

Work function tuning of tin-doped indium oxide electrodes with solution-processed lithium fluoride

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ABSTRACT

Solution-processed lithium fluoride (sol-LiF) nanoparticles synthesized in polymeric micelle nanoreactors enabled tuning of the surface work function of tin-doped indium oxide (ITO) films. The micelle reactors provided the means for controlling surface coverage by progressively building up the interlayer through alternating deposition and plasma etch removal of the polymer. In order to determine the surface coverage and average interparticle distance, spatial point pattern analysis was applied to scanning electron microscope images of the nanoparticle dispersions. The work function of the sol-LiF modified ITO, obtained from photoelectron emission yield spectroscopy analysis, was shown to increase with surface coverage of the sol-LiF particles, suggesting a lateral depolarization effect. Analysis of the photoelectron emission energy distribution in the near threshold region revealed the contribution of surface states for surface coverage in excess of 14.1%. Optimization of the interfacial barrier was achieved through contributions from both work function modification and surface states.

1. Introduction

The ability to tune the electrode work function by the insertion of an interlayer has enabled the optimization of charge injection and collection efficiency in organic electronics [1]. In particular, charge selectivity and improved energy level alignment has motivated the development of various interlayers, such as n-type oxides, e.g., TiO₂ and ZnO, for preferential electron transport [2] and p-type oxides, e.g., MoO₃, WO₃, NiO_x, for hole transport [3]. Self-assembled monolayers of organic dipolar molecules have also been presented as a means for controlling the surface dipole of the electrode; the polarization strength can be tuned by careful selection of the functional groups on both ends to specify the desired shift of the modified electrode work function [1,4,5]. More recently, conjugated polyelectrolytes, which appear to have dynamic dipoles that can switch direction depending on the direction of the applied electric field, have been used in organic light emitting diodes and transistors

[6,7]. However, some of the most widely used interlayers have been thermal evaporated LiF and other alkali halides and alkali metals [8], where the exact mechanism by which these materials enhanced charge collection/injection remains the subject of debate [9,10].

Meanwhile, rapid advances in the low-cost solution processing of organic electronics [11], as exemplified by the roll-to-roll manufacturing of polymer solar cells [12], have motivated the development of a solution processed alternative to thermal evaporated LiF [13]. In contrast to thermal evaporated LiF, which decreases the surface work function of tin-doped indium oxide (ITO), solution-processed LiF (sol-LiF) actually increases the work function [13]. In fact, incorporation of the sol-LiF at 14.4% coverage into a conventional ITO/sol-LiF/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) layer (PEDOT:PSS)/poly(3-hexyl-thiophene):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM)/thermal LiF/Al photovoltaic device showed a 6-fold increase in photon conversion efficiency over the same device without sol-LiF [14]. Since LiF interlayers have been shown to enhance charge collection efficiency at both electrodes, they are most likely providing a means to fine-tune the energy level alignment between the electrode and the organic active layers.

The work function, Φ , is the difference in energy between an electron at the Fermi level just inside the surface and at rest in vacuum [15], and a key technique to measure it is photoelectron emission yield spectroscopy. When irradiated with a UV source, electrons with a kinetic energy greater than the apparent photoemission threshold, φ , will be ejected from the specimen. The fastest, i.e. most energetic,

