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SCIENTIFIC REPORT

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Host: Prof. Dr. Karina Morgenstern, Institut für Festkörperphysik, Abteilung für atomare und molekulare Strukturen, Leibniz Universität Hannover, Hannover (DE)
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Purpose of Visit

Integration of molecular switches into larger circuits requires arranging them on surfaces. This project contributes to the understanding of switches based on isomerization reactions in direct contact to the technologically important silicon surface. So far there exist reports on switches based on the *cis-trans* isomerization of azobenzene derivatives induced by various stimulants, mostly electrons. The majority of these works has been carried out on metallic surfaces, preferably Au(111). We here adsorb 4-anilino-4'-nitroazobenzene molecules on a Si(100) substrate and investigate the influence of this substrate on the switching properties.

Description of the work carried out during the visit

First of all, I prepared a clean atomically flat Si(100) surface. This process requires extremely good UHV conditions as well as a high purity of sample holders, manipulators etc.

During this visit in Hannover I focused on understanding the influence of the silicon surface on electron and light induced conformation and configuration changes of 4-anilino-4'-nitroazobenzene. These experimental studies will be compared to calculations performed by M. Hermanowicz and Prof. M. Radny using spin resolved density functional theory methods.

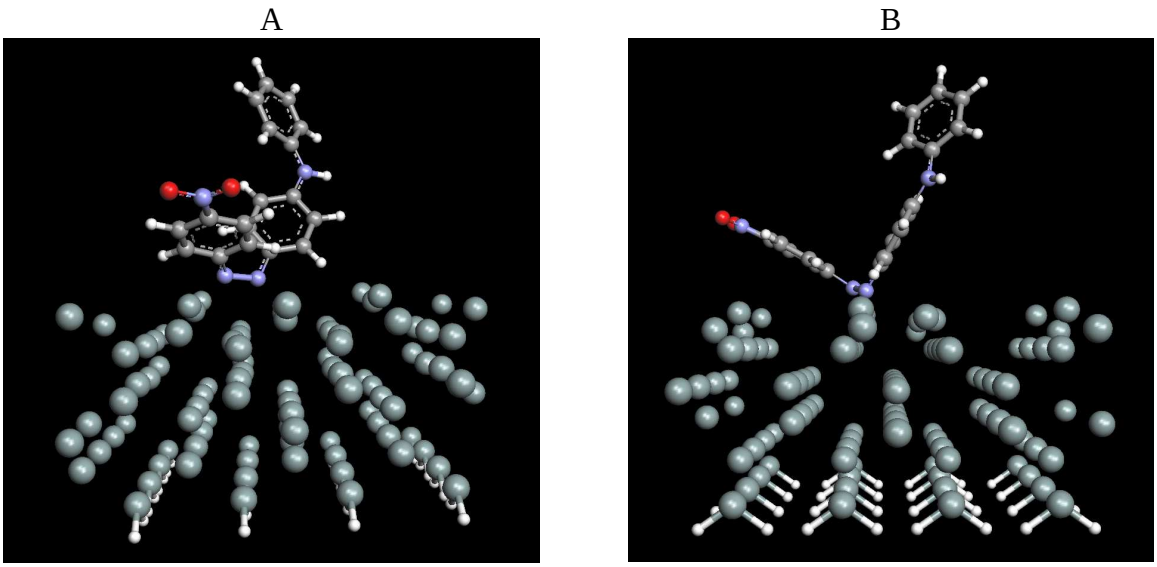

Fig. 1. Simulated structure of one of the possible adsorption structures of 4-anilino-4'-nitroazobenzene on Si(100)-(4x2); A – view perpendicular to silicon dimer rows, B – view in parallel to the silicon dimer rows

Figure 1 presents one of many possible structures of the molecule adsorbed on Si(100)

obtained using geometry optimization by means of energy minimization in the PM6 algorithm.

The experiments were performed with a low temperature STM. Low temperature is necessary to establish a stable adsorption structure of molecules on a very reactive substrate such as Si(100), because a higher adsorption temperature (above 100K) usually leads to dissociative adsorption such as in the case of water molecules causing the C-defects on the Si(100) surface. Low temperature eliminates diffusion as well as desorption of the molecules due to thermal energy.

The molecules were sublimated *in-situ* in UHV system onto the Si(100) substrate. After this preparation, molecules in several forms were found on the surface. The configurational and conformational changes were induced via electrons and via light illumination.

Description of the main results obtained

The clean Si(100) surface was obtained after several flash procedures in a UHV chamber with a base pressure on the level of $5x10^{-11}$mbar. During the flash the pressure was kept below $7.5x10^{-10}$mbar. Fig. 2 shows clean silicon surface with a density of defects on the level of 0.015 nm^{-2}.

