Supporting Information

Transparent conductive oxide nanocrystals coated with insulators by atomic layer deposition

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1. Synthesis Techniques

1.1 Synthesis of films comprised of ZnO nanocrystals

Films comprised of ZnO nanocrystals were deposited using a similar reactor to one described previously. The total reactor consisted of three separate gas streams, which were combined upstream of a quartz plasma reactor tube, followed by a supersonic nozzle where ZnO particles were accelerated into the deposition chamber downstream.

The three gas streams were controlled with mass flow controllers (GE50A, MKS Instruments). The first stream contained 30 standard cubic centimeters per minute (SCCM) of pure oxygen, the second contained 300 SCCM of pure argon. The third stream contained a mixture of argon and diethyl zinc (DEZ). The flow of DEZ was estimated to be 3.4 SCCM from a flow of 20 SCCM of argon passing through a bubbler of room temperature DEZ at a total pressure of 94 Torr. At the quartz tube, where the streams were combined, the total pressure was 12 Torr. We estimate that the partial pressures of argon, oxygen, and DEZ at the inlet to the reaction zone were 10.9, 1.0, and 0.1 Torr respectively. The total flow through the tube, which is the sum of the three streams, was approximately 350 SCCM.

The synthesis of nanoparticles took place within the plasma generated in the quartz tube. The quartz tube had an outer diameter of 19 mm and an inner diameter of 17 mm. Two aluminum rings served as the electrodes for the plasma, which was generated by applying a 13.56 MHz radiofrequency signal through an impedance matching network. The height of each electrode was 10 mm, separated by a 1 cm gap. The power provided by the RF power supply was maintained at 35 W. Within the plasma, DEZ and oxygen reacted to form ZnO nanocrystals.

The gas and particles were accelerated through a nozzle which measured 0.8 x 20.0 x 67.0 mm (LxWxH). Downstream of the nozzle, the pressure was 0.55 Torr. Since the pressure ratio across the nozzle was 22, the flow was choked. Films were deposited for 45 seconds by moving the substrates back and forth under the particle beam.

1.2 Synthesis of films comprised of colloidal ITO nanocrystals

ITO nanocrystals were synthesized using adaptations of methods reported in the literature. 5.4 at% Sn doped In2O3 was synthesized by heating mixture 1.37 mmol In(acetylacetonate)3, 0.09
mmol Sn(acetylacetonate)$_2$Cl$_2$ in 17.5 mmol oleylamine to 110°C for 10 min followed by 250°C for 2 hours under an N$_2$ atmosphere. Nanocrystals were crashed with ethanol, decanted, and dispersed in organic solvent several times. The resulting nanocrystals were 9.5 ± 1.75 nm in diameter as measured by scanning transmission electron microscopy.

1.3 Atomic layer deposition of HfO$_2$ and Al$_2$O$_3$

Atomic layer deposition (ALD) was carried out in a custom built reactor. The sample chamber consisted of a stainless steel tube in a Lindberg/Blue tube furnace operating at 180°C. As-deposited thin films comprised of ZnO nanocrystals on glass and Si substrates were loaded into the sample chamber. The sample chamber was sealed and pumped down to a base pressure of 0.60 Torr with 30 SCCM of continuously flowing argon (CK gas supply, 5N purity) regulated by a mass flow controller (GE50A, MKS instruments). The samples were allowed to outgas for a period of 600 seconds before ALD. Precursor pulse and purge times were controlled using LabView software. For both depositions, water was used as the first pulse followed by a purge time to evacuate the chamber of any excess water. The purge was followed by a precursor pulse and subsequent purge to complete one ALD cycle.

For HfO$_2$ growth, tetrakis(dimethylamino)hafnium (TDMAH, STREM chemicals, 98+%) was used as the hafnium precursor. The TDMAH temperature was 75°C. For one complete ALD cycle of H$_2$O-purge-TDMAH-purge, the timing sequence was 0.25-25-0.25-25 where the units are seconds. A total of 40 cycles were carried out at a growth rate of 1.1 Å/cycle to fill in the pores to approximately 98% total solids volume fraction, as determined by x-ray fluorescence and spectroscopic ellipsometry.