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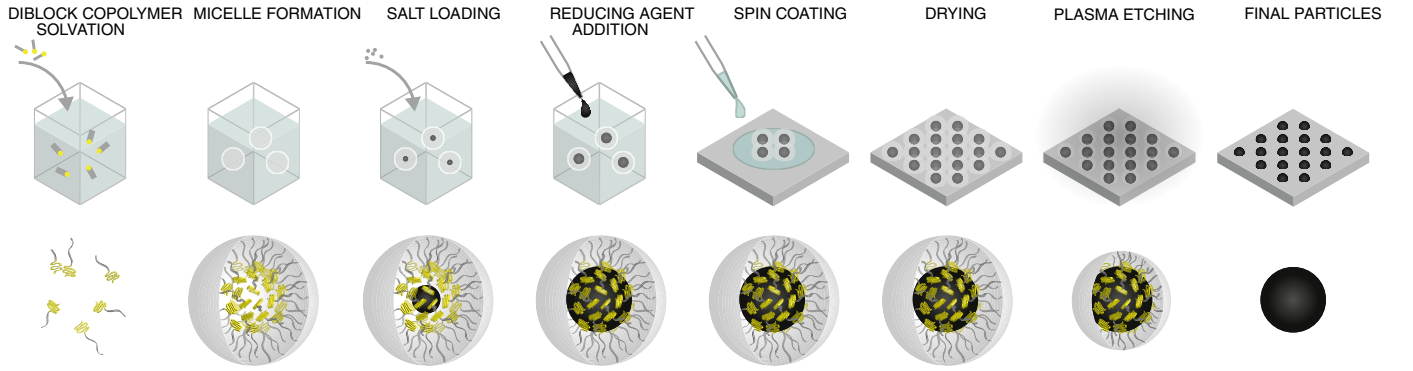


Fig. 1. The synthesis LiF nanoparticles in solution in reverse polystyrene-*block*-poly2vinylpyridine diblock co-polymer reactor vessels.

electrons would be those at the Fermi level, while the slowest electrons would be those with energy equal to Φ . A negative deviation of φ from Φ can be attributed to emission from surface states [16,17].

Adsorbates on the surface can induce surface dipoles [15]. The consequent formation of a dipole layer can also change the emission threshold of the substrate [18]. When the density of these dipoles is increased, mutual interactions reduce the effective dipole moment ("depolarization") [4,19], which is reflected in modulation of φ [15].

An important side effect of the solution process protocol for LiF is the ability to tune the electrode work function, measured by Kelvin probe, via control of the surface coverage. The tuning of Φ by LiF nanoparticles has been attributed to depolarization [13]. The increase in coverage entailed a decrease in interparticle separation, giving rise to increasing depolarizing interaction between surface dipoles induced by the LiF. As the sol-LiF processing enables the progressive build-up of the electrode bilayer, it provides the means to investigate the degree of work function shift with interlayer morphology. The results would reveal

insight into how modification of the electrode structure impacts the interfacial properties. In this contribution, we provide further evidence that the degree of increase of the work function of ITO is tunable via its surface coverage by sol-LiF; we also substantiate the participation of surface states in tuning the degree of increase.

2. Experimental details

Details can be found in Aytun et al. [13] for the synthesis of LiF nanoparticles in solution by using reverse diblock copolymer nanoreactors. Briefly, as shown in Fig. 1, polystyrene-*block*-poly 2vinyl pyridine diblock copolymer (P1330-S2VP; Polymer Source Inc., Montreal, Canada) was dissolved in toluene. Lithium hydroxide non-hydrate (Merck KGaA, Darmstadt, Germany) was loaded into the micelle core, and then buffered 40% hydrofluoric acid (Merck KGaA, Darmstadt, Germany) was added to the loaded micelle solution. The micelles loaded with size-monodisperse particles were deposited onto tin-doped indium oxide

