

Domain fracture and recovery process of metal phthalocyanine monolayers via NO₂ and H₂O

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CuPc ultrathin films (5 monolayers) are employed to detect NO₂ in chemFETs [organic thin film transistors (OTFTs)]; while the NO₂ causes OTFT degradation, H₂O restores OTFT performance. To develop an atomic understanding of this H₂O induced performance recovery, NO₂/CuPc/Au(111) was exposed to H₂O, then observed using ultrahigh vacuum scanning tunneling microscopy. After dosing NO₂ (10 ppm for 5 min) onto CuPc monolayers under ambient conditions, domain fracture is induced in CuPc monolayers, and CuPc aggregates are formed near new grain boundaries, consistent with dissociative O adsorption between CuPc molecules and Au(111). Conversely, after exposing H₂O onto a fractured CuPc monolayer for 30 min, fractured domains merge, then large area domains are generated. As the duration of H₂O exposure increases to 4 h, second layer growth of CuPc molecules is observed on the CuPc monolayers consistent with H₂O breakdown of CuPc aggregates which have formed at the domain boundaries. The results are consistent with H₂O driving the removal of atomic O between CuPc molecules and Au(111) consistent with previous sensing results. © 2015 American Vacuum Society.

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I. INTRODUCTION

Organic semiconductors have been applied for pressure, temperature, or chemical sensors.^{1–15} Unlike inorganic materials, the organic molecules can be deposited on substrates by not only vacuum deposition, but also by solution based processes such as spin coating, spray, or simple dipping coating.^{16–22} Metal phthalocyanines (MPc) are an attractive sensing material because they are robust under ambient conditions and high temperature.^{23,24} For example, the molecular structure of MPcs is intact when annealing below 673 K, and only few acidic agents can induce MPcs decomposition. Moreover, the electronic properties of MPcs molecules can be tuned by replacing the central metal atom or adding functional groups to the phthalocyanine rings. Although clean CuPc molecules are intrinsic semiconductors in vacuum, they can be doped to P-type by exposure to an oxidizing agent. Conversely, F₁₆CuPc, which has 16 F atoms replacing the hydrogens in CuPc, is doped N-type after exposure to an oxidizing agent.^{25–30}

Previously, the mechanism for threshold bias (V_{th}) shift in MPc organic thin film transistors (OTFT) sensor (chemFETs) induced by high coverage dosing of strong binding analytes was elucidated.³¹ As the MPc layer is exposed to a high coverage of NO₂, NO₂ dissociates into NO and atomic O on MPc surfaces. After dissociation of NO₂, O migrates and binds between the CuPc and the Au surface,

thereby lifting the CuPc molecules and inducing domain fracture. Existence of atomic O and O induced domain fracture were confirmed by XPS and scanning tunneling microscopy (STM). Since bound atomic O between MPc and Au has a high binding energy, domain fractures can only be physically reversed by annealing above 423 K. A similar process was observed after O₃ exposure, another O donor.^{31–33} Generated domain boundaries can act as an energy barrier to charge transfer in OTFT resulting in irreversible V_{th} shifts. Consequently, chemically induced domain fracture in the MPc layer is consistent with being one important source of the irreversible V_{th} shifts observed in MPc OTFTs.^{34–40}

Previously, it was shown that exposure of H₂O onto CuPc OTFT induces recovery in the sensing response of OTFT films aged in air.⁴¹ Weak binding analytes, such as H₂O or O₂, do not cause the aging effect directly, whereas high binding analytes, such as NO₂, induce an increase in off-state current and a positive threshold voltage shift, which also can be observed in air aged OTFT, consistent with an increase of fixed charge and trap states.^{31,41} This aging effect can be recovered by exposing the CuPc film to humidified clean air at 300 K which induces a decrease of threshold voltage and improvement on/off ratio. However, this recovery process has not been elucidated at the molecular level. Here, ultra-high vacuum scanning tunneling microscopy (UHV-STM) imaging of the CuPc monolayer after exposure to NO₂ and H₂O elucidates the above described recovery process with visualization at the molecular level.

