_{0,m}(I)$ the I migration prefactor, and $D_{0,break}(I_2)$ the di-interstitial break up prefactor.

We assume that there is no I_2 interaction with {311} defects because the interaction is energetically less favorable based on the relative structure rearrangement required for the capture into "chain-like" defects, and also
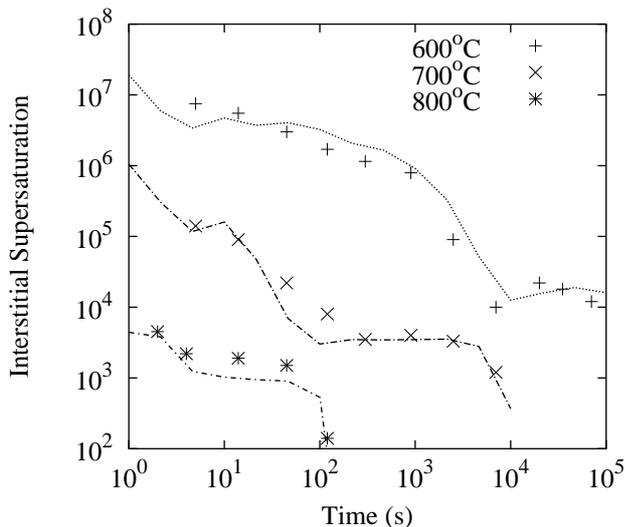
FIG. 4: Interstitial supersaturation as a function of time for three different annealing temperatures after 40 keV, $2 \times 10^{13} \mathrm{cm}^{-2}$ self implantation. Symbols correspond to experimental values taken from Ref. 22. Lines represent simulations using the model presented in this work, that includes mobile I_2.
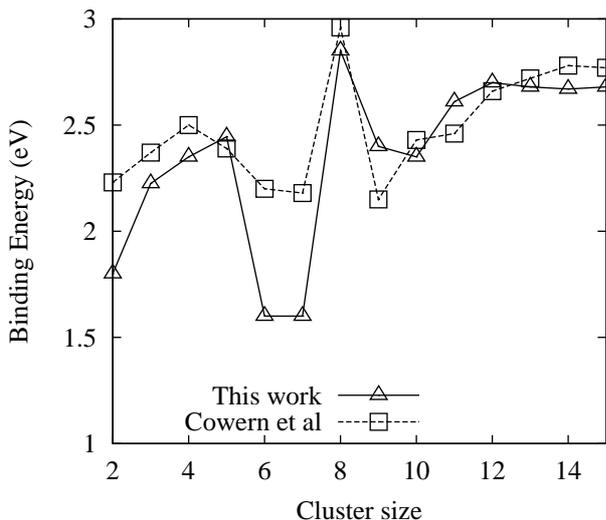
FIG. 5: Binding energies of interstitial clusters, $E_b^I(I_n)$, as a function of their sizes. Squares: previous model including only mobile I.[22] Triangles: present model.

because it is not necessary for the {311} defects dissolution (it can be done through single I emission).

We have tested the resulting model, that includes the mobile I_2, through the simulation of the measured time evolution of the I supersaturation (TED measurement[22]) and the {311} defects dissolution as determined from direct transmission electron microscopy (TEM) measurements.[1] To perform the simulations, we use MARLOWE[23] to generate the implantation cascades and the atomistic kinetic Monte Carlo (kMC)

code DADOS[12] to simulate the subsequent annealing. Fig. 4 shows the experimental time evolution of the I supersaturation (self-interstitial concentration relative to that of equilibrium conditions, C_I/C_{I^*} at different temperatures[22]) inferred from the boron diffusion enhancement induced by a post-implant anneal. Simulated results, which are also displayed in the same graph, are in good agreement with the experiments. It is important to point out that, in comparing our simulations with the TED measurements,[22] we have assumed that the boron broadening directly provides a measure of the I supersaturation. This is so because, as discussed above, boron diffusion is mainly through B_i, which is formed from I+B. In this way the presence of I_2 does not increase the B_i concentration, which is still assumed to be the main responsible for boron diffusion.

The same set of binding energies for I_n was used in all the simulations and is plotted in Fig. 5, together with the average of the three sets (one for each temperature) used in Ref. 22. The most remarkable difference is the weak binding energy of cluster sizes 6 and 7, that act as a bottleneck for cluster growth. The presence of a bottleneck is necessary to obtain the stepwise shape in the supersaturation time evolution, otherwise the mobile I_2 is capable of bridging the bottleneck of cluster size 8, precipitating the formation of {311}. With our assumption of I_2 emission and capture from the small clusters, a bottleneck of two consecutive, relatively unstable cluster sizes is needed. Following Ref. 22 we have supposed that the two consecutive, less stable cluster sizes are 6 and 7. As it can be seen in Fig. 5, we need larger energy oscillations, more in agreement with the oscillation amplitude of the theoretical values[8] which also exhibit two consecutive, less stable clusters at sizes 6 and 7. Our simulations are very sensitive to the I_2 binding energy (used as a fitting parameter) and yield a value of $E_b(I_2) = 1.8$ eV. This is in good agreement with LDA calculations,[8] but is somehow lower than values obtained with TBMD (2.2 eV).[5]

As another test, Fig. 6 shows the total number of interstitials contained in {311} clusters after implantation, as function of annealing time. The experimental data are from Ref. 24 and the simulations have been performed using the same parameters as for Fig. 4. For I_n clusters with $n > 15$, binding energies are assumed to tend asymptotically to $E_b^I(\{311\}) = 2.7$ eV, that best fits the dissolution curves. This binding energy corresponds to a {311} cluster activation energy of 3.7 eV, in good agreement with 3.6 eV from Ref. 24.

