Colloidal quantum dot solids

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4. Colloidal quantum dot inks for single-step-fabricated field-effect transistors

Ligand exchange, the process of removing the surfactants from the surface of colloidal quantum dots is a crucial step in making the solid films conductive. Performing it on solid films leads to cracks, increased disorder and the formation of defects. Hence the formation of thick, device-grade films have only been possible through layer-by-layer processing, limiting the technological interest for quantum dot solids. Solution-phase ligand exchange before deposition allows for the direct deposition of thick, homogeneous films suitable for device applications. In this paper, fabrication of field-effect transistors in a single step is reported using blade-coating, a scalable, industrially relevant technique. Most importantly, a post-deposition washing step results in device properties comparable to the best layer-by-layer processed devices, opening the way for large scale fabrication and further interest from the research community.

This chapter is based on a submitted article with the following list of authors:

4.1. Introduction

The practical bottleneck in the fabrication process is the difficulty of forming high quality (i.e. crack-free, dense, ordered) thick arrays in a single step. As-synthesized CQDs are capped with long, insulating organic ligands that passivate the CQD surface and allow their colloidal dispersion. These ligands need to be removed or exchanged to achieve electronic coupling of QDs in solids. Such ligand exchange is usually performed on CQDs which are already assembled in thin film that causes serious cracking and limits to work with rather thin layers, and a layer-by-layer approach is often used to achieve the necessary film thickness and quality. In the last decade, a number of methods to perform ligand exchange in liquid phase prior to the formation of CQD solids were reported.

Replacement of the hydrophobic, organic ligands by small, highly-charged inorganic ones is accompanied by the migration of the CQDs from the original apolar solvent to a polar one. Chalcogenidometallate complexes, chalcogenides, halides, pseudohalides, and halometallates have been proposed for such processes. Halides and halometallates show the most prospects for solar cell applications due to the better electronic passivation of the CQD surface. FETs based on inorganic-capped PbSe inks have been reported with electron mobilities ranging from 0.03 to 2 cm²/Vs (depending on annealing temperature and further surface passivation steps) using spin-coating, a non-scalable technique only useful in laboratory research. Thiocyanate-passivated inks based on larger PbS nanocubes results in 0.1 cm²/Vs mobility for both electrons and holes, but with low current modulation. Clearly, the prospects are enormous, but most works focus on the material chemistry or the solar cell performance, while very little was reported on the fabrication and electronic property control.

In this work, we synthesized small diameter PbS CQD inks stabilized by inorganic iodide (I⁻) and iodoplumbate (PbI₃⁻) complex ligands in a highly polar medium, and investigated the quality of the resulting dispersions. We fabricated high performing field-effect transistors (FETs) by blade-coating, and we identified the removal of excess ligands as a key step in optimizing the electronic properties of the films. We show the prospects of the approach by achieving 0.12 cm²/Vs electron mobility and 10⁶ on/off ratio in FETs fabricated in a single deposition step at mild temperature.

4.2. Ink formation and properties

We prepared halide- and halometallate-stabilized PbS CQD inks following the phase transfer method developed by Dirin et al. (see Figure 4.1). Two ligand solutions were used: pure methylammonium iodide (MAI) dissolved in N-methylformamide (NMF), and a 1:1 mix of MAI and PbI₂ also in NMF (from here referred to as MAPbI₃). The oleate-capped CQDs dispersed in hexane were exposed to the NMF solutions under stirring; successful phase transfer of the CQDs was indicated by bleaching of the apolar phase and darkening of the NMF phase. After purification, the inorganic-capped CQDs were
dispersed in propylene-carbonate (PC) for film formation. Details of the procedure are found in the Experimental methods section.

Absorbance and photoluminescence spectra of the CQD inks are shown on Figure 4.1(b-d), and the extracted peak positions and Stokes-shift values are collected in Table 4.1. The peak in the absorption spectrum corresponding to the first excitonic transition shows decreasing maximum intensity, increasing width and a mild red-shift upon phase transfer, compared to the oleate-capped CQDs. The broadening can be caused by energy disorder due to varying thickness and composition of the shell. The red-shift can be partially assigned to the different dielectric permittivity ($\varepsilon_r$) of the environment; following the considerations of Takagahara, replacing hexane ($\varepsilon_r = 1.9$) with PC ($\varepsilon_r = 64$) by itself can cause a red-shift of several 10 meVs. On the other hand, we see a difference between the peak positions of the two PC dispersions, which may be caused by the different size and dielectric properties of the iodide ion vs. the PbI$_3$ complex, causing a marginal increase of effective size of CQDs, and thus a lower confinement in the latter case.