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II. EXPERIMENT

Deposition of CuPc monolayers and STM imaging were performed in an Omicron ultrahigh vacuum chamber (main chamber: 1×10^{-10} , STM chamber: 2×10^{-11}). The single crystal Au(111) surface was cleaned by multiple cycles of sputtering with a 1 kV of Ar^+ ion beam (RBD instruments) with a background pressure of 6×10^{-5} Torr and annealed at 773 K for 30 min. This process was repeated until the surface was atomically flat. The CuPc monolayer was prepared by depositing thick overlayers on the Au(111) surface at 373 K by organic molecular beam epitaxy with an effusion cell (Eberl MBE-Komponenten). Subsequently, the multilayer of CuPc on Au was annealed at 623 K for 5 min to form a flat-lying monolayer on the Au(111) surface because the CuPc-Au interaction is stronger than the CuPc-CuPc molecular interaction.⁴²

Exposures to NO_2 and H_2O were performed in ambient conditions. CuPc monolayers on Au(111) were transferred from the UHV chamber through the load lock and introduced into the atmosphere for NO_2 and H_2O dosing. NO_2 dosed CuPc monolayers were formed with 10 ppm NO_2 in a dry synthetic air mixture. After dosing NO_2 , H_2O was dosed via a bubbler under ambient conditions, and amount of dosed H_2O was controlled by the dosing time. Dosed CuPc monolayers were returned to the UHV chamber, and transferred to the analysis chamber sample stage at 95 K. All STM images were obtained using electrochemically etched W tips.

III. RESULTS AND DISCUSSION

In order to observe the structure transition of CuPc monolayers on Au(111), CuPc monolayers were exposed to a high dose (10 ppm for 5 min) of NO_2 ; afterwards, the surface was imaged by UHV-STM. In Fig. 1(a), the deposited

clean CuPc monolayer Au(111) is shown as a crystalline single domain on each Au(111) step, and very few defects are observed in STM images. The characteristic Au(111) herringbone reconstruction also is observed through the single monolayer of CuPc. The inset image shows molecular structure of CuPc; a Cu atom at center of the CuPc molecule is imaged as a dark hole, and the four aromatic benzene rings surround central Cu form bright features. As shown Figs. 1(b) and 1(c), after dosing 10 ppm of NO_2 for 5 min at 300 K (~ 2.3 ML assuming $1 \text{ L} = 1 \times 10^{-6}$ Torr sec), the images reveal domain fracture and reorientation of CuPc molecules consistent with previous reports.³¹ Due to NO_2 dosing, the single crystalline CuPc layer disappears and is replaced by a polycrystalline CuPc monolayer. The average domain size in the clean CuPc monolayer is larger than 332 ± 16 nm and limited by only the Au(111) step size, whereas NO_2 dosed CuPc monolayer has a domain size of 46.8 ± 6 nm. Previous reports confirm that as NO_2 is dosed onto the CuPc monolayer, dissociation of NO_2 into NO and O occurs on the CuPc surface, then atomic O diffuses between CuPc and Au(111) because the CuPc/O/Au binding energy is higher than the O/CuPc/Au binding energy.³¹ The migration of O to lie between CuPc and Au(111) induces a lifting of the CuPc molecules. Domain boundaries are generated by displacement of CuPc, and the remaining CuPc molecules undergo rearrangement along generated domain boundaries. These displaced CuPc molecules mix with hydrocarbon from ambient air to form aggregates along the domain boundaries of the CuPc monolayer. This domain fracture cannot be reversed spontaneously without annealing above of 423 K.

