GROWTH, INTERACTION PHENOMENA AND PHASE DIAGRAM OF HETEROMOLECULAR ADSORBATES ON METAL SURFACES: THE MODEL SYSTEM PTCDA+CUPC/AG(111)

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Interfaces between organic semiconductors and metals have been investigated intensively in order to improve and develop future electronic devices. In this context the formation of molecular blends (i.e., heteromolecular layers containing at least two different types of molecules, usually charge donors und acceptors) on metal surfaces is of great interest. In this context, we have so far investigated structural and electronic properties of prototypical systems (PTCDA, NTCDA and several metal-Phthalocyanines on noble metal surfaces) using LEEM/PEEM, LEED, STM, NIXSW, ARPES, orbital tomography and STS.

Here we report a novel thermodynamic phase diagram for molecular blends formed by PTCDA+CuPc on Ag(111). In the submonolayer regime, two homo- and three heteromolecular ordered structures occur with different stoichiometry. Large eutectic regions exist in the phase diagram, caused by the opposite intermolecular interaction of the components – repulsive for CuPc, attractive for PTCDA. We find that the repulsive species cause the formation of a 2D lattice gas, the density of which determines the stability of all other phases. Critical values of the gas-phase density are the basis for understanding this constant-volume phase diagram that perfectly describes our experimental observations. We envisage the general validity of this type of phase diagram for binary systems containing gas-like phases.

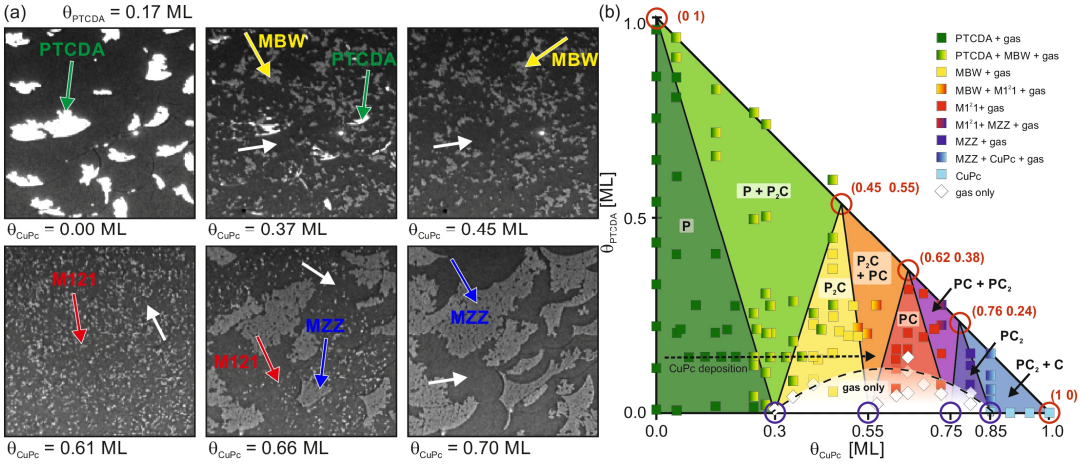

Fig. 1. (a) Bright-field LEEM images recorded during deposition: Initially, the Ag(111) surface is covered by 0.17 ML PTCDA (upper left image). Subsequently, 0.7 ML CuPc were deposited, as shown by the following five LEEM images. The original PTCDA islands (marked by green arrows) are sequentially transformed to MBW (yellow), M121 (red) and MZZ islands (blue), according to the stoichiometry sequence. (b) Phase diagram for PTCDA/CuPc heteromolecular submonolayer structures at 300K: Experiment and thermodynamic model. Colored areas and data points mark the regimes of pure and eutectic phases as obtained from model and experiment, respectively. A dotted arrow indicates the path of the experiment shown in (a). The model is based on more than 20 LEEM experiments with different initial coverages. Abbreviations: P = PTCDA, C = CuPc; Sequence and stoichiometry of the phases: PTCDA (P) – MBW (P2C) – M121 (PC) – MZZ (PC2) – CuPc (C).

Keywords: metal-organic interfaces, molecular blends, phase diagram, LEEM/PEEM