Theoretical investigation of in situ k-restore processes for damaged ultra-low-k dielectrics

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Ultra-low-k (ULK) materials are essential for today’s production of integrated circuits (ICs). However, during the manufacturing process the ULK’s low dielectric constant (k-value) increases due to the replacement of hydrophobic species with hydrophilic groups. We investigate the use of plasma enhanced fragmented silylation precursors to repair this damage. The fragmentation of the silylation precursors octamethylcyclotetrasiloxane (OMCTS) and bis(dimethylamino)-dimethylsilane (DMADMS) and their possible repair reactions are studied using density functional theory (DFT) and molecular dynamics (MD) simulations.

I. INTRODUCTION

Gordon Moore predicted that the number of transistors per integrated circuit (IC) would double biennially [1]. To achieve this goal today’s microelectronic industry uses materials with low dielectric constants (k-value): ultra-low-k (ULK) materials. Pores and hydrophobic species in the ULK materials are the reason for their low k-value. However, the hydrophobic species, in particular methyl groups, are prone to be replaced by hydrophilic, polar groups during the manufacturing process due to active radicals and highly energetic vacuum-ultraviolet photons [2]. The substitution of Si-CH$_3$ bonds with Si-H bonds (H-damage) leads to an increased k-value. In air contact, this H-damage can further react to an OH-damage by forming Si-OH bonds [3] or lead to adsorbed water molecules [4].

Three repair mechanisms to re-decrease the k-value were suggested in literature [2]: The UV assisted thermal curing, the silylation process and the k-restore via hydrocarbon plasma. Either of the these mechanisms has its own assets and drawbacks. The UV assisted thermal curing removes the hydroxyl groups and water molecules from the material by breaking the bonds with UV radiation and high temperatures. However, in order to cure the damage completely, temperatures of about 600 – 1000 deg C are required [2]. Because of the ULK’s porous structure, this results in the compression or collapse of the material [3].

The k-restore via hydrocarbon plasma is based on methane fragments. These fragments are supposed to diffuse into the porous material to repair the damage by replacing undesired Si-OH bonds with Si-CH$_3$ bonds. Experiments showed that the fragments instead build a carbon rich layer on the surface [6], thus no repair takes place. However, the carbon rich layer can protect the ULK material from further damage.

The silylation precursors, on the other hand, replace the damaged bonds with Si-CH$_3$ bonds at low temperatures (T $<$ 300 degC). However, the size of the precursors (6-9 Å) prevents them from diffusing into deeper regions of the damaged ULK material. Therefore, the repair via silylation is limited to the surface [7].

An obvious alternative for the in-situ k-restore is the plasma fragmentation of silylation precursors, the so-called plasma repair process. This repair process is distinguished as it combines the good repair behavior of the silylation process with the good diffusion behavior of the hydrocarbon plasma, while at the same time only requiring a temperature of 80 degC [8].

In our theoretical study we analyze the reaction energies of numerous fragmentations and selected repair reactions. Based on these findings, fragmentation and reaction pathways can be identified, which are likely to occur in experiments. Finally we compare our results with the experimental investigation of Köhler et al. [5].

II. REPAIR FRAGMENTS

The combination of the advantages of both the silylation and the hydrocarbon plasma process in the plasma repair process is achieved by the plasma enhanced fragmentation of silylation precursors. For our theoretical analysis we considered eight different fragments which are shown in figure 1. They can be obtained from the silylation precursors bis(dimethylamino)-dimethylsilane (DMADMS, figure 3a) and octamethylcyclotetrasiloxane (OMCTS, figure 3b).

As can be seen in figure 2k, the silylation and plasma repair processes display an identical repair behavior. This includes the disadvantage that some silylation precursors/plasma repair fragments can only repair one damaged site, resulting in a steric hindrance for other repair processes in the close vicinity. However, the fragments from the plasma repair process are about half the size of the silylation precursors (2.5-5 Å vs. 6-9 Å) and thus can repair the deeper region of the damaged ULK materials. Further, the plasma repair process does not result in additional molecules that are a possible source for further damage if they do not evaporate from the ULK material.
Also, opposed to the silylation process, the plasma repair process can cure H-damages in addition to OH-damages. It can be deduced from figure 1 that not all repair fragments can repair both damage types. This is due to the H-repair depending on oxygen atoms, whereas the OH-repair requires the silicon atom to have at least one dangling bond. Further, if the repair fragment contains exactly one methyl group, then the fragment is prone to further damage.