![Diagram](image)

**Figure 4.1.** (a) Schematic of the solution-phase ligand exchange process; (b-d) optical absorbance, steady-state photoluminescence spectra and PL decay curves of PbS CQD dispersions integrated over the whole peak width.

The photoluminescence (PL) spectra show a similar trend as the absorption, without significant broadening. The Stokes-shift marginally increases upon ink formation, and is typically around 120 meV. The increased Stokes-shift is expected in a highly polar environment, given the higher dipole moment and consequent higher dipolar screening of the excited state in CQDs. Moreover, energy transfer between CQDs can also cause a
shift in the peak position in presence of larger disorder. The quality of the samples was further confirmed by measuring the PL decay. Long lifetime in the microsecond range was observed for all three samples. The organic-capped CQDs show a single recombination process with 3.1 μs lifetime. The decay becomes slightly biexponential upon ligand exchange with lifetimes around 1 and 4 μs, with the latter being the dominant for both samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption (eV)</th>
<th>Emission (eV)</th>
<th>Stokes-shift (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS-OA/HX</td>
<td>1.29</td>
<td>1.18</td>
<td>111</td>
</tr>
<tr>
<td>PbS-MAI/PC</td>
<td>1.27</td>
<td>1.15</td>
<td>120</td>
</tr>
<tr>
<td>PbS-MAPbI₃/PC</td>
<td>1.25</td>
<td>1.13</td>
<td>125</td>
</tr>
</tbody>
</table>

*Table 4.1. Absorption, emission peak positions, and Stokes-shift for the original dispersion and the formed inorganic inks.*

*Figure 4.2. TEM images of (a) pristine and (b) washed PbS-MAPbI₃ CQD assemblies, the scale bars are 100 nm; AFM images of (c) pristine and (d) washed PbS-MAPbI₃ thin films.*
4.3. Ink-based FETs

We prepared FETs based on the CQD inks to test their electronic properties and prospects in practical applications. Si/SiO\textsubscript{2} substrates were used as bottom gate, and the ITO/Au electrodes were patterned before the deposition of the active layer. CQD films were formed using blade-coating, an upscalable and controllable technique, in inert atmosphere at relatively low (100°C) temperature. After drying the solvent the particles appear surrounded by the ligand material in a TEM, and the films appear smooth and crack-free under AFM (see Figure 4.2.). We observe an electron-dominated ambipolar behavior, as shown on Figure 4.3(a-b). The general properties are similar to the layer-by-layer processed inorganic-capped PbS CQD solids reported earlier, but the electron currents in the as-deposited films are slightly lower for the same geometry and measurement conditions.\textsuperscript{3,21,22} We observed a strong improvement in electron transport upon immersion of the pristine films into pure methanol for 3 minutes, while the hole current remains the same.

![Figure 4.3. Influence of MeOH washing on the FET properties: (a) p- and (b) n-channel transfer curves of the PbS-MAI and PbS-MAPbI\textsubscript{3} samples before and after washing with MeOH, and (c) mobility and threshold values extracted from the transfer curves. The color coding is consistent throughout the figure, the arrows indicate the sweep directions.](image)

We obtained the carrier mobility and threshold voltage values from the linear regime transfer curves using the gradual channel approximation. Electron mobilities around 10\textsuperscript{-3} cm\textsuperscript{2}/Vs are found in the pristine films, which are lower than the literature standards.\textsuperscript{21,22} The values improve an order of magnitude with both ligands upon washing using methanol, reaching values exceeding 10\textsuperscript{-2} cm\textsuperscript{2}/Vs, and being on a par with previous reports. The hysteresis in the n-channel decreases upon washing. On the other hand, the hole mobility does not change after washing the samples, and remains around 10\textsuperscript{-5} cm\textsuperscript{2}/Vs. Importantly,
both electron and hole transport appears to be better in the MAPbI$_3$-treated PbS CQD solids compared to the PbS-MAI samples, which can give partial explanation to the fact that the complex ligands are shown to work better for the fabrication of efficient solar cells.\textsuperscript{23} At the same time, both electron and hole threshold voltages shift towards more positive values. The threshold voltage in a thin-film transistors is estimated as

