

Chemical sputtering of a-C:H films by simultaneous exposure to energetic Ar⁺ ions and water vapor

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Abstract. Amorphous hydrocarbon films (a-C:H) were exposed to a beam of 800 eV Ar⁺ ions. The temperature of the films was varied between 110 and 800 K. When backfilling the chamber with water vapor during ion bombardment there is a marked increase of the erosion rate at and below 200 K, while there is no influence on the erosion rate at room temperature and above. We explain the observed synergism by an ion-induced reaction between adsorbed water molecules and the film surface in which volatile erosion products are formed.

1. Introduction

Chemical sputtering is a process in which bombardment by energetic and chemically reactive species leads to an erosion rate which exceeds the sum of the erosion rate due to the chemically reactive species at thermal energies and the rate expected for pure physical sputtering due to the energetic species [1]. The kinetic energy and chemical reactivity can either be supplied by a single species or by two separate beams, one of energetic, non-reactive and one of chemically reactive species.

Chemical sputtering of (hydro-) carbon solids was, e. g., observed due to bombardment with hydrogen ions [2, 3, 4], nitrogen ions [5, 6], oxygen ions [7], and by combined exposure to noble gas ions and thermal hydrogen atoms [8, 9].

More recently, we have reported on the chemical sputtering by simultaneous bombardment with 400 eV Ar⁺ ions and thermal molecular oxygen [10]. It was found that the resulting erosion yields (removed carbon atoms per incident ion) can exceed the pure physical sputtering yields by more than an order of magnitude at room temperature, whereas no reaction of the films with oxygen molecules alone can be observed at this temperature. At flux densities of ions and O₂ of $4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ and $6 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$, respectively, i. e., an O₂/ion ratio of approximately 10 000, a yield of ≈ 4 was observed.

In this article we show that simultaneous bombardment by Ar⁺ ions and water also leads to chemical sputtering of a-C:H if the surface temperature is sufficiently low.

2. Experiment

Experiments were performed in the particle-beam experiment MAJESTIX. A detailed description of the setup is available in Ref. [11]. A hard a-C:H film is deposited onto a silicon wafer in a preparation chamber. After deposition it is transferred *in vacuo* into the UHV experiment chamber. The substrate holder can be cooled by cold nitrogen gas to a minimum temperature

of 110 K and heated resistively up to ≈ 900 K. The temperature of the a-C:H film is measured by a thermocouple clamped to the sample surface. In cooling mode, the temperature is held constant at the desired value by cooling with constant settings and simultaneous heating.

An ion gun capable of producing mass-selected ion beams at energies in the range of 10–1000 eV creates an Ar^+ beam. In all experiments reported in this paper, the ion energy was set to 800 eV and the ion flux density was held constant at $4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. H_2O is introduced into the chamber from a small water-filled container connected to the chamber via a pressure-controlled thermovalve in a remote position. The water pressure in the chamber is derived from the mass spectrometry signal of mass 18 which was calibrated by comparison with an ion gauge at higher water pressure. From the water partial pressure the flux density of water to the walls can be easily calculated by

$$j_w = p \sqrt{\frac{1}{2k_B T m \pi}}, \quad (1)$$

where $T = 300$ K is the temperature of the chamber walls, p is the water partial pressure, k_B is the Boltzmann constant, and m is the mass of a water molecule.

The film thickness is monitored by ellipsometry at a constant laser wavelength of 632.8 nm. Using the known carbon density of the films, the erosion rate can be expressed in units of removed carbon atoms per unit area and unit time. The yields reported in this article are these rates normalized to the incident ion flux density.

