Chemical sputtering of carbon films by argon ions and molecular oxygen at cryogenic temperatures

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The experiments demonstrate the existence of a synergistic interaction of molecular oxygen and energetic ions with amorphous carbon leading to enhanced erosion; although the samples, amorphous hydrogenated carbon films, are not gasified by O_2 at room temperature, additional ion bombardment at the same temperature leads to erosion rates that drastically exceed those of physical sputtering. Investigation of the temperature dependence from 400 down to 113 K shows that the erosion rate increases with decreasing temperature.

Exposure to an oxygen plasma is a standard approach for the etching of carbon-based thin films which provides high rates. Examples of applications are patterning processes in microelectronics fabrication [1–3], the removal of diffusion-barrier carbon coatings on polyethylene terephthalate bottles prior to recycling [4], and the cleaning of optical components in synchrotron beamlines [5]. More recently it has also attracted considerable attention for the removal of redeposited hydrocarbon films in magnetic-confinement nuclear fusion experiments [6–12].

In the etching process, CO, CO_2, as well as—in case of hydrogen in the film—H_2O and H_2 are formed as volatile erosion products [13]. The underlying microscopic mechanisms leading to the formation of these volatile species are manifold, as the surface is bombarded by a combination of neutral O_2 and oxygen ions (O^+, O_2^+, O_3^+), as well as the radical species O and O_3.

Neutral oxygen molecules alone lead to combustion of carbon at elevated temperatures. For amorphous hydrocarbon films (a-C:H), combustion starts above 500–600 K [14, 15]. The thermal oxygen radicals, atomic oxygen [16] and ozone [17], exhibit much higher reactivity at moderate temperatures, and there is indication that their reactivity toward a-C:H is still significant at room temperature. Bombardment of carbon with an oxygen ion beam leads to what is known as chemical sputtering or reactive ion etching [18–20]; in addition to physical sputtering the ions react chemically at the end of their range and form CO, CO_2, and H_2O, leading to highly enhanced sputtering yields and significantly lower threshold energies.

In the case of an oxygen plasma, where all the mentioned species impinge simultaneously on the film surface, mutual interactions between these species are to be expected. Such synergistic interactions are also known from other systems such as silicon etching in fluorine-containing plasmas [21] or the etching of a-C:H by thermal atomic hydrogen plus noble gas ion bombardment [22, 23]. Landkammer *et al.* [24] and Jacob *et al.* [7] have investigated the erosion of a-C:H in oxygen electron-cyclotron-resonance plasmas. The erosion rate shows a weak temperature dependence and increases strongly with ion energy. These two dependences make it clear that both thermally activated chemical reactions and ion-collisional effects play a role. Concerning the latter it was shown by using different mixtures of noble gases and oxygen for the plasma that it does not principally matter which ion species produces the damage [13]. In summary, Landkammer [13] concluded that the dominant mechanism of oxygen plasma erosion is a two step process in which ion bombardment induces defects at which thermal oxygen species can chemically react to form H_2O, CO, or CO_2.

The question thus arises whether thermal molecular oxygen contributes to this synergistic erosion or if the more reactive but usually less abundant O or O_3 are required. To answer this question, we have studied the erosion of a-C:H by combined bombardment with thermal, molecular oxygen and chemically nonreactive Ar^+ ions with energies of 50 and 400 eV, respectively.

The experiments were performed in the setup MAJESTIX, which is described in detail in [25]. A hard a-C:H film is deposited on a silicon substrate in a preparation chamber and then transferred *in vacuo* to the experiment chamber. A mass-selected Ar^+ ion beam is produced by an ion gun and focused on the center of the sample. Molecular oxygen is supplied to the chamber by a constant gas flow while the chamber is continuously pumped. The O_2 flux density onto the substrate is calculated from the resulting oxygen partial pressure. Variation of the pressure is achieved by varying the O_2 flow with a pressure-controlled thermovalve. The temperature of the substrate is controlled by either heating the substrate resistively, cooling the whole substrate holder with cold nitrogen gas, or both simultaneously. The temperature is measured with a thermocouple on the sample surface. In cooling mode, temperatures down to ≈ 110 K are feasible. Time-resolved measurement of the film thickness is achieved by *in situ* ellipsometry. This sensitive technique allows to measure film thickness changes of below one monolayer and rates of less than 10^{10} C atoms $cm^{-2} s^{-1}$, $\approx 10^{-6}$ nm/s.