III. COMPUTATIONAL DETAILS

We used both density functional theory (DFT) and molecular dynamics (MD) to investigate the fragmentations of the silylation precursors and the repair reactions of the gained repair fragments. For the DFT calculations we used Dmol\(^3\) [9, 10] as implemented in Materials Studio (Accelrys, Version 6.0) [11]. We chose the PBE functional in combination with the DNP(3.5) basis set [12]. The convergence criteria were set to \(10^{-5}\) Ha for the geometry optimizations and to \(10^{-6}\) Ha for the scf cycles. In cases of problematic convergence thermal smearing up to 0.008 Ha was activated. Because the automatic orbital cutoff value of methyl being below the value for silicon containing species, it was fixed to 4.6 Å for all calculations. The Grimme DFT-D correction was also used.

For the MD calculations we used Gulp [13] as implemented in Materials Studio (Accelrys, Version 6.0) with the ReaxFF 6.0 force field [14] [17], as well as Lammps [18] with the ReaxFF force field as parametrized by Kulkarni et. al [19]. With the former program geometry structures were optimized until a stationary point was reached. Using Lammps a dynamical calculation at a temperature close to 0 K was performed until a convergence of \(10^{-6}\) Ha was reached, followed by a minimization at 0K with a convergence criteria of \(10^{-10}\) Ha.

We compare the DFT and MD results to determine the reliability of the used force fields. This is done with the aim to study larger clusters and surfaces in future studies as such systems are too large to be handled with DFT methods. If not otherwise stated, all reaction energies were calculated for temperatures of 0 K.

IV. MODEL SYSTEM

In order to mimic the high energy of the plasma-generated fragments of the silylation precursors, we study the fragmentation reactions at a temperature of 700 deg C. We limit the studied fragmentation reactions to the ones that result in our desired plasma repair fragments from figure 1. Further, we restrict the reactions to those leading to exactly one or four repair fragments with possible closed-shell residues for the DMADMS and the OMCTS fragmentation, respectively.

We constructed a silicon oxide cluster model to investigate the effectiveness of selected repair fragments, the influence of surrounding atoms on the repair behavior and the reliability of the used force fields in comparison to DFT results. Thus, the silicon oxide cluster consists of the damaged site and two rings of surrounding silica atoms which mimic steric hindrance and stabilize the structure (see figure 2).

With a sum formula of \(\text{Si}_{86}\text{O}_{135}\text{H}_{73}\)-OH and \(\text{Si}_{86}\text{O}_{135}\text{H}_{73}\)-H for the OH- and H-damage, respectively, our cluster is at the limit of a computationally reasonable size for DFT. Therefore, to decrease the computational costs for the DFT calculations the 73 hydrogen atoms of the cluster (see figure 2), which together with the outer silica atoms (see dark blue hexagon in figure 2) are basically acting as saturating atoms and were fixed during the geometry optimizations in Dmol\(^3\). Thus the fixed boundary of the cluster is similar to the rigid structure of real ULK materials.

V. FRAGMENTATION REACTIONS

We focus our work on the fragmentation reactions of the silylation precursors DMADMS and OMCTS. The DMADMS fragmentation can only result in oxygen-free fragments. Thus, only reactions that lead to the repair...
fragment Si(CH$_3$)$_x$ and closed-shell residues were studied (figure 3a). Here, we find that among all endothermic fragmentations, the one leading to Si(CH$_3$)$_3$ is the most probable reaction path. The remaining three reactions show similar reaction energies between 3-3.5 eV. In conclusion, for DMADMS the chance to form small repair fragments which are prone to damages (SiCH$_3$) is low.

Figure 2. a) Exemplary silylation and plasma repair processes. The silylation process with DMADMS and HMDS also results in residual molecules dimethylamine (DMA) and trimethylaminosilane (TMAS) in comparison to the plasma repair process with Si(CH$_3$)$_2$ and SiO(CH$_3$)$_3$. b) the silicon oxide cluster model for the OH-damage The atoms highlighted in light blue show the OH-damage region. The hexagons on the cluster illustrate the freely optimized silica dodecagons that provide a steric hindrance (orange) and the geometrically constrained boundary silica dodecagons which stabilize the structure (dark blue).