The domain fracture in the CuPc monolayer induced by NO_2 dosing can be chemically recovered by introducing

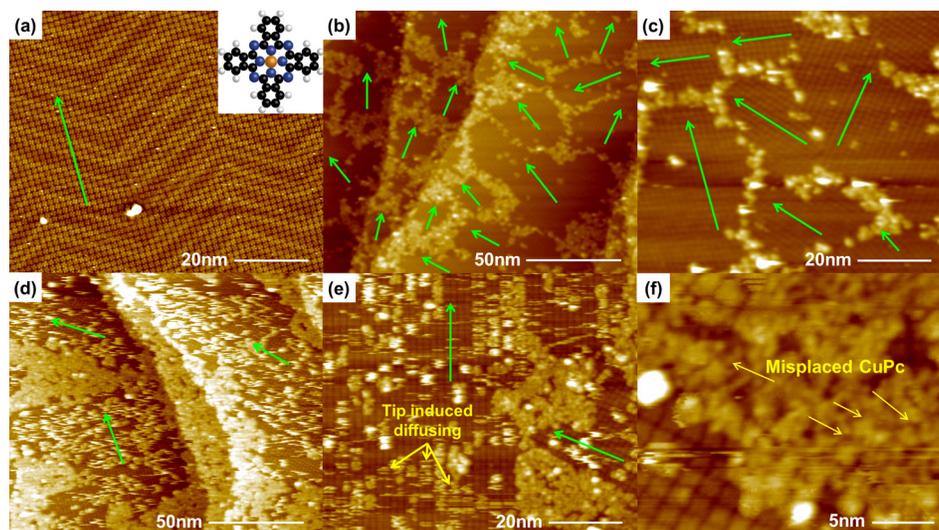


Fig. 1. (Color online) Empty-state STM images ($V_s = 2.0$ V, $I_t = 20$ pA) of a CuPc monolayer. Arrows indicate orientation of CuPc molecules and show multiple domain directions. (a) Clean CuPc monolayer deposited by MBE on Au(111). Inset image shows the schematic molecular structure of CuPc (b) CuPc monolayer dosed with 10 ppm of NO_2 for 5 min at 300 K (~ 2.3 ML), and annealed at 323 K for 10 min ($V_s = 2.0$ V, $I_t = 20$ pA). (c) Zoomed STM image of NO_2 dosed CuPc monolayer (d) CuPc monolayer dosed with 10 ppm of NO_2 for 5 min, then exposed to H_2O for 5 min under ambient conditions (~ 40 GL). Arrows show three domain directions. (e) Zoomed STM image of $\text{H}_2\text{O}/\text{NO}_2$ dosed CuPc monolayer. The tip induced diffusion of H_2O induced adsorbates are shown arrow. (f) High resolution rendered STM image of domain boundaries, after exposure to H_2O . Arrows indicate misplaced CuPc molecules near domain boundaries.