Figure 1 shows the erosion yield, i. e., the number of car-
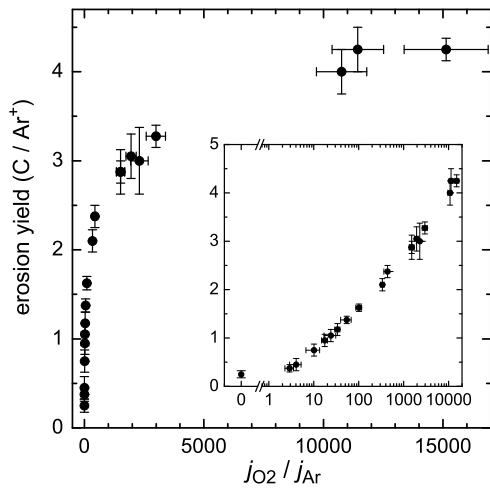
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FIG. 1: Dependence of the erosion yield (removed C per incident Ar^+) on the ratio j_{O_2}/j_{Ar^+} at a sample temperature of 300 K. The ion energy was 400 eV and the ion flux density was constant at $4 \times 10^{12}\,cm^{-2}\,s^{-1}$.

FIG. 2: Dependence of the erosion yield (removed C per incident Ar^+) on surface temperature. The ion and O_2 flux densities were constant at 4×10^{12} and $1.1 \times 10^{16}\,cm^{-2}\,s^{-1}$, respectively. The lines are guides to the eyes.

bon atoms removed per incident Ar^+ ion, as a function of the neutral-to-ion flux ratio j_{O_2}/j_{Ar^+}. The ion energy is 400 eV and the ion flux density is constant at $4 \times 10^{12}\,cm^{-2}\,s^{-1}$ while the flux density of oxygen is varied. The sample temperature is 300 K. At $j_{O_2}/j_{Ar^+} = 0$, erosion is entirely driven by physical sputtering with a yield of 0.25. As soon as a certain O_2 flux is added, the erosion rate begins to increase rapidly. At $j_{O_2}/j_{Ar^+} = 4$, the yield is already 0.45, and at the highest investigated flux ratio of 1.14×10^4, the yield reaches more than four removed carbon atoms per ion. For comparison, the maximum physical sputtering yield of hard a-C:H under Ar^+ bombardment is ≈ 1.2 at 15 keV, as predicted by TRIM.SP [26] simulations. The linear presentation of the data in Fig. 1 shows a slower rise of the yield with increasing flux ratio, indicating that the ion flux starts limiting the erosion rate.

The observed enhancement of the erosion rate over physical sputtering in the presence of molecular oxygen is a clear indication that the oxygen molecules react chemically with the surface if it is bombarded by ions. The involvement of chemical reactions makes an investigation of the temperature dependence very desirable. At elevated temperatures, O_2 is known to oxidize and gasify a-C:H without the involvement of ion bombardment. It therefore seems especially interesting to investigate the synergistic erosion process below room temperature.

