

Photoelectric and Tensometric Properties of a Metal Phthalocyanine-Silicon Junctions

Alexander Malik
Electronics Department, INAOE
amalik@inaoep.mx

Salvador Alcántara
CIDS, BUAP, Mexico
salvador@siu.buap.mx

Jose Luis Sosa
CIDS, BUAP, Mexico

Abstract

New photoelectric and tensometric properties of metal-organic semiconductor-semiconductor sensors have been obtained on structures prepared by deposition of different metal – phthalocyanine (MePC) films on silicon substrate. In these sensors the MePC film serves as leak insulator. If a trapezoidal voltage bias is applied to sensor, the photocurrent amplification caused by transition processes in structure takes a place. Under uniaxial compression applied to sensor, a drastically changes of the electrical properties have been obtained. This effect is connected with tensoresistive properties of MePC films.

1. Introduction

Thin films of organic semiconductors on various substrates have attracted much attention due to their successful application in optical and electronic devices. The family of the phthalocyanines (PCs) presents one of the most promising candidates for organic thin films. These systems offer excellent film growth properties, high chemical and thermal stability as well as possessing advantageous electronic properties [1]. The heterocyclic molecule PC shows a flat conformation with all atoms of the molecule located in one plane (called molecular plane). In MePC a metal atom occupies the center of the molecule. Within the crystal structures the molecular planes of MePC molecules stack parallel to each other building columns of PC molecules [2]. The single crystal substrates support an ordered “lying” growth morphology, and this order of molecules causes strong anisotropy of the transport properties along and normal to the molecular planes [3]. Thus, it's possible to wait a slight transversal conductivity in sandwiched metal-MePC-semiconductor structures likewise a metal-insulator-semiconductor (MIS) structures with leaky insulator that are very attractive as different types sensors due to their fabrication simplicity. However, a controllable carrier transport in MIS structures is connected with carriers tunnelling through an insulator that requires complicated fabrication process of thin (less than 10 nm thickness) of this layer. From this point of view, sufficient interest presents the MIS structure where

tunnelable insulator is changed on thick MePC film with controllable transverse conductivity (leaky insulator), fabrication of that is simple and reproducible. Aside from, it's possible to predict intuitively that limited conductivity of this layer at certain conditions of optical generation rate may promote the accumulation of minority photogenerated carriers at the boundary insulator/substrate causing transition from MIS structure to convention MOS capacity. Below, we show that by this way new optical sensors with internal gain can be designed.

The effect of pressure is studied also on the electrical conductivity of different MePC films [4]. At the first time, we present significant tensometric effect in structures with MePC films under uniaxial compression. This effect can be used for design of a sensitive pressure sensor.

2. Experimental details

MePC films (Me = Ni, Co, Pt, La) were deposited on cleaned n-type silicon substrates with carrier concentration of 10^{15} cm^{-3} . Aluminium non-transparent and titanium semitransparent films with area $2 \times 3 \text{ mm}^2$ were used as a gate electrode. Cross-section of the structures investigated is shown on Fig. 1.

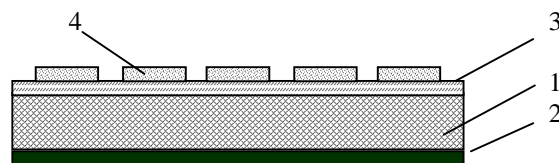


Figure 1. Cross-section of devices investigated:
1 - silicon substrate; 2 – back metallic electrode;
3 – MePC film; 4 – metallic gate electrode.

The dynamic current-voltage (I-V) measurements were performed using a Wavetek pulse/function generator and a Tetronix TDS 3012 oscilloscope. In the reverse bias direction the gate contact was biased negatively relative to substrate. Grating monochromator and light-emitting diodes (LED) were used for photoelectric measurements. Experiments with uniaxial

compression were performed with device, set-up of which is shown on Fig. 2.

