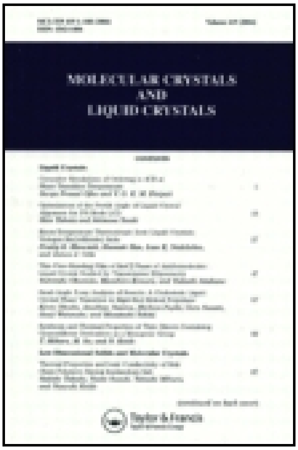

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

IN-PLANE RESISTANCE OF AN ULTRA THIN GOLD FILM: INFLUENCE OF A COPPER PHTHALOCYANINE OVERLAYER

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Version of record first published: 07 Jan 2010

To cite this article: A. Bourlange, B. J. Hickey, S. D. Evans, A. Pecchia, B. Movaghar, R. W. Kelsall & N. Boden (2004): IN-PLANE RESISTANCE OF AN ULTRA THIN GOLD FILM: INFLUENCE OF A COPPER PHTHALOCYANINE OVERLAYER, Molecular Crystals and Liquid Crystals, 413:1, 81-90

To link to this article: http://dx.doi.org/10.1080/15421400490432614

Mol. Cryst. Liq. Cryst., Vol. 413, pp. 81/[2217]–90/[2226], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490432614

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We have constructed an apparatus to evaporate ultra thin films of Copper Phthalocyanine (CuPc) on ultra thin gold epitaxial film grown by MBE, which thicknesses are in the range of 30 Å. We present STM pictures of CuPc on ultra thin gold which show a columnar alignment perpendicular to the substrate and preliminary in-situ resistance measurement of the hybrid device. Using theoretical modeling on a simpler system, we calculate the electronic properties and estimate the expected changes in the quantum and temperature dependent resistance of the thin gold layer, when it is covered by a discotic overlayer.

Keywords: growth; metal; organic; resistance; thin film; transport

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INTRODUCTION

Our aim is to learn how to self-assemble or grow one-dimensional molecular wires onto 2-dimensional substrates. For this purpose it was decided to make hybrid systems comprising of a thin film of discotic liquid crystal (DLC) on an ultra thin, quantum confined, metallic or magnetic substrate as seen in the Figure 1. Typical DLCs of interest are hexaalkoxytriphenylene (HAT) derivatives [1], hexabenzocoronenes (HBC) [2], and copperphthalocynine derivatives (C*u*Pc) [3]. Adsorption of gases within the DLC matrix may be manifest as detectable ac resistivity changes in the metal film. This type of device, unlike others based on plasmon-resonance spectroscopy or IR reflectance, offers in principle the advantage of miniaturisation and simple electronic interconnection.

Complementary studies have established that the conductivity of ultra thin gold films is sensitive to adsorption of self-assembled thiol monolayers, and that this in turn is sensitive to exposure to N_2 [4]. The resistivity of a 50 Å Ca film has also been found to increase by 6% on absorption of an overlayer of C_{60} [5]. The emphasis in our work is to exploit the one-dimension transport properties of the DLC overlayers. Excitons generated in the organic layer and recombining at the metal surface could generate signals that could be used in imaging devices.

EXPERIMENT

Device Construction

Discotic liquid crystals were evaporated using a purpose built chamber (OMBD). The sample was carried on the transfer holder from the fast-entry-lock to the MBE growth chamber and then to the top of the OMBD.

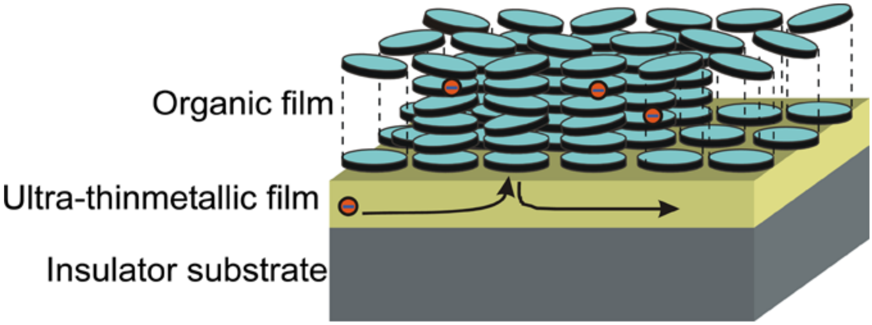

FIGURE 1 Hybrid system architecture. (See COLOR PLATE VII)

