UNIVERSITÄT DUISBURG ESSEN

SFB 616

Organic Molecular Nanowires: The growth of DiMe-PTCDI on KBr(001) and NaCl(001)

M. Lange, M. Fendrich, C. Weiss, T. Kunstmann, and R. Möller

Fachbereich Physik and Center for Nanointegration Duisburg Essen (CeNiDE), Universität Duisburg-Essen, D-47048 Duisburg

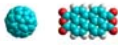
CeNIDE CENTER FOR NANOINTEGRATION DUISBURG-ESSEN

C4

Motivation: DiMe-PTCDI on alkali halide (001) surfaces

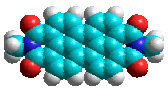
Topic of interest: growth of organic molecules on insulating surfaces (→ molecular electronics,…)

Model system:
- Alkali halide(001) surfaces, easy to prepare
- Prototypical organic semiconductor molecules (C_{60} [1], PTCDA [2,3])

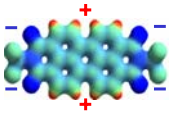


BUT: no "controlled" growth so far
e.g. on KBr(001): C_{60} (fractal islands)
PTCDA (3d crystallites)

New candidate: DiMe-PTCDI



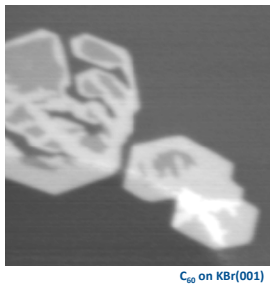
N,N'-dimethylperylene-3,4,9,10-bis(dicarboximide)



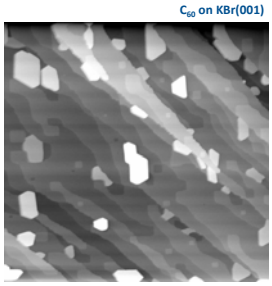
DiMe-PTCDI: charge distribution negative oxygens

studies e.g. on Ag(111), Ag(110) [4]

Goal (hopefully!): Growth of controlled molecular structures on insulators, low dimensional structures?



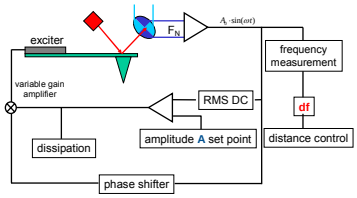
C_{60} on KBr(001)



PTCDA on KBr(001)

Technique: frequency modulation (FM) – AFM

- Sample is brought near an oscillating silicon cantilever with tip
- Tip-sample forces change the resonance frequency, distance control keeps the frequency shift df constant: atomic resolution imaging also on insulating surfaces possible
- Second control loop keeps amplitude A constant: external driving energy = **dissipated energy**



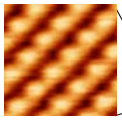
Scheme of the control loops in FM-AFM

Experimental details

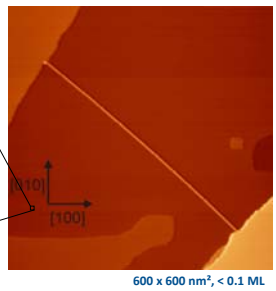
- Experiments performed in UHV
- Microscope: Omicron AFM/STM in non-contact – mode (@ 300 K)
- Sample preparation: KBr(001)/NaCl(001) single crystals (Korth, Germany)
  in situ – cleaving
  heating to 450 K after cleavage
- Evaporation of various amounts of DiMe-PTCDI from home-built crucible (sample @ 300 K)
- Flux control: quadrupole mass spectrometer

Experiments: DiMe-PTCDI on KBr(001)

Low coverage:
- Molecules form long "wires":
  < 10 nm wide, 600 nm long
- Wires stretched over substrate terraces
- Pinned at step edges
- Not stable otherwise?
- Between wires: atomic resolution of KBr, no wetting layer of molecules