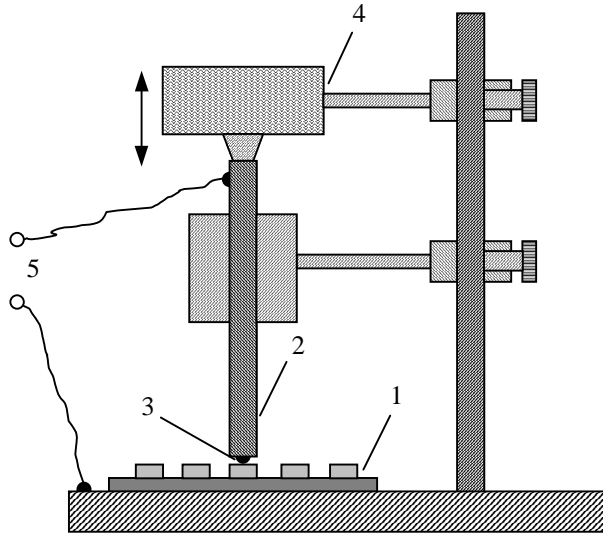


Figure 2. Set-up of device for the tensometric measurements:

- 1 – the structure investigated; 2 – plunger;
- 3 – metallic ball ($d = 1 \text{ mm}$); 4 – pressure transducer; 5 – electric contacts.

This device allows making the tensometric measurements of I-V characteristics under a static load applied to plunger as well as under a dynamic load with piezoelectric transducer.

3. Experimental results and discussion

3.1. Photoelectric properties

Fig. 3 shows the I-V characteristics (load resistor is $50 \text{ k}\Omega$) at dark and at different illumination levels from LED ($\lambda = 930 \text{ nm}$) for Ti/CoPC/nSi sensor with semitransparent titanium gate and thin CoPC film used as leaky insulator.

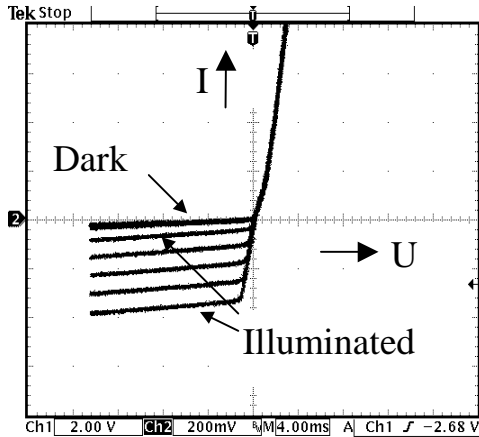


Figure 3. $I(\text{Ch2})$ - $V(\text{Ch1})$ dependencies of Ti/CoPC/nSi sensor.

Character of the I-V characteristics allows making some conclusions about a carrier transport mechanism in this structure. A slight current suppression at low voltage bias indicates a considerable transparency of CoPC film for photogenerated holes. It can be connected with high transversal conductivity of this type MePC film.

The responsivity of this type of sensor (in order of 0.3 A/W at $\lambda = 930 \text{ nm}$) is shown on Fig. 4. The value of the spectral response is limited by transparency of titanium gate. A short wavelength response is limited by energy gap ($\approx 2 \text{ eV}$) of CoPC films.

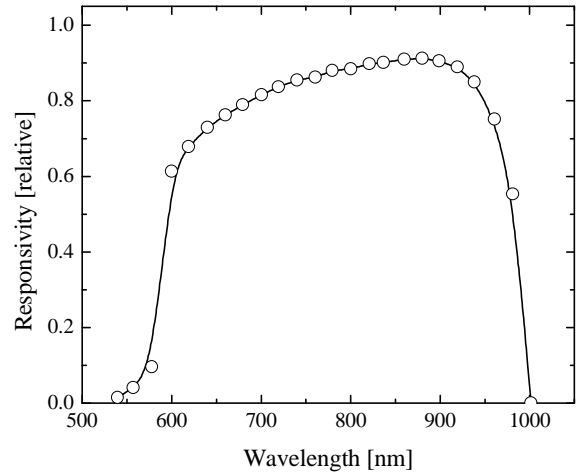


Figure 4. Responsivity of Ti/CoPC/nSi sensor

Another situation has been obtained when LaPC film is used as leaky insulator. The transverse conductivity of this film is much less. Thus, at certain illumination conditions and a voltage bias it is possible to observe an accumulation of photogenerated holes at LaPC/Si boundary. At that, an inversion layer appears at silicon surface and the structure has behaviour likewise to MOS capacitor.

