

Hyperthermal Neutral Ar Atom Sputtering of Multilayer Thin Films of *p*-Xylene Adsorbed on Rh(111)[†]

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Hyperthermal neutral Ar atoms ($\langle E \rangle = 12$ eV) were used to sputter molecules from thin films of *p*-xylene adsorbed on Rh(111). This was done for several different film thicknesses, and the energy and intensity of the sputtered *p*-xylene was measured as a function of both the incident angle of the Ar and the ejection angle of the sputtered *p*-xylene. The first layer is not sputtered. For thicker films, up to a coverage equivalent to ~ 16 layers, molecules are ejected from the surface with a yield of at most 0.05 and a translational energy of under 1 eV. For multilayer films, these results show little, if any, dependence on the film thickness. This atom-based technique is envisaged as an alternative to ion sputtering for depth profiling of organic thin films. Since it involves only low-energy neutral species, charging effects are mitigated. Moreover, the incident neutral inert gas species does not react with the surface nor alter the chemical composition of the film.

Introduction

The sputtering of materials by collisions with high-energy particles has been extensively studied. Much of the work involves the use of ion beams, which are relatively easy to produce and focus.^{1,2} One analytical use of sputtering is to characterize surfaces and do molecule specific depth-profiling, in conjunction with techniques such as secondary ion mass spectroscopy and X-ray photoelectron spectroscopy.^{3,4} For organic films, a problem arises in that high-energy ions can damage the surface, changing the composition.^{3–5} One technique to mitigate this problem is to use large polyatomic ions such as C_{60}^+ , which do not damage the surface in the same way as monatomic ions.^{3,4,6–8} The large ions can partially decompose on the surface, however, which can affect the results.³

Another possibility, to be explored in this paper, is to use beams of hyperthermal neutral inert gas atoms to sputter organic thin films. With energies of at most a few tens of electron volts, no reactivity with the adsorbates, and no adsorption on the surface, this provides a potentially good way to sputter away the organic molecules without creating any artifacts. There have been other studies that used neutral inert gas atom beams to desorb organics,^{9–11} but they have all involved only monolayer or submonolayer coverages on a metal substrate. In the experiments covered in this paper, we used a high-intensity pulsed beam of hyperthermal Ar ($\langle E \rangle = 12$ eV). The model organic film used was a multilayer of *p*-xylene adsorbed on a Rh(111) substrate. This surface was chosen because *p*-xylene forms ordered overlayers on the Rh(111) surface. We can make angle and energy resolved measurements on the sputtered molecules, and with the known morphology of the surface possibly extract information on the sputtering mechanism. Xylene is also of modest molecular weight and has a small adsorption energy, which from simple binary collision considerations could potentially give good sputtering yields.

Experimental Details

Details of the experimental methods and apparatus have been covered previously,^{12–14} and only a brief summary will be presented. The scattering occurs in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. The Rh(111) crystal is mounted on a rotating manipulator so that the incident polar angle (θ_i) can be varied. The crystal can also be resistively heated and cryogenically cooled with liquid N_2 . There is a separately rotating, double-differentially pumped quadrupole mass spectrometer (electron-bombardment ionization, $\sim 1^\circ$ fwhm angular resolution) to detect the scattered *p*-xylene at different final angles (θ_f). Energies were determined by measuring the time-of-flight (TOF) with a multiscaler system. The major component in the cracking pattern of *p*-xylene is 91 AMU, and it was this mass that was detected in the scattering experiments.

The hyperthermal translational energy Ar atoms were produced with a pulsed laser-breakdown source.^{15,16} The average kinetic energy of the Ar was 12 eV with a full-width-half-maximum of 5.2 eV. The Rh(111) substrate was cleaned between experiments by O_2 exposure at 900 K, followed by annealing at 1200–1300K.