For Al$_2$O$_3$ growth, trimethylaluminum (TMA, Sigma-Aldrich, 97%) was used as the aluminum precursor. The mechanism of growth can be found in the literature. For one complete ALD cycle of H$_2$O-purge-TMA-purge, the timing sequence was 1.0-60-1.0-60 where the units are seconds, and 40 cycles were used to fill in the film with insulating amorphous Al$_2$O$_3$ at a growth rate of 1.1 Å/cycle.

After deposition, the sample chamber was vented to atmospheric pressure using argon, and then opened. Samples were removed promptly and cooled to room temperature for characterization.

2. Characterization methods

2.1 Transmission electron and scanning electron microscopy

Transmission electron microscopy (TEM) images were acquired using an FEI Tecnai G2 Spirit TEM with a thermal emission gun operating at 120 kV. ZnO nanocrystals synthesized in the plasma reactor were deposited on copper TEM specimen supports for approximately 1 second. The supports consist of an electron-transparent lacey carbon layer for mechanical support and a 3 nm continuous carbon layer to support the particles.

Cross-sectional scanning electron microscopy (SEM) images of the coated and uncoated ZnO nanocrystals deposited in Si substrates were taken using an FEI Nova NanoSEM 2301. Prior to
imaging, a thin layer of Au was sputtered on the surface to enhance the images. The optimal imaging parameters are listed below in Table S1 for a magnification of 200,000x. The images were processed using ImageJ software.

**Table S1.** SEM parameters used to resolve the ALD coated and uncoated thin films comprised of ZnO nanocrystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Accelerating voltage</th>
<th>Spot size</th>
<th>Working distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated ZnO</td>
<td>15.0kV</td>
<td>3.0</td>
<td>5.2mm</td>
</tr>
<tr>
<td>Al₂O₃ coated ZnO</td>
<td>30.0kV</td>
<td>3.0</td>
<td>6.8mm</td>
</tr>
<tr>
<td>HfO₂ coated ZnO</td>
<td>10.5kV</td>
<td>3.0</td>
<td>5.1mm</td>
</tr>
</tbody>
</table>

2.2 *Scanning transmission electron microscopy*

Scanning transmission electron microscopy (STEM) images were acquired using a Hitachi S-5500 SEM. Colloidal ITO nanocrystals were drop-cast onto copper TEM grids and allowed to dry under ambient conditions. Nanocrystal images were processed to determine size distribution using ImageJ software.

![Figure S1](image.png)

**Figure S1.** ITO nanocrystal sizing analysis. (a) STEM image of ITO nanocrystals with 50 nm scale bar. (b) Histogram of ITO nanocrystal size distribution.
2.3 Spectroscopic Ellipsometry

Spectroscopic ellipsometry was carried out using a J.A. Woollam and Company α-SE spectroscopic ellipsometer. The spectra were fit using a Bruggeman effective medium approximation considering a biphasic mixture of ZnO and air voids to determine the porosity and thickness of the thin films comprised of ZnO nanocrystals.

Table S2. Ellipsometry data obtained from three ZnO nanocrystalline thin films. Two of these films were coated with Al₂O₃ and HfO₂. Three samples are listed, but these are representative of a much larger sample set.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ALD</th>
<th>Thickness (nm)</th>
<th>ZnO volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>209 ± 6</td>
<td>34 ± 0%</td>
</tr>
<tr>
<td>2</td>
<td>Al₂O₃</td>
<td>205 ± 4</td>
<td>34 ± 1%</td>
</tr>
<tr>
<td>3</td>
<td>HfO₂</td>
<td>182 ± 5</td>
<td>34 ± 1%</td>
</tr>
</tbody>
</table>

2.4 Electrical measurements for ITO nanocrystal samples

Sheet resistance measurements of thin films comprised of Sn doped In₂O₃ (ITO) nanocrystals on glass substrates were carried out in an Ecopia HMS-5000 using a 4-point contact arrangement. Indium contacts were placed at the corners of the sample to improve electrical contact between the Ecopia’s gold spring contacts and the sample.

Four samples were measured: two duplicates were coated with Al₂O₃ by ALD using the same conditions as ZnO (see section 1.3 above) and two duplicates were left uncoated. For the coated ITO samples, a current of 100µA was used. The uncoated samples were also measured using a 100µA current initially. However, within 36 hours of ambient exposure, increased sheet resistance made it necessary to reduce the current to 50µA for the remaining measurements.