\[ V_{th} = \phi_{ms} \pm \frac{qN_d}{C_i} \pm \frac{qN}{C_i} \]  \hspace{1em} \text{Eq. 4.1} 

where $\phi_{ms}$ is the difference of the Fermi levels of the gate metal and semiconductor, $n$ is the trapped charge density in the gate dielectric (cm$^{-2}$), $N$ is the bulk carrier concentration (cm$^{-3}$), and $C_i$ is the gate capacitance (Fm$^{-2}$).\textsuperscript{24} Besides the actual charge carrier concentrations, changes in $\phi_{ms}$ can also cause a threshold shift. The workfunction difference is affected by shifting conduction and valence band energies (relative to the gate contact work function) due to surface dipoles at the SiO$_2$ or CQD surface, or changing Fermi-level in the semiconductor (relative to the band edges) through doping. Ionic compounds such as the ligands stabilizing the dispersions can result in significant dipole moments, if well-organized at an interface. In CQDs, especially strong shifts in the energy levels up to 2 eV have been observed through dipoles located at the CQD surface,\textsuperscript{25-27} and similar range of workfunction shifts were observed in ZnO,\textsuperscript{28} but these factors cannot be accounted for the whole threshold shift. Hence a changing carrier concentration in the CQD film or at the interface is likely the main cause. The 2D charge density difference can be estimated from the values ($\sim$10 V for both ligands and both charge carriers) as $\Delta n = C_{ox} \Delta V_{th}/e$ to be in the range of $10^{12}$ cm$^{-2}$, or $\sim$0.1 elemental charge per CQD. This carrier density change can be either related to the CQD layer or the SiO$_2$ surface. Assuming a band edge density of states ($N_C$) from the CQD density ($\sim$4 nm center-to-center distance in cubic arrangement) to be around $6\times10^{19}$ cm$^{-3}$, the distance of the Fermi-level from the middle of the band gap can be calculated:

\[ \Delta E_F = E_g/2 + kT \ln\left(\frac{N}{N_C}\right) \]  \hspace{1em} \text{Eq. 4.2} 

In the presence of $10^{12}$ cm$^{-2}$ charges in the first ($\sim$4 nm thick) monolayer from the oxide interface, the Fermi-level shift is approximately 0.5 eV. This shift would alter $\phi_{ms}$ by the same amount; the observed threshold shift is thus at least partially stemming from a changing SiO$_2$ surface charge.

We must point out the discrepancy between the direction of the threshold shift and the mobility increase. In an earlier work, we reported that air exposure results in a positive threshold shift in PbS CQD FETs; this effect was accompanied by a decrease in electron mobility, as expected from the underlying trap formation mechanism.\textsuperscript{29} Moreover, n-doping the active layer in similar devices results in a negative threshold shift and higher electron mobility.\textsuperscript{21} In this case, however, a positive threshold shift is accompanied by a mobility increase, suggesting that more than a single mechanism should be considered to explain these experimental results.
4.4. Effect of post-deposition washing

<table>
<thead>
<tr>
<th>Sample</th>
<th>treatment</th>
<th>Abs (eV)</th>
<th>A₁ (eV)</th>
<th>E₁ (eV)</th>
<th>w₁ (eV)</th>
<th>A₂ (eV)</th>
<th>E₂ (eV)</th>
<th>w₂ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS-MAI</td>
<td>pristine</td>
<td>1.27</td>
<td>0.34</td>
<td>0.98</td>
<td>0.045</td>
<td>0.93</td>
<td>1.07</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>washed</td>
<td>1.26</td>
<td>0.32</td>
<td>0.99</td>
<td>0.046</td>
<td>0.78</td>
<td>1.04</td>
<td>0.064</td>
</tr>
<tr>
<td>PbS-MAPbI₃</td>
<td>pristine</td>
<td>1.26</td>
<td>0.18</td>
<td>0.97</td>
<td>0.061</td>
<td>0.89</td>
<td>1.05</td>
<td>0.078</td>
</tr>
<tr>
<td></td>
<td>washed</td>
<td>1.25</td>
<td>0.55</td>
<td>0.97</td>
<td>0.073</td>
<td>0.59</td>
<td>1.05</td>
<td>0.077</td>
</tr>
</tbody>
</table>