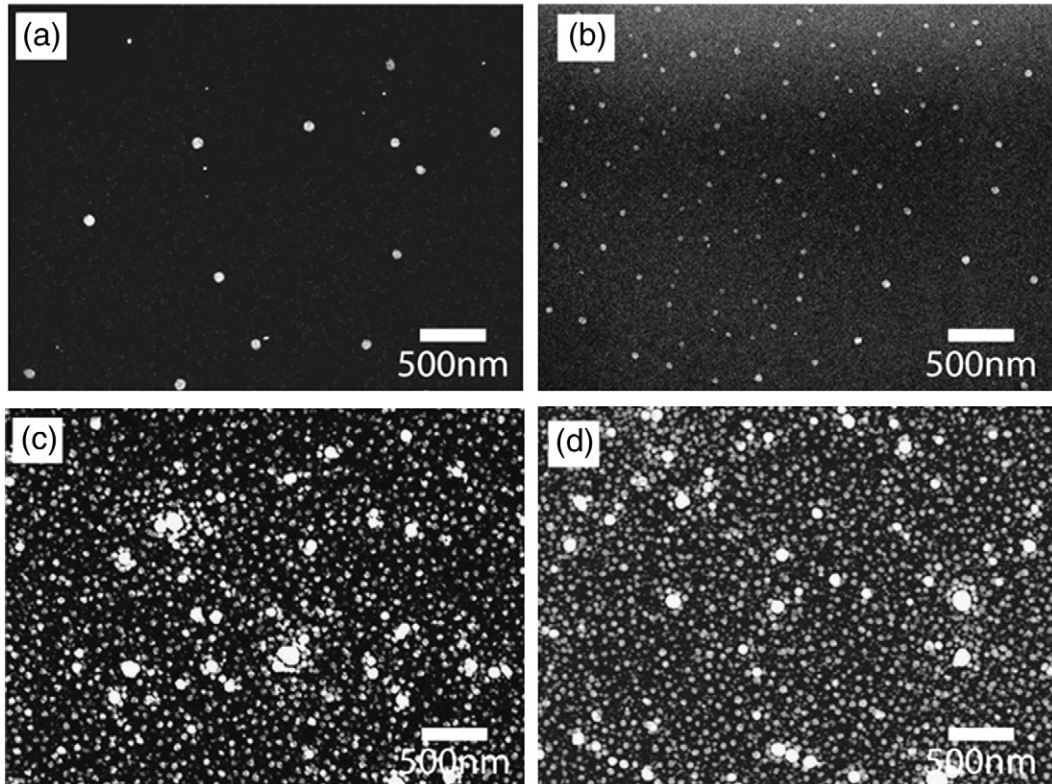


Fig. 2. Images of LiF nanoparticles on single crystal silicon wafer substrates used for spatial point pattern analysis, showing a) 0.5% coverage, b) 1.1% coverage, c) 14.1% coverage, and d) 21.8% coverage.

Table 1

Surface coverage and average interparticle spacing for the 4 different nanoparticle dispersions produced.

# of deposition layers	Surface coverage	Avg. Interparticle Spacing [nm]
1x LiF	0.5%	394.6
3x LiF	1.1%	177.1 ^a
5x LiF	14.1%	63.3
7x LiF	21.8%	58.3

^a Highest probability nearest neighbor position.

(ITO; smooth, 30 $\Omega/\square$, TFD Inc., Anaheim, California) and on Si wafer pieces. The particle distribution on ITO and on single crystal silicon wafer substrates is comparable. However, since Si substrates present a more uniform background than the sub-grain boundary structure of ITO, single crystal Si wafer substrates were used to facilitate the image processing and analysis. In order to achieve varying degrees of surface coverage (repetitions of 1x, 3x, 5x, and 7x), layer deposition was successively alternated between spin coating (2000 rpm, 40 s) and oxygen plasma etch removal of the polymer (1.5 h at 29.6 W RF power; Harrick PDC-002, Ithaca, New York). The nanoparticle distribution on the Si surface was imaged under a 3 keV beam in the scanning electron microscope (SEM; LEO Supra 35VP, Oberkochen, Germany). Surface coverage and average interparticle spacing were quantitatively determined by spatial point pattern analysis, in which ImageJ [20] and the spatstat package [21] of the statistical software, R, [22] were applied to the SEM

micrographs. The work function of the sol-LiF-modified ITO surface was measured by photoelectron emission yield spectroscopy (PEYS; Riken Keiki AC-2, Tokyo, Japan). A deuterium lamp was used as the UV source, and the incident light was adjusted from $h\nu = 3.4$ to 6.2 eV by a grating monochromator. Electrons emitted into air from the solid surface, irradiated by a 4 mm $\times$ 4 mm spot, were detected by an air-filled counter (open counter) equipped with two grids—one grid quenched the counter discharge using an external circuit, while the other grid suppressed the positive-ion bombardment. The certified repeatable accuracy for the measurement of the work function using this method is 0.02 eV [23].