Figure 3. Fragmentation of silylation precursors at $T = 700$ deg C from DFT calculations. a) Four different possible fragmentation reactions of DMADMS. b) Twelve different possible fragmentation reactions of OMCTS.
We restricted the studied fragmentation reactions of OMCTS to the ones that result to four repair fragments from figure 1 with possible residual molecules (figure 3b). In accordance with the DADMS fragmentation, the OMCTS fragmentation reactions are also endothermic, however they require about five times the energy of the DMADMS fragmentation reactions. This finding can be explained easily by the fact that at least four strongly polar SiO-bonds need to be broken in OMCTS, in contrast to only two SiN-bonds in DMADMS.

The energetically favored reaction for OMCTS is fragmentation VII into four SiO(CH3)2 fragments as it demands the least amount of bond breaking. Among the remaining studied fragmentation, the ones leading to at least one SiO(CH3)2 fragment or fragments with three methyl groups are preferential (see reactions I, II, III, VI, XII), regardless whether they contain an additional oxygen atom. Thus, both the DMADMS and the OMCTS fragmentation suggest that larger repair fragments are advantageous.

Based on their dominant repair fragments, OMCTS should show a better repair effect than DMADMS. This is due to the fact that Si(CH3)3 as the dominant repair fragment of DMADMS is only able to cure exactly one OH-damage while at the same time providing steric hindrance for further repair reactions in its close vicinity. OMCTS’s dominant repair fragment SiO(CH3)2, on the other hand, is able to cure both an OH- and H-damage at the same time, while leaving more space for other nearby repair reactions. Thus more repair reactions should take place with OMCTS as the plasma enhanced fragmented silylation precursor.

The fragmentation of OMCTS at T=0K was chosen as a test case for the reliability of the used MD forced fields (see figure 1). As to be expected, the MD results differ from the energies gained by DFT. However, they still agree on the favored fragmentation reaction for OMCTS (fragmentation VII). Further, both Gulp and Lammps with the Kulkarni force field have an average mean squared error of 14.9 and 15.0 eV, respectively. Excluding the large derivation of Lammps for fragmentation VIII, its average mean squared error decreases to 9.4 eV. Fragmentation VIII is also an indicator that the oxygen-oxygen interaction parameter in the Kulkarni force field needs to be optimized to obtain quantitatively correct results. In summary, it can be said that both Lammps and Gulp are nearly equally reliable when trends in the fragmentation of silylation precursors are to be studied. However, the use of both MD force fields is restricted to a qualitative analysis only.

VI. PLASMA REPAIR PROCESS

The second focus point of our study was to investigate the performance of the repair fragments and whether MD could be used for the simulation of the plasma repair process on more complex surface models. For example, to study simultaneous repair processes or to analyze the diffusion behavior of the repair fragments into a porous ULK cluster, larger model systems with dimensions of about 10 x 10 Å would be required. Such systems are too large to handled by DFT and thus MD with a well parameterized force field needs to be employed.

For this purpose we investigated the plasma repair process with MD and DFT on a silicon oxide cluster as described in the section ‘Model System’ and shown in figure 2. We restricted our studied repair reactions to those repair fragments that DMADMS and OMCTS favor during their fragmentations. We show the resulting reaction energies of the repair reactions in figures 5a) and b) for the OH- and H-repair, respectively.

The main conclusion that can be drawn about the reliability of the used MD force fields is that while Lammps with the Kulkarni force field provided the correct trends for the OMCTS fragmentation, it is not suited for studying the plasma repair process, because it unsystematically under- and overestimates the reaction energies.

Results from Gulp also differ from the DFT energies which are taken as a reference. However, Gulp still conserves the general trend of the reaction energies and thus could be used to approximately study the plasma repair process, if a large error range of up to 2 eV is taken into consideration. While this is sufficient for a first analysis of the performance of the plasma repair process on the system shown in figure 2b, an improvement of the existing force field is necessary to gain reliable results of the repair behaviors or diffusion processes for more complex systems including pores and methyl groups.

Looking at the repair reactions themselves, the results state that (nearly) all repair reactions are highly exothermic because of the reactive fragments produced in the plasma. Therefore, both damage repairs will take place when the repair fragments come into contact with the

![Figure 4. Fragmentation of OMCTS with MD and DFT. The fragmentation energies of the twelve OMCTS fragmentations from figure 3b) are obtained from MD and DFT calculations at T=0K.](image)
Figure 5. The energies of the damage repair reactions gained from Dmol³, Gulp and Lammps. a) OH-repair reactions and b) H-repair reactions.

damaged ULK material. The DFT and Gulp calculations further indicate that the repair of an H-damage is energetically more favorable than the repair of an OH-damage.

