Solution-Processed Inorganic Thin Film Transistors Fabricated from Butylamine-Capped Indium-Doped Zinc Oxide Nanocrystals

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Indium-doped zinc oxide nanocrystals (IZO NCs), capped with stearic acid (SA) of different sizes, were synthesized using a hot injection method in a noncoordinating solvent 1-octadecene (ODE). The ligand exchange process was employed to modify the surface of IZO NCs by replacing the longer-chain ligand of stearic acid with the shorter-chain ligand of butylamine (BA). It should be noted that the ligand-exchange percentage was observed to be 75%. The change of particle size, morphology, and crystal structures were obtained using a field emission scanning electron microscope (FE-SEM) and X-ray diffraction pattern results. In our study, the 5 nm and 10 nm IZO NCs capped with stearic acid (SA-IZO) were ligand-exchanged with butylamine (BA), and were then spin-coated on a thermal oxide (SiO2) gate insulator to fabricate a thin film transistor (TFT) device. The films were then annealed at various temperatures: 350 °C, 400 °C, 500 °C, and 600 °C. All samples showed semiconducting behavior and exhibited n-channel TFT. Curing temperature dependent on mobility was observed. Interestingly, mobility decreases with the increasing size of NCs from 5 to 10 nm. Miller-Abrahams hopping formalism was employed to explain the hopping mechanism insight our IZO NC films. By focusing on the effect of size, different curing temperatures, electron coupling, tunneling rate, and inter-NC separation, we found that the decrease in electron mobility for larger NCs was due to smaller electronic coupling.

Key Words : Indium-doped zinc oxide, Nanocrystal, Thin film transistor, Solution process, Coupling energy

Introduction

Recently, numerous developments in using semiconductor oxide nanocrystals (NCs) in thin film transistors (TFTs) have been reported.1,2 Especially, many studies have been carried out on indium-doped ZnO (IZO) thin films for the active channel layers of TFTs,3-5 due to their good carrier mobility, excellent environmental stability, and high transparency. In our study, the ester elimination reaction was employed in synthesis of IZO NCs capped with stearic acid ligand,6,7 as summarized in Scheme 1. The stearic acid group has played a role as a large insulating barrier that significantly limits electron transport between NCs.8,9 A simple and effective way to enhance the electron transport efficiency is the ligand exchange approach, in which the long and insulating native ligand of the as-synthesized NPs is replaced by a short ligand molecule. The stearic acid group on the surface of IZO NCs was replaced by butylamine groups as shown in Scheme 1, with the aim of strengthening the electron transport efficiency between nanocrystals.9-11 For a full understanding of the electron transport properties, we are interested in electron coupling energy which provokes the electron tunneling between the NCs.8,9,12 According to the Einstein-Smoluchowski equation, mobility (μ) and electronic coupling between the neighbor (V) of the two NCs has the following relationship,8,9,13,14

\[ \mu = \frac{e^2}{2\hbar k_B T} s^2 V \]  

where e, h, k_B, T, and s are the electron charge, Planck constant, Boltzmann constant, temperature, and inter-nanocrystal (inter-NC) separation, respectively. When two or more NCs are in close proximity to each other, their wave function can interact (couple), forming a molecular orbital delocalized over several NCs or even propagating throughout the entire array of NCs. The quantum mechanical coupling between the energy levels can be expressed in term of the coupling energy V,

\[ V = \hbar \Gamma \]  

Scheme 1. IZO NCs capped by stearic acid (SA) was synthesized by ester elimination reaction,6,7 then the IZO NCs capped by SA was ligand exchanged with butylamine over 2 days.10

\[ \frac{e^2}{2\hbar} k_B T \]  

\[ s^2 V \]  

where e, h, k_B, T, and s are the electron charge, Planck constant, Boltzmann constant, temperature, and inter-nanocrystal (inter-NC) separation, respectively. When two or more NCs are in close proximity to each other, their wave function can interact (couple), forming a molecular orbital delocalized over several NCs or even propagating throughout the entire array of NCs. The quantum mechanical coupling between the energy levels can be expressed in term of the coupling energy V,
where $\Gamma$ is the tunneling rate between two NCs neighbors. Using the Einstein-Smoluchowski equation, the tunneling rate can be approximated as:

$$\mu = \frac{e^2}{2k_B T} s^3 \Gamma$$

(3)

In this article, the synthesis and electron properties of IZO NCs capped by butylamine were performed in order to explore and determine the factor that dominates the mobility by focusing on the effect of size, curing temperature, electron coupling, and tunneling rate along with the inter-NC separation. As confirmed by X-Ray diffraction spectra, as the size increases the mobility decreased. We consider two mechanisms which could explain this phenomenon in the IZO NCs capped by butylamine (BA-IZO NCs), namely the hopping formalism of Miller-Abrahams and the characteristic crossover diameter of our material.13

**Experimental**

**Chemicals.** The chemicals used included Indium(III) acetate (In(Ac)₃, 99.99%, Aldrich), zinc(II) stearate (Zn(St)₂, Aldrich), Stearic acid (SA, 95% Aldrich), 1-octadecanol (ODA, 97% Alfa Aesar), 1-octadecene (ODE, 90% Aldrich), butylamine (BA, 99.5% Aldrich). All chemicals were used without further purification.

**Synthesis of IZO Nanocrystals.** We used stearic acid as the capping agent to synthesize different sizes of IZO nanocrystals. Earlier, Jin et al. used a similar capping agent for synthesizing the 20 nm IZO NCs.6 The following synthesis route was a modification of the Jin et al. method for our experimental purpose. We denoted the synthesized particle as IZO-5 nm and IZO-10 nm, corresponding to the average diameters of 5 nm and 10 nm, respectively.