The I_2 contribution to self-diffusion is negligible in equilibrium with the parameter values of this model. Indeed, the product $D_{I_2}C_{I_2}^*$, D_{I_2} being the I_2 diffusivity and $C_{I_2}^*$ its equilibrium concentration, has an activation energy of

$$2E_f(I) + E_m(I_2) - E_b(I_2) = 6.7\mathrm{eV}.$$

This energy is much higher than the ~ 4.9 eV measured in metal-diffusion[25] experiments. Therefore $D_{I_2}C_{I_2}^*$ is
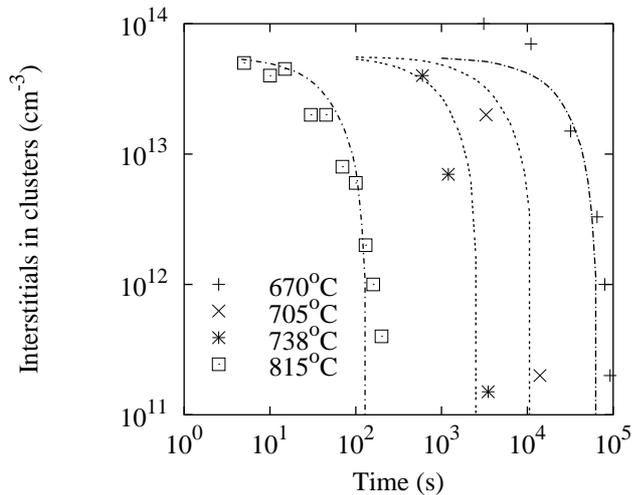
FIG. 6: Self-interstitial concentration in clusters as a function of annealing time and temperature, after a 40 keV, 5×10^{13} cm^{-2}, Si implant. Symbols are experimental data from Ref. 1. Lines represent the simulations using the model presented here, which includes mobile I_2.

much lower than the dominant $D_I C_I^*$ contribution, corresponding to single interstitials. In contrast, in local quasi-equilibrium conditions, I_2 effects will be more important for high I concentrations because the I_2 supersaturation ($C_{I_2}/C_{I_2}^*$) and I supersaturation are related by $C_{I_2}/C_{I_2}^* = (C_I/C_I^*)^2$. In consequence, the role of I_2 (e.g. in possible reactions with B_mI_n clusters) will be much more prominent in TED than in OED conditions.

It is worth pointing out that the inclusion of I_2 mobility requires a revision of not only the energy parameters for self-interstitial clusters I_n, as we have done so far, but also those for the clusters formed by interstitials and dopants. In particular, the B_mI_n clusters are thought to play a central role in boron diffusion and electrical deactivation in high damage conditions because they immobilize active boron. These clusters nucleate only in high interstitial concentration regions. In the model for boron proposed in Ref. 26, the precursor of B_mI_n clusters is supposed to be BI_2. In our picture the formation of BI_2 via I_2+B would lead to nucleation even in low interstitial concentration regions due to the migration of

stable, mobile I_2. Therefore a revision of the boron cluster nucleation process and, in general, of the B_mI_n energy parameters is needed, but this is beyond the scope of this paper. The mobile I_2, with its high room temperature diffusivity, could also be a candidate to explain the room temperature dopant deactivation observed after a shallow damage implantation.[27]

IV. CONCLUSIONS

In conclusion, we have developed a comprehensive, physically based model that is able to reconcile the high I_2 diffusivity reported in theoretical calculations, with other theoretical and experimental constraints. We have analyzed some implications of such a new mobile species. Interstitial cluster binding energies, in particular had to be readjusted, mostly for small sizes.

However, attempts to also account for the different surface I recombination length observed in OED and TED experiments (by assigning a different surface sink efficiency for I and I_2) failed to comply with other restrictions imposed by some theoretical and experimental data.

The overall picture that emerges from this study is that the theoretically predicted mobile I_2 can be included, but it does not seem to play a critical role in boron TED simulations, at least when no boron clustering occurs: the dominant boron flux is still controlled by the single I, which sees the surface as an almost perfect sink. From the practical point of view of silicon process simulation, this means that, as far as we can conclude from the analysis presented in this work, it is not necessary to include a new species (the mobile I_2) in the conventional process simulators: the single I can be made to account for the missing mobile I_2. We should warn again that these conclusions are applicable only under the conditions investigated in this study, i.e., when no boron clustering occurs. Whether the presence of mobile I_2 plays a relevant role in the boron clustering/deactivation process, still remains to be seen. Calculations of B_mI_n cluster energies as well as possible mobilities of BI_2 and B_2I_2 (two extra atoms each like the mobile I_2)[28] will help elucidate and model the mechanisms involved in such processing conditions.

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