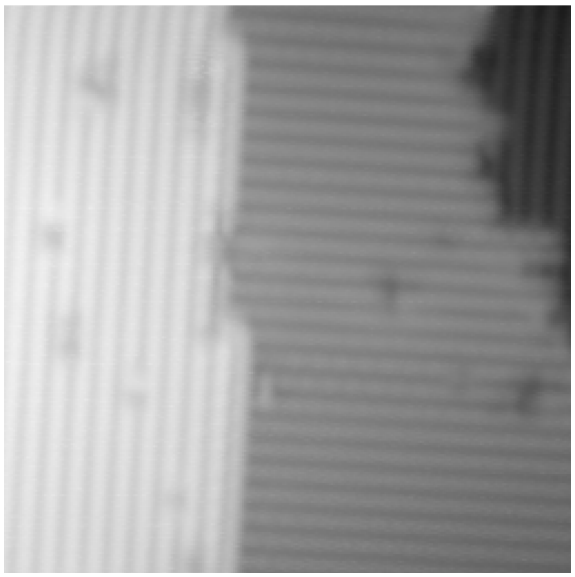

Fig. 2. STM image of a clean Si(100) surface; scan size 21nm x 21nm, I_t=49pA, V=2.5V

The molecules were sublimated onto the substrate at a temperature of 25K from a Knudsen cell at the temperature of 400K and a pressure of $1.5x10^{-8}$mbar. The base pressure in the preparation chamber was at the level of $5x10^{-11}$mbar. After the evaporation the sample was immediately transferred into the STM and cooled down to a temperature below 6K.

A B

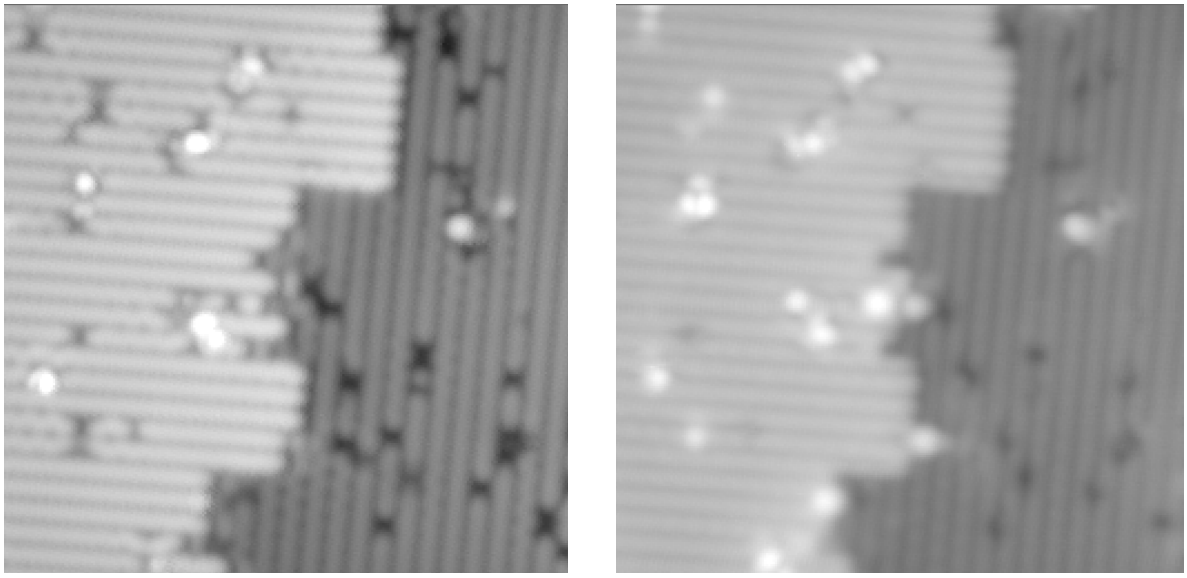

Fig. 3. STM image of molecules adsorbed on Si(100); A – unoccupied states, B – occupied states; image size 21nm x 21nm, I_t= 30pA, V_A= -2.5V, V_B= 2.5V

Fig. 3 depicts various structures of adsorbed molecules. Molecules are imaged differently in both occupied and unoccupied states. Fig. 4 shows a high resolution image of one of the most common adsorption structures in both polarizations. The defected structure of silicon around the adsorption site is clearly visible.

