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 gas ion bombardment [22, 23]. Landkammer et al. [24] 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 H2O, CO, or CO2.

The question thus arises whether thermal molecular oxygen contributes to this synergistic erosion or if the more reactive but usually less abundant O or O2 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 O2 flux density onto the substrate is calculated from the resulting oxygen partial pressure. Variation of the pressure is achieved by varying the O2 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 1010 C atoms cm−2 s−1, ≈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 \(4 \times 10^{12}\) and \(1.1 \times 10^{12}\) cm\(^{-2}\) s\(^{-1}\), respectively. The lines are guides to the eyes.

Carbon 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 \(1.14 \times 10^4\), 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 \(\approx 1.2\) 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 an activation energy of 0.03 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.