Table 4.2. Absorption peak positions and parameters of double Gaussian fits to the steady-state PL data of films prepared from PbS-MAI and PbS-MAPbI₃ inks, with and without washing in MeOH; A - intensity, E - peak position, w – Gaussian width.

To explain the observed behavior we investigated the photophysical properties of the films. The absorbance, steady-state and time-resolved PL data are shown on Figure 4.4, the extracted absorption and PL spectra peak positions and decay lifetimes are listed in Table 4.2 and 4.3. Interestingly, no redshift, only a minor broadening is observed upon film formation (see data in Table 4.1 and 4.2, and direct comparison in the Appendix). The peaks show a minor shift of <10 meV towards lower energies upon washing with MeOH (Fig. 4.4(a)). Both the PL peak positions and decay lifetimes of the films are different than those of the respective inks. All steady-state PL spectra can be fitted with a double Gaussian function, indicating the emission from two distinct states (see the fits in the Appendix). A stronger peak is centered around 1.05-1.1 eV, and a weaker one is just below 1 eV. In general, washing increases the weight of the lower energy emission sites, giving an effectively red-shifted emission. The decay curves also show biexponential dynamics, with one lifetime around 100 ps, and one in the range of 600-1000 ps. The overall decay becomes faster upon washing, mainly due to an increasing rate of the slower process, and the effect is stronger in the PbS-MAI thin films. The red-shift and the faster decay suggest that the electronic coupling decreased or trap-mediated emission increased in the film upon washing in MeOH.

<table>
<thead>
<tr>
<th>Sample</th>
<th>treatment</th>
<th>τ₁ (ps)</th>
<th>τ₂ (ps)</th>
<th>τ₁ weight (%)</th>
<th>τ₂ weight (%)</th>
<th>τ eff (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS-MAI</td>
<td>pristine</td>
<td>146</td>
<td>1086</td>
<td>0.41</td>
<td>0.59</td>
<td>296</td>
</tr>
<tr>
<td></td>
<td>washed</td>
<td>131</td>
<td>655</td>
<td>0.53</td>
<td>0.47</td>
<td>211</td>
</tr>
<tr>
<td>PbS-MAPbI₃</td>
<td>pristine</td>
<td>144</td>
<td>1056</td>
<td>0.41</td>
<td>0.59</td>
<td>294</td>
</tr>
<tr>
<td></td>
<td>washed</td>
<td>119</td>
<td>807</td>
<td>0.40</td>
<td>0.60</td>
<td>245</td>
</tr>
</tbody>
</table>

Table 4.3. Lifetimes of the PL decay in films prepared from PbS-MAI and PbS-MAPbI₃ inks, with and without washing in MeOH.
Figure 4.4. (a) Absorbance spectra, (b) steady-state PL spectra and (c) PL decay of films prepared from PbS-MAI and PbS-MAPbI₃ inks, with and without washing in MeOH; (d) elemental analysis obtained from EDX data of organic capped PbS, and PbS-MAPbI₃ CQDs with and without washing; (e) schematic showing the ligand removal upon washing.

In order to prove the ligand removal, we determined the layer composition using energy-dispersive X-ray spectrometry (EDX). We obtained Pb/S and I/S ratios for the original, oleate-capped CQDs, and the pristine and washed samples prepared using the PbS-MAPbI₃ ink (Fig. 4.4(d)). The original particles show an excess lead, as expected for the synthetic method used. We observe a large amount of iodine and a strong increase in the Pb/S ratio upon phase transfer, showing that we effectively stabilize the PbS-MAPbI₃ ink by an iodoplumbate complex attached to the CQD surface. Upon washing with methanol, the Pb/S and I/S ratios both decrease, indicating partial removal of the capping complex, making the barrier between the CQD cores thinner, more “transparent”.