3. Results

Spatial point pattern analysis was performed on SEM images of the sol-LiF-modified Si substrates, as shown in Fig. 2. The results for surface coverage are summarized in Table 1 for each sample of different particle dispersions. Analysis of the particle distributions can be used to differentiate between and quantify different types of order, of which there are three primary categories: regular (repulsive interactions), complete spatial randomness (non-interacting), and clustered (attractive interactions) [24]. In contrast to complete randomness, the other extreme for particle distribution is complete crystallographic order, which for two dimensions would be a hexagonal close-packed lattice. For the lowest surface coverage (0.5%), the cumulative nearest neighbor distribution function ($G(r)$) (Fig. 3a), Ripley's K function (Fig. 3b) [25] and pair

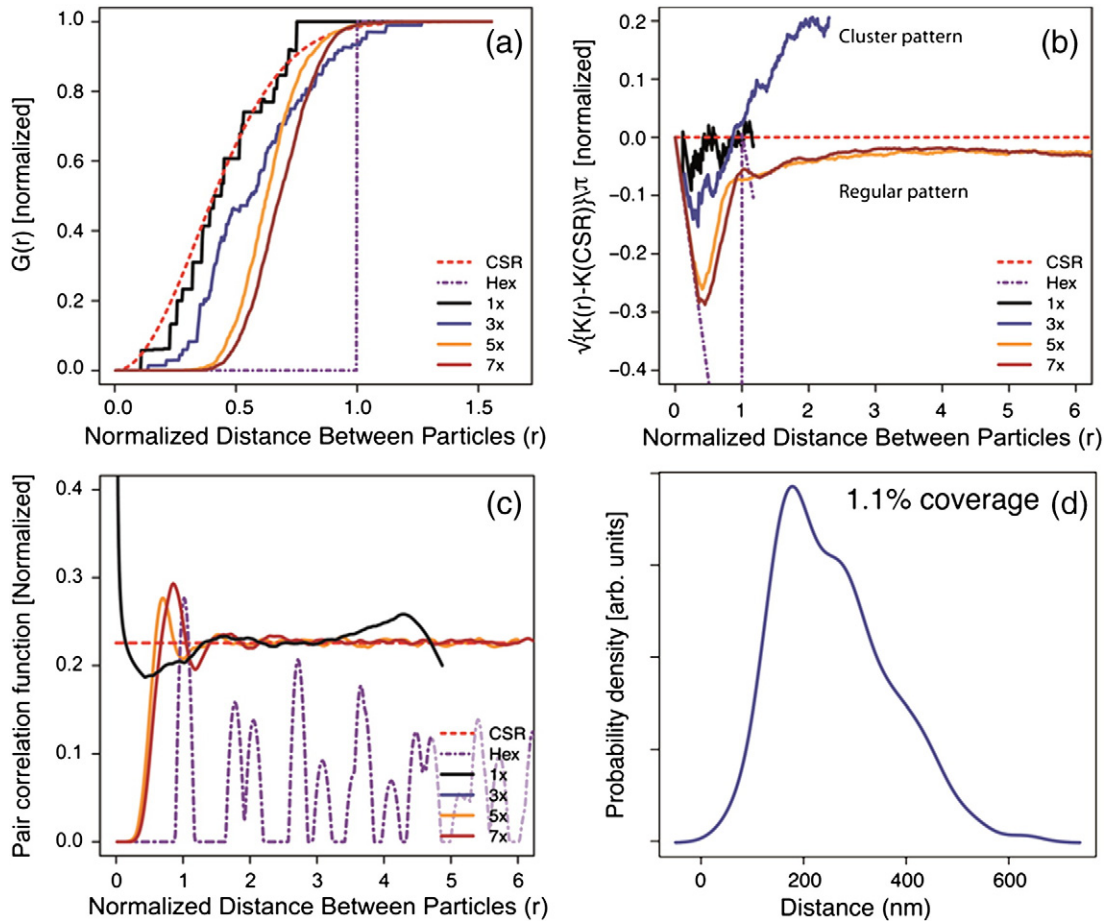


Fig. 3. Spatial point pattern functions for 1x (0.5%), 3x (1.1%), 5x (14.1%), 7x (21.8%) sol-LiF nanoparticle dispersions on single crystal Si. All are normalized to a hexagonal lattice dispersion with similar density of particles per unit area. Expected values for complete spatial randomness (CSR) and the 2D hexagonal close packed lattice are also given for comparison. a) Cumulative nearest neighbor distribution function ($G(r)$); b) Difference spectrum for the linearized Ripley's K function compared to CSR (dotted red line): clustered patterns lie above the CSR line, while ordered regular patterns fall below the line; c) pair correlation function: due to clustering effects, the PCF of 3x coverage is meaningless and not shown; d) Distribution of nearest neighbors for 1.1% coverage (3x dispersion) showing three nearest neighbor values, at 177.1 nm, 300 nm, and 410 nm, representing the particle and cluster distances respectively.

correlation function (Fig. 3c) all indicate complete spatial randomness of the particles. As the surface coverage increases, the particle dispersion starts to show clustering behavior, as observed in the Ripley's K function—indicative of the second nearest neighbor distribution—at larger particle separations in Fig. 3b for 1.1% coverage. This is also supported by the nearest