Fig. 5 shows the experimental results obtained for Al/LaPC/nSi sensor at conditions when dc and a trapezoidal voltage bias are applied to structure.

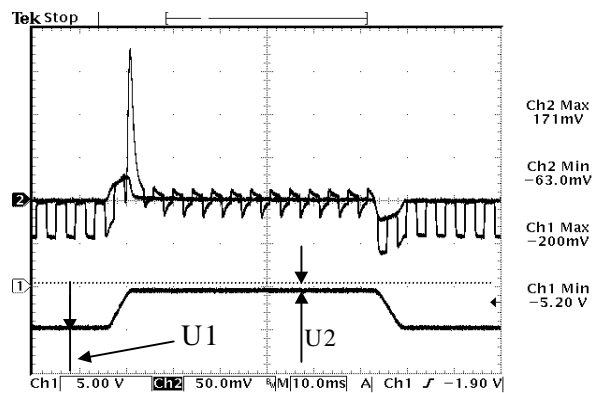


Figure 5. Time-dependent current (Ch2) characteristic of Al/LaPC/nSi photodetector obtained at applying of combined voltage bias (Ch1).

When applied voltage (U_1) is enough to create a sufficient electric field within the LaPC layer, photogenerated holes have the possibility to recombine with electrons from Al gate and some steady photocurrent is observed. To clarify this operating mode, we illuminate the structure by a square-wave modulated light. At that, the photoresponse repeats the light modulation form. When applied voltage bias (U_2) decreases at a certain level, the electric field within the LaPC layer decreases. The holes transport through the LaPC layer is diminished also, and an accumulation of holes at LaPC/Si boundary takes a place. In this situation the structure is likewise MOS capacitor in an inversion mode. At that, a differentiation of the photoresponse is obtained. From Fig. 5 one can see the transition process taken the place in the trailing edge of the trapezoidal voltage pulse bias, when the level of voltage bias applied to structure is decreased from U_1 to U_2 with velocity dU/dt . This process presents the transition of the sensors from MIS to MOS behaviour.

Appearance of a current depolarisation peak conducts the transition to this operating mode. The peak amplitude (I) depends on dU/dt rate and the structure capacity (C) in an inversion mode ($I \cong C \times dU/dt$). The value of capacity is determined by charge (Q) accumulated in a potential well formed at a voltage bias U_1 . This charge $Q = I_{ph} \times T_{stor}$, where I_{ph} – is the photocurrent value, and T_{stor} – is a time interval when U_1 is applied (a storage time).

Fig. 6 shows the depolarisation photocurrent peak at different T_{stor} values for Al/LaPC/nSi sensor illuminated with near infrared LED. The incident optical power is 2×10^{-7} W.

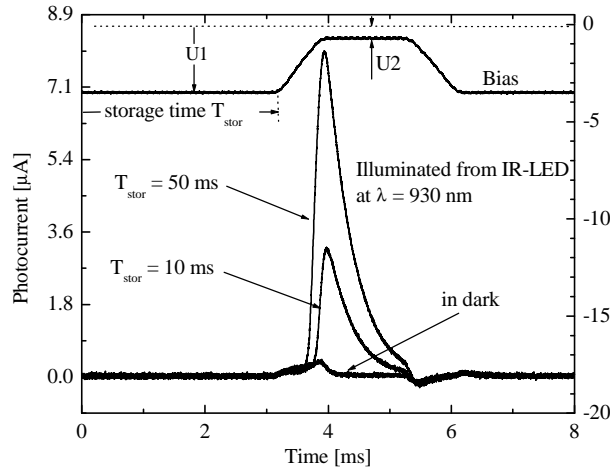


Figure 6. Depolarization photocurrent of Al/LaPC/nSi sensor at LED illumination

Sensitivity of sensor occurs only in the edge of Al non-transparent contact. Taking it into account, the responsivity of sensor was calculated as 40 A/W.