The overall picture can be interpreted as follows. The lack of the red-shift upon drying indicates that the confinement is not altered by a reduced interdot spacing, and suggests that the ligand shell stabilizing the dispersions prevents significant electronic coupling. This, however, is changed by washing: the red-shift and shorter lifetimes indicate that electronic coupling is induced, or trap states become active; these effects both can be caused by
washing away ligands from the CQD surface. The mobility, being limited by single dot-to-dot tunneling events, is strongly dependent on the barrier; hence the observed increase in the mobility suggests that the red-shift is at least partially related to an increased coupling through partial removal of the ligand shell. Excess ligands bound to the surface and shielded by a counterion (that make up the stabilizing shell in polar solvents) can cause a shift in the energy levels of the CQDs by forming surface dipoles, uncompensated charges on the CQDs can shift the Fermi-level, and the same ions can also shield trapped charges at the SiO$_2$ surface. The partial removal of the ligands can thus result in all three previously mentioned effects possibly shifting the threshold in the FETs, but the magnitude of the shift suggests that the SiO$_2$ surface is the main and major origin of it.

By optimizing the substrate treatment and the deposition process, we fabricated high performing FETs based on the PbS-MAPbI$_3$ ink; the characteristics of a representative device are shown in Figure 4.5. Good linear and saturation behavior is observed in the output curves (panel a), with lower relative hysteresis for electrons than holes. An injection barrier is observed at room temperature for electrons, but not for holes, as shown on Figure 4.6. We measure mobilities up to 0.12 cm$^2$/Vs for electrons and $10^{-4}$ cm$^2$/Vs for holes. We observe on/off ratios $>$10$^6$ in the n-channel, and up to 10$^3$ in the p-channel. These data are comparable to the best samples fabricated using conventional layer-by-layer deposition and ligand exchange of PbS thin films, but are now prepared in a single deposition step, confirming the prospects of the solution-phase ligand exchanged CQD solids for optoelectronic applications.
Figure 4.5. Behavior of a representative FET fabricated in a single deposition and washing step using the PbS-MAPbI$_3$ ink: (a) output, and (b) p-type and (c) n-type transfer characteristics.
Figure 4.6. Low drain, high gate bias output curves in the (a) n-channel and (b) p-channel showing injection barrier for electrons, but not for holes.

4.5. Conclusion

In summary, we show that blade-coating inorganic-capped CQD inks is a facile way to fabricate high quality thin films and FETs showing performances as good as the state of the art CQD devices prepared by solid-state ligand exchange. We show that the as-prepared films contain a large amount of ligands that limit the electron transport, which can be largely improved by a post-deposition washing step. Partial removal of the ligands significantly increases the electron mobility, and causes a positive threshold shift, likely through influencing the oxide surface. Broader application of these findings could be the next step towards highly efficient solar cells and optoelectronic devices based on colloidal quantum dot solids.

4.6. Experimental methods

Materials: Lead (II) acetate trihydrate (PbAc$_2$·3H$_2$O, ≥ 99.99%, Aldrich), bis(trimethylsilyl)sulfide (TMS$_2$S, Aldrich), 1-octadecene (ODE, 90%, Aldrich), oleic acid (OA, 90%, Aldrich), ethanol (Fluka), hexane (Aldrich), chloroform (Aldrich), methanol (Aldrich) were used as received.

CQD synthesis: PbS-OA CQDs were synthesized according to a previously reported method. For the synthesis of 3.1 nm PbS CQDs, a lead precursor solution consisting of 1.5 g PbAc$_2$·3H$_2$O in 47 mL ODE and 2.8 mL OA was vacuum dried for an hour at 120 °C in a three-neck reaction flask. Than atmosphere was then switched to argon and the temperature was subsequently changed to 105 °C. After that, the heating mantle was removed and a sulfur precursor of 420 µL TMS$_2$S in 10 mL of dried ODE was quickly injected. After 3 minutes of growth the flask was cooled down to room temperature by an ice bath. Hexane (39 mL) and ethanol (102 mL) were added to the crude solution, followed by centrifugation to separate the CQDs. Two more washing steps were performed by re-dispersion in hexane (39 and 18 mL on the first and second washing steps respectively) and
precipitation by ethanol (45 and 21 mL respectively). One extra-washing step was performed by re-dispersion CQDs in 3 mL chloroform and precipitation by 3 mL methanol. The final pellet was dissolved in 4mL of anhydrous chloroform and filtered through 450 µm PTFE filter. The particles were dried in mild vacuum and dispersed in hexane at the required concentration before ligand exchange.

