2D07

Electrical Properties of Copper Phthalocyanine in the Course of Thin Film Formation

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【Introduction】In-situ measurement of the electric conductivity of an organic thin film during vacuum deposition is a new technique for studying the growth morphology and charge carrier transport properties of organic semiconductors as a function of film thickness. By performing the experiment in ultra-high vacuum the effect of atmospheric water vapor and oxygen doping is minimized, allowing the material properties of highly pure organic material deposited to be directly assessed in relation to its proximity to an insulating surface.

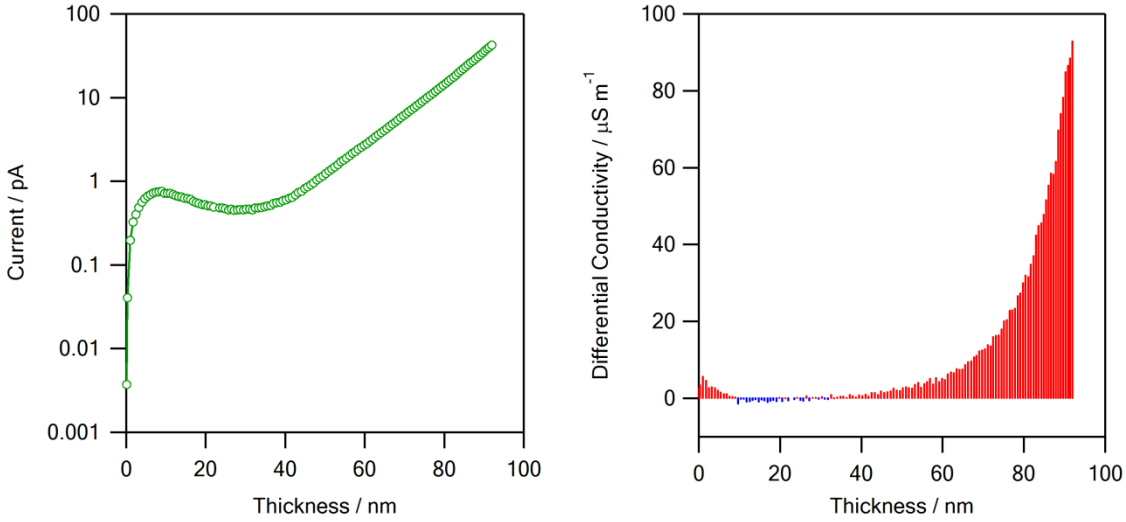
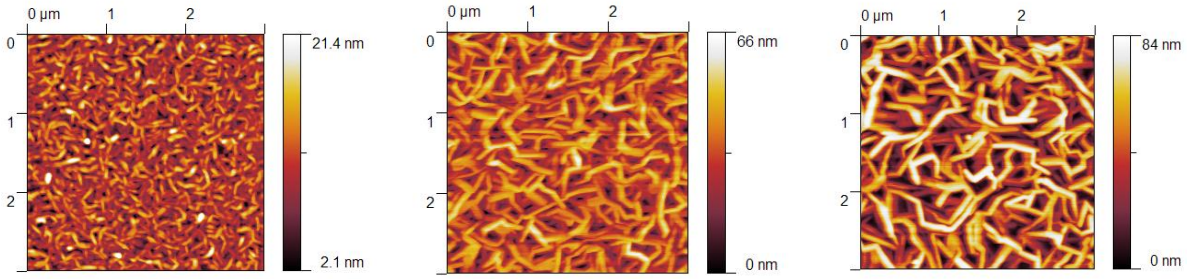


Figure 1. Sample current and differential conductivity at 10 V applied bias for CuPc on sapphire [0001] at 125 °C.

【Experimental】Copper phthalocyanine (Aldrich 99%+) (CuPc) was purified by vacuum sublimation a total of four times, and was transferred to the vacuum chamber directly after the final sublimation run with minimal air exposure. 10 x 10 x 0.5 mm single crystal sapphire (Al_2O_3) [0001] substrates were obtained from Shinkosha. After annealing in air for 5 h at 1000 °C, the substrates were pattered with 5 nm / 100 nm vacuum deposited Cr / Au electrodes, and degassed in vacuum for 1 h at 150 °C immediately before use. The electrode spacing was 0.1 mm. 4 nm square films were deposited over the electrodes through a shadow mask. Film thickness was monitored by a quartz crystal microbalance (Ulvac CTM-6000) and the sample current under an applied bias of 10 V was measured by

a Keithley model 6587 picoammeter/sourcemeter. The deposition rate was 2.1±0.2 nm min^{-1}. The sample temperature during deposition and measurements was 125.0±0.1 ℃. The pressure was maintained under 1×10^{-5} Pa at all times.

The bias voltage was pulsed in order to continually subtract the baseline signal. The pulse polarity was alternated to monitor and correct for sample charging induced by the pulsed waveform. The current resolution is 10 fA. After the film deposition the dependence of the sample current on bias voltage (I-V curves) and temperature (Arrhenius plots) was determined. The samples were later removed from the vacuum chamber and the surface morphology confirmed by AC mode atomic force microscopy (Picoscan Plus / Nanoworld NCST tips).



7 nm CuPc　　45 nm CuPc　　93 nm CuPc

Figure 2. Ex-situ AC AFM images of the CuPc film for various thicknesses.

【Results and Discussion】 The film current through CuPc on sapphire [1000] is shown in Figure 1 as a function of film thickness from 0 to 93 nm. A steep initial rise up to about 7 nm is followed by a region between 7 nm to 32 nm where the sample current decreases. The current rises exponentially after 32 nm to a maximum of 42 pA at 93 nm at which point the deposition was stopped. The high currents are transient however, and decay to 10% of the maximum value within 3 hours. The thermal activation energy of conduction and integral film conductivity measured 24 hours after deposition was 0.82 eV (90-125 ℃) and 4.6×10^{-8} S m^{-1}, respectively. Conductance is Ohmic at bias voltages of up to 10 V.

Representative AFM images for various thicknesses of CuPc film on sapphire [0001] are shown in Figure 2. The grain size is noticeably smaller for the 7 nm film, while the 45 nm and 93 nm films are qualitatively very similar, but in all cases the grains appear to be interconnecting with considerable open volume.

The results indicate that a highly conductive CuPc layer forms below 7 nm, followed by a relatively thick insulating layer in which larger grains form but interconnectivity remains relatively poor. Above a threshold thickness about 32 nm the conductivity of the material is transiently enhanced by the adsorbing molecules.