3. Results and Discussion

Figure 1 shows the erosion rate as a function of sample temperature for bombardment by Ar^+ ions only and for combined $\text{Ar}^+/\text{H}_2\text{O}$ exposure. The right-hand-side ordinate shows the corresponding erosion yield, i.e., the rate divided by the constant ion flux density. The open circles show the case without water. The rate is independent of temperature and in good agreement with TRIM.SP [12] calculations (dotted line) of physical sputtering assuming a surface binding energy of 2.8 eV [13]. An additional water flux density of $2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ (solid circles) does not alter the erosion rate at room temperature and above. However, when cooling the substrate to temperatures of 200 K and below the erosion rate increases significantly over the pure ion bombardment case, indicating a synergistic erosion process, or in other terms chemical sputtering. Doubling the water flux density at 110 K almost doubles the erosion rate (solid star). At water flux densities in excess of roughly $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ no erosion of the film is observed at 110 K. Instead, the growth of an ice layer is seen in the ellipsometry signal. By increasing the sample temperature the ice layer can be evaporated again and the ellipsometry signal returns to that of the original a-C:H film.

Hence, it appears most likely that the mechanism underlying the observed increase in erosion rate at lower temperatures is an ion-induced reaction between oxygen in the adsorbed water and carbon from the a-C:H film, leading to the formation of volatile carbon oxides.

We apply a simple adsorption–desorption model to describe the surface coverage of a-C:H by water as a function of surface temperature T . The quantity Θ denotes the fraction of the surface covered by H_2O . We calculate its steady-state value by considering one adsorption and two desorption processes. The adsorption rate of the incident flux density j_w of water molecules is described by $j_w p (1 - \Theta)$, where p is a coverage-independent adsorption probability. The adsorption is only accounted for if the molecule adsorbs on the uncovered fraction $(1 - \Theta)$ of the a-C:H film. Assuming a fixed desorption energy E_d , the thermal desorption of adsorbed molecules happens with the rate $n_0 \nu \exp(-E_d/k_B T) \Theta$, where n_0 is the maximum areal density of water molecules and ν is a frequency factor. Another mechanism by which Θ is reduced is the consumption of H_2O in the erosion process. For simplicity we assume that the rate of this depopulation is equal to the chemical sputtering rate which we write as $j_{\text{ion}} Y_0 \Theta$, where j_{ion} is the

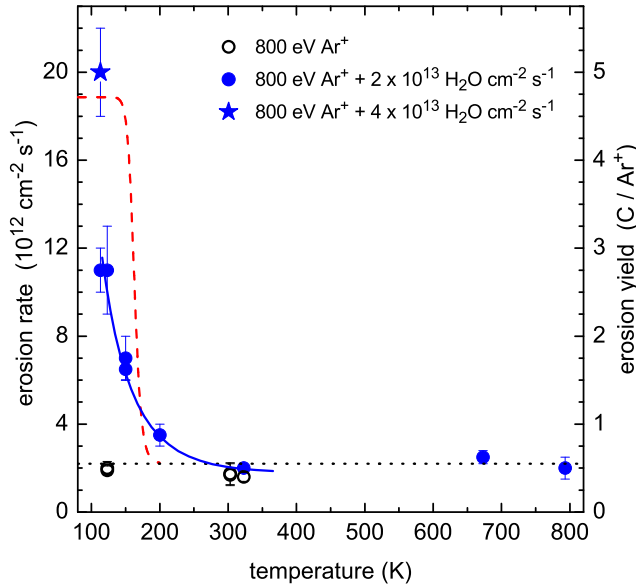


Figure 1. Erosion rate (left scale) and yield (right scale) as a function of surface temperature for bombardment by Ar^+ at 800 eV at a flux density of $4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ and different H_2O flux densities. The dotted line indicates the physical sputtering yield calculated with TRIM.SP. The dashed line is the result of Eq. (3). The solid line is a guide to the eye.

ion flux density and Y_0 is the chemical sputtering yield on a fully H_2O -covered surface. Thus, the temporal change of Θ reads

$$n_0 \frac{d\Theta}{dt} = j_w p (1 - \Theta) - n_0 \nu \exp(-E_d/k_B T) \Theta - j_{\text{ion}} Y_0 \Theta. \quad (2)$$

In steady state the time derivative vanishes and we can solve for Θ . Finally, the erosion yield is given by

$$Y = Y_{\text{phys}} + Y_0 \Theta = Y_{\text{phys}} + \frac{j_w p Y_0}{j_w p + n_0 \nu \exp(-E_d/k_B T) + j_{\text{ion}} Y_0}, \quad (3)$$

where Y_{phys} is the physical sputtering yield as calculated with TRIM.SP.