neighbor distribution function (Fig. 3d), which can be resolved into three nearest neighbor peaks, for the particles and the clusters. Around the first nearest neighbor distance, Ripley's K function also indicates regularity within each particle cluster at such low coverage (Fig. 3b). This suggests that with low surface coverage, the micelles tend to deposit at the same locations, leading to clustering; however inside the cluster, the particles show some regularity. As the coverage increases, the micelles begin to cover areas not already occupied by nanoparticles, leading to a significant increase in the surface coverage for multiple spin coating and etching passes. At higher coverage, 14.1 and 21.8%, the particle distribution no longer shows any clustering, with clear indication of short range order. Though not approaching long range hexagonal close-packing, the pair correlation function shows both first and second order peaks, indicating more regularity than complete spatial randomness (Fig 3c).

Photoelectron emission yield spectroscopy was performed to determine the surface work function of the sol-LiF-modified ITO films. Because ITO is a degenerate semiconductor, the electronic band structure model for a metal can be applied to analyze the quadratic increase in photoelectron yield with the incident photon energy [26]. Recognizing that $Yield^{1/2} \sim (E_{kinetic} - E_{incident})$ for $E_{incident} > \phi$, the surface work function Φ can be extrapolated from a fit of the linear portion of the energy curve. The energy curves are presented in Fig. 4, while the shift in extrapolated work function values is summarized in Fig. 5. The bare ITO sample was exposed to the same oxygen plasma treatment conditions as the 0.5% LiF coverage sample. An increase in work function on the order of 0.13 eV can be expected for oxygen plasma etched ITO [13], which typically has a work function of 4.7–4.8 eV [27,28].

4. Discussion

For determining the work function shift of ITO by sol-LiF modification, PEYS was suitable for comparing ITO with varying sol-LiF surface coverage. In a degenerate n-type semiconductor, like ITO, Φ approaches the value of ϕ , which is very sensitive to bulk doping and to the surface

