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At the interface between organic radicals and $TiO_2(110)$ single crystals: electronic structure and paramagnetic character†

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We find that in a paramagnetic pyrene derivative of the nitronyl nitroxide radical deposited on rutile $TiO_2(110)$ single crystals the molecules keep/lose their paramagnetic character depending on the local substrate hydroxylation. The first molecular layer may act as a ''buffer'' on which intact organic magnets are grown.

Titanium dioxide is a transparent insulating oxide, and it is the most investigated single crystalline system among all metal oxides.[1–3] On one hand, it is considered the model system for the surface science of metal oxides; on the other hand, the potential of its applications as a material is enormous, ranging from medicine to electronics.[1–3] A major role in its popularity is certainly played by the studies on TiO_2 as a catalytic support.[1–3] TiO_2 exists mainly in three different crystallographic phases: rutile, anatase, and brookite. The rutile $TiO_2(110)$ surface is the most stable surface configuration. This surface under the (1×1) reconstruction is characterized by parallel rows of Ti atoms running along the [001] direction, alternated with rows of bridging oxygen atoms. The oxygen atoms protrude above the surface plane and they dominate the surface topography.[1–3] The ultra high vacuum (UHV) surface preparation consists of alternating cycles of sputtering and annealing. It is well known that this treatment gives rise to an oxygen deficient surface, because some bridging oxygen atoms are removed.[1,3] The consequent vacancies originate occupied band gap states that have Ti^{3+} 3d character and in X-ray photoemission (XPS) are mirrored by the presence of a shoulder in the low binding energy range of the Ti2p main line. However, freshly prepared surfaces may undergo fast hydroxylation (also in UHV) because of the reaction of the bridging oxygen vacancies with OH groups due to a residual water partial pressure in the UHV chamber.[4]

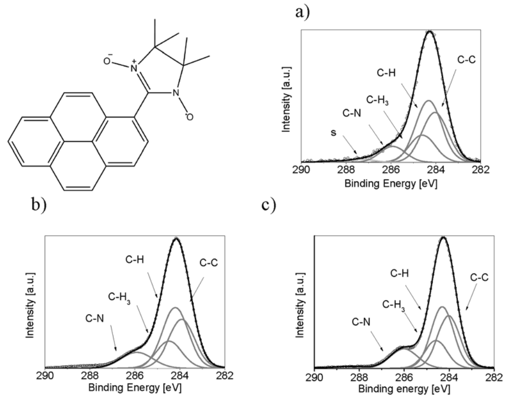

Fig. 1 Thickness dependent C1s core level spectra (together with their peak-fit analysis) of NitPyn thin films deposited on rutile $TiO_2(110)$ single crystals. (a) 0.3 nm nominally thick film. (b) 0.5 nm nominally thick film. (c) 1.0 nm nominally thick film. The NitPyn molecular structure is also shown.

Here we describe the interface properties of a pyrene derivative of the nitronyl nitroxide radical (4,4,5,5-tetramethyl-2-(pyrenyl)-imidazoline-1-oxy-3-oxide, NitPyn, Fig. 1) deposited on rutile $TiO_2(110)$ single crystals by using XPS investigations. We have previously demonstrated its successful deposition on gold under controlled conditions preserving the paramagnetic properties of the molecule.[5] The results identify some useful concepts in engineering new purely organic-based magnets and open the way to fruitfully exploiting organic molecular beam deposition (OMBD) to assemble NitPyn on a solid surface in view of future technological applications. The importance of organic radicals is that they are purely organic molecules with at least one unpaired electron that therefore originates a magnetic moment.[6–8]

In the last few decades, almost no attention has been paid to the deposition of organic radicals on a substrate. This is due to the fact that it is generally believed that these materials are not stable. In actual fact, however, in 1991 the first stable purely organic ferromagnet based on a nitronyl nitroxide was already synthesized by M. Tamura *et al.*[9] Only rare attempts to study the

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† Electronic supplementary information (ESI) available: Experimental details, Tables S1–S3 with all fit parameters for XPS C1s core level spectra, Tables S4–S6 with all fit parameters for XPS N1s core level spectra, XPS spectra obtained after film annealing at 790 K, XPS Ti2p core levels of two surfaces with different densities of Ti^{3+} 3d states and relevant pK_a/pH values in solution. See DOI: 10.1039/c3cc45693e

evaporation of this class of molecules have been reported:[10–12] all efforts were focused on the archetypal *p*-nitrophenyl nitronyl nitroxide[9] in the micrometre range thickness, characterized by a crystal packing reproducing those of the different bulk phases. Very recently other research groups have drawn their attention to organic radicals deposited under UHV conditions on gold.[13–17]

We are presently focusing our efforts on the investigation of NitPyn deposited on silicon dioxide, sapphire, and titanium dioxide, *i.e.*, technologically relevant surfaces. Our work on metal oxides is motivated by the fact that, besides the interest in the investigation of a new organic–oxide system, it is clear how the coupling of such materials with a purely organic radical may also lead to new developments in device engineering.

