Supplementary Material: Organic Thin Films of 6T and PF6T

I. PREPARATION OF MOLAR MIXTURES

First, pure 6T and pure PF6T films were grown in ultrahigh vacuum on native silicon oxide (SiO_x) by thermal evaporation and deposition. The growth rate was monitored with an oscillating quartz crystal microbalance (QCM). The film thickness was measured *ex situ* after growth with X-ray reflectivity and a scaling factor, which relates growth rates to changes in oscillation frequencies, has been evaluated. Subsequently, a rate calibration was carried out in order to assign evaporation temperatures T to growth rates r following the exponential law $r(T) = a \cdot \exp(b \cdot T)$. Taking into account that the volume of 6T is 0.856 of the volume of PF6T[1,2] allows to grow films with molar mixing ratios, which means that the mixing ratio refers to the number of molecules. For instance, a molar 6T:PF6T 1:1-mixture requires a ratio of 0.856 Å/min : 1.000 Å/min for the growth rates. In order to gain a total growth rate of 2 Å/min for all blends we have to apply Eq. (1) to the growth rate of each kind of molecule respectively (indicated with index i) such that the new rates satisfy Eq. (2) and (3). The resulting growth rates are shown in Tab. I. Finally, pure films and 6T:PF6T 3:1, 2:1, 1:1, 1:2, and 1:3 blends were grown by coevaporation on three different substrates, native silicon oxide, thermally oxidized silicon, and quartz glass, for a duration of 50 minutes with a total growth rate of 2 Å/min, resulting in a mean thickness of approximately 10 nm.

$$r_{new,i} = \frac{r_{total}}{r_{old,6T} + r_{old,PF6T}} \cdot r_{old,i} \tag{1}$$

$$r_{new,6T} + r_{new,PF6T} = r_{total} \tag{2}$$

$$\frac{r_{new,6T}}{r_{new,PF6T}} = \frac{r_{old,6T}}{r_{old,PF6T}} \tag{3}$$

Molar Mixing Ratio 6T:PF6T	Growth Rate in Å/min
pure 6T	2.0
3 : 1	1.4 : 0.6
2 : 1	1.3 : 0.7
1 : 1	0.9 : 1.1
1 : 2	0.6 : 1.4
1 : 3	0.4 : 1.6
pure PF6T	2.0

TABLE I. Scaled growth rates for molar mixtures and a total growth rate of 2 Å/min.

II. EXAMINATION OF THE MIXING RATIO

The mixing ratio of the 1:1 blend grown on thermally oxidized silicon was analyzed by X-ray photoelectron spectroscopy (XPS) using a monochromatic Al Kα X-ray source with a photon energy of $h \cdot f = 1.4867\,\mathrm{keV}$ and an angle of incidence of 60°. The kinetic energy E_{kin} of photoelectrons was measured by a hemispherical analyzer from 750 eV to 1500 eV with a resolution of 1 eV and averaged over two measurements. The results are plotted in terms of binding energies $E_b = h \cdot f - E_{kin}$, see Fig. 1. There are fluorine, carbon, and sulfur peaks visible. The fluorine peak does of course not appear in the spectrum of pure 6T. Furthermore, there are oxygen and silicon peaks stemming from the substrate.

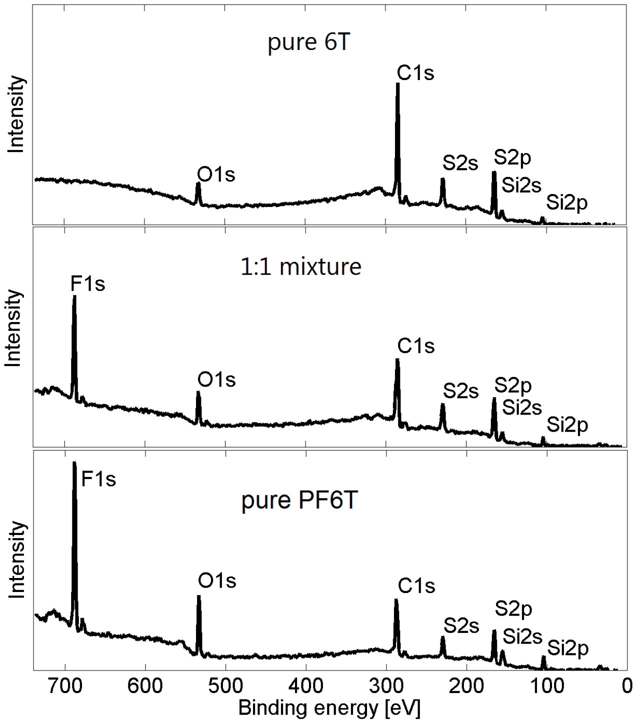

FIG. 1. XPS of pure films and a 1:1 blend 10 nm thin and grown at 300 K on thermally oxidized silicon

This survey was followed by measurements of the peaks with a higher resolution of 0.1 eV averaged over 10 measurements. The Voigt profiles of the XPS peaks were fitted with multiple Lorentz-Gauß curves and their intensities determined as area underneath the curve. The fitted intensities are shown in Tab. II.