Figure 2 shows temperature-dependent erosion yields at two different ion energies of 50 and 400 eV and at a constant flux ratio of $j_{O_2}/j_{Ar^+} \approx 3000$. Surprisingly, the yield increases toward lower temperatures in the whole investigated range from 415 to 113 K. Additionally, the yields at the higher ion energy are higher, which can be ascribed to the more effective damage production.
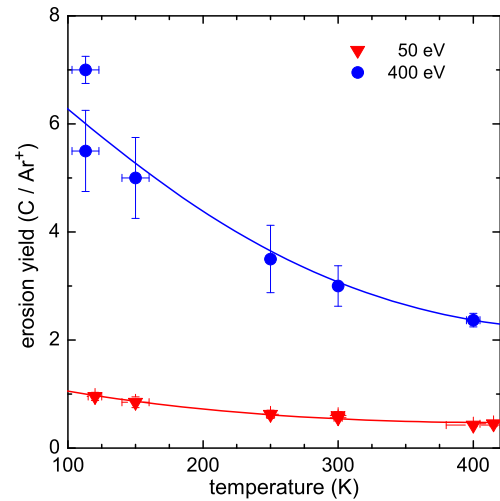
The existence of the ion/O_2 synergism in the erosion of carbon materials was proven earlier by Vietzke *et al.* [27], who investigated graphite erosion under 5 keV Ar^+ ion bombardment in a background of thermal oxygen. A quadrupole mass spectrometer was used to detect the released species and showed CO production in the whole investigated temperature range between 300 and 1500 K. In an analogous fashion to our experiments, the CO signal increased with decreasing temperature between 800 and 300 K. The difference in the temperature below which the increase is observed might be due to the different sample materials, a-C:H and graphite, respectively.

The observed synergism recalls another synergism in a-C:H erosion, namely, that between ion bombardment and atomic hydrogen [22, 23, 28–30]. In this case, the proposed explanation [23] was that ion bombardment creates dangling bonds at and below the surface which become passivated by H. By repeated such events hydrocarbon molecules are formed which leave the surface. In principle the synergism between ions and O_2 could be explained by a similar mechanism. It is worth noting, however, that, whereas in the hydrogen case the atomic radical is required, in the oxygen case the O_2 molecule provides sufficient reactivity. The mechanism in the hydrogen-plus-ions case, however, hardly provides an explanation for the low-temperature enhancement, and indeed no such increased erosion at low temperature was found in corresponding experiments with Ar^+/H [31].

A similar increase of the erosion rate with decreasing temperature was found for the chemical sputtering of silicon with noble gas ions and fluorine species [32, 33]. A difference compared with our case is, however, that here the chemically reactive precursor, either F atoms or XeF_2, leads

to spontaneous etching (without ion bombardment) already below room temperature. While the spontaneous etch rate due to F atoms decreases in the temperature range from 300 to 77 K [32], it increases below 300 K in the case of XeF_2. The temperature dependence below approximately 300 K for both chemical sputtering with Ar^+/XeF_2 and spontaneous etching with XeF_2 was explained in terms of a temperature-dependent steady state physisorbed XeF_2 coverage [34, 35]; increasing temperature leads to an increasing desorption rate of XeF_2 which is bound to the surface with $\approx 0.03 \text{eV}$. The rate of the ion-induced chemical erosion reaction is proportional to the XeF_2 coverage and hence decreases with increasing temperature.

It seems reasonable to assume a similar mechanism for chemical sputtering of a-C:H by Ar^+/O_2: Oxygen molecules adsorb at the surface without a barrier and thus with a temperature-independent rate. This adsorption is counteracted by thermal desorption, hence leading to a decreasing oxygen coverage of the surface with increasing T. Ion bombardment induces reactions between the adsorbed oxygen species and the a-C:H film whereby volatile carbon oxides and water are formed. The rate increases with ion energy due to increasing damage production and with increasing oxygen flux density due to a shift of the steady state coverage toward higher coverages, thus qualitatively explaining the experimentally observed energy and flux dependence. It should be noted that this mechanism implies that the erosion yield depends explicitly on the oxygen flux density and not only on the flux ratio.

In summary, we have unambiguously observed a synergism between thermal oxygen molecules and energetic Ar^+ ions in the erosion of a-C:H films; while O_2 alone does not erode a-C:H in the investigated temperature range, its presence during Ar^+ ion bombardment leads to an enhancement of the sputtering rate of more than an order of magnitude compared to physical sputtering. The erosion yield was found to increase with the neutral-to-ion flux ratio as well as with ion energy. Temperature-dependent measurements revealed that the yield increases with decreasing temperature in the range of 400–110 K. A reasonable explanation for this phenomenon is the buildup of a temperature-dependent oxygen coverage as a precursor for ion-induced volatile oxide formation.

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