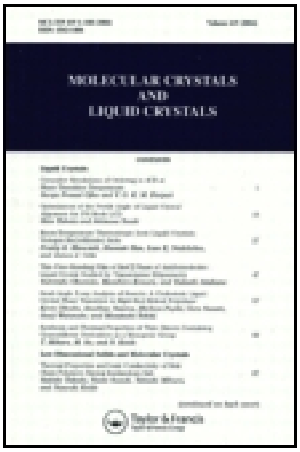

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Surface Chemistries and Photoelectrochemistries of Thin Film Molecular Semiconductor Materials

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SURFACE CHEMISTRIES AND PHOTOELECTROCHEMISTRIES OF THIN FILM MOLECULAR SEMICONDUCTOR MATERIALS

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Abstract Thin films of vacuum deposited trivalent and tetravalent metal phthalocyanines (Pc), and derivatives of perylenes (Pe), have been explored by a combination of ultrahigh vacuum deposition, surface spectroscopic characterization techniques, and measurement of photoconductivity and photocurrent spectral responses involving a) interdigitated array microcircuits (MC), and b) photoelectrochemical cells. Of particular interest has been the way adsorbed molecules such as O_2 and NH_3 affect the photoconductivity of these thin film materials, and the effect on photoactivity of the formation of a sharp interface between a phthalocyanine and a perylene. Multiple chemisorption sites are implicated for molecules such as O_2 and NH_3 on trivalent metal Pc thin film surfaces. These sites may either increase or decrease photoconductivity, depending on the partial pressure of the adsorbant, and the coverage of molecules competing for the same chemisorption sites. Photoelectrochemical modification of the Pc surface introduces submonolayer coverages of metals like Ag, providing a chemisorption site for molecules such as NH_3, thereby improving the performance of these photoconductivity-based chemical sensors. Photoelectrochemical techniques can be used to characterize Pc/Pe bilayers, since the electrolyte provides a noncorrosive, optically transparent electrical contact. Photocurrent yield spectra, obtained from two different illumination directions, have been used to estimate the width of the interfacial region which is most active for exciton dissociation in the Pc/Pe bilayer. Transient photocurrent yields in Pc/Pe multilayers (up to 16 total layers), show that the photocurrent increases linearly with the number of Pc/Pe interfaces. These increases occur up to the point where the width of the individual layers becomes narrower than the interface resolution that our present vacuum deposition technologies can provide.

INTRODUCTION

Impurity effects on the photoconductivity of condensed phase cyclic conjugated molecules such as phthalocyanines and perylenes continue to be of interest, primarily because of the application of these molecules in electrophotography and in emerging technologies such as electroluminescent displays, solar energy conversion systems, chemical sensors, and photonic devices utilizing optical nonlinearities[3,4,5]. These materials can show extreme sensitivity in both their dark and photoelectrical properties, to the chemistries occurring at the interfaces between the molecular material and either a) metals or semiconductors, b) gas or solution phase adsorbants, or c) other molecular materials with a significantly different electron affinity. Such areas are shown schematically in Figure 1 and are discussed in more detail below.