Sample preparation and XPS investigations were performed both in our laboratory and at the BESSY II synchrotron source (Berlin, Germany) at the UE52-PGM-PES. No degradation of the samples was observed on the time scale of all presented experiments.

Fig. 1 shows the C1s core level spectra obtained for samples of different NitPyn nominal thicknesses, together with their best fit curves. The fitting procedure is described in detail in ref. 5, the fitting parameters are given in Tables S1–S3 in ESI.†

While the fit curves of the C1s core level spectra show the expected characteristic four main components, the N1s core level spectra (Fig. 2) are different with respect to the relative spectroscopic lines obtained on powder,[5] and physisorbed NitPyn on gold[5] and sapphire[18] substrates.

In the C1s core level spectra the aromatic carbon sites (C–C and C–H bound carbons), the carbons of the methyl group (CH_3), and the carbons bound to nitrogen (C–N) contribute to the spectroscopic lines. The components, assigned according to ref. 5, are in good stoichiometric agreement, indicating that the molecule is intact and the pyrene substituent does not interact strongly with the surface.

The N1s core level spectra of an intact mesomeric nitronyl nitroxide radical are characterised by a single peak.[5] We observe two phenomena characterising the XPS N1s core level spectra at the NitPyn–TiO_2(110) interface: a shift of the main peak towards lower binding energy with respect to the N1s main peak binding energy observed on gold (401.9 for a 1.0 nm thick film on TiO_2(110) and 402.2 eV on gold) and a complex spectral line shape. In order to understand the physics and the chemistry of this interface, we apply a best fit procedure[5,19,20] to the spectra (see Fig. 2 and Tables S4–S6 in the ESI†). We are able to identify two line contributions for the spectra obtained for a 0.3 nm nominally thick film as in Fig. 2a: one at 400 eV and the second one at 398 eV. The first contribution is due to photoelectrons emitted from nitrogen atoms bound to hydrogen atoms, the contribution at 398 eV indicates nitrogen atoms involved in a bond with titanium. These assignments are in agreement with the interpretation of N1s core level spectra of various organic adsorbates on TiO_2(110).[21–23] Upon increasing the film thickness, a peak (corresponding to the one observed for intact molecules deposited on gold and sapphire) appears at 401.9 eV, while the XPS lines due to contributions involving N–H and Ti–N bonds decrease in relative intensity (see Fig. 2c and d, and Tables S4–S6 in the ESI†).

The experimental spectra together with the fit analysis give a detailed picture of the investigated NitPyn–TiO_2(110) interface: the clean TiO_2(110) surface, although with few oxygen vacancies, originating very few Ti^{3+} 3d state contributions, may favour water adsorption/dissociation leading to the coexistence of hydrolysed and clean surface regions.[4,24] The nitronyl nitroxide radical derivatives in solution show the tendency to spontaneously lose an oxygen atom, without further decomposition.[25] The compounds are still stable and can be reconverted to the initial one with appropriate chloroperbenzoic acid treatment. All compounds (*i.e.*, independently from the substituent) may be reversibly protonated without decomposition.[25] Due to the catalytic properties of the rutile TiO_2(110) surface, the reactions observed in solution may be favoured at the interface leading to the consequent bonding of the nitrogen atoms to the hydrogen/titanium atoms, depending on the adsorption site. Upon increasing the film thickness, the interaction with the substrate decreases, the spontaneous release of oxygen from the nitronyl nitroxide radical is quenched leading to the presence of intact molecules. Note that in our previous work we have demonstrated by using XPS and electron spin resonance spectroscopy that we are able to evaporate NitPyn without molecular degradation and preserving its paramagnetic character;[5] therefore the molecules land on the substrate in their intact structural form, as it is also demonstrated by the fact that XPS spectra of thicker films show the main line related to the intact nitronyl nitroxide radical. It is the interaction with the substrate that causes the discussed spontaneous reaction.