The oscillating crystal monitor, as well as all lateral components of the chamber, are mounted using linear travelling adapters to allow the transfer of the sample from the bottom to the top of the chamber. The resistive heater is composed of a tantalum wire holding a boron nitride crucible. Tantalum has been chosen for its good mechanical and refractory properties, but also for its fairly high electrical resistance, which enables us to use a reasonably low power supply (max 10 A, 10 V). The crucible is then heated through this Ta wire to reach the evaporation temperature, which is typically 250°C for *Cu*Pc and 200°C for HAT6.

Resistivity Measurements

In situ resistivity measurements were carried out using the four-point probe technique. A special sample holder was built so that resistivity could be measured continuously during the growth of the film. Since there are two growth chambers we needed a device that could be transported and connected in vacuum. In our device four Ta fingers have been predeposited on the substrate by sputtering before being inserted in the vacuum chamber on a specially designed molybdenum block holder. Figure 2 shows a top and side view of this sample holder. The substrate is held by a piece of boron nitride, which has four holes to let pass through the Ta wires, which assure the contact. These wires are connected to four tantalum tubes and the latter are hold with a large piece of ceramic screwed on the Mo block. To control thermal expansion and therefore the risk of contact loss during the cleaning process of the substrate, all the metallic components of the system are made of the same metal (Ta), which has a low expansion coefficient. Pressure contacts are made to the Ta probes. In this way we could measure the resistivity of the Au film during the deposition. This was particularly useful to establish when the film was continuous. In the OMBD, the sample was mounted into a special holder (see Fig. 3) where the temperature was also continuously monitored. Ceramic tubes around the Ta wire of the source and on top of the source have been added to limit thermal and photoelectric interference during the resistance measurement.

The ultra thin epitaxial gold films have been evaporated on a buffer layer of 5 Å of Fe at room temperature in a molecular beam epitaxy system (MBE) at 0.1Å/sec under a vacuum of less than 10^{-10} mbar. The Fe buffers were grown on a thermally cleaned MgO(100) at 0.1 Å/sec at 450 K and annealed at 720 K. The *Cu*Pc has been evaporated at 0.1 Å/sec in an organic molecular beam deposition chamber with a vacuum of 10^{-7} mbar. The sample temperature and the sheet resistance were recorded in the OMBD. The proximity of the source heated the sample from room temperature (293 K) to 320 K at the end of the *Cu*Pc evaporation. The temperature