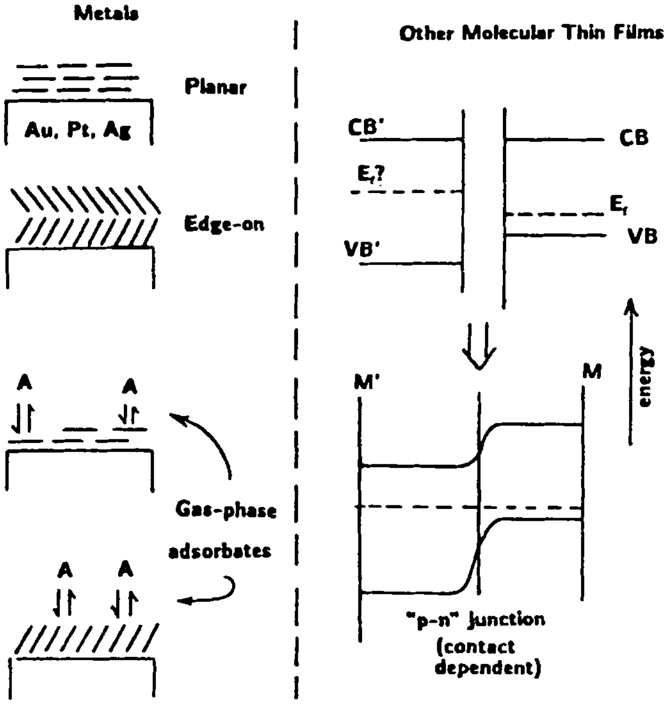

Figure 1 - Schematic of Interfacial Processes

Excitons formed as the result of photon absorption are generally assumed to dissociate and form mobile charge carriers by one of two mechanisms. These are an intrinsic mechanism where dissociation occurs at structurally distinct sites such as aggregate sites surrounded by monomers, or terrace or kink sites in an otherwise orderly array of molecules; or an extrinsic mechanism where impurity sites with fixed charges provide a local electric field gradient to assist exciton dissociation. The studies described here demonstrate: 1) how low coverages of small molecule adsorbants on a Pc thin film affect the photoconductive response; and 2) how the formation of a Pc/Pe interface creates a narrow region with a steep electric field gradient, which controls almost all of the photoactivity of the thin film assembly. Both effects are consistent with an extrinsic exciton dissociation mechanism, and in the first case, lead to the development of a new detection mode for gas sensing using phthalocyanine thin films.

EXPERIMENTAL

The preparation and vacuum deposition of the Pc and Pe thin films has been described in detail elsewhere (6). GaPc-Cl, InPc-Cl and perylene tetracarboxylicdianhydride (PTCDA) were deposited from temperature-controlled Knudsen cells with apertures and shutter assemblies which allowed for deposition rates from ca. 0.05 to 4 equivalent monolayer per minute. Deposition chambers used had base pressures of ca. 10^{-7} torr (Pc/Pe multilayers) or ca. 10^{-10} torr (chemisorption studies). In both cases the coverage of the thin film was quantitated with a quartz crystal microbalance (quantitated by profilometry), which was also used in the second chamber to monitor the uptake of adsorbants such as O_2 and NH_3. The UHV chamber was also equipped for monochromatic illumination of an interdigitated array microcircuit (MC), upon which the Pc or Pe film was deposited, so that dark conductivity and photoconductivity could be measured during the deposition process, as well as during the adsorption of various other molecules introduced after film formation. Microcircuits used in the UHV studies were provided by Motorola, and consisted of 59 interdigitated gold fingers, 100nm high, spaced at 3.1 microns. Microcircuits used in the sensing studies were either the same Au circuits, or were ca. 400 $PtSi_x$ interdigitated fingers, 100nm high, spaced at either 4 or 6 microns, provided by Burr-Brown. Gas sensing studies were carried out in a vacuum-compatible cell which allowed for illumination of the MC, and where the Pc-coated MC and QCM were simultaneously operated. Photoelectrochemical modification of the Pc/MC was performed in another cell which allowed for coverage of the MC with a small drop of electrolyte (1 ml). Photoelectrochemical studies of Pc, Pe and Pc/Pe bilayers and multilayers were carried out in previously described electrochemical cells, where the thin film assembly is immersed into transparent electrolytes. The thin films were deposited on conductive substrates such as SnO_2/glass or Au/polymer, both semitransparent, thus allowing for illumination of the thin film from the substrate side first (backside, BS, illumination) or from the electrolyte side first (frontside, FS, illumination).

