I. INTRODUCTION

The goal of efficient, low cost solar energy conversion has motivated many investigations of nanostructured materials for photovoltaic applications.1–3 Organic–inorganic hybrids are one promising class of novel materials that combine organic components and inorganic nanostructures through chemical and/or physical interactions.4 Organic films containing lead chalcogenide nanoparticles are one such hybrid material that have been the subject of intense study.2,5,6 Lead sulfide (PbS) nanoparticles allow for a size tunable bandgap due to quantum confinement effects, have large extinction coefficients,7 and are thus under consideration for use as the near-IR active component nanocomposite films. It is hypothesized that the surface metal overlayers to complete electrical contact with these delocalized charge carriers. As shown schematically in Fig. 1, ion modification shares some characteristics with plasma polymerization, which has been previously used for surface modification of nanoparticles.10 The acetylene ions used in ion-assisted deposition behave both as catalysts and reagents by energetically inducing bonding between condensed phase species and forming adducts with the neutral reagents.11–15

X-ray photoelectron spectroscopy (XPS) was employed to probe photoconductivity of the PbS nanoparticle–4T composite films. For insulating and semiconducting samples, it has been observed that surface charging can shift the measured binding energies in an X-ray photoelectron (XP) spectrum.16–19 Ineffective filling of holes due to photoemission results in the buildup of a positive surface potential. Monitoring the shifts in XP spectra due to this surface charge buildup allows for examination of changes in the local electrical conductance of different components in a sample. The use of XPS for probing photovoltaic effects in heterostructured materials has been reported in various works.20–24

Surface potential shifts related to external electron gun stimulation and/or illumination via laser or other light sources are observable in XP spectra of composite semiconductor surfaces.25 For such surfaces, it has been demonstrated that photovoltaic and photoconductive properties are related to static or quasistatic shifts of XPS peaks. Furthermore, these shifts can be qualitatively studied by using films on conductive substrates. This XPS technique examines the charging/discharging process during laser illumination, without the need for metal overlayers to complete electrical contact with these delocalized nanocomposite films. It is hypothesized that the surface chemistry and heterojunction bonding within the nanocomposite films affect photocharging, and in turn can be probed by XPS. XPS measurements performed upon green laser
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N
N

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phene was thermally evaporated onto the substrates. This sexithiophene, mass spectrometric analyses (not shown, to be varied from 413 to 513 K to maintain a 1:1 fluence with the ceramic crucible (LTE 11 000 K, 1 cc, Kurt J. Lesker, Pitts-

4, Sigma-Aldrich, St. Louis, MO) evaporated from a heated substrate with oligothiophene (sexithiophene, CAS 88493-55-

eous PbS clusters were simultaneously deposited onto the Si surface. The metal aperture allowed for four different distinct regions to be deposited simultaneously onto the Si substrate, as shown in Fig. 2. The four regions were 4T only, 4T with acetylene ions (denoted as 4T + ions), 4T with PbS nanoparticles (denoted as 4T + PbS), and 4T with both PbS nanoparticles and acetylene ions (denoted as 4T + PbS + ion). The films were made in three replicate samples for analysis.

II. EXPERIMENT

A. Sample preparation

Sample preparation was performed in Chicago, IL, using the methods shown schematically in Fig. 1. Silicon wafers [P-doped, n-type Si (100) wafers, Atomergic Chemical Corporation, Melville, NY] were used as substrates and were hydrogen terminated by hydrofluoric acid etching to leave at most a minimal oxide layer. PbS clusters were formed in a magnetron condensation source by reactively sputtering a Pb metal target in an Ar/H2S gas mixture, as previously described.8,9 The gaseous PbS clusters were simultaneously deposited onto the Si substrate with oligothiophene (sexithiophene, CAS 88493-55-4, Sigma-Aldrich, St. Louis, MO) evaporated from a heated ceramic crucible (LTE 11 000 K, 1 cc, Kurt J. Lesker, Pitts-

burgh, PA). The oligothiopehene sublimation temperature was varied from 413 to 513 K to maintain a 1:1 fluence with the PbS clusters, as monitored with a quartz crystal microbalance.

While the oligothiophene sample purchased was nominally sexithiophene, mass spectrometric analyses (not shown, to be presented elsewhere) found that predominantly quaterthioprene was thermally evaporated onto the substrates. This resulted from the lower sublimation temperature of 4T compared with sexithiophene and the ~10% 4T content of the oligothiophene mixture as received from the vendor (as verified by mass spectrometric analysis).