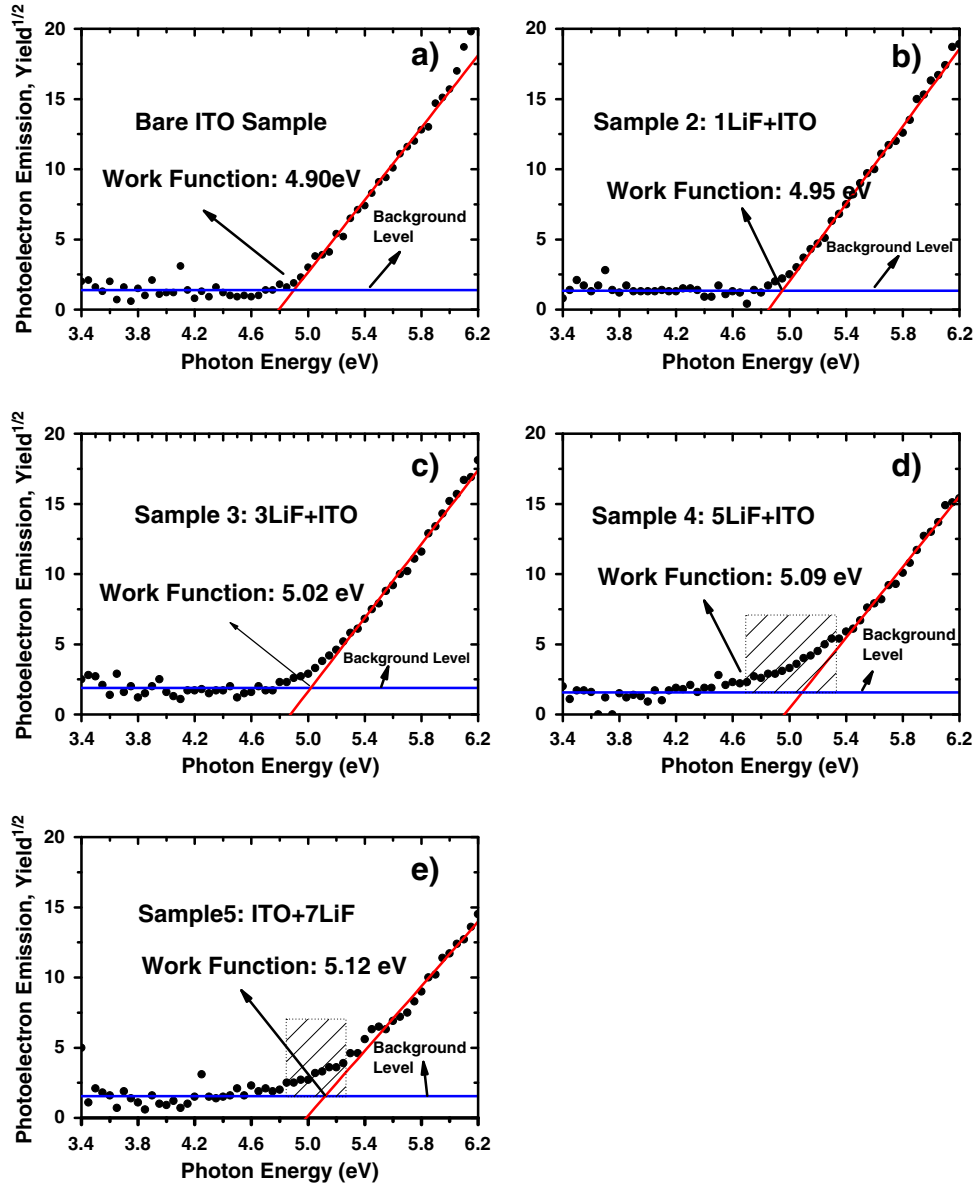


Fig. 4. (Photoelectron emission yield)^{1/2} vs. incident photon energy curves are presented for a) bare ITO, b) ITO with a single deposition of sol-LiF (0.5% coverage), c) ITO with three deposition/etch cycles of sol-LiF (1.1% coverage), d) ITO with 5 deposition/etch cycles of sol-LiF (14.1% coverage), and e) ITO with 7 deposition/etch cycles of sol-LiF (21.8% coverage).