The growth of an ordered *p*-xylene monolayer adsorbed on Rh(111) has been extensively studied.^{17–20} Exposure at a surface temperature of $T_s = 300$ K leads to a $c(2\sqrt{3} \times 4)rect$ structure. Dosing was done with a room temperature beam of *p*-xylene in He, produced by bubbling He through a reservoir of *p*-xylene and expanding it through a 200 μm nozzle. The dosing rate was ~ 0.2 – 0.3 monolayers/s, estimated by monitoring the scattered *p*-xylene signal with the detector and with a residual gas analyzer. When a clean, $T_s = 300$ K Rh(111) surface was exposed, there would initially be little, if any, scattered *p*-xylene. After a few seconds, the signal would rise rapidly. If the exposure were stopped at this point, the He diffraction spectrum of the surface was consistent with the $c(2\sqrt{3} \times 4)rect$ structure; further dosing did not change the spectrum. Therefore, the length of time between initial exposure and the rapid rise in *p*-xylene signal was assumed to be the time needed to reach complete monolayer coverage. Figure 1a shows a helium diffraction spectrum for the Rh(111) $\langle 10 \rangle$ direction. There are some small

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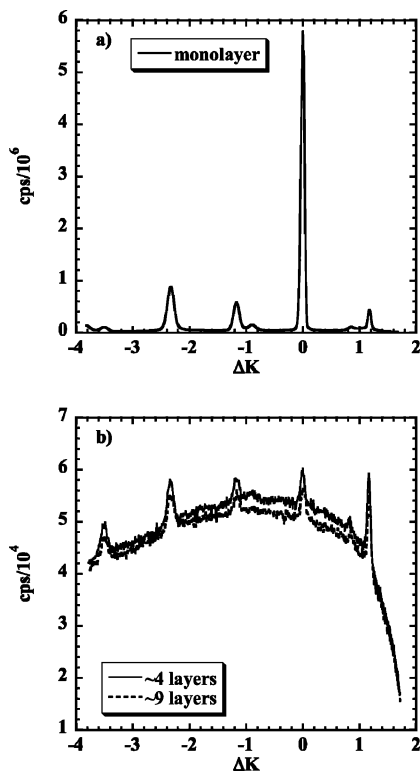


Figure 1. Elastic He diffraction spectra taken along the Rh(111) $\langle 10 \rangle$ azimuth. Conditions were $\theta_i = 45^\circ$, $\langle E \rangle (\text{He}) = 19.5$ meV, and $T_s = 125$ K.

superlattice features, but the principle diffraction features occur at positions consistent with a repeat distance of 10.7 \AA , as expected for this azimuth.^{17,18}

Higher coverage was produced by further dosing the monolayer covered surface at $T_s = 150$ K. By monitoring the scattered *p*-xylene signal, it appeared that the sticking coefficient was close to 1, and so coverage is estimated by exposure time as a multiple of the time needed to produce a monolayer coverage at $T_s = 300$ K. Figure 1b shows the He diffraction for higher coverages of *p*-xylene. The positions of the diffraction features indicate that any ordered areas have the same general structure as the monolayer. The features are narrow, which indicates long-range coherence, but are greatly attenuated with respect to those of the monolayer, and set on a large incoherent background. These observations indicate that there is some surface order in the overlayers, possibly as ordered regions between areas of disorder. It is also not clear whether the coverage is uniform, as expected with layer-by-layer growth, or the surface consists of various thicknesses of *p*-xylene. For these experiments, the He diffraction spectra were very similar at all coverages greater than a monolayer, as shown in Figure 1b. Therefore, it is reasonable to state that the surface morphology was similar for all of the coverages greater than a monolayer.

Temperature-programmed desorption (TPD) measurements could be made from *p*-xylene covered surfaces either before or after hyperthermal Ar exposure. Taking TPD spectra involved measuring desorbed *p*-xylene signal while the surface temperature was ramped. For a given dosing time, the comparison between the amount of *p*-xylene before and after hyperthermal Ar exposure gives a measure of the amount ejected from the surface from the Ar exposure. TPD measurements were not useful for absolute coverage measurements, as the monolayer apparently decomposes on the surface; no intact molecules of *p*-xylene are detected when the monolayer was heated.

