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| Note | |

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# Molecular dynamics simulation study on substrate temperature dependence of sputtering yields for an organic polymer under ion bombardment

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Substrate temperature dependence of sputtering yields in organic polymer etching processes has been examined with the use of molecular dynamics (MD) simulations. The simulation results indicate that structural weakness arising from high substrate temperatures alone is not sufficient to account for the experimentally observed strong dependence of sputtering yields on substrate temperatures. In other words, thermal desorption is likely to increase significantly at high substrate temperatures in reactive ion etching processes of organic polymers. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2433132]

Reduction of dielectric constants of insulating materials in integrated circuits (ICs) is one of the major challenges in the semiconductor industry.[1] As low dielectric constant (i.e., low-$k$) materials, organic polymers have been widely examined for such applications.[2–4] In typical dual damascene processes,[5–7] insulators are etched by plasmas to form trenches and holes (i.e., vias), into which highly conductive metal is deposited to form interconnect wires.[8,9] For plasma etching of organic polymers, $N_2/H_2$ and/or $NH_3$ gases are often used as source gases. Organic polymer etching rates in reactive ion etching processes are known to depend sensitively on the substrate temperature.[3,10,11] In this work we attempt to clarify the mechanism of such strong substrate temperature dependence of organic polymer etching rates, using molecular dynamics (MD) simulations.

In general, one may expect there are two major mechanisms that can possibly cause the increase of sputtering yields as the substrate temperature. One is structural weakness of organic polymers at higher temperatures due to stronger thermal oscillations. It affects a fast sputtering process, where atoms/molecules that are less firmly bound to the surface due to the high temperature tend to be removed by and immediately after the impact of each injected species. The other is increased thermal desorption at high-substrate temperatures. Thermal desorption is a slow thermodynamical process, where some surface atoms/molecules occasionally gain sufficiently high energy from thermal fluctuations that overcome the potential energy that binds them to the surface. With MD simulations, the former mechanism can be well investigated as sputtering (i.e., removal) of surface atoms/molecules takes place soon after each ion impact. On the other hand, the latter process, i.e., thermal desorption cannot be simulated by MD simulations in a straightforward manner due to its extremely long time scale.

In Ref. 12, etching mechanisms of an organic polymer poly (1,4-phenylene), which is also called polyparaphenylene (PPP), by hydrocarbon radical beam injections are studied with MD simulations. It was found that hydrogen atoms chemically break carbon bonds in the substrate whereas higher momenta carried by carbon atoms sputter surface atoms that are weakly bound to the surface. In the MD simulations of Ref. 12, the substrate temperature was set at room temperature and the thermal desorption process was neglected. Here we examine similar etching processes at elevated substrate temperatures, using the same MD simulation techniques. The interatomic potential functions for hydrogen and carbon covalent bonds are those proposed by Brenner.[13] The two-body van der Waals interaction[14] is also included.

Figure 1 shows the initial substrates of PPP at (a) 300 K and (b) 600 K. As in Ref. 12, PPP chains are laid almost in parallel in the $x$ direction of the simulation box. The periodic boundary conditions are imposed in the horizontal directions. It is seen that the substrate is more expanded by thermal oscillation at a higher temperature. The horizontal cross section of the simulation box is approximately 4 $nm^2$. As etching proceeds, more PPP chains are added from the bottom, which emulates an infinitely deep substrate. Here we present simulation results for the substrate temperatures of 300, 450, and 600 K. The substrate is subject to bombardment of C or $CH_4$ at the translational kinetic energy of 50 eV with the vertical injection angle (i.e., in the negative $z$ direction in Fig. 1). All atoms are assumed to be charge neutral and we interpret highly energetic impinging species as beam ions.

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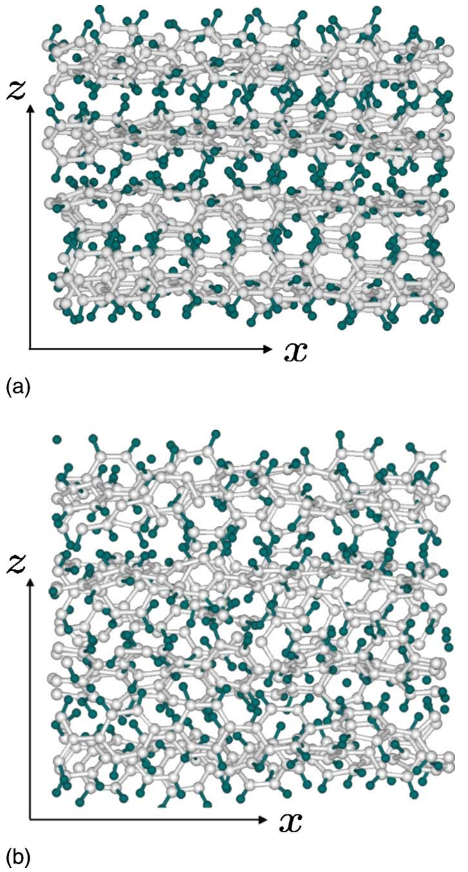

FIG. 1. Horizontal views of the initial PPP substrates at (a) 300 K and (b) 600 K. The dark and white spheres represent hydrogen and carbon atoms. The bond between two C atoms is depicted by a white bar and that between C and H atoms by a dark bar.