6T:PF6T	F1s I [kCPS]	C1s (C-F) I [kCPS]	C1s (C-other) I [kCPS]
pure 6T	-	-	103.5
1:1 mix	112.1	37.6	69.7
pure PF6T	192.3	52.5	28.2

6T:PF6T	S2s I [kCPS]	$S2p_{1/2}$ I [kCPS]	$S2p_{3/2}$ I [kCPS]
pure 6T	40.5	23.5	31.9
1:1 mix	40.4	-	-
pure PF6T	32.3	19.4	19.5

TABLE II. Intensities of XPS peaks of pure films and the 1:1 mixture 10 nm thin and grown at 300 K on thermally oxidized silicon in kilo counts per second integrated over the entire peak area.

The peak intensity I can be evaluated from the atomic concentrations n, the flux of photons f, and the atomic sensitivity factor ASF due to $I = n \cdot\ f \cdot\ ASF$. Tabulated ASF-values for many chemical elements can be found in the literature, but it is said that the deviation from one experimental setup to another often amounts to more than 10%[3]. Equation (4) directly follows from $I = n \cdot\ f \cdot\ ASF$ and was used in order to determine the mixing ratio:

$$\frac{I(S2s)}{I(F1s)} = \frac{n(S2s) \cdot f \cdot ASF(S2s)}{n(F1s) \cdot f \cdot ASF(F1s)} \tag{4}$$

The ratio of the S2s and the F1s peak intensities in pure PF6T was determined from the measurement. The ratio of atomic concentrations n in pure PF6T was evaluated from the chemical formula $C_{24}F_{14}S_6$. There are 6 sulfur and 14 fluorine atoms within each PF6T molecule. The ratio of sulfur to fluorine is 6/14. Then it was possible to determine the relative ratio of ASF-values for the S2s and the F1s peak by Eq. (4). The flux f of photons is the same for all measurements and cancels out. An ASF-ratio of 0.39 resulted, which is close to the literature value of 0.33[3].

Inserting the measured S2s and F1s peak intensities of the mixed film and the previously determined ASF-ratio of 0.39 into Eq. (4) delivers the ratio of sulfur to fluorine atoms in the mixed film. An ideal 1:1 mixture should have a sulfur to fluorine ratio of $(2 \cdot 6)/(1 \cdot 14)$. Both, 6T and PF6T contribute 6 sulfur atoms each, but the 14 fluorine atoms of PF6T appear only once. After determining the deviation of the sulfur to fluorine ratio of our sample from the ideal ratio and calculating the fraction of PF6T molecules, the fraction of PF6T in the mixed thin film turned out to be 47%. The mixing ratio of 6T:PF6T is then $53/47 = 1.13{:}1.00$.

III. X-RAY DIFFRACTION EXPERIMENTS

The in-plane q_{xy}-values from the GIXD profiles of the pure films and the blends grown at 300 K on native silicon oxide (thickness 12 nm) are compiled in Tab. III.

6T:PF6T	[1/Å]	[1/Å]	[1/Å]	[1/Å]	[1/Å]	[1/Å]	[1/Å]
pure 6T	-	-	-	1.38	1.60	-	1.96
3:1	0.54	-	1.00	1.38	1.60	-	1.95
2:1	0.53	-	1.06	1.38	1.60	-	1.96
1:1	0.50	0.75	0.96	-	-	1.80	-
1:2	0.49	0.75	0.96	-	-	1.81	-
1:3	0.50	0.75	0.94	-	-	1.78	-
PF6T	0.49	0.78	0.94	-	1.70	-	1.90

TABLE III. q_{xy}-values of the various blends grown at 300 K on native silicon oxide (thickness 12 nm) in comparison with pure 6T grown at 308 K on native silicon oxide (thickness 20 nm).

IV. ATOMIC FORCE MICROSCOPY

Atomic force microscopy (AFM) was applied in intermittent contact mode using a NanoWizard II AFM head from JPK instruments. An n-type silicon probe with a tip radius of less than 10 nm attached to an aluminium coated cantilever with a drive frequency of 343.5 kHz and a spring constant of 14 - 15 μm from AppNano was used. The scanned region is 3 × 3 μm^2. A tip velocity of 2.4 $\mu m/s$ and a low line rate of 0.4 Hz was necessary to allow the tip to follow the high columnar shaped islands of PF6T. The high target amplitude of 3.0 V and a drive amplitude of 0.019 V with a setpoint around 2.20 V were crucial for probing the sticky PF6T films and all blends containing PF6T. The evaluation of surface profiles was done with the Gwyddion software.

V. ABSORPTION MEASUREMENTS

Absorption measurements were performed in transmission at normal incidence on quartz glass for wavelengths in the range of 190 nm to 1100 nm, corresponding to an energy range from 1 eV to 6 eV, with the Varian Cary 50 UV-VIS spectrophotometer. Eq. (5) evaluates the absorption k from the measured transmittance $T = I/I_0$ and I_0 is the intensity after passing quartz glass without organic film and I is the intensity after passing the glass with an organic layer on top. With the help of the Kramers-Kronig relation ship, see Eq. (6) we can determine the corresponding index of refraction n for the in-plane component. Note that the integral goes from zero to infinity but only a finite region of k can be measured such that there is small uncertainty for the evaluated n at high energies.

$$k = -\frac{1}{d} \cdot \frac{\lambda}{4 \cdot \pi} \cdot ln\,(I/I_0) \tag{5}$$

$$n(E) = 1 + \frac{2}{\pi} \cdot PV \int_0^{\infty} \frac{E' \cdot k(E')}{E'^2 - E^2} dE' \tag{6}$$

VI. REFERENCES

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