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## Stable Polymeric Light-Emitting Devices

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### Abstract

This is a final report of a two-year LDRD project on fabrication of light emitting diodes. Using layer-by-layer self-assembly technique, we have deposited multilayer thin films on conductive indium tin oxide (ITO) surfaces by alternating a polymer PDDA (or polydiallyldimethylammonium chloride) and a macrocycle NiPc (or nickel phthalocyanine). An oscillation of the surface electronic potential was observed with Kelvin Probe in alternative deposition of PDDA and NiPc. The average gap of this surface potential difference between NiPc and PDDA monolayer is about 400 mV. This oscillation behavior of surface potential or work function are mainly due to the modulation in electron affinity of ITO when different monolayers of PDDA or NiPc was bound to its surface. The electron affinity can be decreased as large as 0.5 eV with only one PDDA monolayer on ITO.

### Background and Research Objectives

It has been demonstrated that self-assembly techniques can be used to fabricate artificial thin films for a number of high-tech applications such as optoelectronic devices.<sup>1-4</sup> While comparing with Langmuir-Blodgett method, spin-coating, and other thin solid film depositions,<sup>5-10</sup> layer-by-layer (LBL) assembling of oppositely charged polymeric and organic materials such as conducting polymers, optical chromophores, metal complexes, or semiconductor nanoparticles can be considered as a new and simple approach to thin-film fabrications. LBL assembling of functional multilayer for new optical and electronic device applications appears to be promising. The unusual electronic and optical phenomena can emerge from the interface or surface in such heterostructures between assembled bilayers or multilayers. Therefore it could be very interesting to study the interfacial properties and their behaviors in these self-assembled systems.<sup>11-12</sup>

Kelvin probe is a technique that uses a vibrating capacitor to measure the difference of work functions [i.e. the contact potential difference (CPD)] between metals, semiconductors, and liquid interfaces.<sup>13,14</sup> As a direct, noncontact method, it has been widely used on determining the surface potential of monolayers of organic molecules on conducting or semiconducting solid effectively.

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<sup>15-21</sup> For example, researchers reported their progress on controlling the work function of semiconductor surface through molecular modification of its surfaces. The resulting surface electric properties are a function of surface modifiers; for example, dicarboxylic acids were chemisorbed onto CdTe, CdSe, CuInSe<sub>2</sub>, GaAs and InP as monolayers.

In this two-year LDRD final report, we present our studies on controlling the surface work functions because these properties in turn control charge injection efficiency and ultimately polymer light emitting efficiency. The first goal of this project was to assemble superior polymeric LEDs in a layer-by-layer manner and measure device performance (e.g., charge injection, electroluminescent, or EL, and optical efficiency). Our second goal was to assemble these polymeric materials into integrated multilayer thin-film structures in which electron and hole injection and transport are optimized so that they recombine in an efficient radiative decay process to yield high EL efficiency.

### **Importance to LANL's Science and Technology Base and National R&D Needs**

Because electron transfer underpins many advanced research areas, it is important to understand electron transfer or charge injection mechanisms at interfaces of metals, oxides, and organic polymers. Scientifically, such an understanding will positively impact areas such as communication systems, semiconductor devices, and advanced optoelectronics.

Technologically, defense-related devices and instruments continue to require better and higher performance LEDs. For example, ultrabright displays are needed for fighter jets in conditions of strong sunlight. Furthermore, LEDs are needed in virtually all facets of life, ranging from research equipment to home entertainment systems.

Polymeric LEDs also can be fabricated into flexible thin films and adapted into many unusual places where conventional inorganic LEDs cannot be applied (e.g., a roll-up display). Using self-assembly techniques, as well as conductive polymers as electrodes and conjugated polymers as light emitters, greatly simplified the fabrication of polymeric LEDs in air and water, compared to processes that require clean-room technology. Because of their simpler processing, easy tunability of electronic properties, and adaptability in device structures, polymeric LEDs will provide brighter and richer colors, thereby perhaps playing an important role in future technologies such as communication and information.

### **Scientific Approach and Accomplishments**

In this report, we studied the "engineering" of electrode work function through surface modifications using polymers and functional organic materials. The precise control of surface properties was achieved with layer-by-layer techniques of molecular assemblies.

