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Control of the interfacial potential barrier for metal/n-GaAs diodes has been achieved using thin interlayers of the organic semiconductor, tin phthalocyanine (SnPc). The I-V characteristics for organic-modified Ag/S:GaAs diodes indicate a change from rectifying to almost ohmic behavior as the thickness of the SnPc interlayer is increased. Modeling reveals thermionic emission to be the dominant transport mechanisms for all diodes (ideality factors, n<1.3). Unlike other organic interlayers in similar device structures, SnPc reduces the effective barrier height by influencing the space charge region of the GaAs. The change in barrier height deduced from the I-V characteristics ((0.26 ± 0.02) V) is similar to the band-bending measured using core-level photoelectron spectroscopy for SnPc growth on the S-passivated n-GaAs(001) surface ((0.22 ± 0.04) eV) and is much larger than previously reported for other similar systems.

The considerable interest in the electrical and optical properties of organic molecular semiconductors reflects their increasingly widespread use in organic and hybrid inorganic-organic devices[1-6]. Much of this activity has been focused on understanding and controlling key parameters such as the interface potential barriers. In hybrid devices such as organic-modified Schottky diodes, two main approaches have been used for controlling the barrier height: monolayers of adsorbates[1] and thin organic films[2-6]. Using a range of organic molecules, inorganic Schottky diodes have been modified by monolayer adsorption on the substrate surface[1]. The barrier height has been changed by ≤ 0.12 V, but to achieve a continuous range many different molecules are required. Thicker organic interlayers of small conjugated molecules have also been successfully used to modify effective barriers. The metal/Si diode conductivity has been controlled by including a range of organic interlayers[2,3] and a similar approach has been used for metal/GaAs[4,5,6] and metal/InP diodes[6]. Reduction of the effective barrier height in these systems is relatively small (< 0.15 V) and is due to image-force lowering[5]; increases in barrier height are due to transport through the organic film and the interface energetics[2-6]. These effects require thick organic interlayers (> 5 nm)[4].

However, it now emerges that one class of organic semiconductor, metal phthalocyanines, can be used to continuously vary the barrier height for III-V semiconductors over a wide range using film thickness in the sub-5nm regime, and where the current transport is determined by a change in the true barrier height defined by the substrate space charge region.

GaAs Schottky diodes, modified by organic interlayers, are of considerable interest in high frequency applications[6] and the effect of tin phthalocyanine (SnPc) interlayers in Ag/n-GaAs diodes are reported here. Since ordered organic films are known to be facilitated by chalcogen-terminated (001) surfaces[7], the n-GaAs substrates were chemically prepared to provide a stable S-terminated surface (S:GaAs)[8]. The diodes were fabricated in a controlled, ultra-high vacuum

(UHV) environment: thin interlayers of high-purity SnPc were grown with sub-nm precision[9] and Ag contacts were deposited and characterized in-situ using I-V measurements. The composition, structure and energetics were monitored using photoelectron spectroscopy and electron diffraction during UHV fabrication.

Fig. 1 shows the I-V characteristics for the Ag/S:GaAs diode (curve a) and for similar diodes containing SnPc interlayers of increasing thickness from 1nm to 4 nm (curves b-d). The saturation current in these semi-logarithmic plots increases by over four orders of magnitude as the thickness of the organic film is increased, indicating a reduction in the effective barrier height to the point where the contact becomes almost ohmic.

Charge transport through such organic-modified diodes can in general be modeled by considering the series potential differences across four regions: the inorganic substrate, the organic/inorganic interface, the organic film and the metal/organic interface. A complete model must also allow for parallel conduction paths in each of these regions. The complex expression that results can be simplified by recognizing the dominant transport mechanism in each region and eliminating less important factors. For diodes with very thin organic interlayers, transport through these layers, the metal/organic and organic/inorganic interface potentials and the image force lowering at the organic-inorganic interface can be neglected[4,10,11]. Furthermore, by selecting moderately-doped GaAs substrates, the effect of tunneling through the inorganic-organic barrier can be almost eliminated[10,11].