RESULTS AND DISCUSSION

Chemisorption Phenomena on UHV-grown GaPc-Cl Thin Films

Figure 2 shows the photocurrrent yield spectrum of a thin film of GaPc-Cl (ca. 20 nm thickness) on the Au microcircuit at a base pressure of

10^{-10}torr immediately after deposition. The spectrum is in qualitative agreement with the absorbance spectrum of a thin film of comparable thickness and has been corrected for power fluctuations in the excitation source, and for the nonlinearity of the photocurrent response with the incident light intensity (see below). The dark current response of such a thin film is at or below detection limits (0.1 picoamp), and the contrast between photoconductivity and dark conductivity is ca. 10^4:1. Activation

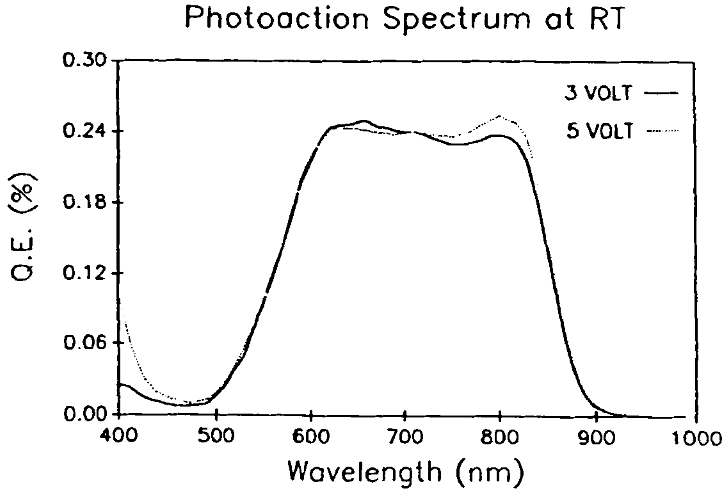

Figure 2 - Photocurrent Yield Spectrum for GaPc-Cl

energies determined for photoconductivity were ca. 0.1 eV and for dark conductivity were ca. 1-1.5 eV[3]. As expected, the photocurrent yield, i_{ph}, of this assembly was not linear with light intensity, I_o, over the illumination power density range of 0.008 to 0.08 watts/cm^2 (several different wavelengths), but instead follows the empirical relationship $i_{ph} = KI_o^{\alpha}$, where K is a constant reflecting the quantum efficiencies for absorption of the photon, and radiative and nonradiative energy transfer back to the ground state, and collection of mobile electrons and holes. The coefficient (α) has been seen to vary from ca. 0.2 to 1.0 and higher in certain cases(7). For the UHV prepared and characterized GaPc-Cl thin films the value of (α) was ca. 0.8 over the full spectral range shown in Figure 2, and over an electric field gradient range (ca. 0.03 to 2 x 10^4 volts/cm).

The interaction of such Pc thin film surfaces with O_2 has been reported previously[3,7], and has now been the subject of additional study. The importance of the interactions of O_2 with molecular electronic materials has been repeatedly emphasized (3). Figure 3 shows the photocurrent yield of the GaPc-Cl/MC (632.8nm) as O_2 was admitted to the UHV chamber. Upon initial exposure to O_2 in the pressure range below ca. 10^{-3} torr, the photoconductivity declines sharply to ca. 70% of the initial value. This pattern persists until much higher O_2 partial pressures and exposure times are achieved, whereupon the photoconductivity increases to a value ca. 2.4x the original level in UHV. Interestingly, the effect caused by the initial exposure to O_2 is not reversible whereas the photoconductivity enhancement caused by the higher pressure exposures is reversible, even if O_2 is removed (by pumping and bakeout) after several days of exposure at