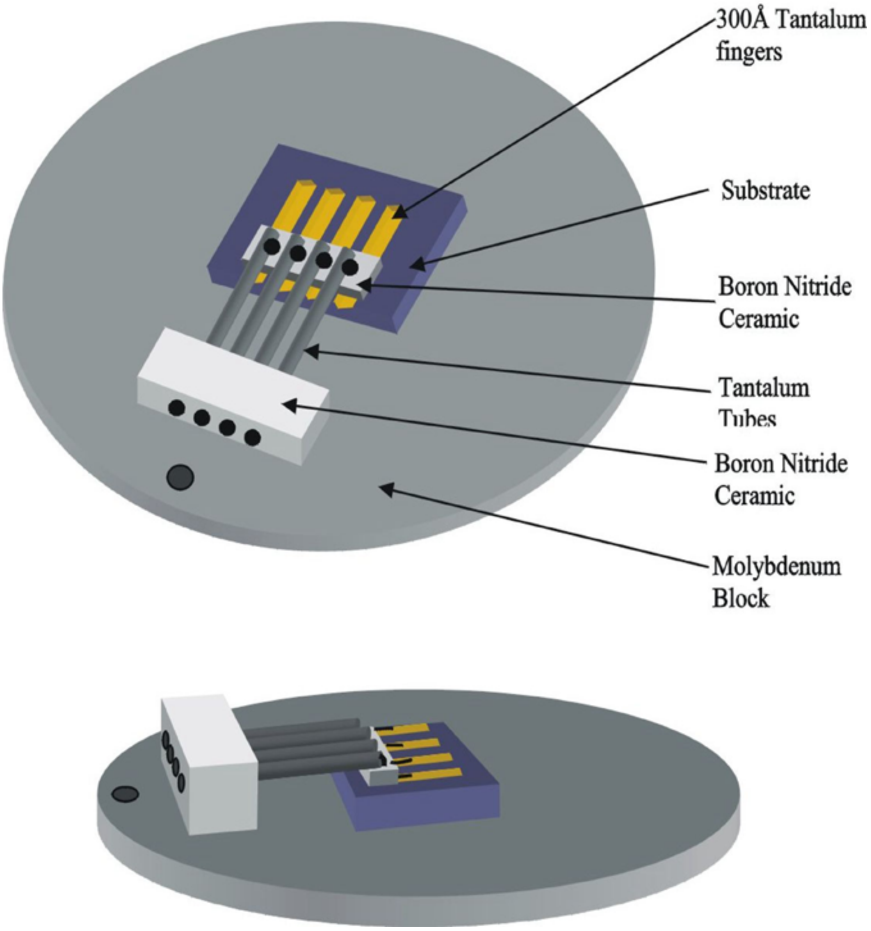

FIGURE 2 *In-situ* resistance system on the sample holder. (See COLOR PLATE VIII)

and the sheet resistance are recorded during each stage of the cycle and the results are plotted as a function of the time cycle as shown on Figure 4.

The initial experimental deposition was made by using *Cu*Pc because this material has a proven record of high quality vapour deposition and ordering. It has been vapour deposited successfully and STM characterised many times, showing that the molecular discs lie flat on the substrate. The composition and structure of the CuPc thin films have been studied with STM and Raman spectroscopy. To observe the orientation of the molecule on the surface, STM images have been taken before and after the deposition of the molecules on thick gold layers. A typical example of these

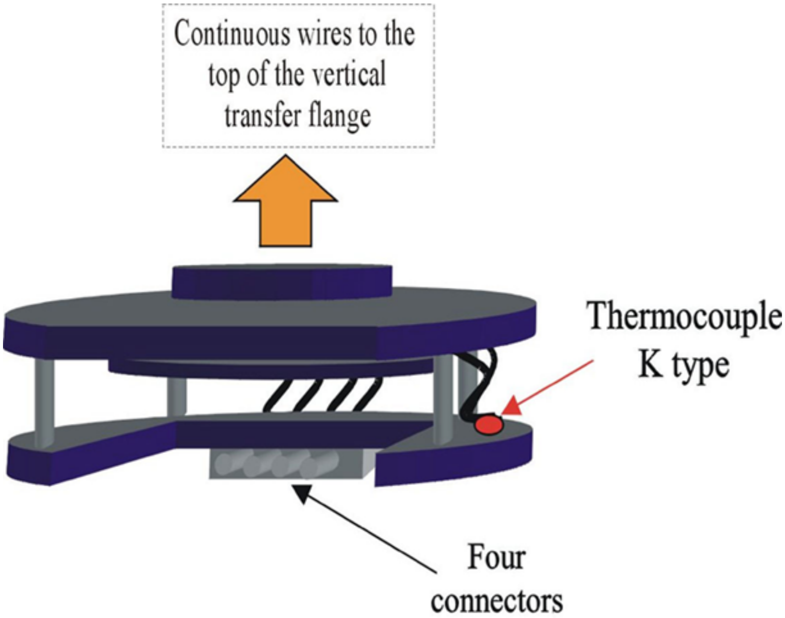

FIGURE 3 Connection for the in-situ measurement on the manipulator in the OMBD. (See COLOR PLATE IX)

scans is presented in Figure 5, which shows the surface of the gold thin film (a) and the atomically resolved molecules on the surface (b). The metallic gold film presents terraces of 10 nm wide, which allow the CuPc molecules to lie flat. The molecules form also a hexagonal array.

The distance between two cores is 13 ± 0.2 Å. As it is smaller than the normal distance between two cores, we can consider that the molecules have a slight angle in regards of the metallic surface. This angle corresponds at 21 degree confirming earlier work on CuPc evaporation.