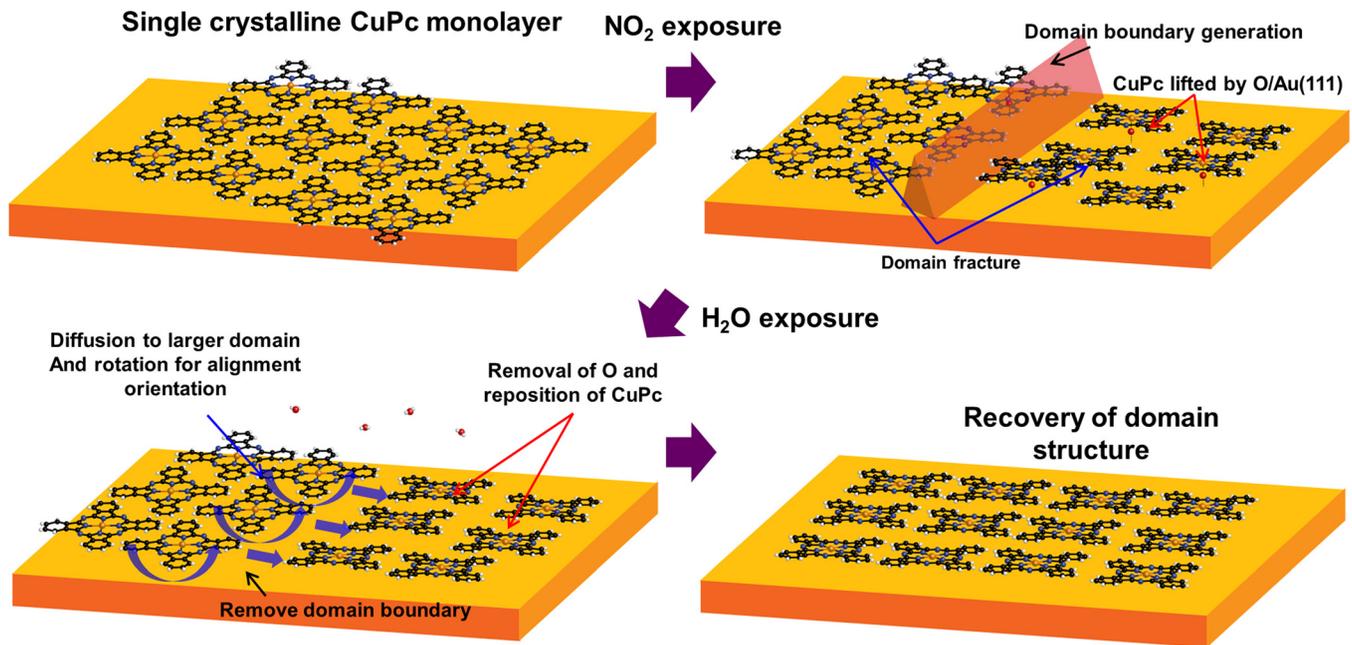


Fig. 2. (Color online) Schematic diagrams show suggested recovery process of CuPc domain structure. Dosing NO₂ onto a CuPc monolayer induces the domain fracture in the CuPc layer, while exposing H₂O leads to recovery of the single crystalline CuPc layer.

H₂O at room temperature, consistent with previous OTFT sensing data.⁴¹ After dosing 10 ppm of NO₂ for 5 min on the CuPc monolayer (~2.3 ML), H₂O from a bubbler was dosed onto the NO₂/CuPc/Au(111) surface for 30 min at 300 K

(~40 GL exposure), as shown in Figs. 1(d) and 1(e). Comparing the large area images of Fig. 1(d) with Fig. 1(b), although the density of adsorbates on the CuPc monolayer dosed with H₂O/NO₂ is higher than on CuPc monolayer