Regarding the most effective repair fragments for the OH- and H-damage, DFT and Gulp results are in agreement that these are Si(CH₃)₃/SiOCH₃ and SiO₂(CH₃)₂/SiO(CH₃)₃/SiO₂CH₃, respectively. Among these repair fragments, SiOCH₃ and SiO₂CH₃ have the disadvantage that they are prone to develop new defects (refer to figure 1). The remaining repair fragments, on the other hand, are rather large and thus will prevent other repair processes to take place in the close vicinity. This means that while the repair reactions are all strongly exothermic, not a 100% repair of the damage will be achieved due to steric hindrances and the susceptibility of the repair fragments with only one methyl group to form new defects.

If the above listed repair fragments are compared to the dominant fragments of the OMCTS and DMADMS fragmentation, then it can be seen that SiO(CH₃)₂ as the dominant repair fragment of OMCTS is one of the least effective repair fragments, while Si(CH₃)₃ as the dominant repair fragment of DMADMS is the most effective OH-damage repair fragment. However, the energetically next favored fragments of OMCTS (refer to reactions I, II, VI and XII in figure 3b) are all very effective plasma repair fragments for both the OH- and H-damage. Thus, OMCTS should still demonstrate a good repair performance, which is even better than the repair effect of DMADMS. The last assumption can be made because the reaction energy for the H-repair is over 1 eV higher than for the OH-repair, which is the only damage DMADMS can cure.

A. Comparison with ULK-fragments

In [20] we studied the repair performance of all repair fragments shown in figure 1 with identical DFT settings but with another, much smaller model system. This model system consists of small ULK-fragments (see example in figure 6), which possess only one silicon atom together with OH- and H-defects as well as saturating H atoms. In analogy to the silicon oxide cluster, a part of the ULK-fragment was fixed during geometry optimizations. Specifically, all atoms outside the in blue and pink highlighted areas in figure 1 were fixed.

In figure 6 we compare the repair reactions of this study with the results from [20]. The motivation for this comparison is the unsatisfactory performance of the MD force fields and the high numerical effort of the DFT calculations for the silicon oxide cluster. For both OH- and H-repair reactions the results with the small ULK-fragment and with the extended cluster model agree very well energetically. Thus, when assessing only the effectiveness of new repair fragments the computationally less demanding ULK-fragments can be employed. The ULK-fragment model system is sufficient to quickly and at the same time qualitatively correctly describe the repair behavior of plasma fragmented silylation precursors.

B. Comparison with Experiments

In a final step we compare our theoretical results with the experiments carried out by Köhler et al. [8]. They investigated the repair with plasma enhanced fragmented OMCTS and DMADMS, in particular the repair of surface and sidewall damages. Köhler et al. found that both fragmented silylation precursors minimize the surface damage, with OMCTS showing an improved repair performance compared to DMADMS. This is in agreement with our result that the repair of H-damages and thus oxygen-containing repair fragments possess more strongly exothermic reaction energies and thus the use of OMCTS results in a better repair effect.
With the repair of sidewall damages Köhler et al. investigated the correlation between the repair process and OMCTS-flow together with the use of the gas additives oxygen or methane. The presence of oxygen led to a highly improved repair of the damages. This can be understood by our result that only oxygen containing repair fragments yield exothermic reaction energies for the repair of H-damages. Thus, the repair of H-damages is strongly increased by the availability of oxygen.

VII. CONCLUSION

We have shown that the fragmentation of DMADMS requires less energy than the OMCTS fragmentation. However, their dominant fragmentation reactions and the resulting primary repair fragments, indicate that the plasma repair will be less effective for DMADMS in comparison to OMCTS. Further, (nearly all of) the favored fragments from the OMCTS fragmentation are very effective repair fragments for both the OH- and H-damage, while the favored repair fragment of DMADMS can only repair OH-damages. These results are in good agreement with the experimental study carried out by Köhler et al.

By comparing DFT and MD results we can conclude that for using MD to simulate the plasma repair process with larger and more realistic silicon oxide structures which include pores, the existing force fields need to be optimized. However, Gulp with the ReaxFF 6.0 force field can be used for a first investigation of the qualitative trends.

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