Contact potential differences (CPDs) are measured after each deposition of PDDA or NiPc layer on ITO. Fig. 1 shows the measured CPD values vs the number of PDDA and NiPc layers. First, this result indicates that the surface potential of ITO electrodes has been changed due to the deposition of PDDA or NiPc layers on it. Once a single layer of PDDA is deposited on to ITO electrode, its CPD value shifts to  $\sim 500$  mV in reference to blank ITO. In other words, its work function is decreased by 0.5 eV. Interestingly, the CPD value of PDDA coated ITO decreases to  $\sim 100$  mV after a NiPc layer is added on top of a previous PDDA layer. There are some up-and-down shifts of the CPD values as the multilayer deposition is carried out, but the average gap between PDDA and NiPc remains relative constant,  $\sim 400$  mV. This proves that the relationship between surface potential and number of alternative layers is periodic and the net effect to work function of multilayer-modified electrodes is the same as a few layers with a single repeated periodicity. This result is also consistent with the conclusion we reported before.<sup>6,7</sup> For sample with the depositions less than 50 layer-pairs, a linear increase in both absorption and thickness monitored by UV-vis absorption spectra and X-ray reflectivity measurements indicate that local structure of PDDA and NiPc molecules do not change much, especially the local solid-state environment or NiPc's electronic properties.

Actually, the change in work function comes from a modification in electron affinity and/or an alteration in band bending. Therefore the total change in surface potential is equal to the sum of the modulation in band bending and electron affinity. If the self-assembled monolayers have ligand properties that alter the density of the surface states, then band bending should also occur.<sup>15</sup> According to reports by Cahen D. *et al*, both electron affinity and band bending can be changed under this situation.<sup>18-20</sup> For example, work function of semiconductor modified by chemisorption of organic compounds such as dicarboxylic acid derivatives. However, on the chemisorption of a series of benzoic acid derivatives with vary dipole moments, CPD measurements reveal that molecular modification only affects the work function by altering the electron affinity while band bending is not affected significantly.<sup>16,17</sup> In other words, the presence of a dipole layer affects the electron affinity only. Therefore, we expect that the effect on work function from deposition of oppositely charged polymers or macrocycles on ITOs comes predominant from electron affinity contributions.

ITO is a degenerate *n*-type semiconductor and generally behaves like a metal. But ITO is not quite as conductive as a metal, thus it still possesses some semiconductor surface characteristics. Indeed, Moons *et al.* verified that the presence of a depletion layer in bare ITO.<sup>22</sup> For example, after porphyrins were spin-coated onto ITO substrate, band bending was altered on ITO surface and shifted by 30 and 90 meV with different porphyrin species, respectively.

Due to the formation of a typical *n*-type depletion layer on bare ITO, there are some negative charges existing on the surface of ITO, thus promoting the growth of positively charged PDDA monolayer through electrostatic attractions. The formation of PDDA on ITO surfaces generates a dipole, pointing towards ITO, thus lowering electronic affinity and decreasing its work function. In other words, it is easier for the surface-localized electrons to transfer into the vacuum from Fermi level after the formation of PDDA/ITO dipole layers. When the negatively charged NiPc layers was deposited on top of PDDA layers, another new opposite dipole layers forms and these total contributions sum up to a net dipole close to the blank ITO's electron affinity. Therefore the CPD values shift back to  $\sim 100$  mV. This same effect remains after depositing many alternating PDDA-NiPc layers with LBL technique. If this modification of work function came from an alteration of ITO's band bending, it would have stopped the oscillation after the second bilayers on ITO substrates. Therefore we concluded that this oscillation pattern in work function is mainly due to modulation in ITO's electron affinity. Each new dipole layer forms with its deposition, which adjusts the work function. These results reveal that Kelvin probe is a very effectively tool on monitoring dipole changes of surface monolayers.