The strong deviation of the spectral line from the spectra obtained for the NitPyn powder or physisorbed molecules clearly indicates that NitPyn is not physisorbed on TiO_2(110). In the case of physisorption, the molecular orbitals at the interface stay almost unperturbed, showing only a single peak in the N1s core level spectra, thus we can deduce that NitPyn

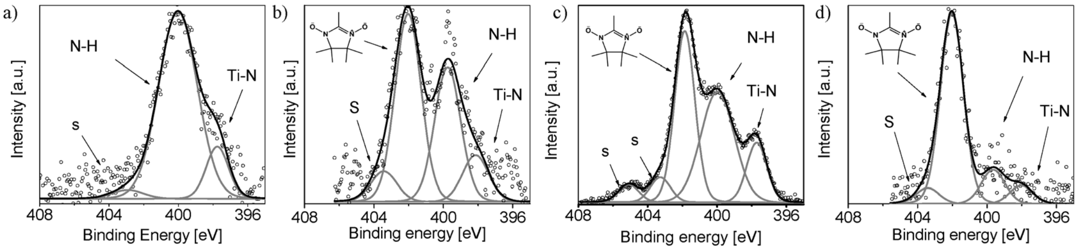

Fig. 2 Thickness dependent N1s core level spectra (together with their peak-fit analysis) of NitPyn thin films deposited on rutile TiO_2(110) single crystals. (a) and (b) 0.3 nm nominally thick film deposited on two surfaces with different Ti^{3+} 3d state densities (17% and 3% respectively, see ESI†). (c) 0.5 nm nominally thick film. (d) 1.0 nm nominally thick film.

molecules are chemisorbed on titanium dioxide. To support this conclusion we perform a series of annealing experiments to determine the desorption temperature of the molecules. The experiments show that the molecules are still present on the surface after annealing up to 790 K just below the annealing temperature used for the preparation of the (1×1) reconstructed surface (see Fig. S1 in the ESI†). This result evidences a strong chemical interaction between NitPyn and $TiO_2(110)$.

As mentioned, rutile $TiO_2(110)$ single crystals are extensively investigated, nevertheless, there is still a strong debate on some aspects like water adsorption/dissociation related to the oxygen vacancy density. Therefore, although the focus of our work is on the organic magnet, at this point we would like to mention two other main observations related to the surface preparation: (1) we have observed the spectroscopic lines due to contributions involving N–H both for very thin films deposited on almost ideally prepared surfaces (up to 4% of Ti^{3+} 3d states) and vacancy rich surfaces (up to 20% of Ti^{3+} 3d presence) (compare Fig. 2a and b, and Fig. S2 and S3 in the ESI†). This would indirectly hint to the fact that water dissociation/adsorption also occurs on almost ideally prepared surfaces. This result is in agreement with recent investigations on water adsorption/dissociation on rutile $TiO_2(110)$.[24] Note that we have the presence of a small residual water partial pressure in the UHV chamber, because NitPyn is thermal-sensitive: we avoid standard baking out procedures, simply adopting low temperature (at around 350–370 K, max 18 hours) bake-out of the Knudsen cell.

(2) Comparing the Ti 2p core level spectra before and after NitPyn deposition, we do not see a healing of the Ti^{3+} d states. The healing at room temperature of the contributions associated with the Ti^{3+} was reported in earlier studies.[26] Recent UHV experimental and theoretical research does not support the healing phenomenon.[4,27] The Ti^{3+} d states are localised below the conduction band and the formation of a pair of hydroxyl groups does not remove/compensate them.[4] This is in agreement with recent calculations that show that their charge is distributed over several titanium atoms, mostly located in the second layer.[3]

An important aspect is that in the very thin films of NitPyn the difference in Ti^{3+} 3d state density that mirrors the oxygen vacancy density is related to higher/lower percentage of molecules that forms a bond with hydrogen atoms, as it can be seen comparing the N1s spectra in Fig. 2 for two films having the same nominal thickness but deposited on two differently prepared surfaces (Fig. 2a: $\sim$17% Ti^{3+} 3d state and Fig. 2b: less than 4% Ti^{3+} 3d state): the molecules show the tendency to favour a bond with the hydrogen atoms, when the hydroxyl population is high enough.

In conclusion, we observe at the interface between NitPyn and $TiO_2(110)$, in the sub- and monolayer regimes, a strong chemisorption of the molecules. The chemisorption perturbs the mesomerism of the nitronyl nitroxide radical, implying the fact that those molecules bound to hydrogen or titanium atoms lose their initial paramagnetic character. The first layer of NitPyn deposited on rutile $TiO_2(110)$ has a mixed nature consisting of molecules with their paramagnetic character and molecules that have lost their paramagnetic character depending on their adsorption site, *i.e.*, ideal *versus* hydrolysed sites.

We believe that our work clarifies the phenomena occurring at the NitPyn–$TiO_2(110)$ interface, with particular attention devoted to the electronic and magnetic properties. This may stimulate further systematic work on the processes involving purely organic magnets at the interface with metals and metal oxides.