A B

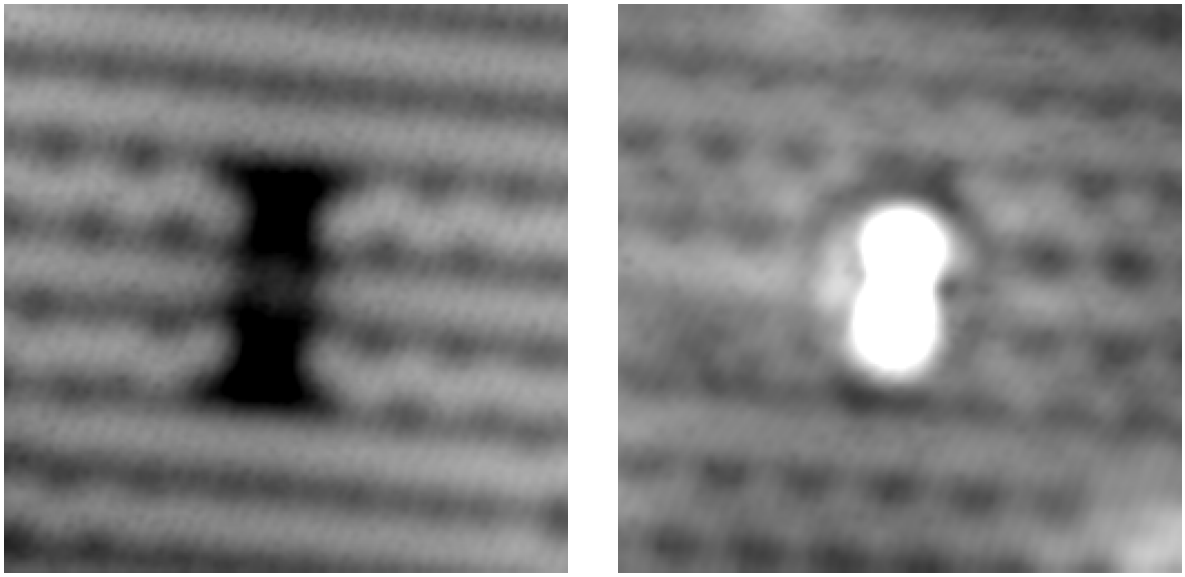

Fig. 4.A high resolution STM image of one of most common adsorption structures; A – unoccupied states, B – occupied states; image size 5nm x 5nm, I_t= 200pA, V_A= -2.5V, V_B= 2.2V

In order to characterize the electronic structure of the adsorbed molecules and to determine the influence of the adsorption configuration on this structure, I carried out STS measurements on both the clean substrate and on individual molecules in different configurations. An example of the obtained spectra is shown in Fig. 5. Peaks characteristic for silicon disappear and we can observe a lowest unoccupied molecular orbital of the molecule (LUMO) at around 2.3eV. This peak may be LUMO +1 or even +2 as the energy gap of Si

makes peaks lower in energy than 1.7eV invisible is STS spectra. The calculations of electronic structure will provide an answer.

Furthermore, in order to characterize the switching properties, inelastic electron tunneling manipulation were performed at different conditions within the range from zero energy to decomposition of the molecule.

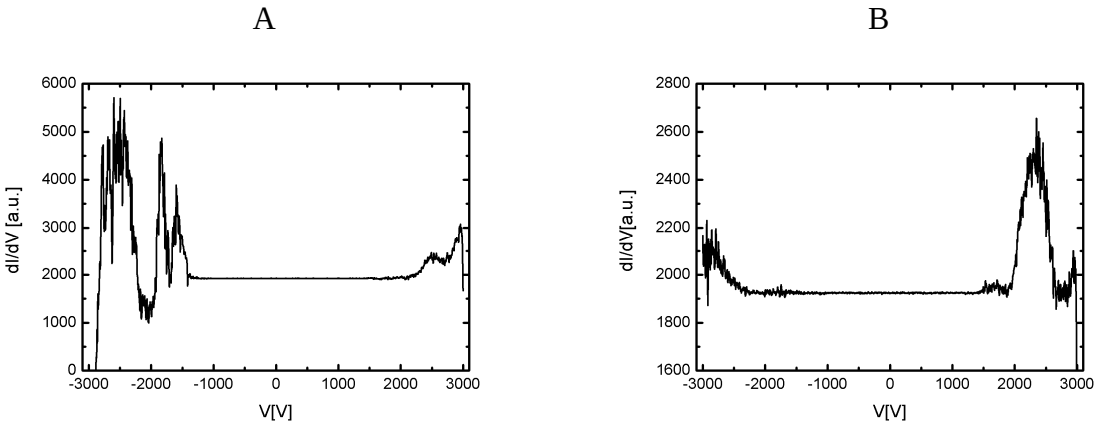

Fig. 5. dI/dV spetra; A – on clean Si(100); B – on the molecule presented in Fig. 4. Lock-in parameters for spectroscopy: f_{mod}=479.1Hz, V_{mod}=6mV,

Finally, surface processes were induced by exposing the sample to light from a mercury lamp. Light induced configurational changes are observed for species, which at present are interpreted as parts of the 4-anilino-4'-nitroazobenzene and not whole molecules. Yet the calculations of all possible adsorption structures may disprove this interpretation.

The temperature of the sample during the illumination reached 25K. In situ annealing was performed in order to discriminate thermal from photo-induced processes. An experiment with annealing the sample up to 100K induced further changes in the structure of adsorbed molecules.

Projected publications/articles resulting or to result from the STSM

The data obtained during my stay at the Leibniz University Hannover are currently analyzed. DFT calculations are in progress. It is planed to present them in the near future at scientific conferences. Moreover an article "Electron and light induced processes of 4-anilino-4'-nitroazobenzene adsorbed on Si(100)" will be prepared for publication.