Theoretical Modelling

We first considered the resistivity of an ultra-thin metal film grown on top of an ideal insulator. The band structure of the metal film was treated in the effective mass *jellium* approximation. It was assumed that the buried interface was a perfect specular reflecting interface. The exposed surface was assumed, to first order, to be perfectly flat, and the surface corrugation is treated to first order scattering theory. The roughness was treated following the method of Ashcroft and Trivedi [7] and Calecki [8]. Within the relaxation time approximation of the Kubo-Greenwood formula, we

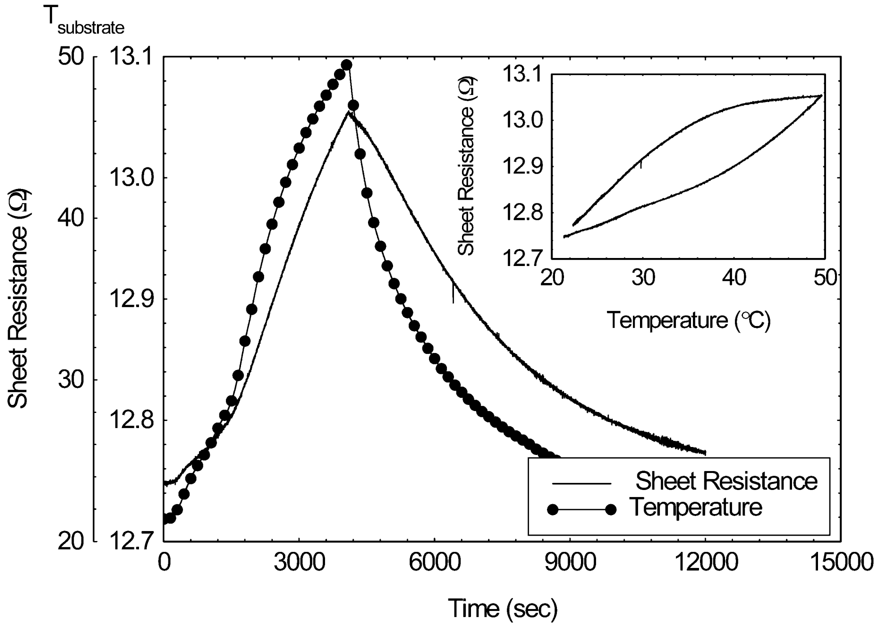

FIGURE 4 Sheet resistance and temperature measurement in-situ. (inset) Analysis of the data: Sheet resistance in function of the temperature.

included random impurity scattering and electron-phonon interaction. The phonon bands were assumed to be the same as in the bulk, the effect of quantum confinement on the phonon modes was neglected. This is indeed

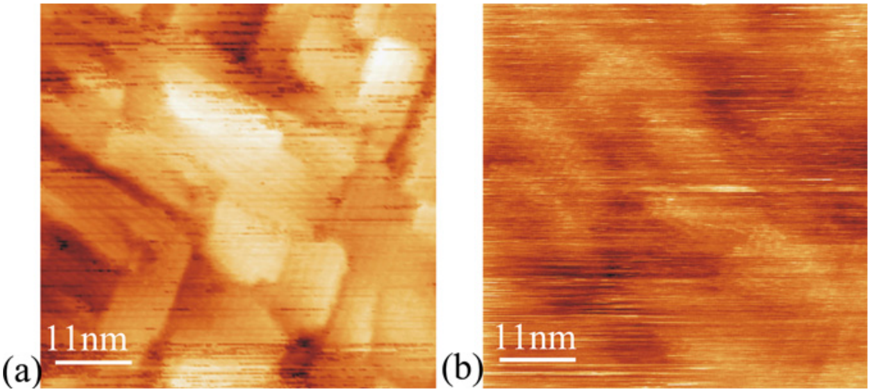

FIGURE 5 STM topographic images of (a) ultra thin gold surface, (b) 5 nm of CuPc thin film deposited on the same sample. (See COLOR PLATE X)

justified within the present modelling accuracy. The results are shown in Figure 6. The main conclusions at this stage are that: surface scattering is the dominant source of resistance in very thin metals d $< 5\,\mathrm{nm}$, but this was known already. The effect of temperature on the resistance at room temperature becomes important at thicknesses above 2 nm.