Thus, proposed sensor has an internal gain of the order of 100 and can be used for registration of weak optical signals.

3.2. Tensometric properties

In the course of our investigations we obtained that the character of I-V characteristics of metall/MePC/nSi structures with thin MePC intermediate layer depends on a force of pressure contact used for contacting with a metallic gate electrode.

Fig. 7 shows the I-V characteristics of Ti/NiPC/nSi structure at low (above) and high (below) contact pressure.

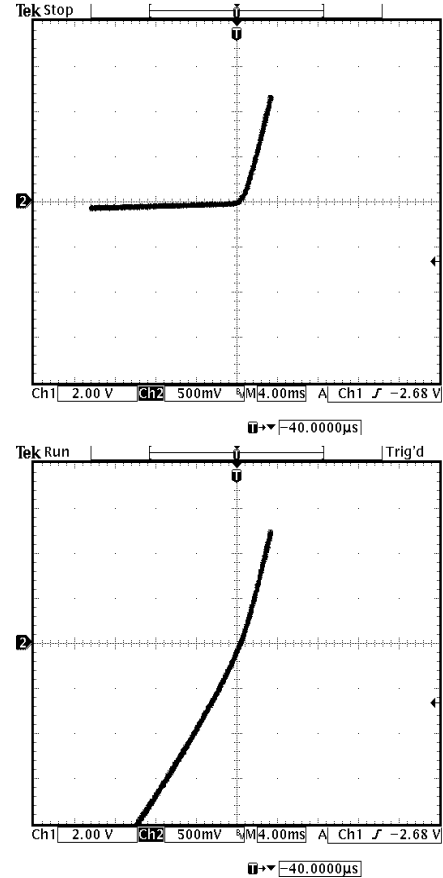


Figure7. I-V characteristics of sensor at two forces of pressure contact

The same changes of I-V characteristics have been obtained also in structures with NiPC, PtPC and LaPC thin films.

Drastically changes of I-V characteristics can be connected with a tensorresistive effect obtained by Berlin *et al.* [4] in MePC film with divalent metals.

Supposing “lying” grow morphology of MePC films on silicon substrates (see Introduction), it is possible to explain results obtained under uniaxial compression by changing of carrier transport mechanism in the direction normal to substrate.

The uniaxial compression to reduces to overlapping of π -orbital nearest molecules causing increasing of carriers mobility and conductivity in the direction normal to the molecular plane.

In our structures this located area with high conductivity plays a rule of an electric shunt and significantly influences on character of I-V characteristics.

To check our estimates, we made experiment shown on Fig.8. Here, tan uniaxial compression was applied on some distance from electrical contact to gate.