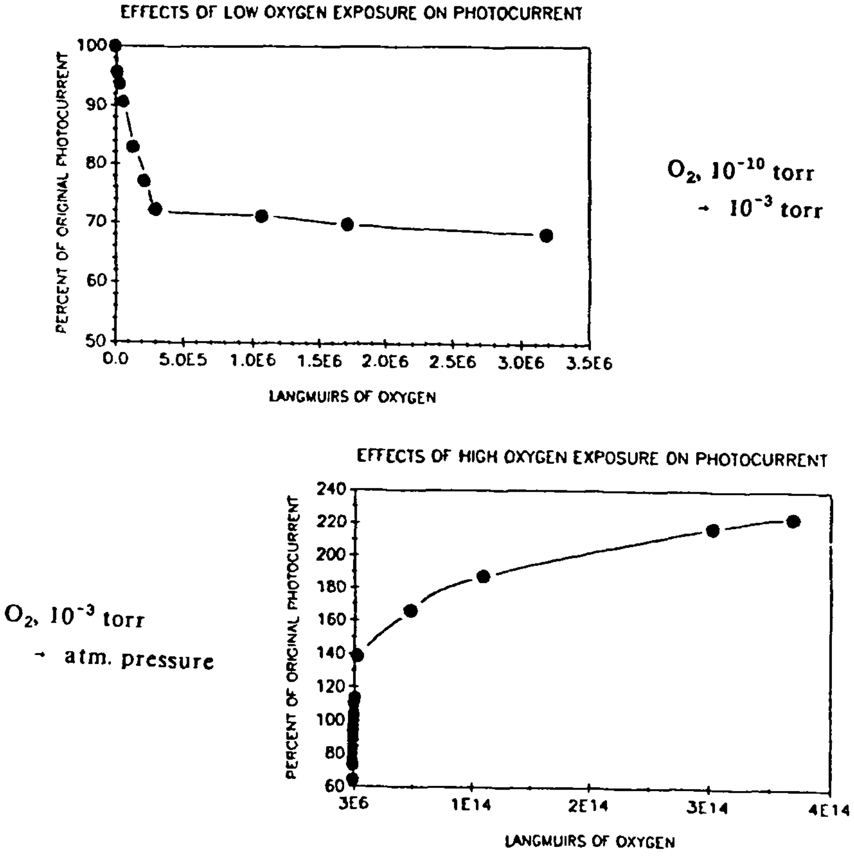

Figure 3 -- Photoconductivity changes upon exposure to O_2

atmospheric pressure. Persistent ESR signals of free radicals (10^{17} - 10^{18} spins/cm^3) in Pc powders (including GaPc-Cl) have been noted when the Pc has been exposed to high partial pressures of O_2 (6), which we believe correlate with the increased photoconductivity regime in Figure 3. Also of note is that the dark conductivity is not increased by the initial O_2 exposure in Figure 3, but is seen to steadily increase with the higher partial pressure exposures, to the extent that the contrast between photoconductivity and dark conductivity for the highest O_2 exposure is decreased to ca. 100:1.

Detailed studies of NH_3, TCNQ and NO_2 chemisorption will be reported elsewhere. In summary, the action of NH_3 on the photoconductivity of the GaPc-Cl and InPc-Cl thin films prepared in UHV appears to be due to interactions principally with electron trap sites, that exist even in highly purified materials. On the other hand, a molecule like TCNQ enhances photoconductivity apparently through the formation of sites of fixed charge where exciton dissociation is facilitated.

The photoconduction mechanisms for such UHV prepared and characterized, polycrystalline Pc films can be summarized as follows:

a) The creation of mobile charge carriers in the "pure" material is still largely an extrinsic process, as deduced by the low activation energy for photoconduction. Bimolecular processes such as electron-hole pair recombination and exciton-exciton annihilation events determine the efficiency of charge production, and lead to nonlinearity in photocurrent response with light intensity.

b) The action of O_2 at low partial pressures is to form stable complexes with Pc's, and/or with impurity sites in the material (e.g. another Pc) that act as electron traps for mobile electrons, but do not contribute to a change in the efficiency for their production (no change in the exponent for the photocurrent versus light intensity relationship).

c) At higher O_2 partial pressures, under illumination, these or similar O_2-Pc complexes dissociate to form stable $O_2^{\cdot-}$ and $Pc^{\cdot+}$ states, which lead to increased dark conductivity (and therefore more efficient transport of mobile charge), but which also experience bimolecular recombination, leading to a further lowering of the exponent in the i_{ph} versus I_o relationships. After doping of the Pc films with high O_2 partial pressures, a small percentage of the overall photocurrent also appears to be due to migration of stable ionic species, thus contributing to charging currents and asymmetries in the current/voltage relationship.

