A NEW STRUCTURE OF BENZOIC ACID ON Cu(110) INCLUDING COPPER ADATOMS STM INVESTIGATIONS AND DFT CALCULATIONS

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The feature sizes in semiconductor technology have been reduced very fast and continuously so that the feature size reduction seems to hit, physical and economical limits. Furthermore the tools to investigate nanoscale objects have improved tremendously, mainly driven by the invention of scanning probe methods. So it is a promising opportunity to replace the known systems by integrating molecules in electronic circuits [1].
It is necessary to develop reproducible contacting methods of molecules to some, usually metallic electrodes, and secondly to find suitable molecule/metal combinations that provide the desired functionality reliably.

In this report we will focus on the second point. The carboxylate/copper system is a promising alternative to the thiol/gold systems which are studied in many other projects, for instance in [2,3,4]. Today an advantageously employed metal for wires or interconnects in electronics industry is copper, due to its low resistance. Copper in combination with new dielectric materials is thought to have the prerequisites for developing integrated circuits with decreasing switching times, reduced heat dissipation and higher reliability. According to this strategy it is essential to get a fundamental understanding of the organic/copper interface, like the carboxylate/copper interface for example we are focusing on.
Carboxylic acids are chosen because both oxygen atoms of the carboxyl group link with the copper surface. The carboxylates create ordered monolayers. Because of this binding situation (angles) the carboxylate/copper system has less structure formation possibilities than the thiol/gold system for example. If a copper surface with [110]-direction is chosen, the specific surface structure (lines) leads additionally to a confinement of the spatial diffusion possibility of the molecules on the surface and further to a texturing with a preferred direction. With increasing coverage, several large area and large domain with well ordered structures occur containing species oriented both parallel and perpendicular to the surface with defined unit cells [5].
To get a statement about the basic geometries and electron transport properties, benzoic acid (C_6H_5COOH) is deposited from the gas phase on Cu(110) surfaces and the arising benzoate monolayers are characterized by UHV-STM.
By topographical analysis with the UHV-STM we found some of the structures described by Frederick and Barlow [5,6] e.g. the close-packed c(8x2)-structure (see fig. 1) of all upright standing molecules.
Beside the structures shown there, we found a new structure with a higher packing-density of the molecules in the monolayer (see fig. 1). This structure can be described as structure with a (1 1, -4 2) periodicity. All molecules in this structure are upright standing with a packing-density of one molecule per three outermost surface copper atoms. Compared to the packing-density of the common c(8x2)-structure with four copper surface atoms per molecule, this represents a strong increase in the molecular packing-density and the structure with the highest surface coverage, observed so far. Looking at the height-profiles of the close-packed phase, a slight elevation of around 0.25 nm is found for the central molecule row, leading to the suggestion of an adatom stabilized structure.

Matching the new structure to the copper lattice, results in energetically unfavourable adsorption sites for every second row of molecules, supporting the adatom suggestion.
By DFT calculations, the overall energies of the adatom structure and a structure without adatoms are computed. The calculations show, that the structure without adatoms is unstable and relaxes into an energetically even less favourable structure. Both structures, relaxed and unrelaxed, are energetically less favourable, than the adatom stabilized structure. The evolution of the adatom stabilized surface is also supported by the observation of benzoate-adatom complexes on the surface for lower coverages in literature [7].
A model of the surface structure built by benzoic acid on a Cu(110) surface including copper adatoms based on STM investigations with linescans and height-profiles will be presented. The stability of the new structure will be discussed based on DFT-calculations.

References:

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Figures:

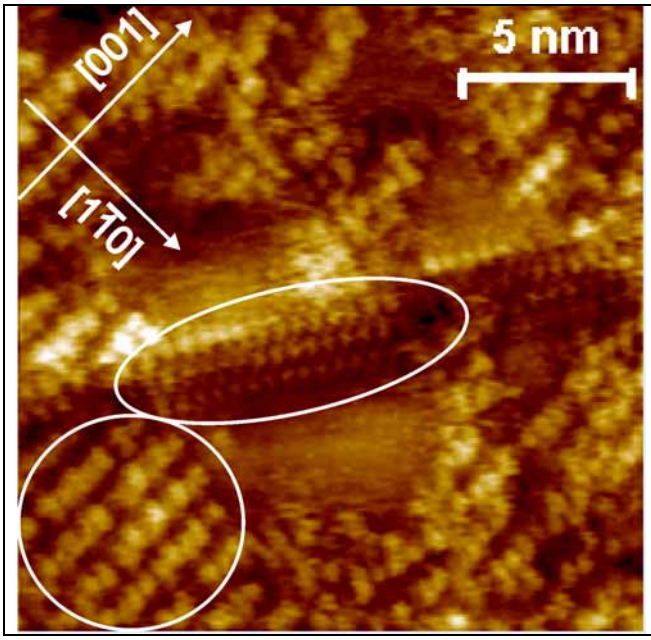

Fig. 1 STM-Topography of benzoic acid on a Cu(110) surface. The lower left circle assigned an area with a c(8x2)-structure of all upright standing molecules. The structure in the upper right area is a higher packed structure of upright standing molecules and is based on molecules situated on copper adatoms.