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Scanning Tunnelling Microscopy and Spectroscopy on Alkali Doped Copper Phthalocyanine

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Abstract. An insulator-metal-insulator transition is observed in thin-film transport experiments of four different, isostructural metal phthalocyanines molecules upon intercalation with alkali atoms. This transition is attributed to band filling of electronic bands originating from the molecular orbitals of the phthalocyanine. In order to investigate the microscopic electronic properties of these films we have performed scanning tunneling spectroscopy on high quality films grown on Si(001). Details of the growth mode and crystal structure of the films are also reported.

Many interesting phenomena occur in organic materials at high carrier density [1]. Particularly interesting is the case of alkali doped C_{60} [2] in which the carrier density can be tuned by intercalation of alkali atoms. This results in different electronic states, such as a metallic, a superconducting [3] and a Mott-Hubbard insulating state [4].

Similar to C_{60}, molecular films of different phthalocyanines(Pc)-based molecules can be turned into metals and again into insulators upon doping with alkali atoms. This transition is due to progressive filling of electronic bands originating from individual molecular orbitals of different symmetry. Electrical transport measurements performed on different metal-phthalocyanines (MPc's) molecules such as CuPc, NiPc, CoPc, and FePc show that at low and high doping concentrations the MPc film is insulating and in the intermediate region it is metallic [5].

In order to further investigate the microscopic electronic properties of these films, we discuss here scanning tunnelling spectroscopy (STS) measurements performed on Potassium doped CuPc films.

The MPc's are a large class of molecules [6] consisting of an identical planar ring of carbon, nitrogen and hydrogen atoms, surrounding one individual atom of a different metallic element (see Fig. 1). The metallic ion can be chosen among a large number of elements and determines the electronic properties of the molecules [7] (e.g. their spin). The electrical and magnetic properties of undoped MPc's have been studied experimentally in the past and it is known that some of the MPc's exhibit ferromagnetism, depending on the crystal structure [8, 9]. It is also known that electron

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and hole conductivity can be induced using a field effect transistor configuration [10, 11]. So far, however, metallic conductivity has never been reported.

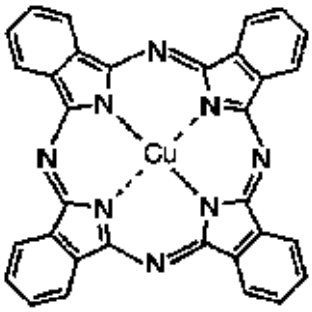

FIGURE 1. Structure of a CopperPhthalocyanine molecule

Our work is based on scanning tunnelling microscopy (STM) and spectroscopy (STS) performed on alkali-doped thin films of CuPc. Film deposition, doping, scanning probe characterization and spectroscopy are performed *in-situ* in a single ultra high vacuum system with a base pressure of 10^{-11} mbar. The CuPc films are thermally evaporated from a Knudsen cell on a Si surface. The films are a few monolayers thick and are deposited at elevated temperature on a 2x1-reconstructed Si(001) surface. Chemical doping is achieved by exposing the film to a constant flux of alkali atoms generated by a current-heated getter source.

Figure 2 shows the STM images of four CuPc films which are few monolayers thick. The film morphology shows a fully closed first monolayer and highly ordered islands typical of the Stransky-Krastanov growth mode. The size of the domains increases with increasing the substrate temperature.

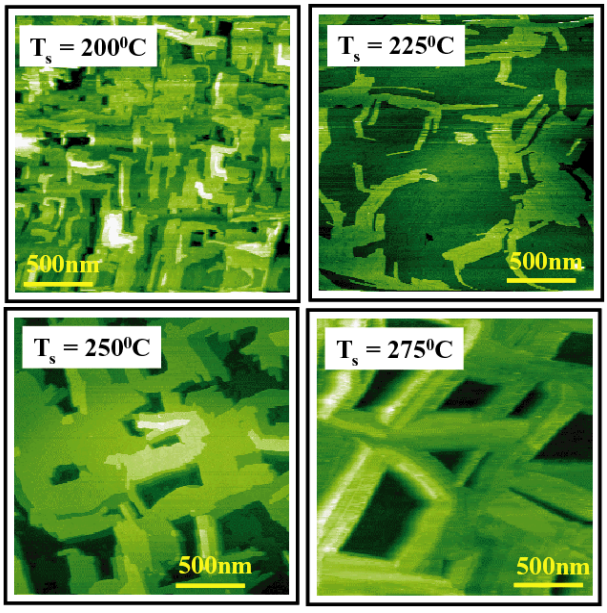

FIGURE 2. STM images of a CuPc film grown at different substrate temperatures.

High-quality STM images of undoped CuPc films exhibiting molecular and submolecular structure are shown in Fig. 3. Ordered molecular rows, all aligned in the same direction are visible upon zooming in on a molecular terrace. The terrace height and the inter-molecular separations in the STM image permit to identify the crystal structure of our films as the α-form of CuPc, consistent with previous literature studies of CuPc film deposition under similar conditions [12]. Zooming in further on the molecular rows gives access to sub-molecular details. The yellow and purple lines correspond to the phenyl ring of the uppermost CuPc molecules, as shown by the identically colored dots in Fig. 3.