Photoconductivity-based GaPc-Cl and InPc-Cl Gas Sensors

Pc/interdigitated MC assemblies have been repeatedly cited as potential chemiresistor gas sensors for molecules such as NH_3, NO_2, etc.[8]. Dark conductivity changes have principally been used, with considerable variablility in response noted, depending upon the electron donating or accepting nature of the analyte molecule, the type of Pc used, the nature of the substrate, the preparation and purification of the Pc, and the presence of other interferent molecules. Because photocurrent generation (mainly through the extrinsic mechanism) is a near-surface phenomenon in insulating or doped insulator solids, it can be expected that an increase in sensitivity would be realized by measuring photoconducitivity changes in the presence of the analyte gas[7]. If interaction with the analyte produces resolved absorbance bands, selective detection of certain analytes may also be expected.

Initial experiments have shown that NH_3 and O_2 compete for at least one of the chemisorption sites at the surface of GaPc-Cl or InPc-Cl thin $h\nu$ films[7]. In addition, NH_3 chemisorption appears to occur at two distinct sites, with only one influencing photoconductivity. Experiments to date suggest that NH_3 intereacts with a trap site for electrons when exposed to the Pc surface bathed in N_2 at atmospheric pressure, causing the

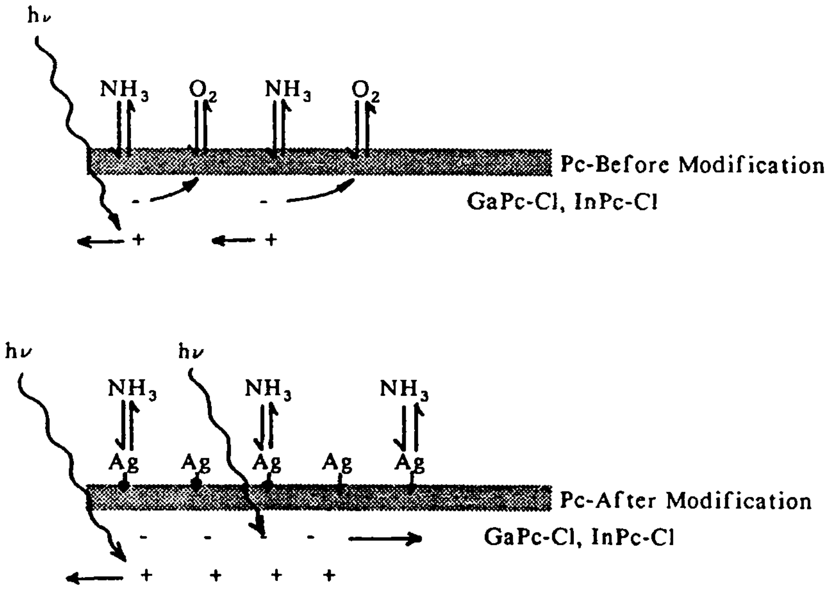

Figure 4 -- Influence of metal sites on the chemisorption of NH_3 and the photoconductivity of GaPc-Cl or InPc-Cl

photoconductivity to increase. Part-per-thousand levels of NH_3 in N_2 produce detectable increases in photoconductivity with no discernable change in dark conductivity. Extending this detection limit to the ppm level, and/or detection of NH_3 at room temperature in normal atmosphere is problematic, since no detectable changes in photoconductivity occur in either instance.

Intentional addition of impurity sites in the near surface region however, can enhance the response of a photoconductive Pc thin film to a molecule such as NH_3 at room temperature(7), even in the presence of large excesses of O_2. The presumed influence of an added impurity, such as a metal at submonolayer coverage, is shown schematically in Figure 4. Several different metals lend themselves to photoelectrochemical deposition on molecular photoconductor or several inorganic photoelectrode surfaces, including Ag, Au, Pt, Cu, Hg, etc. We have previously shown that coverages of these metals high enough to produce 100 nm diameter nuclei can be used to selectively decorate crystallites of Pc's with differing absorbance bands, to the extent that they can be subsequently imaged by surface analytical techniques(9). For the present studies, the Pc/MC assemblies are covered with a 1 microliter drop of electrolyte, ca. 10^{-6}M in the metal ion of choice, illuminated with light