Acetylene ions with 50 eV kinetic energy were generated by a Kaufman ion source (IBS 250, 3 cm, Veeco/Commonwealth Scientific, Plainview, NY)15 and used to modify the films simultaneous with 4T and PbS cluster deposition. The ion source was mounted ~45° from the surface normal. An aperture was placed directly in front of the sample perpendicular to the organic doser and 37° from the normal of the CBD source. The metal aperture allowed for four different distinct regions to be deposited simultaneously onto the Si substrate, as shown in Fig. 2. The four regions were 4T only, 4T with acetylene ions (denoted as 4T + ions), 4T with PbS nanoparticles (denoted as 4T + PbS), and 4T with both PbS nanoparticles and acetylene ions (denoted as 4T + PbS + ion). The films were made in three replicate samples for analysis.

B. XPS analyses

X-ray photoelectron spectra were collected in Ankara, Turkey using a commercial XPS spectrometer (K-Alpha, Thermo Fisher Scientific) with monochromatized Al Kα x-ray source. The spectrometer was able to probe the sample with a small x-ray spot size between 30 and 400 μm. All core level spectra were charge referenced to C 1s, taken to be at 285.0 eV, and fit using commercial software (XPS PEAK FIT 4.1). The instrument was also equipped with a flood gun as an external electron source and an additional argon ion source for neutralization of the sample surface. The electron flood gun was operated at 0.5 eV and 100 mA for all the measurements reported in this work. The sample holder was grounded and samples held by Au clamps. The optical stimulus was provided by a continuous wave (cw) 532 nm (2.3 eV) green laser outputting 50 mW (GCL532, CrystalLaser, Reno, NV). The schematic in Fig. 2 represents the photoilluminated XPS measurement.24,26

III. RESULTS AND DISCUSSION

A. Elemental and chemical analysis of films

The survey x-ray photoelectron spectra (not shown) verified the composition of the nanocomposite films as consisting of Pb, S, and C with only a small O signal due to minor oxidation. The average elemental composition for all three samples and four regions is presented in Table I. Although samples were kept under vacuum after preparation, they were sent from Chicago to Ankara and thus were exposed to atmosphere, which caused some oxidation. Carbon content increased slightly for films with ion modification compared to those without, as expected upon the introduction of carbonaceous acetylene ions. Correspondingly, the Pb and S components from all contributions for ion-modified films slightly decreased. Introduction of PbS nanoparticles led to the appearance of a Pb peak. Oxygen content also slightly increased for ion-modified films, likely due to the formation of oxidizable radical sites.

The quoted errors in the elemental compositions of Table I reflect sample-to-sample fluctuations in film thicknesses,
Table I. Elemental composition of four different types of quaterthiophene (4T) films: with (4T + ion) and without (4T) ion bombardment as well as with PbS nanoparticles (4T + PbS + ion and 4T + PbS, respectively).

<table>
<thead>
<tr>
<th>Film region</th>
<th>%O</th>
<th>%Pb</th>
<th>%C</th>
<th>%S_{4T}</th>
<th>%S_{4T-PbS}</th>
<th>%S_{PbS-Surf}</th>
<th>%S_{PbS-Core}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4T + ion</td>
<td>3.5 ± 0.9</td>
<td>—</td>
<td>74.3 ± 1.7</td>
<td>22.2 ± 1.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4T + PbS</td>
<td>7.4 ± 1.3</td>
<td>—</td>
<td>76.0 ± 1.8</td>
<td>16.6 ± 1.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4T + PbS + ion</td>
<td>6.8 ± 1.9</td>
<td>7.3 ± 3.3</td>
<td>67.4 ± 3.9</td>
<td>8.0 ± 2.2</td>
<td>5.2 ± 1.4</td>
<td>1.9 ± 0.6</td>
<td>3.4 ± 1.6</td>
</tr>
<tr>
<td>4T + PbS + ion</td>
<td>6.7 ± 1.8</td>
<td>4.7 ± 1.4</td>
<td>73.2 ± 3.7</td>
<td>6.9 ± 2.0</td>
<td>5.0 ± 0.5</td>
<td>1.3 ± 0.3</td>
<td>2.2 ± 0.8</td>
</tr>
</tbody>
</table>

Comparison of core level spectra on samples with and without C\textsubscript{2}H\textsubscript{2}\textsuperscript{+} ion modification indicates enhanced bonding within the nanocomposite film. The ratio of S\textsubscript{4T-PbS}/Pb for the 4T + PbS samples was 0.7 ± 0.4, but this ratio increased to 1.1 ± 0.3 for the 4T + PbS + ion samples, indicating that ion modification increased the coupling between the nanoparticles and 4T. Further experiments on samples that were only minimally air exposed supported the increase in nanoparticle–4T bonding (results not shown, but to be presented elsewhere).