The MD simulation is performed under conditions of constant total energy (i.e., microcanonical conditions) for 1.6 ps in the case of 300 K and for 2.4 ps in both 450 and 600 K cases after each injection. Before the next injection, the substrate is rapidly cooled to the preset substrate temperature (in 0.4 ps in the 300 K case and in 0.6 ps in the 450 K/600 K cases) and the same simulation cycle is repeated for about 1000 times, which corresponds to the dose (i.e., fluence) of $2.45 \times 10^{16}$ cm$^{-2}$.

For more details of the simulation method as well as simulation results at 300 K, the reader is referred to Ref. 12.

First we simulated single C atom injections into a PPP substrate at 300, 450, and 600 K substrate temperatures. In all cases, carbon deposition was observed and the deposition rate was found to be independent of the substrate temperature.

As to $CH_4$ injections, the net erosion yields for H and C atoms obtained from MD simulations are given by the solid and dashed curves as functions of the injection dose in Fig. 2. As in Ref. 12, the net erosion yield $Y_\alpha$ of species $\alpha$ is defined as $Y_\alpha = Y_\alpha^s - I_\alpha$, where $Y_\alpha^s$ is the sputtering yield for $\alpha$ atoms, i.e., the number of $\alpha$ atoms removed or reflected from the surface per injection and $I_\alpha$ is the number of $\alpha$ atoms that reach the surface as the incoming species per injection, i.e., $I_C = 1$ and $I_H = 4$ in the case of $CH_4$ injections. Obviously, $Y_\alpha > 0 (Y_\alpha < 0)$ means net removal of $\alpha$ species from (accumulation of $\alpha$ species in) the substrate. The net erosion yield at a specific dose in Fig. 2 is that averaged over $4.8 \times 10^{15}$ cm$^{-2}$ of injections around the dose value. As in Ref. 12, the net erosion yields given in Fig. 2 were obtained from the average of five independent MD simulations with different sequences of $CH_4$ injections. It is clearly seen in Fig. 2, both $Y_C$ and $Y_H$ increase more rapidly and saturate at higher average values at higher temperatures. The systems may be viewed to have reached almost steady state after around the dose of $11 \times 10^{15}$ cm$^{-2}$. Therefore we have averaged $Y_C$ and $Y_H$ over the dose from $1.1 \times 10^{16}$ to $2.4 \times 10^{16}$ cm$^{-2}$. shown in Fig. 2 and plot them as functions of the substrate temperature in Fig. 3. Here the error bar represents the standard deviation of the level of yield fluctuation over the same dose also shown in Fig. 2. It is clearly seen that the net erosion yields (and therefore the sputtering yields) increase with the substrate temperature. We have also observed that the yields of major sputtered species such as H, $H_2$, and $CH_3$ hardly depend on the substrate temperature and almost the same as those at the substrate temperature of 300 K given in Ref. 12.

The temperature dependence of sputtering yields given in Fig. 3 is, however, significantly weaker than those observed in typical experiments. In many reactive ion etching processes of organic polymers, much stronger substrate temperature dependence has been observed. For example, it is reported in Ref. 11 that the etch rate of parylene-N increases more than ten times when the substrate temperature increases from 373 to 523 K. Our simulation results given above indi-

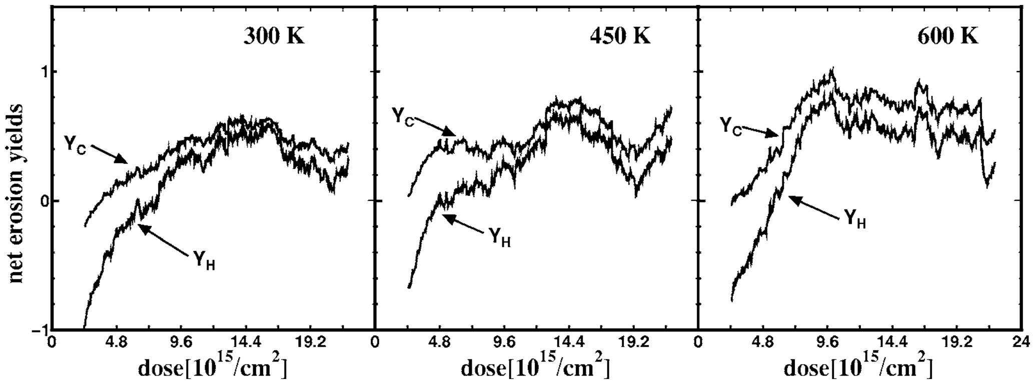

FIG. 2. The net erosion yields $Y_H$ and $Y_C$ under $CH_4$ injections into PPP substrates as functions of injection dose for substrate temperatures of 300, 450, and 600 K.