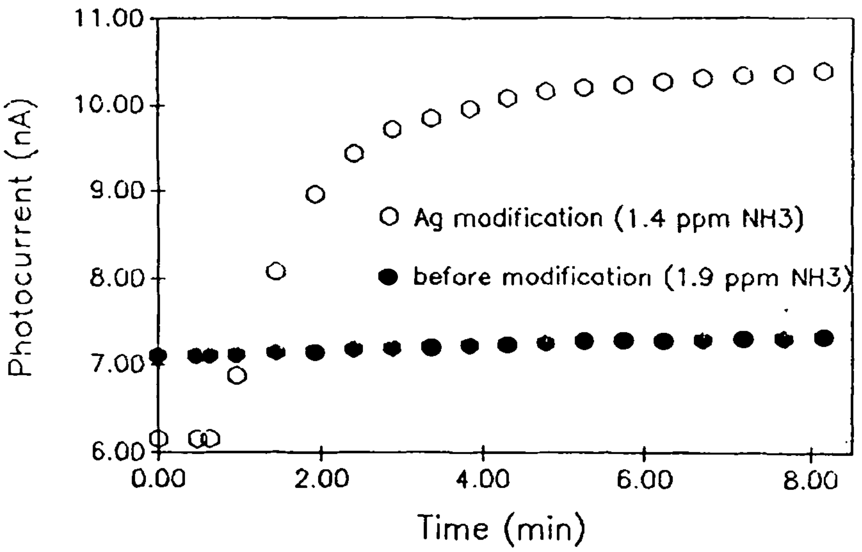

Figure 5 -- Room temperature photocurrent vs. time with 1 ppm NH_3/N_2, before and after Ag modification

from a He-Ne or diode laser source, and the metal ion exhaustively electrolyzed (reduced) from the drop with the MC under potentiostatic control. Normalizing for the geometric area of the device, this leads to coverages of metal on the Pc surface of 0.25 to 1 monolayer. Figure 5 demonstrates the time dependence of the photocurrent reponse of an InPc-Cl/MC assembly (Pc = 40nm thickness) to the introduction of 1 ppm NH_3, before addition of Ag, and after the photoelectrochemical Ag-decoration (ca. 0.5 monolayer Ag) of that sensor surface. In both cases the Pc/MC assembly was held at a temperature of 25°C in flowing N_2 for several minutes before introduction of the analyte. Little if any change in photocurrent reponse was seen at 1 ppm NH_3 before the modification, whereas an easily detectable change was observed following addition of the Ag sites to the surface. We hypothesize that at low Ag coverages, the Ag sites are in intimate electrical contact with sites responsible for electron trapping, implying a coordinative bonding of at least part of the Ag at that site with molecular species at the Pc surface. Chemisorption of NH_3 to that Ag site, involving electron donation, is apparently successful in chemically compensating some of the electron trap sites, and/or in changing their energies to make the trapping process less favorable. The result of this type of surface decoration is that the Pc/MC sensor sensitivity to ppt levels of NH_3 in the N_2 stream is enhanced by at least a factor of seven, while the competition of NH_3 and O_2 for the same chemisorption sites is suppressed to the extent that reasonable responses (detectable photocurrent increases) to ppt levels of NH_3 in atmosphere, at room temperature, are achieved(7b). The response time to steady state of such sensors is also decreased by a factor of at least 10x following metal modification. Recent experiments suggest that careful selection of decorating metals is necessary to extend this reponse to ppm levels of NH_3, since for metals where the interaction with NH_3 is strong, saturation of the chemisorption sites occurs at the ppm level, and additional photocurrent changes are difficult to detect. Metals with significantly lower affinities for NH_3 may actually provide more reasonable analytical reponses (monotonic photocurrent changes with increasing NH_3 levels, greater reversibilty).

VOPc/PTCDA Bilayers and Multilayers

Another method of intentionally introducing regions for exciton dissociation involves producing a bilayer of two dissimilar molecular materials, such as a phthalocyanine and a perylene. The anticipated

difference in electron affinities of such systems, and the measured difference in ionization potential (UPS), leads to the approximate band diagram of Figure 1, where formation of the interface between the two materials leads to a sharp electric field gradient(10,11).
Previous studies of such assemblies have demonstrated that the "p-n like" junction formed between a Pc and Pe thin film can be used in a solid state photovoltaic device capable of delivering a photopotential of several hundred millivolts, and a power conversion efficiency of ca. 1%(10). The extent to which the electric field generated by this assembly extends away from the interface will ultimately determine the population of excitons which will encounter that field and contribute to photocurrent generation.