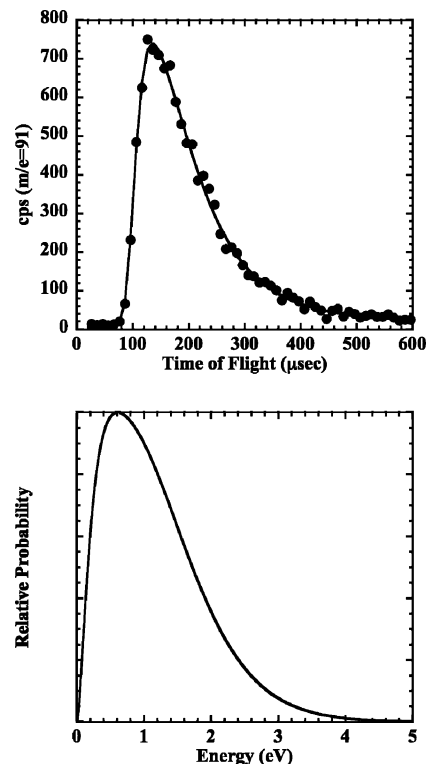


Figure 2. (a) Example TOF spectrum of sputtered *p*-xylene, using $m/e = 91$. The points correspond to the data, the line to a fit used to derive the energy and intensity of the sputtered molecules. Conditions are $\theta_i = 45^\circ$, $\theta_f = 30^\circ$, $\langle 10 \rangle$ azimuth, $T_s = 125$ K, and an average translational energy of 12.0 eV for the Ar. (b) The derived energy distribution for intact *p*-xylene molecules.

It was also possible to extract kinetic data from the TPD data. For the thick overlayers, the data is readily fit with a simple zeroth-order Arrhenius equation, $\text{rate} = \nu \exp(-E/k_B T)$, giving a value of $E = 16.4 \text{ kcal/mol} = 0.71 \text{ eV/molecule}$. This value can be used as an approximate value for the binding energy of a *p*-xylene molecule.

Results and Discussion

Figure 2 shows an example TOF spectrum with the nonlinear least-squares fit to the data and the energy distribution derived from the fit. Figure 3 shows a series of TOF spectra for *p*-xylene sputtered from eight layers, taken at different detector angles with 12 eV Ar incident at $\theta_i = 45^\circ$. Figures 4–6 show the average final energies and total intensities for the sputtered *p*-xylene derived from fitting the TOF Spectra. For the intensity plots, the data have been normalized by the incident Ar intensity and corrected for the instrument function and incident flux variations due to the different incident and final angles; the values are directly comparable between plots. To estimate the sputtering yield (number of sputtered *p*-xylene molecules/number of incident Ar atoms), we first compared the mass spectrometer signal of the hyperthermal pulsed beam with that of a continuous atom beam of Ar, made from a conventional nozzle source, for which the flux was known. With this information, and the TPD signal after exposure to hyperthermal Ar, we calculate a yield of at most 0.05.

Figure 4 shows the results for eight layers along a $\langle 10 \rangle$ azimuth and at different incident angles. All show a decrease in the intensity of the sputtered *p*-xylene as a function of the final angle examined. The translational energy appears to peak at a final angle greater than normal, but there are insufficient

