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## RECTIFICATION IN FULLERENE (C<sub>60</sub>)-PHTHALOCYANINE THIN FILM SANDWICH STRUCTURES

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Bilayer sandwich structures were fabricated by the sequential thermal evaporation of gold, copper phthalocyanine (CuPc), C<sub>60</sub> and gold onto sapphire substrates. When the current-voltage characteristics of a freshly made device are measured in an atmosphere of argon, fairly strong rectification is observed. When the bilayer device is exposed to ammonia vapor, the rectification slowly decreases and almost disappears. If the device is then placed under vacuum and the ammonia removed, the initial conditions slowly return. We attribute the rectification to the formation of a *p-n* junction.

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### 1. Introduction

Many inorganic rectifiers are based on the *p-n* junction. Copper phthalocyanine is a molecular semiconductor which can be easily *p*-doped [1], whereas C<sub>60</sub> behaves as an *n*-type semiconductor [2]. Both materials can be sublimed at around 400°C to make robust microcrystalline thin films. Hence a device formed by the sequential evaporation of C<sub>60</sub> and CuPc films may act as a *p-n* junction and rectify current.

### 2. Experimental

The copper phthalocyanine was purified by two sublimations under dynamic vacuum. The fullerene, C<sub>60</sub>, was purchased from Hoechst and used without further purification. Devices were fabricated on sapphire substrates. A thin layer of chromium was deposited, 10 nm in thickness, followed by 30 nm of gold to form the bottom electrode. The evaporation of the organic layers was carried out in an argon atmosphere glovebox, with a copper phthalocyanine film deposited first, followed by C<sub>60</sub>. The organic films were between 500 and 1000 nm thick, as determined by a depth profiler. The devices were exposed to air for about one minute during transfer to a metal evaporation chamber for deposition of the top gold electrode. The top gold electrode was deposited slowly, at a rate of 0.2 Å/s, in order to prevent short circuits through the organic layers. The active device area, formed by the overlap of the electrodes, is 1 mm<sup>2</sup>.

Current-voltage measurements were performed with a Keithley 230 voltage source and a Keithley 617 electrometer, at room temperature and in the dark. Initial measurements were made on a freshly made device, in an argon atmosphere. The device was then exposed to ammonia vapor for 24 hours, by attaching a vessel containing 25% aqueous ammonia to the measurement chamber. After  $I/V$  measurements were made on the ammonia saturated device, it was placed under a vacuum of  $5 \times 10^{-6}$  torr for 16 hours, and further  $I/V$  measurements taken.  $I/V$  measurements were also made on gold/CuPc/gold and a gold/C<sub>60</sub>/gold devices.

### 3. Results and discussion

The  $I/V$  characteristics of a freshly made gold/CuPc/C<sub>60</sub>/gold bilayer device are shown in Fig. 1a. The device rectifies current fairly strongly. The rectification ratio, which is the ratio of the forward bias current to the reverse bias current, is 350 at ten volts. The forward bias condition is observed when a positive voltage is applied to the copper phthalocyanine side of the device. A gold/CuPc/gold device does not rectify current, as seen in Fig. 1b. A gold/C<sub>60</sub>/gold device exhibits some slight rectification, with a rectification ratio of 10, at ten volts, as seen in