2.5 Fourier transform infrared spectroscopy (FTIR)

ZnO nanocrystals synthesized via the non-thermal plasma route outlined above were deposited on polished crystal KBr IR windows (Sigma-Aldrich, 13x2 mm). Two of the samples were coated immediately with Al₂O₃ and HfO₂ by ALD using the processes above; the third sample was left uncoated. FTIR measurements of all three samples were carried out using a Thermo Nicolet Nexus 470 with 64 scans per sample. The FTIR sample chamber was purged for 5 minutes with dry air prior to analysis. This allowed any carbon dioxide and water in the vapor phase to exit the sample chamber. The samples were carefully monitored using a spectra preview built into the software which continuously collects the spectra during the dry air purge prior to the actual data collection. No observable change in the signals corresponding to physisorbed water and chemisorbed hydroxide was seen during this time. The raw sample spectra were plotted against each other in the range of 4000-400 cm⁻¹ to create Figure 3 in the main text. The evolution of two specific signals were tracked corresponding to the chemisorbed at 3600 cm⁻¹ and physisorbed water at 1500 cm⁻¹ on the ZnO surface according to the results from Noei, et al.⁴
2.6 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Indium references between 1 and 200 ppm were made by dilution of indium standard solution (Fluka Analytical) with 2% nitric acid. Tin references between 0.1 and 2 ppm were made by dilution of tin standard solution (Fluka Analytical) with 2% hydrochloric acid. Spectra of references were fit to a line which nanocrystal data was fit to. ITO nanocrystal ICP-OES solutions were made by dissolving nanocrystals in 37% hydrochloric acid over a day followed by dilution with ultra-pure water to yield a 2% acid solution.

3. In situ electrical probe system

The in situ electrical measurements were conducted using a home-built sample holder situated in a quartz tube that was inserted into a Lindberg/Blue tube furnace. The sample holder was made from insulating Macor glass with phosphorus bronze electrical spring contacts set up for sheet resistance measurements in the van der Pauw configuration. The bottoms of the spring contacts were coated with gold by thermal evaporation to prevent oxidation-induced contact resistance. The spring contacts were connected by an insulated wire and fed through one end of the furnace where they were connected to a Keithley 2400 source-meter controlled by LabView software. A single gas inlet was fixed at the opposite end of the tube furnace. The Ar and H₂ gas streams (CK gas supply, 5N and 4.5N purity, respectively) were regulated separately by Omega Engineering mass flow controllers (FMA5514A for AR, FMA5510A for H₂) and allowed to mix before entering the tube furnace. An exhaust line was placed at the electrical feedthrough end. The reactor was kept at a pressure of 825 Torr during the experiment to not allow air to enter the chamber during Ar and H₂ exposure.

Thin film samples were secured to the sample holder and inserted into the tube furnace. The furnace was brought to 200°C over the course of approximately 7 minutes in air. The temperature was also recorded every 5 seconds until the temperature reached 200°C. Continuous data acquisition was also started at the time the furnace was turned on. 0.1 µA of current was passed through one side of the sample, and the voltage drop across the sample was measured on the opposite side. The samples were allowed to anneal in air for 45 minutes including ramp time.

After 45 minutes of annealing in air, the tube furnace was sealed from the gas inlet end. 700 SCCM of Ar was then allowed to enter the chamber pressurizing it to 825 Torr. Ar was passed over the samples at 200°C for a period of 24 hours while continuously monitoring the voltage drop across the sample. After 24 hours, the Ar stream was reduced to 560 SCCM, and 100 SCCM of H₂ was allowed to mix with the Ar and enter the chamber. Again, the voltage drop across the samples was continuously measured at 200°C for a period of 24 hours.

At the end of period, the H₂ stream was tuned off and the Ar flow was returned to 700 SCCM. The furnace was also turned off at this time, and the samples were allowed to cool to room temperature in Ar. The temperature was recorded every minute using an Omega Engineering (HH802U) temperature readout. After cooling to room temperature, the chamber was opened from the gas inlet end. Once the voltage returned to the upper limit of measurement, the program was stopped and the experiment concluded. Figure 2 in the main text shows one representative measurement from a pool of ~20 measurements all qualitatively showing the same result.
Figure S3. System for *in situ* electrical measurements. (a) Shows the full system with the furnace, gas inlet, and electrical feedthroughs. (b) The top side of the sample holder with gold coated phosphorus bronze spring clips and the electrical configuration. (c) The underside of the sample holder showing the stainless steel electrical feedthrough into the quartz tube furnace.
4. References