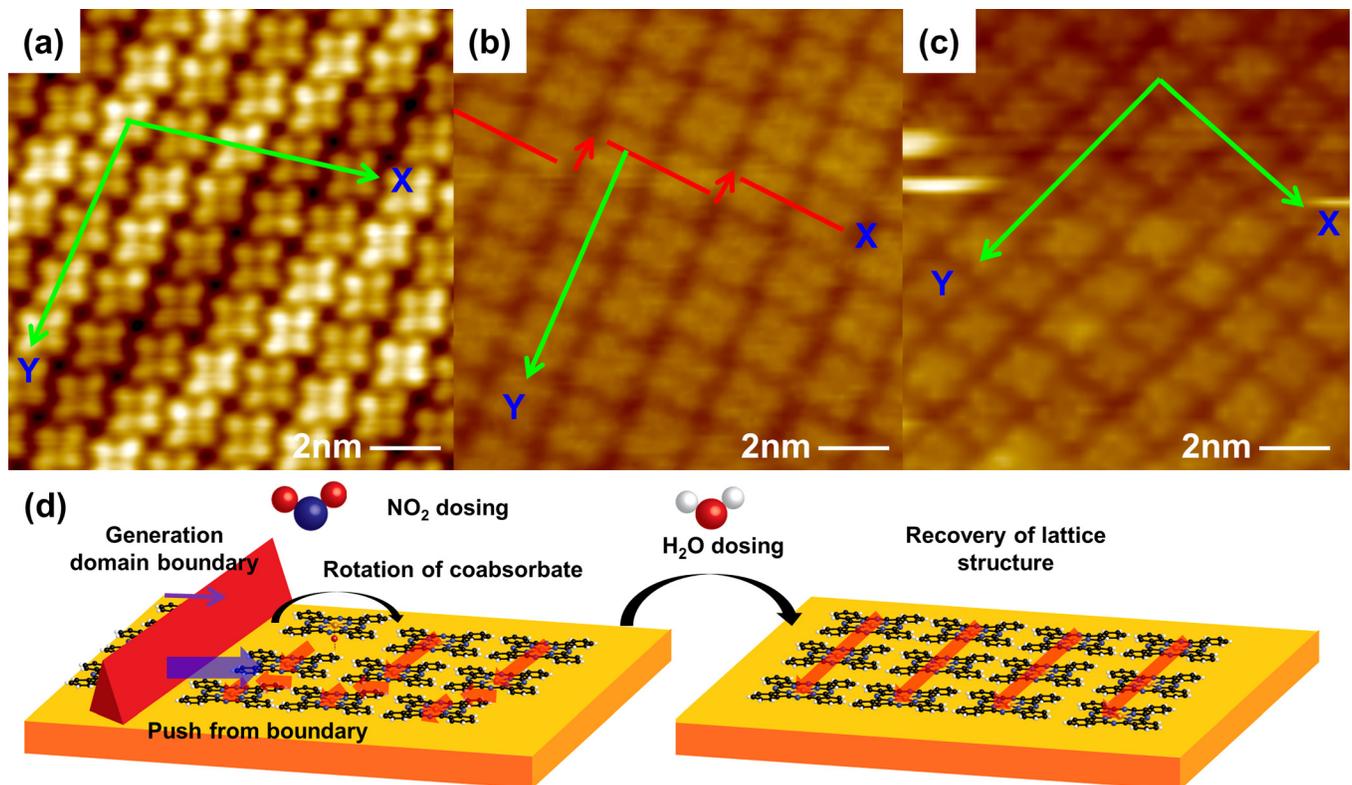


Fig. 3. (Color online) Empty-state STM images of a CuPc monolayer surface. Lines are drawn along the rows of CuPc (a) Clean CuPc monolayer deposited by MBE on Au(111) ($V_s = 2.0$ V, $I_t = 80$ pA). (b) CuPc monolayer dosed with 10 ppm of NO₂ for 5 min at 300 K (~2.3 ML), and annealed at 323 K for 10 min ($V_s = 2.0$ V, $I_t = 20$ pA). (c) CuPc monolayer dosed with 10 ppm of NO₂ for 5 min, then exposed to H₂O for 5 min under ambient conditions (~40 GL). (d) A schematic model of rearrangement of CuPc molecules, following NO₂ and H₂O dosing.

dosed only with NO₂, the density of domain boundaries is significantly decreased by H₂O exposure. In Fig. 1(b), over ten fractured domains are observed on the each Au(111) step on the NO₂ dosed CuPc monolayer. Conversely, after H₂O exposure onto the NO₂/CuPc/Au(111), only one or two domains are detected on the each Au(111) step. As shown by the arrow in Fig. 1(e), diffusion of adsorbates is induced along the scan direction by the STM tip, consistent with the expected weak interaction between the adsorbates and the CuPc molecules. The “H₂O dosing induced adsorbates” are mostly located at domain boundaries. It is noted that “H₂O dosing induced adsorbates” denotes hydrocarbon or other adsorbates introduced onto CuPc layer during H₂O dosing because the samples were exposed to ambient air over 30 min for H₂O dosing. Although the fractured domain structure is recovered by H₂O exposure, islands of CuPc aggregates are still observed along the remaining domain boundaries as shown arrow Fig. 1(f). These misplaced CuPc molecules coexist with H₂O induced adsorbates as complex aggregates. It is noted that since H₂O dosing involves longer exposing of NO₂/CuPc monolayer to ambient condition than NO₂ dosing on CuPc monolayer, additional adsorbates from the ambient air can be introduced on NO₂/CuPc monolayer, resulting in the increases of adsorbates coverage. The H₂O exposure doubles the average domain size from 46.8 ± 6 nm to 95.7 ± 4.9 nm on each gold step. Previous sensing data on OTFTs showed before H₂O dosing, NO₂ induced domain boundaries act as energy barriers to charge transport

consistent with threshold bias shift.³¹ The present studies show that as the fractured CuPc layer is exposed to H₂O, the density of domain boundaries is reduced consistent with the recovery of irreversible sensing response in OTFT. The data are consistent with H₂O reacting with O/Au(111) to form OH/Au(111)^{43–45}