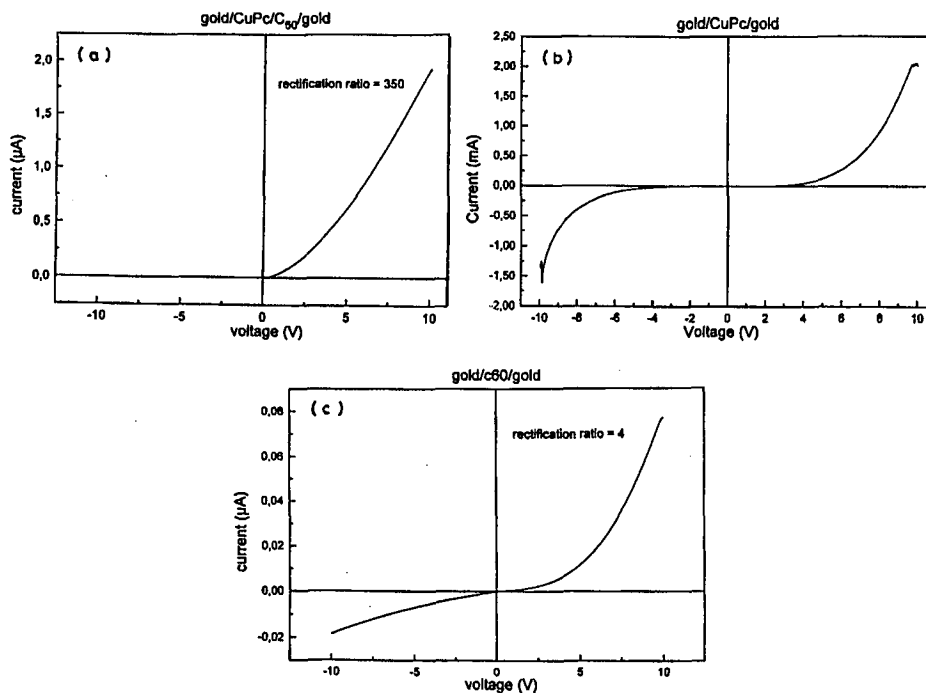


Fig. 1. (a)  $I/V$  characteristics of a gold/CuPc/C<sub>60</sub>/gold bilayer device. (b)  $I/V$  characteristics of a gold/CuPc/gold single layer device. (c)  $I/V$  characteristics of a gold/C<sub>60</sub>/gold single layer device.

Fig. 1c, possibly due to an adsorbed layer of oxygen at one of the organic/metal interfaces [3]. This strongly suggests that the rectification observed in the bilayer device is a result of the junction between the organic layers, and not due to an organic/metal interface.

$C_{60}$  behaves like an  $n$ -type semiconductor, and copper phthalocyanine like a  $p$ -type semiconductor when appropriately doped. It is possible to describe the junction as a  $p$ - $n$  junction, in the manner of classifying classical inorganic semiconductors. This view is supported by the fact that the forward bias condition in a classical  $p$ - $n$  junction occurs when a positive voltage is applied to the  $p$ -type side [4], as is observed with the device described here. Possibly the  $C_{60}$  and phthalocyanine dope each other near the interface, the  $C_{60}$  accepting electrons from the phthalocyanine. The phthalocyanine may also be  $p$ -doped by any oxygen present [5]. When the rectifying device is exposed to ammonia, the rectification slowly disappears; the rectification returns when the device is put under vacuum and the ammonia is pumped off, as seen in Fig. 2a and 2b. Ammonia is an electron donor, and may compensate any  $p$ -doping of the phthalocyanine.

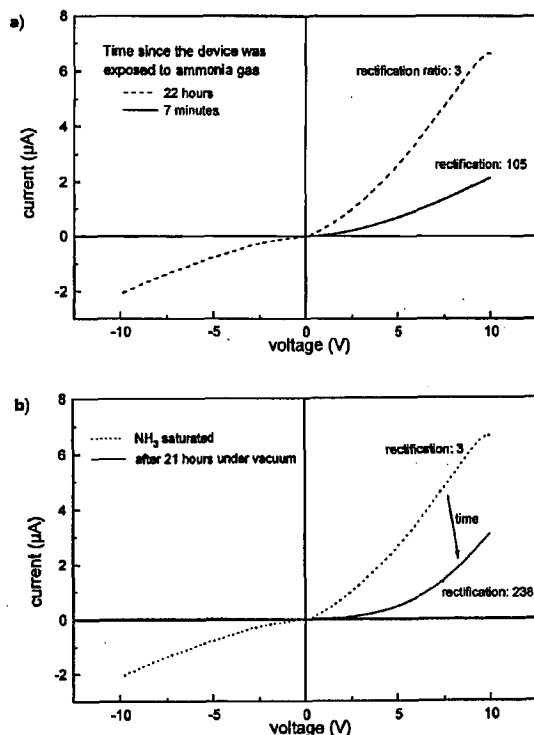


Fig. 2. (a)  $I/V$  characteristics of the bilayer device when exposed to ammonia. (b) Rectification returns when the ammonia is pumped off.

#### 4. Conclusions

A gold/CuPc/C<sub>60</sub>/gold device acts as a current rectifier. This behavior is attributed to the formation of a  $p$ - $n$  junction, with CuPc the  $p$ -type semiconductor and C<sub>60</sub> the  $n$ -type semiconductor. The CuPc is  $p$ -doped by the C<sub>60</sub>, or by oxygen, or both; the  $p$ -doping is thought to be compensated by ammonia, which acts as an electron donor.

#### References

- [1] J. Simon, J.J. Andre, *Molecular Semiconductors*, Springer-Verlag, Berlin 1985, p. 112.
- [2] B. Miller, J.M. Rosamilia, G. Dabbagh, R. Tycko, R.C. Haddon, A.J. Muller, W. Wilson, D.W. Murphy, A.F. Hebard, *J. Am. Chem. Soc.* **113**, 6291 (1991).
- [3] M. Kaiser, W.K. Maser, H.J. Byrne, A. Mittelbach, S. Roth, *Solid State Commun.* **87**, 281 (1993).
- [4] A. Bar-Lev, *Semiconductors and Electronic Devices*, Prentice-Hall, London 1979, p. 102.
- [5] A. Sussman, *J. Appl. Phys.* **38**, 2738, 2748 (1967).