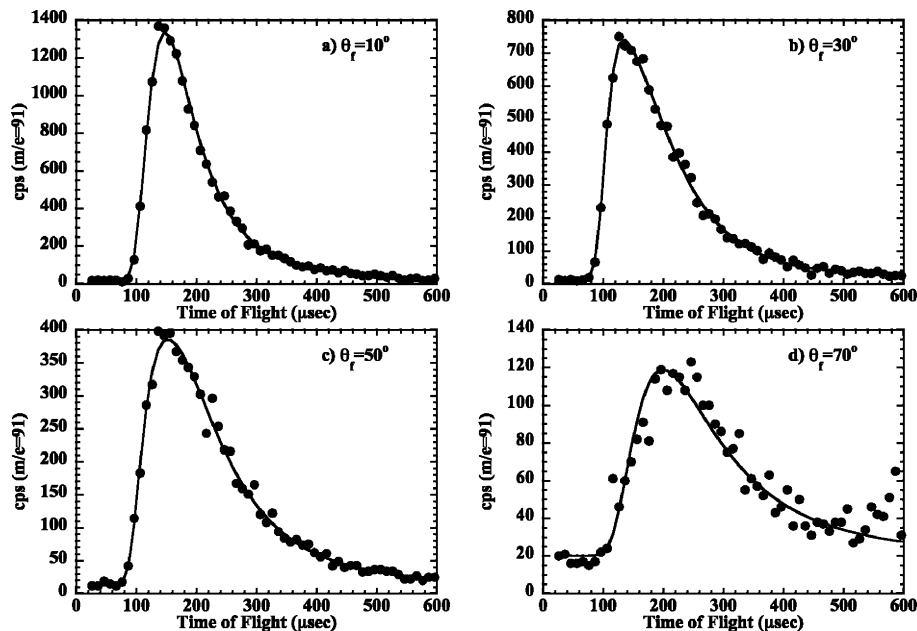


Figure 3. Series of TOF spectra for sputtered *p*-xylene, using $m/e = 91$, taken at different detector angles. Spectra were taken along the $\langle 10 \rangle$ azimuth and at $T_s = 125$ K, with 12 eV Ar incident at 45° . The points correspond to the data, the line to a fit used to derive the energy and intensity of the sputtered molecules. These spectra correspond to data shown in Figure 4.

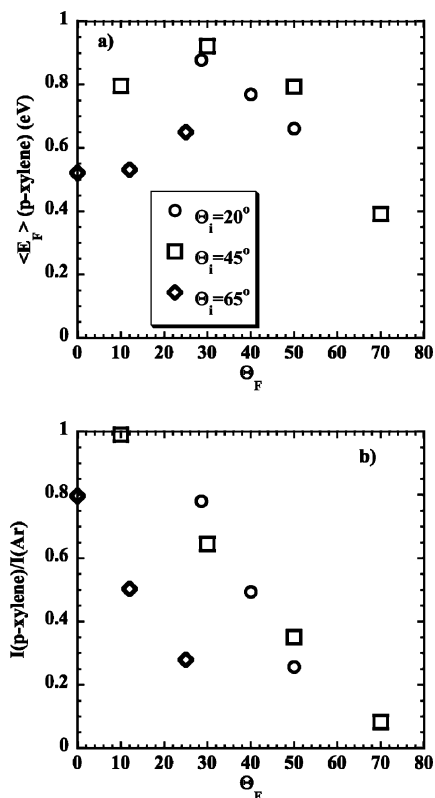


Figure 4. Average energy and integrated intensity for *p*-xylene molecules sputtered from an eight layer thick film as a function of θ_f for three different Ar incident angles. Data was taken along the $\langle 10 \rangle$ azimuth and $T_s = 125$ K.

data to make a precise determination of this angle, and its dependence on the incident angle. For the more normal incident angles, 20° and 45° , the intensity and average energy are the same within the measurement error. In contrast, at $\theta_i = 65^\circ$ there is a systematic shift to a lower yield, with the escaping *p*-xylene having a lower average translational energy. This is consistent with the results of high-energy atom scattering, for

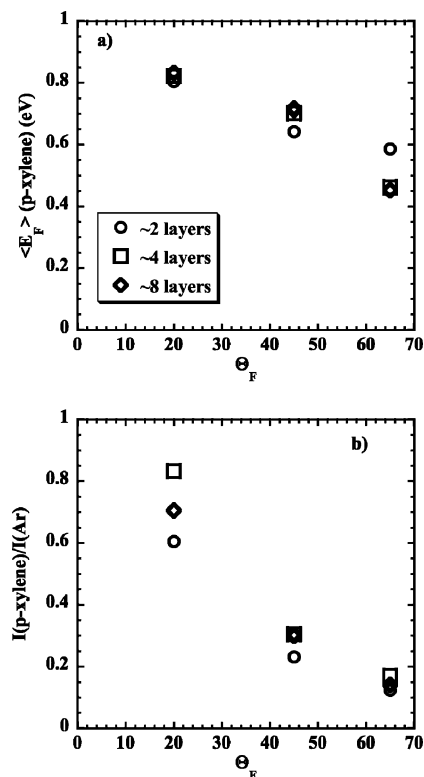


Figure 5. Average energy and integrated intensity for *p*-xylene molecules sputtered from three different coverages. Conditions are $\theta_i = 45^\circ$, $\langle 11 \rangle$ azimuth, and $T_s = 125$ K.

example 0.6 eV Ar incident upon a self-assembled monolayer.²¹ At glancing incident angles, much less energy is transferred to the surface than for incident angles close to the surface normal. This effect would show up in the *p*-xylene experiments as fewer molecules acquiring sufficient energy to escape the surface, and those that do having, on average, a lower translational energy.