The value $Y_{\text{phys}} = 0.55$ was calculated with TRIM.SP. The water areal density is taken as that of ice, $n_0 \approx 10^{15} \text{ cm}^{-2}$. For E_d we take the sublimation energy of ice, which is 0.45 eV [14]. The frequency ν was assumed within the typical range of molecular vibrational frequencies as $1 \times 10^{13} \text{ Hz}$. A reasonable value for p can be derived from the following consideration: The maximum erosion rate shown in Fig. 1 is $\approx 2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ which has to be compared to the corresponding water flux density of $4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. This means, every second H_2O molecule contributes to the erosion process. Hence, it can be concluded that the water depopulation due to chemical sputtering is an important loss term for the water coverage and furthermore, that p has to be greater than 0.5; we set $p = 1$.

Using these values, Y_0 can be derived from the minimum water flux density at 110 K required to grow a thick ice layer. The condition for the threshold to ice growth is that the total adsorption rate, i.e. adsorption on water covered as well as non-covered sites, is equal to the desorption rate at $\Theta = 1$, $p j_w^{\text{ice}} = n_0 \nu \exp(-E_d/k_B T) + j_{\text{ion}} Y_0$. With the experimentally found threshold flux density $j_w^{\text{ice}} \approx 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ we obtain $Y_0 = 25$.

The dashed line in Fig. 1 shows the result of Eq. (3) with $j_w = 2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. The model shows chemical sputtering below approximately 200 K in reasonable agreement with the experiment. However, in the experiment the decrease of the rate with temperature extends over a much wider temperature range than in the model. This discrepancy might be due to coverage-dependent or distributed H_2O desorption energies.

We have recently reported on a similar increase of the erosion rate of a-C:H with decreasing temperature during simultaneous exposure to Ar⁺ ions and molecular oxygen. In that case, our proposed mechanism was an ion-induced reaction of adsorbed O₂ molecules with the film's carbon. Like in the model presented above, the balance between adsorption and thermal desorption leads to a steady-state oxygen coverage which decreases with increasing temperature. Accordingly, the rate of the ion-induced erosion process also exhibits this temperature dependence. The decrease with temperature between 110 and 400 K implies a rather small binding energy of the O₂ molecules of the order of 1 eV. Our experimental facilities do however not allow us to directly determine the oxygen surface coverage of the surface as a function of temperature. The proposed mechanism therefore remains speculative. The observation of an ion-induced reaction between adsorbed water and the a-C:H film, however, supports our proposed model as it shows the general occurrence of this type of reaction.

A clear difference between the Ar⁺/O₂ and Ar⁺/H₂O cases is that in the molecular oxygen case chemical sputtering can also be observed at and above room temperature, whereas in the water case no enhancement over physical sputtering was found. Two possible explanations for this difference are: (i) The adsorption energies of H₂O and O₂—and possibly their distributions—might be different so that there is still oxygen adsorbed at the higher temperatures when offered as O₂ while when offered as water the surface coverage is virtually zero. (ii) At room temperature the chemical sputtering yield in the O₂ case is no longer determined by the reaction of adsorbed oxygen, but by the reaction of incoming O₂ at defects such as dangling bonds. The difference with water could then be due to a lower or vanishing reactivity of H₂O at these damage sites.

4. Summary

Chemical sputtering of a-C:H due to the combined interaction of energetic Ar ions and thermal water vapor was observed at temperatures below ≈ 200 K. Above this temperature no increased erosion compared with physical sputtering was found. We explain the results in terms of an ion-induced erosion reaction between adsorbed water and the film surface. A simple adsorption–desorption rate equation can model both the onset of chemical sputtering with decreasing temperature around 200 K and the transition to ice layer growth with increasing water flux density.

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