The second stage of the theoretical investigations was to analyse the metal/organic hybrid bandstructure formation induced by the ordered self-assembled overlayer of discotic molecules. We took into account the atomic structure and the electronic structure of the adsorbed molecule. Most of the theory work was done on the molecule HATn and was also applied to Hexa-benzo-coronenes. Experience shows that these molecules form highly ordered liquid crystalline phases with molecular wire properties and mobilities with a high degree of anisotropy.

The molecular orbitals and energies were calculated using commercial modelling packages (Gauss and Hyperchem) at Hartree-Fock Ab-initio or semi-empirical level of approximation. The molecules were allowed to approach the surface with the disc parallel to the plane of the metal substrate. The interaction between the molecular orbitals $|m>$ and the electronic band states $|k>$ in the metal are treated using the Newns-Anderson Hamiltonian. This Hamiltonian allows the free electrons $|k>$ in the

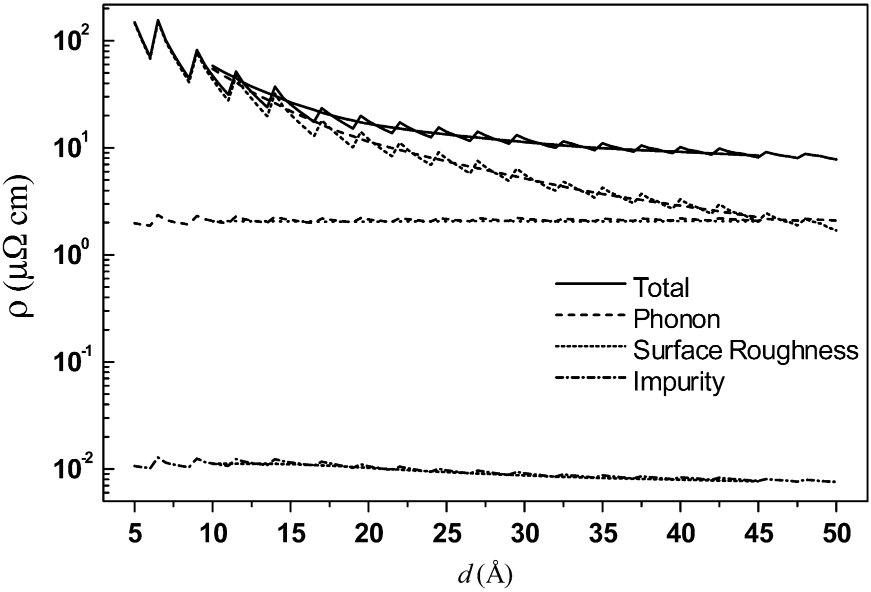

FIGURE 6 Simulation of the resistivity as a function of metallic film thickness. Phonon, surface roughness and impurity contribution are plotted.

metal to change into a molecular state $|m>$ and then come back again into $|k'>$.

When this exchange takes place along a periodic array of discotic molecular columns, then we have a new hybrid Bloch band. The New Bloch energy bands E(k) were computed. The hybrid density of states is shown in Figure 7. The hybrid bands were used to compute the conductivity of the metal film, which is calculated using the Kubo-Greenwood formula. The resistance depends on Fermi level quantities and re-normalised Fermi level shifts. This conductivity model is designed to explain the data in the high temperature range near room temperatures.

In this limit it is legitimate to assume the use of Born type approximations to the scattering amplitudes even though it is well known that multiple scattering processes are important, and that these may give localisation at very low temperatures. When one uses the born approximation, one obtains unrealistically high values of relaxation rates to account for the data. It is possible to justify this, once it is clear that these rates cannot really be due to simple scattering processes. The relative effect on the conductivity of the ultra thin film of a self-organised overlayer of HAT4 is now shown in Figure 8.