In our previous studies,<sup>11</sup> we have measured the current-voltage (*I-V*) characteristics of Al/PDDA with or without NiPc monolayer/*p*-type Si heterostructures. The turn-on voltage is increased to 0.55 V by introducing a PDDA monolayer between Al and Si while a conventional Schottky Al/Si contact has a turn-on voltage of about 0.25 V. The addition of another NiPc monolayer on top of PDDA tunes the turn-on voltage back to 0.4 V despite an increase in total organic film thickness. On the other hand, the Schottky barrier heights, as evaluated from the saturation current at reverse bias, remains essentially the same at 0.7 eV for all heterostructures. The implication is that the conduction at forward bias must be governed by a new mechanism across the interface. According to X-ray reflectivity and ellipsometry studies, there is an ultrathin ( $\sim 0.5$  nm) oxygen-containing layer on the hydrogen-terminated *p*-type Si surface. As a result, the positive charges are being built up at the outer surface, an equal amount and opposite charges (i.e. negative) must exist inside. This is the formation process of the depletion layer on *p*-type Si, which yields a Schottky barrier. When a PDDA monolayer adsorbs on *p*-type Si, it will produce a dipole layer enhancing the total field effect. This phenomenon causes the turn-on voltage shifting up because the migration of electrons from *p*-type Si to Al anode electrode is more difficult than Al/*p*-type Si heterojunction. While a NiPc monolayer absorbs, a new opposite dipole layer will cancel the effect of PDDA monolayer on *p*-type Si surface, hence the turn-on voltage is reduced. In these alternative deposition processes, none of them changes the band-bending of *p*-type Si, thus the barrier height remains the same. These results consist with our measurements of work function on PDDA-NiPc/ITO heterostructures with Kelvin probe technique.

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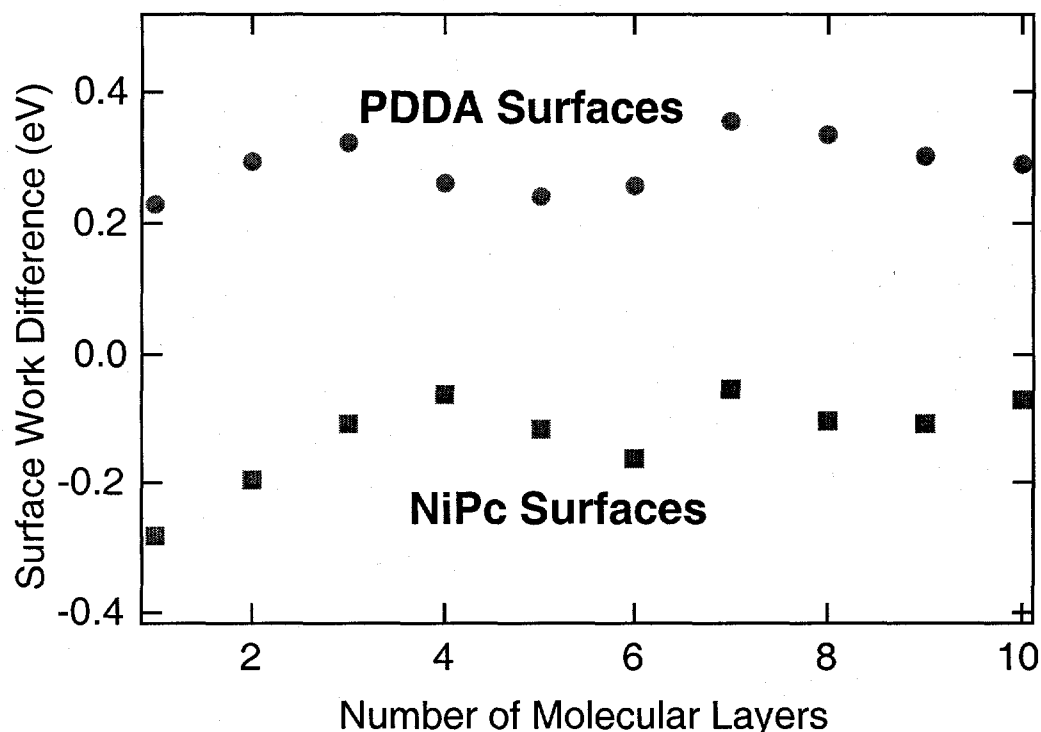
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**Figure 1:** Dependence of the surface work function (eV), of indium tin oxides (ITO) on the surface monolayers of PDPA (square) and NiPc (circle) as a function of deposition layers