

Electronic and structural properties of DiMePTCDI/ S- GaAs(100) interfaces

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Introduction

Planar and highly symmetric molecules like N,N'-dimethyl-3,4,9,10-perylenetetracarboximide (DiMePTCDI) belong to a material class known as organic semiconductors. These molecules interact predominantly via van-der-Waals forces and can form ordered crystalline solids or thin films. The weak van-der-Waals bonding between organic molecules and substrates allows quasiepitaxial growth even in the presence of lattice mismatch. Our work is focused on the modification of semiconductor surfaces and interfaces using such organic semiconductors. The energy level alignment at the interfaces is investigated using Photoemission Spectroscopy (PES) while Near Edge X-ray Fine Structure spectroscopy (NEXAFS) is used to determine the orientation of the molecules.

Experimental

The GaAs(100) surfaces were passivated by etching in S₂Cl₂:CCl₄ (1:3) for ten seconds, followed by rinsing in CCl₄, acetone, ethanol and de-ionised water for 5 seconds each and finally dried in a N₂ flow. Annealing for 30 min at 470°C and a pressure below 5·10⁻⁹ mbar results in sulphur passivated 2×1 reconstructed GaAs(100) surfaces, further on being denoted as S-GaAs. The organic layer is deposited by organic molecular beam deposition (OMBD) onto the S-GaAs substrates with the thickness monitored by a quartz microbalance. Photoemission and NEXAFS spectra were recorded at the Russian-German Beam Line at BESSY. The photoelectron spectra were detected with a CLAM 4 analyser and the NEXAFS studies were performed in the partial photoelectron yield mode. The C1s NEXAFS raw data were divided by the current of the incident X-ray beam and normalized with respect to the absorption at 325eV.

Energy level alignment

Figure. 1 presents an example of valence band structure for the clean S-GaAs(100) surface and after a deposition of a 15 nm DiMe-PTCDI film.

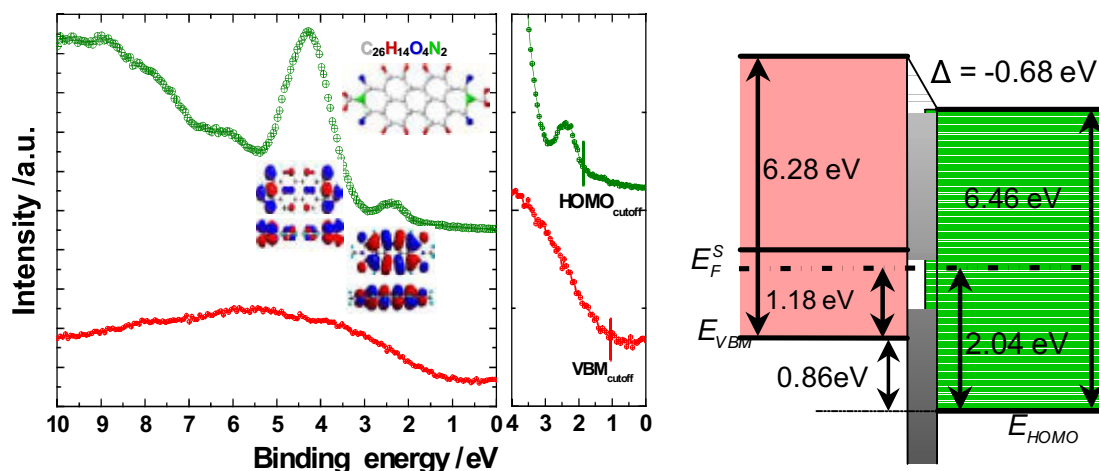


Fig.1: Photoemission spectra of a clean S-GaAs(100) and after evaporation of a 15 nm DiMe-PTCDI film and top view and side view of the calculated molecular orbitals. The energy band diagram for the DiMe-PTCDI/ S-GaAs(100) interface is also shown

The feature with the lowest binding energy in the DiMePTCDI spectrum originates from the highest occupied molecular orbital (HOMO). This molecular orbital has π -character as can be seen from the top and side view of the charge distribution on the molecule calculated using Gaussian 98 (B3LYP/3-21G)¹. Six molecular orbitals contribute to the dominant feature at 4.2 eV binding energy. These orbitals show predominantly π -character and are located around the imide group. Here, E_{HOMO} and E_{VBM} represent the energy edge of the highest occupied molecular orbital of the DiMePTCDI and the valence band maximum of the substrate, respectively, relative to E_F . The $E_{VBM}-E_{HOMO}$ offset is determined to be (0.86 ± 0.10) eV. The ionization energies of (6.28 ± 0.10) eV and (6.46 ± 0.10) eV for S-GaAs(100) and DiMe-PTCDI the interface dipole is determined to be (-0.68 ± 0.10) eV.

Orientation of molecules

In NEXAFS absorption of the incident synchrotron light takes place due to the excitation of an electron from a core shell into the lowest unoccupied states. In perylene derivatives the lowest unoccupied molecular orbitals are derived from the π -electron system with its orbitals oriented perpendicular to the molecular plane. Due to selection rules excitation between the core shell and the π -orbitals takes place if the electric field vector of the incident light has a component parallel to the π -orbitals. Figure. 2 presents selected C-K shell spectra of DiMe-PTCDI for different angles of

incidence. The incident synchrotron light is linearly polarized with the electric field vector lying in the plane of incidence. Due to the orthogonal orientation of the π^* and σ^* orbitals any increase in π^* -resonance is accompanied by a decrease of the σ^* -resonance. The features above and below 288 eV are attributed to unoccupied π - and σ -states, respectively. With increasing angle of

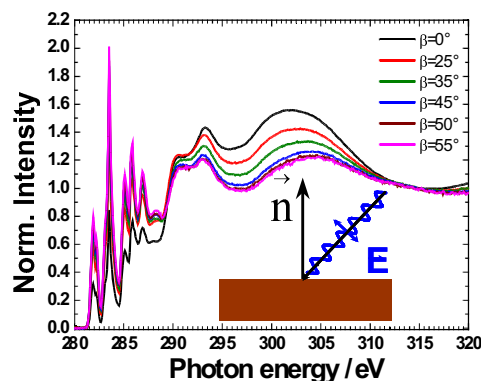


Fig.2: NEXAFS spectra of the C-K edge of DiMePTCDI as a function of the angle of incidence of synchrotron light

incidence the intensity in the π^* -resonance increases. This is a clear evidence that the molecular plane of the molecule is tilted with respect to the substrate surface. In combination with Raman spectroscopy the angle between the (102) plane of crystalline domains and the substrate plane is determined to be $56^\circ \pm 4^\circ$. The long molecular axis of the 2 molecules in the unit cell are deviating from the [110] direction of the substrate by -9° and -48° , respectively.

Summary

The growth of DiMe-PTCDI on S-GaAs(100) surfaces has been investigated using PES and NEXAFS. The valence band maximum of S-GaAs(100) is found to be (0.86 ± 0.1) eV above the HOMO of DiMe-PTCDI. The interface dipole amounts to -0.68 eV with the vacuum level of the DiMe-PTCDI below the vacuum level of S-GaAs(100). NEXAFS investigations show that the molecular planes are tilted with respect to the substrate surface.

Acknowledgements

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2. T. U. Kampen, G. Salvan, A. Paraiian, C. Himcinschi, A. Yu. Kobitski, M. Friedrich, and D. R. T. Zahn, *Appl. Surf. Sci.*, to be published.