Our recent studies have focused on bilayer and multilayer assemblies of vanadyl phthalocyanine (VOPc) and the perylene tetracarboxylicdianhydride (PTCDA), using semitransparent electrode contacts (Au or SnO_2 thin films), and transparent electrolytes, saturated in a redox species for the opposing electrical contact. Our previous photoelectrochemical studies have demonstrated that VOPc forms exclusively p-type photoelectrode thin films, either because of the high oxygen affinity of this material, and/or because of the small amount of self-doping that this material undergoes by demetallation during deposition, releasing the oxovanadium cation into the Pc lattice(6a). Recent studies of PTCDA thin films indicate that it is intrinsically a very lightly doped material, but that interfacial chemistries occurring with the substrate can create a strongly n-type or p-type semiconductor response[12,13]. In our work, the PTCDA thin films, deposited on Au or SnO_2, give n-type photoelectrochemical responses. The difference in apparent flat band potential for the VOPc, (p-type), photoelectrode and the PTCDA, (n-type), photoelectrode, is ca. 0.4 to 0.6 volts, which correlates with the expected difference in ionization potential for these two materials as measured by UPS. The photocurrent yield spectra for the individual photoelectrode materials suggest that the VOPc/solution interface is the most photoactive for mobile charge generation (as revealed from FS and BS illumination studies), whereas the PTCDA films on both Au and SnO_2, indicate that both the PTCDA/solution and PTCDA/substrate interfaces are photoactive, i.e. junction formation occurs at both interfaces(13).

The current/voltage behavior of VOPc/PTCDA bilayers on Au provide an interesting contrast. Where the thickness of both layers is ca. 100nm, with the VOPc contacting the metal, and the PTCDA contacting the electrolyte, a voltage region of ca. 0.7 is observed where diode-like rectification occurs, with the PTCDA acting like the n-type layer and the VOPc acting like the p-type layer. The photocurrent yield spectrum of this bilayer assembly, for both FS and BS illumination, clearly shows that the interfacial region between the VOPc and PTCDA layers is the photoactive region, and not the metal or solution interfaces. Estimates of the thickness of the "active" region can be made by comparing the photocurrent yield in the region for PTCDA absorbance (ca. 450nm), BS vs. FS, and the yield in the region for VOPc absorbance (ca. 650-750 nm)[6,13]. These experiments give a value of the width of the photoactive region below 50nm, implying that the electric field gradient produced at the VOPc/PTCDA interface is quite narrow. This is not consistent with much larger depletion regions for inorganic semiconductor materials, where the bandwidths and mobilities of charge carriers are greater.

To further test the idea that the photocurrent is generated in these assemblies principally at the Pc/Pe interface, a series of VOPc/PTCDA multilayers were created according to $Au/(VOPc/PTCDA)_n$, where n varied from 1 to 8, but where the total film thickness was kept constant, at ca. 200nm. The width of each Pc and Pe layer therefore diminished, and the number of Pc/Pe interfaces increased from 1 to 15. Assuming that the band diagram in Figure 1 provides a reasonable energetic picture of a single interface, a multilayer system might be represented by a series of potential wells, spaced by the thickness of each Pc and Pe layer. The electric field gradient at each interface is expected to remain as steep as in the single interface (bilayer system) until the thickness of each layer becomes less than the distance over which this field extends into the organic solid, and/or less than the dimensional variability imposed by vacuum deposition of these materials as thin films (i.e. the variability imposed by the dimensions of a single Pe or Pc microcrystallite). Once mobile charges have been formed at these interfaces however, trapping and increased recombination velocities would be experienced as a result of the potential wells formed in the middle of each layer. There are several technological applications which would rely on such a multilayer organic device.