**Solution-phase ligand exchange:** Phase transfer into a polar solvent by ligand exchange was performed by exposing the apolar dispersions to a polar solvent containing the inorganic ligands. In a typical procedure, 10 mL of oleate-capped PbS CQDs dispersed in hexanes (~5 mg/mL) was poured on top 10 mL of a 50 mM MAI or MAI:PbI₂ (1:1) solution in NMF. The mixture was stirred at 700-1000 rpm (mild stirring, vortex visible) for 12-24 hours leading to the phase transfer of PbS QDs from the nonpolar to the polar phase resulting in a colorless top phase. The top phase was removed by a syringe, the bottom phase was rinsed three times with hexane (10 mL of hexane each time, vigorously stirred for ~10min). The inorganic-capped CQDs are precipitated by adding 10 mL acetone (and a couple droplets of toluene in case it is necessary), and left to settle for 1-2 h. The solution was completely separated by centrifuging at 16000 rpm for 15 minutes. The supernatant was removed and the pellet was re-dispersed in propylene carbonate at 50-100 mg/ml concentration.

**FET fabrication and characterization:** Substrates for thin films were cleaned by sonication in acetone and isopropanol, and were treated by ozone or vacuum plasma treatment, or longer annealing in inert atmosphere for good wetting. For FETs, 5-40 nm films were formed on Si⁺⁺/SiO₂(230nm) substrates carrying the electrode pattern (10nm ITO/30nm Au) by blade-coating of the PC-based inks. In a typical procedure, 3 µL of the (previously stirred) ink was injected between the blade and the substrate (with a gap of 10 µm) on a table heated to 100°C. The droplet was spread by moving the blade across the substrate at 50 mm/s speed, and the film was let dry on the table. The washing was performed in a Petri-dish by immersion for 3 min at room temperature. The fabrication was finalized by annealing the samples at 120°C for 20 min. The samples for absorption and photoluminescence measurements were drop-cast on quartz substrates at thicknesses around 100nm, and were treated the same way. All fabrication steps were performed in inert atmosphere (<0.1ppm H₂O/O₂).

**Optical and structural characterization:** Samples for optical characterization were prepared on quartz substrates. Absorbance spectra were collected using a Shimadzu UV-3000 UV/Vis/NIR. For the steady-state and time-integrated photoluminescence (PL) measurements, the second harmonic (3.1 eV) from a mode-locked Ti:sapphire laser (Mira 900, Coherent) was used as excitation source. The laser power was adjusted using neutral density filters to 0.3 mW (solutions) or 3 mW (thin films). The excitation beam was spatially limited by an iris and focused with a 150-mm focal length lens. PL was collected into a spectrometer and recorded by Andor 1.7µm InGaAs camera. The time-resolved PL spectra were dispersed by an imaging spectrometer and detected using a Hamamatsu NIR streak camera. For the thin film lifetime, the streak camera was operated in the Synchroscan

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mode with time resolution around 10 ps. For the PL lifetime of OA-caped samples, a slow single sweep unit was used and a pulse picker was employed to reduce the repetition rate of the exciting pulses. FETs were characterized using an Agilent 5262A Semiconductor Parameter Analyzer in a nitrogen-filled glovebox (<0.1ppm H₂O/O₂). AFM images were obtained using a WITEC Alpha SNOM-AFM. TEM and EDX data were collected from samples drop-cast on carbon-coated copper grids using a JEOL 2010, equipped with a LN₂-cooled SiLi detector at 200 kV. The spectra were fitted with the Cliff-Lorimer (MBTS) correction method w/o absorbance, as implemented in the NSS 2.3 software package from Thermo Scientific.

4.7. References


Figure 4.A1. Absorbance spectra of the PbS-MAI and PbS-MAPbI$_3$ inks before and after deposition.
Figure 4.A2. Double Gaussian fits to the thin film PL spectra.