Figure 5 shows the results for different *p*-xylene coverage for $\theta_i = 45^\circ$ along the $\langle 11 \rangle$ azimuth. Within the estimated error bars, the results at any final angle are independent of the

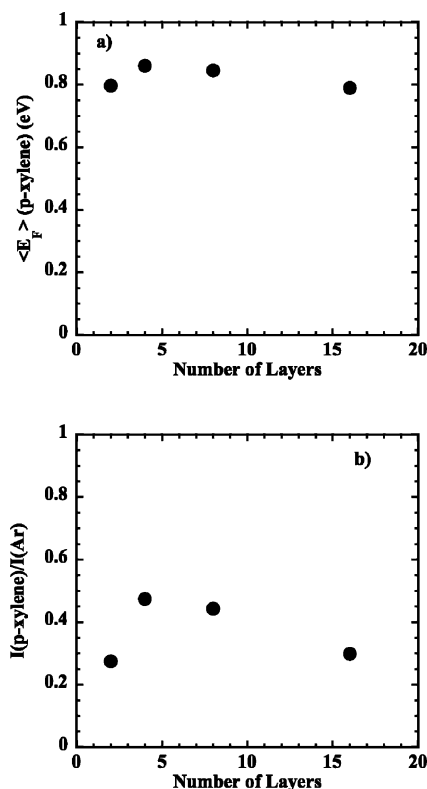


Figure 6. Average energy and integrated intensity for *p*-xylene molecules sputtered from different coverages. Conditions are $\theta_i = \theta_f = 45^\circ$, $\langle 10 \rangle$ azimuth, and $T_s = 125$ K.

coverage. Comparing the results for eight layers with those in Figure 4 shows no significant dependence of the results on azimuth. Figure 6 shows coverage dependent results for $\theta_i = \theta_f = 45^\circ$ and the $\langle 10 \rangle$ azimuth. There appears to be a slight decrease in energy and intensity at 16 layers, but this is very small. For a single layer, there was no $m/e = 91$ detected during hyperthermal Ar exposure, just as there was no TPD signal. Whether the *p*-xylene dissociates when adsorbed or none is sputtered with 12 eV Ar exposure is unknown. On the basis of previous experiments for submonolayer benzene and toluene adsorbed on Au(111),¹⁰ where the collision-induced desorption was ~ 1 , the latter explanation seems unlikely. For the two-layer coverage shown in Figure 6, the relative decrease in signal as compared with higher coverage might be due to the coverage being slightly less than two layers.

Conclusions

Hyperthermal neutral Ar atoms ($\langle E \rangle = 12$ eV) were used to sputter molecules from thin films of *p*-xylene adsorbed on Rh(111). This was done for several different film thicknesses, and the energy and intensity of the sputtered *p*-xylene was measured as a function of both the incident angle of the Ar and the ejection angle of the sputtered *p*-xylene. No *p*-xylene is sputtered from the first layer. For thicker films, up to a coverage equivalent to ~ 16 layers, molecules are ejected from the surface with a yield of at most 0.05 despite the fact that the incident energy is many times the binding energy of the *p*-xylene. The other studies that used neutral inert gas atom beams to desorb

organics^{9,10,22} showed much higher yields, though they involved only monolayer or submonolayer coverages. We presently have no explanation for the low yields that we observed.

The intensity of the sputtered molecules decreases at larger final angles. The translational energy also decreases with larger final angles but possibly also near normal final directions. These results show little, if any, dependence on the film thickness. He diffraction spectra show that the surfaces are at least partially ordered, but there is no obvious dependence on the azimuth. This technique was envisaged as an alternative to ion sputtering for the depth profiling of organic thin films. The advantage of utilizing inert gas atoms rather than ions for sputtering studies is that the overall process involves only neutral species, thus mitigating charging effects, and that a neutral inert gas molecule does not react with the surface and alter the chemical composition of the film.

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