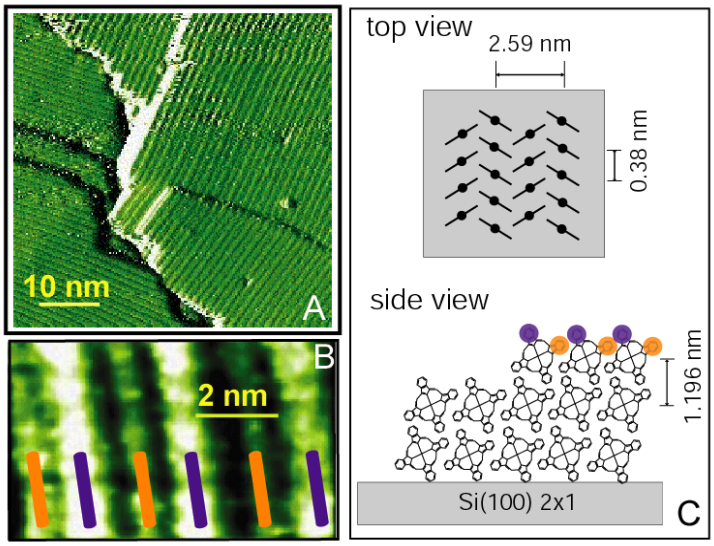

FIGURE 3. A: ordered molecular rows on a terrace. B:details of the molecular rows. C: α-form of CuPc

Figure 4 shows two STM images of a K_xCuPc film in the intermediate doping level (left) and high doping level (right). The high-quality morphology of the film is preserved upon Potassium intercalation, as indicated by the observation of well-defined terraces with sharp edges. The white structure is due to a small fraction (1%) of potassium atoms clustering on the surface of the film.

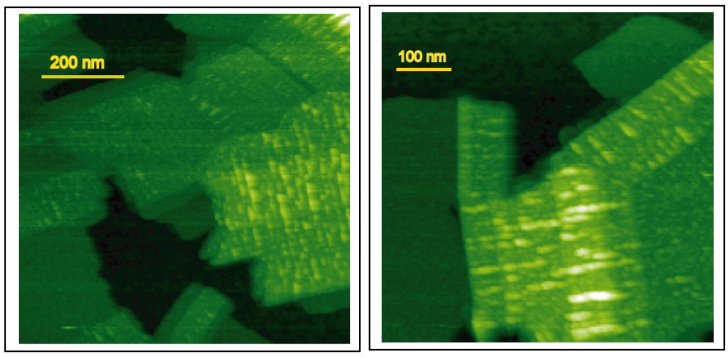

FIGURE 4. STM images of doped CuPc film

We performed scanning tunnelling spectroscopy at different doping concentrations for a CuPc film (Fig. 5). The tunneling I-V characteristics for the undoped films (inset of the Figure 5) show a very large gap. This is because undoped films are highly resistive and a considerable fraction of the voltage applied to the STM tip drops across the CuPc layer. Upon doping, the gap in the I-V tunnelling characteristics decreases (curve *a*) and when the film is doped into the highly conductive state (curves *b* and *c*), a finite slope in the I-V is observed around zero bias. This indicates the presence of a finite density of states at the Fermi energy, as it is expected for a metallic state. Upon overdoping into the insulating state, a gap reappears in the I-V curve (curve *d*).

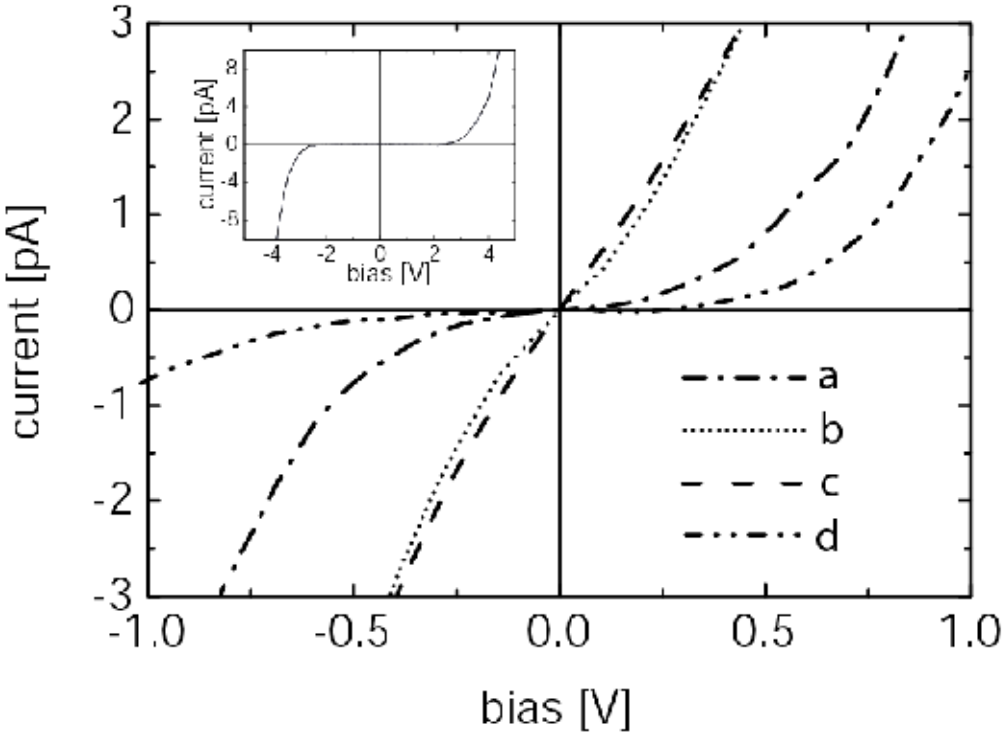

FIGURE 5. Scanning tunneling spectroscopy performed on a CuPc film for different doping levels. Inset: tunneling I-V for the undoped CuPc film

We conclude that the results of tunnelling spectroscopy are fully consistent with the interpretation of the temperature-dependent transport measurements, and they support the picture of an insulator-metal-insulator transition due to band filling.

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