Attempts to extract functional group information from the C 1s peak failed, as this component did not shift significantly for the various changes in chemical environment occurring here. Thus, the C 1s peak was fit with a single component.

Film and nanoparticle morphology was not directly examined here. Prior work showed that well-separated, 3.5 ± 0.9 nm diameter PbS nanoparticles with some degree of crystallinity were formed under conditions similar to those used to prepare the 4T + PbS films.\textsuperscript{8} Those experiments were performed by depositing nanoparticles and organic oligomer onto copper grids for subsequent analysis by dark field scanning transmission electron microscopy. However, more recent attempts to examine changes in film morphology by transmission electron microscopy were hindered by the erosion of the copper grids by acetylene ion bombardment. Further studies of film morphology for the 4T + PbS + ion films are under consideration.

B. XPS analysis of core level shifts due to green laser illumination

All four types of films—4T, 4T + ion, 4T + PbS, and 4T + PbS + ion—showed photoinduced shifts in their core levels. Furthermore, smaller shifts were observed for the ion-modified films, consistent with improved charge transfer and increased photoconductivity. These photoinduced XPS results suggest that ion-assisted deposition leads to enhanced bonding within the 4T organic matrix as well as between the organic matrix and PbS nanoparticles.

The shifts of elemental core spectra due to green laser excitation were measured with the averages of the shifts for all three replicate samples in all four regions presented in Table II. Typical S 2p and Pb 4f spectra in the regions of 4T with PbS nanoparticles with and without ions are shown in Figs. 4 and 5. As seen in Figs. 4 and 5, the dashed lines show the XPS peaks shifting toward higher binding energy for all laser illuminated spectra. Illumination creates a positive potential on the sample surface, which shifts the binding energy of photoelectrons. Increased photoconductivity in the PbS/4T ratios, and/or the oligomer distribution. A slight variation in the Pb to S ratios for the unmodified and ion-modified areas was also observed for different samples. This variation may have arisen from sample heating and/or ion-induced degradation by the ion source, which could have led to evaporation of a small portion of the film simultaneous with deposition.

The S 2p core level spectra of PbS nanoparticle–4T films with and without ion bombardment are shown in Fig. 3. The S 2p core level spectra were deconvoluted into four major sources of sulfur; in addition to the 2:1 spin orbit splitting for S 2p\textsubscript{3/2}/S 2p\textsubscript{1/2} from each individual component. These four components were assigned as S\textsubscript{4T} arising from 4T at binding energy of 164.3 eV, S\textsubscript{4T-PbS} arising from 4T interacting with the PbS nanoparticle at 163.7 eV, S\textsubscript{PbS-Surf}, which is the surface component of PbS at 162.2 eV, and S\textsubscript{PbS-Core}, which is the core component of PbS at 161.3 eV.\textsuperscript{8}

![Fig. 3. S 2p core level spectra of PbS nanoparticles cluster beam deposited into 4T (a) without and (b) with 50 eV acetylene (C\textsubscript{2}H\textsubscript{2}) ion modification. Broken lines are fits to individual components (see the text) and solid lines are composite fit. Closed points are actual data.](image-url)
film causes core level peaks to shift back toward their native binding energies for positively charged surfaces, reducing the shift induced by illumination.23,26

Ion modification shows a decrease in core level shifts in 4T films with and without PbS nanoparticles due to laser illumination. For example, the 4T+ PbS nanoparticles compared with the 4T film. While the smaller photoinduced shift in the S 2p PbS-Core + Surf shift was always ~0.1 eV smaller than the other shifts. Note that the binding energies can be measured to ±0.2 eV.