The data can then be modeled using only thermionic emission and series resistance terms and the expression for the I-V relationship reduces to a form where only three variable parameters are required: the effective barrier height, ϕ_{b0}, the ideality factor, n, and the series resistance, R_S[10,11]. The results of fitting many diodes are summarized in Table I. The mean values for the three parameters are shown along with their statistical errors ($\Delta n = \pm 0.01$, $\Delta \phi_{b0}$

= ± 0.01 V). The low error values reflect the diode uniformity and the variation in the series resistance between each set of diodes is mainly due to different sample dimensions and ohmic back contacts. The low ideality factors indicate that thermionic emission is the dominant transport mechanism for all diodes, and it is clear that the barrier height is significantly reduced with increasing SnPc interlayer thickness.

The quality of the fitting procedure is illustrated in Fig. 2 for a unmodified Ag/S:GaAs diode (a) and one with a 1nm SnPc interlayer (b): the fitted curves (solid lines) coincide with the raw data in both forward and reverse bias. The values for the barrier height ϕ_{b0} and the ideality factor n for the unmodified diode are similar to that reported by Kampen et al[4] but the barrier height reduction for SnPc interlayers is much greater than reported for PTCDA interlayers[4]. The reduction in effective barrier height for the thin 1nm film (Fig 2) is unlikely to be due to image force lowering, and it thus appears that the space charge region in the GaAs is changed. This reduction continues for diodes with 2nm and 4nm SnPc interlayers, at which point the barrier height of 0.34 eV is amongst the lowest reported for n-GaAs. The increasing ideality factor for the 1nm and 2nm films is an indication of the increased tunneling current contribution as the barrier height is reduced. Due to the almost ohmic behavior of the 4 nm interlayer, the series resistance term, although small, becomes dominant and the ideality factor is less reliably extracted.

The I-V characteristics therefore suggest that thin SnPc interlayers reduce the true barrier height at the organic/inorganic interface. To confirm this, the initial stages of growth have been monitored by photoelectron spectroscopy. The energy position of the substrate Ga and As core level emission peaks can be used to monitor directly any changes in the surface Fermi level position with respect to the band edges in these systems since it is known that there are no organic-induced chemical shifts in these systems[9,12]. As the initial position of the surface

Fermi level in S:GaAs(001) can also be directly measured by this technique[12], the Fermi level position relative to the GaAs valence band maximum can be derived from the kinetic energy shift of the GaAs core level emission peaks (Fig 3).

From these data, it can be seen that the GaAs surface Fermi level lies closer to the conduction band minimum when the surface is covered with thin films of SnPc. The solid line is included only as a guide to the eye, but it is clear that the shift occurs within the first few nm and saturates above 2 nm. This indicates a change in the GaAs band profile during the initial stages of SnPc growth that corresponds to a reduction in the GaAs space charge region. This is in stark contrast to PTCDA interlayers in similar diode structures where the GaAs bands are unaffected[4,5]. The correspondence between I-V measurements (change in ϕ_{b0} = (0.26 ± 0.02) V) and interface energetics determined from photoemission experiments (change in GaAs band bending = (0.22 ± 0.04) eV) is seldom as clear due to interaction between the metal layer and the modified substrate. In this case, however, the SnPc/GaAs interface appears unperturbed by the Ag overlayer, and the space charge region in the GaAs remains unchanged by metal contact formation.

It is known that the SnPc film grows uniformly for the first 1.4 nm and forms a physical barrier between the metal and the GaAs substrate, preventing the metal directly contacting the GaAs surface[9]. The SnPc appears to cause a significant modification of interface states even though the organic-inorganic interface appears abrupt and unreactive. The precise origin of the active states at the GaAs/SnPc interface remains unclear, although recent theoretical and experimental studies have reported a finite density of states near the Fermi level in CuPc films[13,14] that suggests that the active states may have their origin in the organic material.