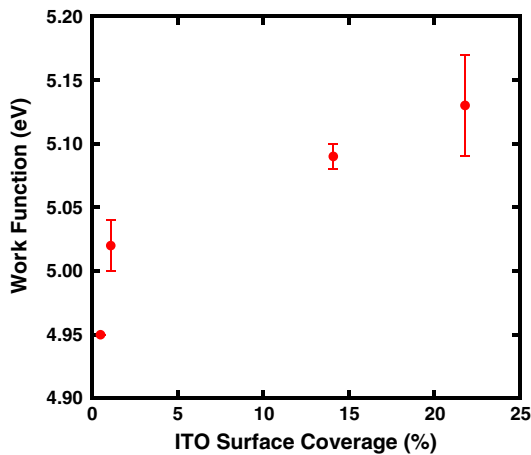


Fig. 5. The variation in work function shift with surface coverage of sol-LiF-modified ITO, as extrapolated from PES energy curves.

state. Because the spot size of incident light is much larger than the average nanoparticle diameter (~ 45 nm), the photoelectron emission signal reflects the average yield from the dispersion of LiF nanoparticles and the exposed, underlying ITO surface.

Two models have been proposed for adsorbate modification of work function: 1) a classical model involving depolarization and 2) a quantum mechanical model involving additional surface states in the band structure of a semiconductor [15].

When adsorbates on the surface induce surface states, shifting charge at the interface formed leads to polarization and forms a dipole layer, which changes ϕ of the substrate [18]. When the density of these dipoles is increased, mutual interactions reduce the effective dipole moment [4,19], which is reflected in modulation of ϕ . This concept, also known as “depolarization”, has been reported in studies of metal adatoms on a semiconductor substrate [15] as well as of strong electron-acceptor, conjugated organic adsorbates on gold [28] and on graphite [29].

The tunability of the work function with surface coverage in Fig. 5 provides further evidence for depolarization of an induced surface dipole upon increasing interaction strength between neighboring LiF particles. It can thus be concluded that the mechanism by which sol-LiF modifies the surface electronic properties of ITO is consistent with the classical depolarization model.

On the other hand, the band states model also appears consistent with our system, when one analyzes the form of the photoelectron emission energy distribution near the threshold. Because atoms at the surface and in the sub-surface monolayers have fewer neighbors than their bulk counterparts, their outer valence electrons have less wave function overlap. They bear closer resemblance to the electrons of isolated atoms, have energy levels closer to those of isolated atoms, and hence contribute states in the bulk bandgap. These surface states appear as a negative deviation of ϕ from Φ . As demonstrated with n-type silicon, the surface states were filled progressively as the energy bands were bent downwards relative to the Fermi energy (at the surface), leading to increased, but slower rising, yield at lower ϕ [16,17].

The bare ITO specimen (Fig. 4a) met the criteria for a metal-like surface, namely a well-defined emission threshold defining the Fermi edge in the yield-energy distribution curves [15]. Depositing sol-LiF onto ITO for a surface coverage of 0.5% (Fig. 4b), did not change the energy distribution at the yield onset significantly. However, as the surface coverage increased to 1.1%, an increase in yield at lower energies was observed (Fig. 4c), consistent with emission from surface states [16,17]. This

increase became more pronounced at 14.1% coverage (Fig. 4d) and was still present at 21.8% coverage (Fig. 4e). The form of the yield-versus-energy curve near threshold arises from photoelectron production and scattering mechanisms, as modeled by Kane. The rate of increase in yield with respect to incident photon energy is slower than that for a metal-like surface, suggesting that the origin of emission stems from states of a lower density than the bulk states [17]. One possible origin of these states may arise from charge transfer, which was observed to increase with surface coverage in core level X-ray photoelectron spectroscopy.

5. Conclusion

Photoelectron emission yield spectroscopy revealed that increasing surface coverage by LiF nanoparticles formed in micelle nanoreactors increased the work function of ITO. The surface coverage was modulated by leveraging the controlled dispersion of LiF nanoparticles through multiple depositions. Moreover, analysis of the energy distribution of photoelectron emission yield near threshold revealed a slower-varying increase at energies below threshold, consistent with emission from surface states. Thus the tunability of the ITO work function appears to be consistent with both the bond model and the band model of surface contributions, and suggests that modification of the interface barrier originates from both depolarization and surface states.

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