Although nearly formed OH is presumed to lie between CuPc and Au(111) after the reaction, OH has weaker bonding than atomic O to Au(111), facilitating diffusion.⁴⁴

In addition, OH may react with additional H₂O again facilitating diffusion on Au(111).^{43,44}

A simplified model is proposed for H₂O removal of atomic O and reformation of large CuPc domains. As shown in top diagram in Fig. 2, initially NO₂ dosing induces lifting of CuPc molecules via dissociative O chemisorption between CuPc and Au(111), generating domain boundaries. However, after H₂O exposure on the NO₂ dosed CuPc layer, O chemisorbates are removed by H₂O and the lifted CuPc molecules are relocated on Au(111) surface. After domain boundaries are eliminated, CuPc molecules diffuse to CuPc molecules of other domains, and rotate to align in orientation.

As H₂O reverses the domain fracture, lattice mismatch induced by NO₂ dosing also is reversed, as shown in Fig. 3. Figure 3 shows internal area of a CuPc domain before and after exposure to NO₂ and NO₂ + H₂O; two different

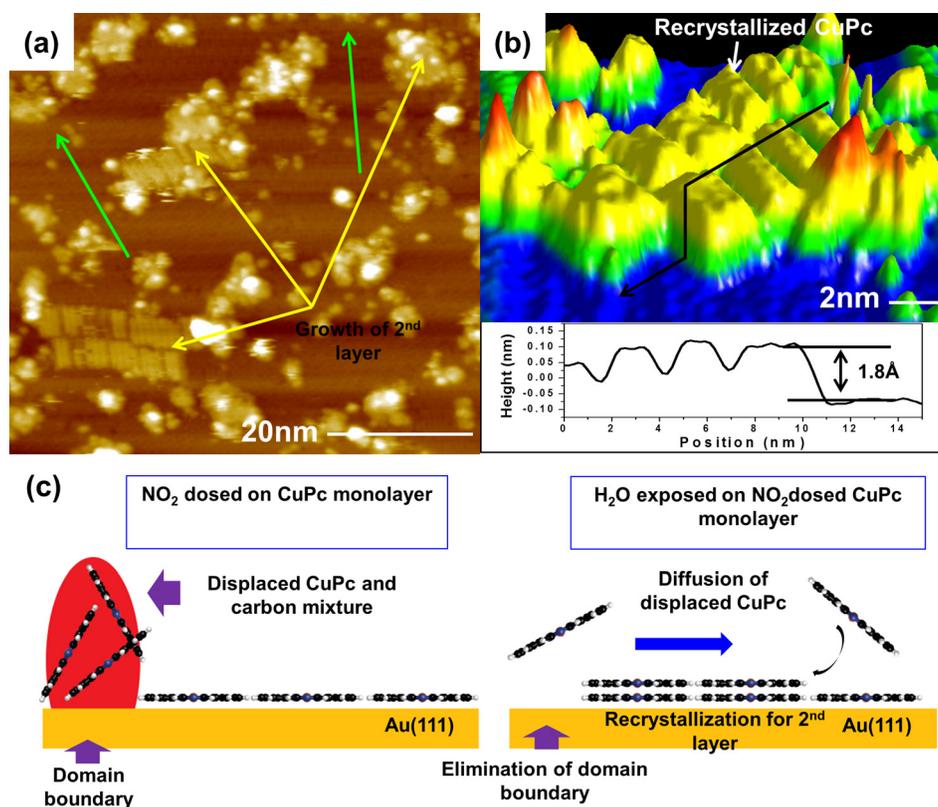


Fig. 4. (Color online) Empty-state STM images of a CuPc monolayer surface. Arrows indicate orientation of CuPc molecules. (a) CuPc monolayer dosed with 10 ppm of NO₂ for 5 min, then exposed to H₂O for 4 h (~320 GL) (V_s = 2.0 V, I_t = 20 pA). (b) Three-dimensional rendering of an STM image of second layer CuPc growth (V_s = 2.0 V, I_t = 40 pA). (c) Schematic model of second growth of CuPc molecules on CuPc monolayer, after H₂O exposure.