Similar calculations were performed for HAT6 and HBC molecules [9]. The effect for HBC is predicted to be larger because of the closer proximity of its HOMO level to the Au Fermi energy. We can, to first approximation, assume that the effect of CuPc molecules on ultra-thin films of *Au* are related to the HA*Tn* and HBC results by a renormalisation of the electronic effective mass [7,8,9]. This, in turn, is related to a renormalisation of the

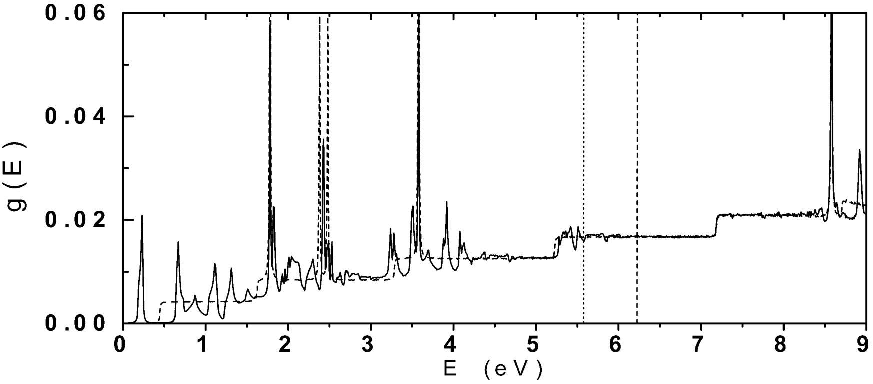

FIGURE 7 DOS diagram of a 10 Å film of *Au*. The continuous lines correspond to the interacting band and the imposed dashed lines correspond to the free bands. The peaks correspond to the molecular core eigenstates of HAT4.

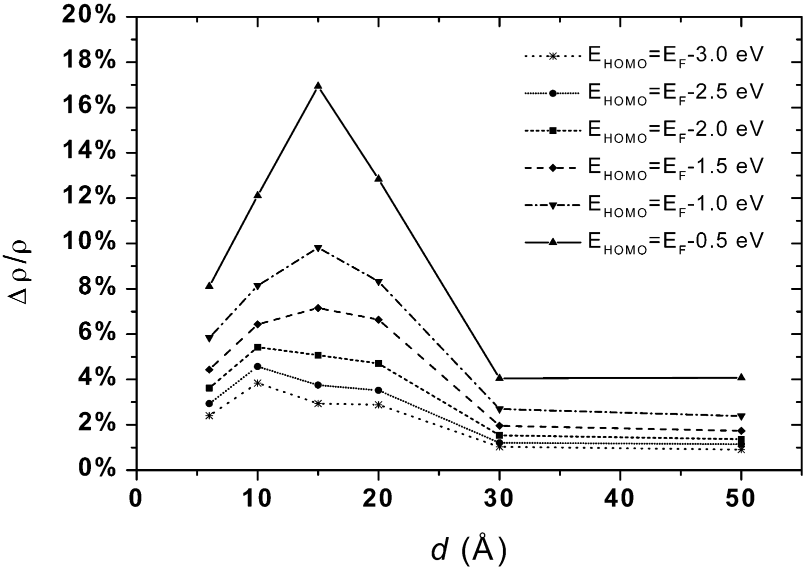

FIGURE 8 Simulation of the relative resistivity change and its dependence of the hybrid band structure with the position of the HOMO energy levels to the Fermi level of the metal.

Homo-Lumo separation in the band coupling term, as explained in reference [9]. The increase in the resistance of the Au film is due to the quantum delay, which is caused by molecular levels virtually trapping periodically the free electrons as they proceed through the slab. This effective mass increase can be estimated by re-normalising our extensive HATn calculations. The theoretical estimates predict a change in resistance of order 4% at a gold thickness of 2 nm. Preliminary measurements carried out recently on a MgO substrate with and iron buffer give values of ~1–2%. Allowing for the fact that is dealing with a more complex system the agreement is at that this very early stage quite satisfactory.

CONCLUSION

We have built a new system comprising an ultra-thin gold film and an organic overlayer both evaporated in UHV. The sheet resistance of the thin metallic film has been measured in-situ. The modelling of such system has been presented and preliminary measurement has shown an increase of this resistance with the presence of the organic overlayer.

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