In addition, the presence of the first NitPyn layer on top of rutile $TiO_2(110)$ single crystals may act as a ''buffer layer'' on which it may be possible to further deposit organised films of intact organic magnets.

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Notes and references

1 U. Diebold, *Surf. Sci. Rep.*, 2003, **48**, 53–229.
2 F. H. Jones, *Surf. Sci. Rep.*, 2001, **42**, 75–205.
3 C. L. Pang, R. Lindsay and G. Thornton, *Chem. Soc. Rev.*, 2008, **37**, 2328–2353.
4 C. Di Valentin, G. Pacchioni and A. Selloni, *Phys. Rev. Lett.*, 2006, **97**, 166803.
5 S.-A. Savu, I. Biswas, L. Sorace, M. Mannini, D. Rovai, A. Caneschi, T. Chasse and M. B. Casu, *Chem.–Eur. J.*, 2013, **19**, 3445–3450.
6 J. S. Miller, *Chem. Soc. Rev.*, 2011, **40**, 3266–3296.
7 I. Ratera and J. Veciana, *Chem. Soc. Rev.*, 2012, **41**, 303–349.
8 D. Gatteschi, A. Cornia, M. Mannini and R. Sessoli, *Inorg. Chem.*, 2009, **48**, 3408–3419.
9 M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi and M. Kinoshita, *Chem. Phys. Lett.*, 1991, **186**, 401–404.
10 J. Caro, J. Fraxedas, O. Jürgens, J. Santiso, C. Rovira, J. Veciana and A. Figueras, *Adv. Mater.*, 1998, **10**, 608–610.
11 J. Caro, J. Fraxedas and A. Figueras, *J. Cryst. Growth*, 2000, **209**, 146–158.
12 S. Molas, C. Coulon and J. Fraxedas, *CrystEngComm*, 2003, **5**, 310–312.
13 F. Grillo, H. Fruchtl, S. M. Francis, V. Mugnaini, M. Oliveros, J. Veciana and N. V. Richardson, *Nanoscale*, 2012, **4**, 6718–6721.
14 F. Grillo, V. Mugnaini, M. Oliveros, S. M. Francis, D. J. Choi, M. V. Rastei, L. Limot, C. Cepek, M. Pedio, S. T. Bromley, N. V. Richardson, J. P. Bucher and J. Veciana, *J. Phys. Chem. Lett.*, 2012, **3**, 1559–1564.
15 S. Mullegger, M. Rashidi, M. Fattinger and R. Koch, *J. Phys. Chem. C*, 2012, **116**, 22587–22594.
16 S. Mullegger, M. Rashidi, M. Fattinger and R. Koch, *J. Phys. Chem. C*, 2013, **117**, 5718–5721.
17 J. Liu, H. Isshiki, K. Katoh, T. Morita, B. K. Breedlove, M. Yamashita and T. Komeda, *J. Am. Chem. Soc.*, 2013, **135**, 651–658.
18 S. Abb, S. A. Savu, A. Caneschi, T. Chasse and M. B. Casu, 2013, submitted.
19 S.-A. Savu, M. B. Casu, S. Schundelmeier, S. Abb, C. Tonshoff, H. F. Bettinger and T. Chasse, *RSC Adv.*, 2012, **2**, 5112–5118.
20 S. A. Savu, S. Abb, S. Schundelmeier, J. D. Saathoff, J. M. Stevenson, C. Toenshoff, H. F. Bettinger, P. Clancy, M. B. Casu and T. Chasse, *Nano Res.*, 2013, **6**, 449–459.
21 P. Y. Jouan, M. C. Peignon, C. Cardinaud and G. Lempérière, *Appl. Surf. Sci.*, 1993, **68**, 595–603.
22 N. C. Saha and H. G. Tompkins, *J. Appl. Phys.*, 1992, **72**, 3072–3079.
23 J. Wei, *J. Appl. Phys.*, 2002, **92**, 6525–6530.
24 D. A. Duncan, F. Allegretti and D. P. Woodruff, *Phys. Rev. B*, 2012, **86**, 045411.
25 E. F. Ullman, *J. Org. Chem.*, 1970, **35**, 3623–3631.
26 L.-Q. Wang, D. R. Baer, M. H. Engelhard and A. N. Shultz, *Surf. Sci.*, 1995, **344**, 237–250.
27 F. Allegretti, S. O'Brien, M. Polcik, D. I. Sayago and D. P. Woodruff, *Surf. Sci.*, 2006, **600**, 1487–1496.