directed lines are superimposed along the rows of CuPc to identify the lattice structure. On the clean surfaces, the molecules form nearly perfect linear arrays along both X and Y axes, as shown in Fig. 3(a). However, after a high exposure of NO₂, the rows of CuPc molecules are aligned along only the Y axis, while almost every two molecules shift about 1/2 unit cell along the perpendicular X axis, as shown with arrow in Fig. 3(b). The data are consistent with a broken symmetry in the lattice structure along one direction induced by the structural transition in CuPc monolayer, as shown in Figs. 3(b) and 3(d). However, as shown in Fig. 3(c), after H₂O exposure onto NO₂ dosed CuPc, the molecular two-dimensional symmetry of CuPc is restored to the clean surface structure, consistent with removal of domain boundaries.

Further dosing of H₂O onto the NO₂ dosed CuPc monolayer induces formation of second layer growth of CuPc on the CuPc monolayer. After exposure of H₂O onto NO₂ dosed CuPc monolayers for 4 h, second layer growth of CuPc molecules is observed with a square lattice structure, as shown in Fig. 4(a). A three-dimensional STM image rendering confirms the periodic array of second layer CuPc, and the height of second CuPc layer is about 0.2 nm, consistent with flat laying layer in Fig. 4(b). This second layer CuPc is not observed before H₂O dosing. It is noted that in the topographical molecular structure of MPc, the height of a MPc is about 0.3 nm. However, since contrast in the STM imaging relies on the probability of electron tunneling as well as the local density of states (LDOS) in the molecules, the height of molecules can be altered by scanning conditions or modification of LDOS in molecules; for example, the height of MPc molecules in STM imaging is changed by adding ligands to the aromatic rings or by changing the central metal atom.⁴⁶ Therefore, if H₂O or NO₂ induced adsorbates reacts with CuPc molecules, the brightness of CuPc molecules can be altered. A simple model is proposed, as shown in Fig. 4(c). As domain boundaries are generated by NO₂, misplaced CuPc molecules are mixed with ambient hydrocarbon to form aggregates near domain boundaries. However, after H₂O is introduced, these misplaced CuPc molecules are detached from aggregates and then diffuse onto the CuPc monolayer to form a crystalline second layer.

IV. SUMMARY AND CONCLUSIONS

To visualize gas induced fracturing and recovery CuPc sensor layers in OTFTs on a molecular scale, NO₂ and H₂O were sequentially exposed onto CuPc monolayer, and the exposed monolayer was imaged after each step. After a large dose of NO₂ onto CuPc monolayers, domain fracture is observed consistent with NO₂ being dissociated into NO and atomic O at CuPc monolayer.³¹ The atomic O diffuses into between CuPc molecules and Au(111), resulting in lifted CuPc molecules and the formation of domain boundaries. In addition, misplaced CuPc molecules mix with ambient hydrocarbon to form aggregates near domain boundaries. However, after dosing H₂O for 30 min at in ambient conditions (~40 GL), fractured domains merge with each,

consistent with electrical recovery in OTFTs. In a simple model, H₂O dosing induces elimination of atomic O adsorption and reorganization of CuPc molecules. Additional H₂O exposure onto NO₂ dosed CuPc monolayer induces the formation of the second CuPc layer on top of first layer due to dispersion of the CuPc-hydrocarbon aggregates at the domain boundaries. This structural transition induced by high binding energy analytes and the recovery process by H₂O serves as a model for the role of crystalline structure in the chemical response of the active layer and the dosimetric sensing behavior in OTFT chemical sensors.

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