

Substrate-induced effects in thin films of a potential magnet composed by metal-free organic radicals deposited on Si(111)

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This Electronic Supplementary Information provides

- 1) Experimental section
- 2) The overview XPS spectrum after NitPyn deposition.
- 3) The table containing the NitPyn stoichiometry and integrated XPS experimental signal intensities for the thin films.
- 4) The overview XPS spectrum after annealing at 570 K.
- 5) XPS profiles extracted from the time-dependent C 1s signal.

1)

EXPERIMENTAL SECTION

Clean Si(111) crystal covered by native oxide were degassed in UHV, without any previous ex-situ treatment, below the temperature at which the oxide is removed. The samples were then repeatedly flashed rapidly to around 1350 K for 1-2 min, until a sharp (1x1) to (7x7) transition was obtained at about 830 C. Finally, the substrate was slowly cooled down to room temperature. The substrate was characterized by XPEEM, LEEM and LEED, which gave a pattern with the expected reconstruction.[1] The measurements have been performed with a SPELEEM (Elmitec, GmbH) installed at Nanospectroscopy beamline (first branch) at Elettra Synchrotron Laboratory.[2] The photon energy was 600 eV. All four detailed core level spectra (C 1s, N 1s, O1s, and Si 2p) were consecutively measured in dispersive plane mode within a cumulative beam exposure time of 120 s to minimize radiation damage. The binding energy was calibrated by using the Si 2p XPS signal at 99.3 eV as a reference. Thin films of NitPyn were prepared in-situ by organic molecular beam deposition (0.7 Å/min evaporation rate, substrate at RT). The nominal thicknesses were measured by using the attenuation of the XPS substrate signal after NitPyn deposition.

[1] F. J. Giessibl, *Science* **267**, 68 (1995).

[2] A. Locatelli, L. Aballe, T. O. Menten, M. Kiskinova, and E. Bauer, *Surf. Interface Anal.* **38**, 1554 (2006).

2)

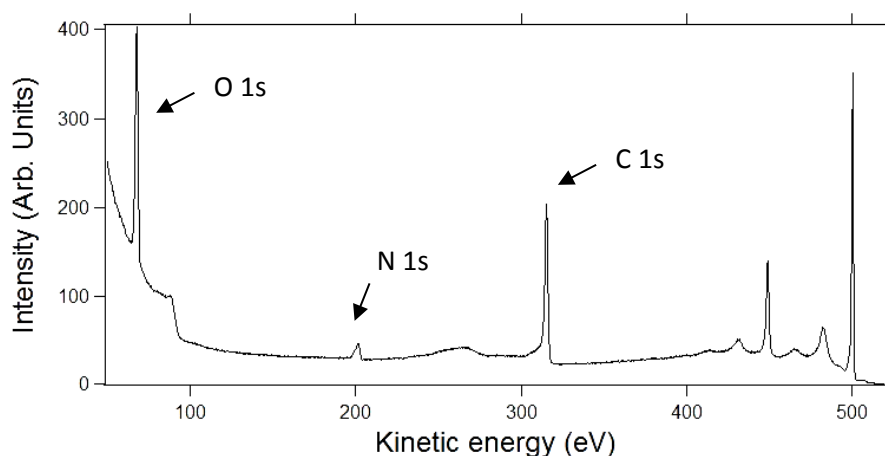


Figure 1S. XPS overview spectra after NitPyn deposition.

The N/C ratio obtained from the spectrum is 0.10. It is calculated taking into account the cross sections (C 1s= 0.168; N 1s= 0.2763) and the microscope transmission.

The molecular stoichiometry N/C ratio is 0.09. Therefore, we find that integrated signal intensities obtained analyzing the XPS curves are in agreement with the theoretical elemental analyses. This means that the stoichiometry of the deposited films corresponds to the quantitative composition of the molecule, indicating deposition without degradation.

3) **Table 1S.** Fit results for the energy positions and relative intensities of the photoemission lines in the C1s spectra. The Lorentzian width is 0.08 eV.

	Energy (eV)	W_G(eV)	Intensity (%)	Stoichiometric Composition (%)
C-C	284.37	1.62	31	30.43
C-H	284.91	1.11	39	39.13
CH₃	285.45	1.14	18	17.39
C-N	286.35	1.35	12	13.04

The C 1s core level spectra were fitted according to a best fit for XPS lines obtained for NitPyn on Au(111) (see Ref. 16) Looking at the chemical structure of the molecule, one would assume a contribution for each chemically nonequivalent carbon site in order to fit the C 1s core level XPS. However, due to the limited resolution of the measurements and the limitation in line width, a fit containing all these contributions is speculative. Therefore, similar carbon sites are merged into groups restricted by constraints based on stoichiometry, electronegativity and bond strength. These constraints are based on the chemical structure and realized via the ratio of the peak area of the single components. For the C-H to C-C, a ratio of 7:9 is extracted and strictly kept. A ratio of 16: 4: 3 is set for C-H + C-C: CH₃: C-N.

4)

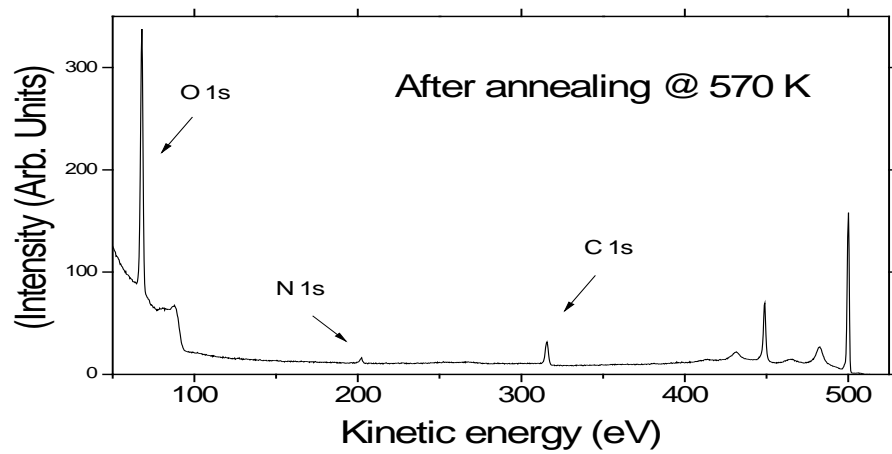


Figure 2S. XPS overview spectra after annealing at 570 K.

5)

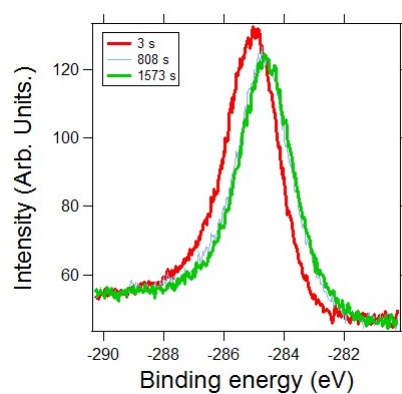


Figure 3S. XPS profiles extracted from the time-dependent C 1s signal, as in Figure 4.