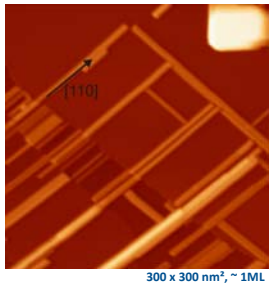


1.5 x 1.5 nm²



600 x 600 nm², < 0.1 ML

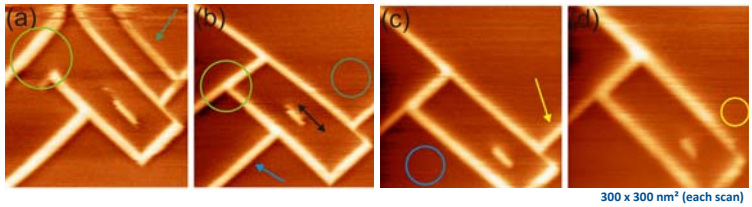
Higher coverage:
- More wires, at least 2 molecular layers high
- Wires stretched between step edges or between other wires
- Preferred orientation: along substrate [110] direction
- Too narrow to scan upon a wire → no molecular resolution



300 x 300 nm², ~ 1ML

No step edges around?

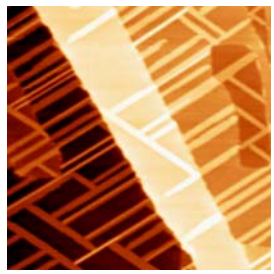
- Well-cleaved KBr crystal, huge terraces (μm)
- Scans ~ 10 min after evaporation of molecules
- Wires move or vanish → high mobility of molecules on the surface



300 x 300 nm² (each scan)

Evaporation on cold crystal (~250 K)

- Height of wires: one layer
- KBr step edges determine the orientation
- Wires as short as possible between steps
- Both [110] and [1̄10] occur when neither direction is preferred by step edges
- KBr steps break into [100] and [010] kinks; kinks might act as nucleation centers
- No molecular resolution possible (sample heating up!)



400 x 400 nm², ~ 0.3 ML

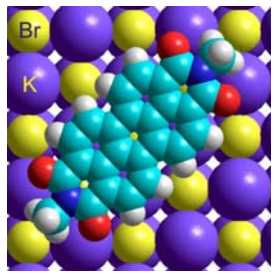
Model: force field calculation + common sense

- Interaction: empirical potential (AMBER) + electrostatic interaction
- Results: optimum position for a single molecule
- [110] preferred, on top of Br ion
- Preferred orientation + close- packed arrangement = wire

Tentative Model:

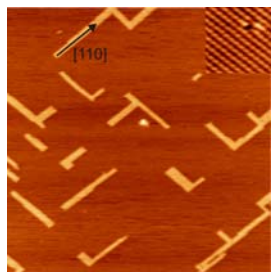
p (2 x 2) – superstructure on KBr(001) (brickwall)

(see also [5])



New Experiments: DiMe-PTCDI on NaCl(001)

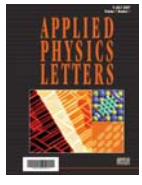
- Wires on KBr unstable (obviously);
- Desirable: more stable wires
- General mechanisms?
- NaCl lattice constant 562 pm (KBr: 658 pm)
- p(2 x 2) – superstructure on KBr: not soooo close-packed
- Molecules form "wires", 2 ML high, [110] direction
- Wires stretched over substrate terraces, not pinned at step edges
- Shape of wires does not change for several hours
- Between wires: atomic resolution of NaCl



400 x 400 nm², 0.2 ML, inset: 3 x 3 nm²

References

[1] S. A. Burke, J.M. Mativetsky, R. Hoffmann and P. Grütter, PRL **94**, 096102 (2005)
[2] T. Kunstmann, A. Schlarb, M. Fendrich, Th. Wagner, R. Möller and R. Hoffmann, PRB **71**, 121403 (**R**) (2005)
[3] S. A. Burke, W. Ji, J. M. Mativetsky, J. M. Topple, S. Fostner, H.-J. Gao, H. Guo, and P. Grütter, PRL **100**, 186104 (2008)
[4] Glöckler et al., Surf. Sci. 405, 1 (1998)
[5] M. Fendrich and T. Kunstmann, APL 91, 023101 (2007)



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Contact

Manfred Lange
Tel. +49 203 379 2137
manfred.lange@stud.uni-due.de
Prof. Dr. R. Möller
Tel. +49 203 379 4220
rolf.moeller@uni-due.de

University of Duisburg-Essen
Institut für Experimentelle Physik
AG Prof. Dr. R. Möller
Lotharstr. 1-21
D-47048 Duisburg
MF/MG Building