Photocconductivity is the convolution of the number of carriers generated per absorbed photon and how fast a carrier moves through the medium under applied field.27 If the conductivity of the surface layer is increased by illumination with an external light source, surface charge decreases due to compensation by available charge carriers.23 Increased photocconductivity is observed here in the reduced binding energy shifts upon laser illumination.

The most likely explanation for the increase in photocconductivity is an increase in chemical bonding, which creates larger conjugated systems that in turn allow increased intramolecular charge transfer. Enhanced bonding in ion-assisted deposition of oligothiophenes has been observed previously11–13 and was predicted by molecular dynamic simulations.14 Ongoing work is exploring a similar mechanism in which the 4T+ PbS + ion films display enhanced covalent bonding between the PbS nanoparticles and the 4T phase, induced by ion-assisted modification.

**TABLE II. Average calculated peak shifts (eV) upon green laser excitation for core level spectra.**

<table>
<thead>
<tr>
<th>Peak</th>
<th>4T + PbS</th>
<th>4T + PbS + ion</th>
<th>4T</th>
<th>4T + ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>S 2p_{4T}</td>
<td>0.43 ± 0.1</td>
<td>0.25 ± 0.1</td>
<td>0.50 ± 0.03</td>
<td>0.35 ± 0.1</td>
</tr>
<tr>
<td>S 2p_{4T-PbS}</td>
<td>0.45 ± 0.1</td>
<td>0.23 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S 2p_{PbS-Core + Surf}</td>
<td>0.33 ± 0.1</td>
<td>0.13 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 1s</td>
<td>0.41 ± 0.1</td>
<td>0.25 ± 0.1</td>
<td>0.52 ± 0.03</td>
<td>0.37 ± 0.1</td>
</tr>
<tr>
<td>Pb 4f</td>
<td>0.37 ± 0.1</td>
<td>0.19 ± 0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**FIG. 5.** Pb 4f core level XP spectra of the PbS nanoparticle with 4T films (4T+ PbS) on Si wafer (a) without and (b) with 50 eV acetylene ion-assisted deposition. Solid lines are fits and closed points are data without illumination, while dashed lines are fits and open points are data with green cw laser illumination. The Pb 4f peaks were fit with only one component.
An alternative explanation for the increase in photoconductivity due to the ion-assisted deposition could arise from an increase in available free charge carriers with the addition of $\text{C}_2\text{H}_4^+$ to the system and an enhancement in charge generation efficiency (i.e., intermolecular charge transfer). However, the validity of this mechanism requires the deposited ions to maintain at least part of their gaseous-state charge upon deposition into the film.

It is known that light-induced carrier generation and diffusion may cause band bending in semiconductors such as doped Si wafers. Photoillumination in semiconductors with a light source whose energy is larger than that of the semiconductors’ bandgap can be described as decreasing band-bending via creation of additional electron–hole pairs, resulting in a further increase in binding energy. A similar photoinduced behavior could be expected for the intrinsically semiconducting PbS nanoparticles, given a bandgap of $\sim 1.4$ eV for the $\sim 3$ nm PbS nanocrystals and 2.3 eV excitation energy of the green laser employed here. However, it is thought that the nanocomposite films studied here exhibit charging shifts mainly due to their significant resistivity. Differentiation between these two processes is not possible with the experiments performed here. It should also be noted that the thickness of these films is $\sim 100$ nm, and the underlying Si substrate was not seen in any XP spectra. Therefore, any photoinduced charging that might have occurred in the Si wafer could not be observed due to the inability of the Si photoelectrons to escape through the nanocomposite film during the XPS measurement.

IV. SUMMARY AND CONCLUSIONS

These experiments demonstrate that cluster beam deposition of semiconductor nanoparticles combined with physical deposition of an organic oligomer can prepare films with a measurable photoinduced response. Furthermore, it is found that this photoinduced response, a type of photoconductivity, can be increased by ion-assisted deposition. The increase in photoconductivity with ion-assisted deposition is analogous to the changes in photodetector and photovoltaic properties of films containing PbS or PbSe nanoparticles observed following chemical or thermal control of the organic ligands on the nanoparticle surfaces. Also, a differential charging event is observed here in which the semiconductor nanoparticles display enhanced photoconductivity compared with the surrounding organic matrix. The cluster beam deposition and ion-assisted deposition strategies can prepare a wide variety of nanocomposite films, indicating their broad potential for photovoltaic and photoconductive applications.

ACKNOWLEDGMENTS

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