Figure 6 shows the photocurrent yield spectra obtained from a bilayer and two multilayer VOPc/PTCDA assemblies, biased at potentials such that electron harvesting occurs at the solution interface (reverse bias conditions for the bilayer assembly). Examination of the current/time behavior following onset of illumination shows that the peak currents increase with an increase in the number of Pc/Pe interfaces, while the steady state current is either unchanged or decreased, consistent with the notion of increased charge trapping and recombination. Through the use of a lock-in-amplifier to demodulate the photocurrent, the photocurrent spectra in Figure 6 reflect the transient current, which is seen to increase almost linearly with increasing number of Pc/Pe interfaces. The largest number of interfaces explored to date reflects a Pc or Pe film thickness of ca. 10nm, which is near the limit of interface integrity available from our present deposition technology. It seems clear therefore, that the electric field gradient at the VOPc/PTCDA interface must be expressed over a distance much narrower than the 50 nm upper limit predicted from the photocurrent yield spectroscopies of the VOPc/PTCDA bilayer described earlier. Since the photocurrent yield of the multilayer assembly increases linearly with number of Pc/Pe interfaces, we hypothesize that the electric field, necessary to achieve a full complement of dissociated excitons, must be expressed across a distance of less than 10 nm, the minimum width of Pc or Pe film used thus far. It should be noted that simply codepositing the VOPc and PTCDA to form single films of ca. 200-400nm thickness produces a system with almost much decreased photoactivity and little rectification, suggesting that interactions on the level of single molecules are not sufficient to create mobile charges and semiconductor-like junctions. It is of interest to determine what the smallest film thickness

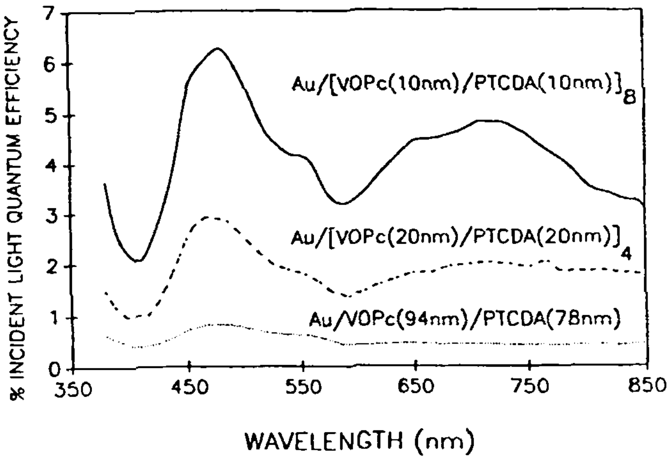

Figure 6 -- Photocurrent yield spectra for a bilayer VOPc/PTCDA and two multilayer VOPc/PTCDA assemblies

would be to create the necessary intermolecular interaction, sufficient to cause photocurrent or electroluminescent behavior suggestive of p-n diode formation. Further experiments focus on producing more highly ordered arrays of the molecular materials, where interface dimensions can be controlled to the diameter of 1-2 molecules.

CONCLUSIONS

It is clear that the role of impurities, either intentionally or accidentally introduced into condensed phase cyclic conjugated systems, such as Pc's or Pe's is critical in determining the electronic properties of the final assembly. It is already understood that rigorous exclusion of O_2 is essential in certain device applications of these materials. On the other hand, prospective applications in gas sensors, where coexistence with O_2 is a device requirement, additional modifications to the near surface region of the molecular thin film may be desirable to provide selective chemisorption sites, and sites capable of suppressing the interaction of the material with O_2. Control of a) photocurrent generation and/or b) recombination following charge injection, can clearly be obtained through the formation of bilayer or multilayer assemblies. The interaction between the two dissimilar molecular materials clearly does not extend far enough from the interface to argue for efficient solar energy conversion with these systems, unless molecular materials are used which have better intrinsic semiconductor properties. Technologies utilizing recombination after charge injection in the dark, to yield luminescence, can clearly be developed from these types of assemblies(11), and will benefit from further developments of deposition technologies which insure sharper interfaces between highly ordered molecular layers.

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