In conclusion, it has been shown that thin SnPc interlayers produce a large reduction in the Ag/n-GaAs barrier height and that this is due to an organic-induced change in the n-GaAs space charge region.

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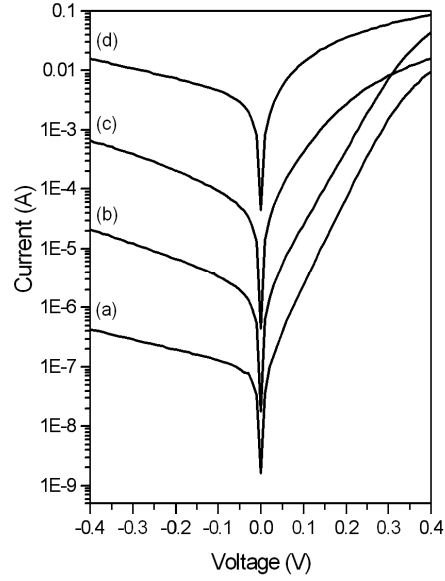|	ϕ_{b0}/V	n	R_S/Ω	$\pm\Delta R_S/\Omega$
Ag/S:GaAs	0.60	1.16	5.8	0.8
1nm SnPc	0.52	1.23	3.6	0.4
2nm SnPc	0.46	1.29	5.4	0.3
4nm SnPc	0.34	1.15	3.9	0.1

Table 1: Fit parameters obtained from the I-V characteristics of SnPc-modified Ag/S:GaAs diodes.

Figure 1: I-V characteristics for a Ag/S:GaAs(001) diode (a) and for Ag/SnPc/S:GaAs(001) diodes of varying SnPc interlayer thickness (1nm(b), 2nm(c), 4nm(d)). The n-GaAs carrier concentration, $N_D = 1\times10^{17}$ cm^{-3}, and the contact area, A = 0.79 mm^2.
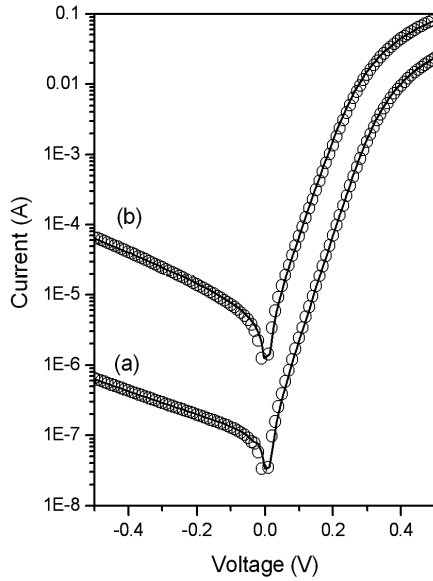

Figure 2: Current-voltage data (open circles) and corresponding fitted curves (solid lines) for a Ag/S:GaAs(001) diode (a) and a Ag/1nm SnPc/S:GaAs(001) diode (b). Both (a) and (b) are modeled using thermionic emission and series resistance terms only, and have a similar ideality factor.
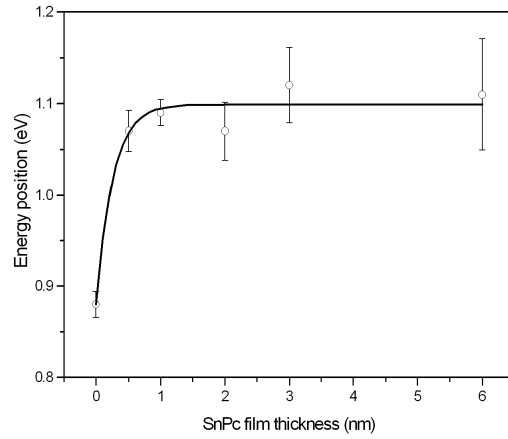

Figure 3: Evolution of the GaAs surface Fermi level position relative to the valence band maximum during SnPc thin film growth. The initial Fermi level position is taken from ref. 12.