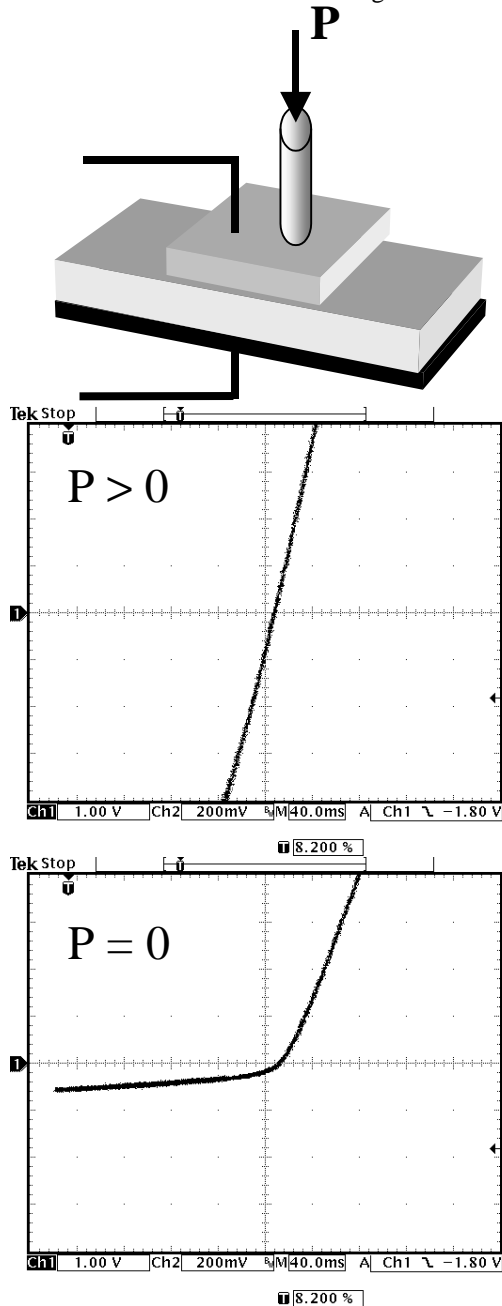


Figure 8. Set-up and I(Ch2)-V(Ch1) characteristics of sensor at uniaxial compression

To demonstrate the possibility of Me/PC/nSi structures as a pressure sensor, a frequency modulated uniaxial compression from transducer shown on Fig.2 was applied to structure. The construction of device allows to register the modulated electric signal (current) (Fig. 9) at some resonant frequency of the device (Fig.2).

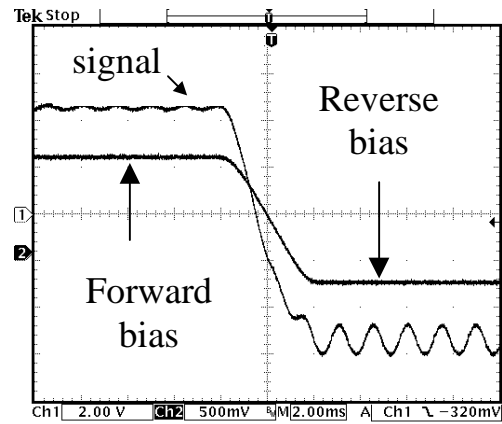


Figure 9. Time-dependent current (signal, Ch2) and voltage bias (Ch1) characteristics of sensor under frequency modulated uniaxial compression

The sensitivity of metal/MePC/nSi pressure sensor is demonstrated on Fig. 10, where one can see the sensor reaction when at the moment t_1 metallic ball with weigh of 0.4 gr. struck a plunger (Fig. 2).

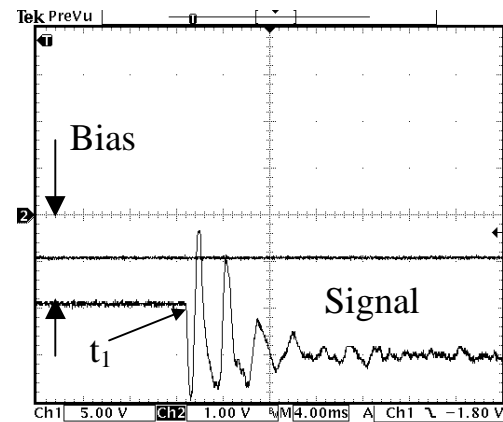


Figure 10. Current signal (Ch2) obtained when metallic ball struck a plunger. The Ch1 presents bias applied to the structure.

4. References

- [1] *Phthalocyanines*, edited by C.C. Leznoff and A.B.P. Lever, VCH Publishers, Weinheim, Germany, 1989-1996, Vols. 1-4.
- [2] J. Simon, J-J. André, *Molecular Semiconductors*, Springer-Verlag, Berlin, Germany, 1985.
- [3] H. Peisert, T. Schwieger, J.M. Auerhammer, M. Knupfer, M.S. Golden, and J. Fink, "Order on disorder: Copper phthalocyanine thin films on technical substrates", *J. Appl. Phys.*, AIP, USA, Vol. 90, 2001, pp. 466-469.
- [4] Y.A. Berlin, N.G. Danielan, *et al.*, "High pressure sensitivity of conductivity observed for phthalocyanine complexes with divalent metals", *Dokl. Akad. Nauk SSSR*, Nauka, Moscow, SSSR, Vol. 282, 1985, pp. 347-349.