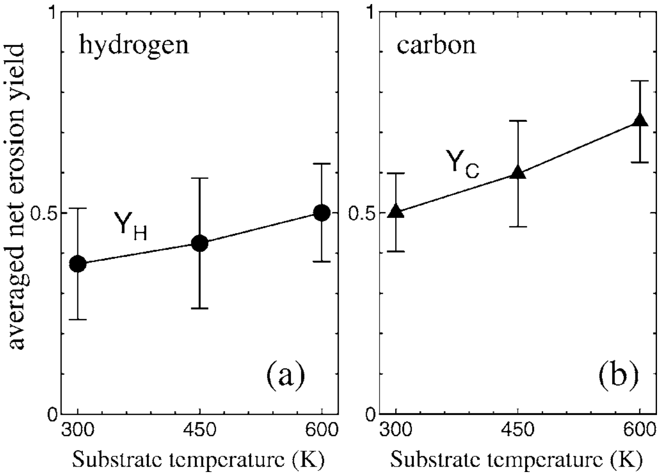

FIG. 3. The net erosion yields (a) $Y_H$ and (b) $Y_C$ in steady state under $CH_4$ injections into PPP substrates as functions of the substrate temperature. The error bar represents the standard deviation of the fluctuation level.

cate that such strong substrate temperature dependence cannot be explained by structural weakness caused by thermal oscillations of substrate atoms.

There may be a few possible reasons to account for such strong temperature dependence of sputtering yields in organic polymer etching. For example, in plasma etching experiments, a high-substrate temperature also heats the gas right above the substrate and the chemical compositions of reactive gas may significantly change as the substrate temperature increases. In our MD simulations, we only inject single species (i.e., $CH_4$ in the case presented here), so this effect is not taken into account. In oxygen beam experiments in Ref. 11, this effect may also be negligible.

Another possibility is the increase of thermal desorption of surface atoms/molecules at a high temperature. As mentioned earlier, it is a slow thermal process, where, in rare occasions, some surface atoms/molecules gain an energy from thermal fluctuations that is higher than their binding potential energy and leave the surface. Clearly MD simulations cannot simulate such slow physical phenomena directly and therefore thermal desorption is neglected in our study. Structural weakness of the substrate at a high temperature combined with ion bombardment may create many atoms and molecules that are weakly bound to the surface via, e.g., van der Waals interactions.

Indeed, in our MD simulations, we have observed that, at a high-substrate temperature, many such atoms and atomic clusters remain to be weakly bound to the bulk substrate (by van der Waals attractive interactions) at the end of each microcanonical simulation period for a single injection. As mentioned earlier, this period was set to be 1.6 or 2.4 ps, depending on the substrate temperature. We have confirmed that if this period were set shorter, significantly more weakly bound species could remain on the substrate surface. On the other hand, when the period was set slightly longer (the length of which was limited by practical computation time), the number of weakly bound species that remained on the substrate surface was confirmed not to change substantially. The fact that we need at least 2.4 ps, rather than 1.6 ps, for the period in the cases of higher-substrate temperatures indicates that, at higher substrate temperatures, more weakly bound species are present on the substrate surface and it takes longer for all such species that are about to leave the surface to actually leave. Therefore, at high-substrate temperatures, we expect that, if we could simulate the dynamics of the system for a significantly longer period than 2.4 ps, a large number of weakly bound species (especially those of smaller molecular sizes) could desorb due to thermal fluctuations. In other words, the thermal desorption process is likely to play an important role in accounting for the strong substrate-temperature dependence of (time averaged) sputtering yields.

In summary, MD simulations have been carried out for hydrocarbon cluster injections into a PPP substrate under different substrate temperatures. In the case of $CH_4$ injections at 50 eV, we observed the increase of sputtering yields with the substrate temperature, but the numerically obtained rate of increase is much smaller than what is expected from various experimental observations. Since slow thermal desorption processes are neglected in the MD simulations and we have observed many atoms and atomic clusters weakly bound to the substrate surface by van der Waals interactions during MD simulations, we conjecture that increased thermal desorption, rather than direct sputtering due to collisions by energetic ion bombardment, at high-substrate temperatures accounts for the strong dependence of etching rate on the substrate temperature during reactive ion etching processes of organic polymers.

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