**Preparation of Indium(III) Stearate (In(St)₃).** In a typical synthesis, In(Ac)₃ (20 mmol) was mixed with SA (80 mmol) and heated to 140 °C under an argon atmosphere for 5 h. The final product, In(St)₃, which was white powder, was washed several times with acetone and dried in a vacuum oven.

**Synthesis of IZO-5 nm.** Synthesis IZO was started with 0.05 mmol of In(St)₃ and 0.95 mmol Zn(St)₂ (the Zn(St)₂:SA ratio was 1:0) and ester elimination reactions were employed, as summarized in Scheme 1. In this procedure, the metal carboxylated salts and 20 g of 1-octadecene (ODE) was degassed under vacuum at 120 °C for 2 h as the precursor, and was then heated to 310 °C. 5 mmol 1-octadecanol (ODA) dissolved in 3 g of ODE at 150 °C was quickly injected into the reaction solution. The reaction temperature was kept at 290 °C for 20 minutes. 25 mL of ethylacetate was used to precipitate nanocrystals. The nanocrystals were collected by centrifugation. IZO nanocrystals were washed several times with isopropyl alcohol and collected by centrifugation. The crystallites were vacuum-dried for 12 h. The extracted powders were dissolved in toluene.

**Synthesis of IZO-10 nm.** Synthesis of NCs was started with 0.05 mmol of In(St)₃, 0.95 mmol Zn(St)₂, and 0.2 mmol of SA (the Zn(St)₂:SA ratio was 1:2) in the presence of 20 g of ODE. The mixture was degassed under vacuum at 120 °C for 2 hours as a precursor, and was then heated to 310 °C. 5 mmol of ODA dissolved in 3 g of ODE at 150 °C was quickly injected into the reaction solution. The reaction temperature was kept at 300 °C for 20 minutes. 25 mL of ethylacetate was used to precipitate nanocrystals. The nanocrystals were collected by centrifugation. IZO nanocrystals were washed several times with isopropyl alcohol and collected by centrifugation. The crystallites were vacuum-dried for 12 hours. The extracted powders were dissolved in toluene.

**Ligand Exchange with Butyl Amine.** IZO NCs powder was redissipated in butylamine as 100 mg mL⁻¹, then enclosed and stirred for 2 days (Scheme 1).10 The butylamine-exchange NCs (BA-IZO NCs) were precipitated with anhydrous methanol, dried, and dispersed in tetrahydrofuran (THF) for storage.

**Preparation of NC Films.** Thin films of BA-IZO NCs, either on a quartz, a silicon substrate or a silicon thermal oxide (SiO₂) substrate, were fabricated using a spin-coating method with BA-IZO NCs solution. The films were then immediately dried for 30 minutes at 80 °C on a preheated hot plate and finally annealed for 2 h at 350 °C, 400 °C, 500 °C, and 600 °C.

**Material Characterization.** Field emission scanning electron microscope (FE-SEM) images of samples were taken using a JEOL ISM-7500F operated at 15 kV. High resolution X-Ray diffractometer images were collected using a X’Pert PRO Multi Purpose X-Ray diffractometer with a Cu Kα source operated at 40 kV and 30 mA. The 2θ angle was scanned from 10º to 90º. Fourier transform infrared spectroscopy (FT-IR) was performed on a spectrum 400 (PekinElmer, U.S.A). All NMR data were collected on the FT-NMR 300 MHz (Varian Inc, Palo Alto, California, U.S.A). Chemical shifts were reported in parts per million (ppm) and Toluene-€ as a solvent. Thermogravimetric (TG) analysis was conducted on a TGA-50H under air condition flow in a range from room temperature to 800 °C. X-ray photoelectron spectroscopy (XPS) was conducted for the IZO thin films of 5 nm NCs and 10 nm NCs on a VG MultiLab 2000 using an Mg Kα (1253.6 eV) source at a pass energy of 20 eV.

**Current-voltage (I-V) Characteristic.** Metal-insulator-metal (MIM) devices were constructed by thermal deposition of the aluminum (Al) top electrode on the IZO NCs thin film using a shadow mask. The thickness and diameter of the Al electrode are about 300 nm and 0.3 mm, respectively. Thin IZO NCs films of only 5 nm NCs were prepared on a p-type silicon wafer of which the resistivity was less than 0.005 Ωcm with a thickness of 525 ± 25 μm. This low-resistivity acts as the back electrode of the MIM devices. Current-voltage (I-V) curves were obtained in an air atmosphere using a HP 4145B semiconductor parameter after contacting the two arm tips of the Si wafer and Al-electrode.
strate was cleaned with piranha solution (sulfuric acid:hydroperoxide = 7:3) and rinsed with deionized water twice prior to use. The BA-IZO NCs solutions of 5 nm and 10 nm were then spin-coated and annealed at 300-600 °C for 2 h in air ambient. The aluminum (300 nm) source and drain electrodes were deposited through a shadow mask.

Results and Discussion

In this approach, ester elimination reaction for synthesis of indium-doped zinc oxide NCs with the best electrical conductivity was employed. In the IZO nanocrystals, the molar concentration of indium is about 6%, while that of zinc is about 94%; this will be discussed in the XPS results below. Several methods can be used to tune the size of nanoparticles during synthesis. In this article, we tried to control the size of nanoparticles by changing the ratio of Zn(St)2 : SA (see Experimental section). The ratio of Zn(St)2 : SA was 1 : 0 and the reaction was maintained at 290 °C. The resulting nanocrystal size was 5 nm, the ratio of Zn(St)2 : SA was 1 : 2 and the reaction was maintained at 300 °C. The resulting nanocrystal size was 10 nm. The X-Ray diffraction spectra of IZO NCs thin films cured at 100 °C are shown in Figure 1. It can be seen that the XRD pattern indicates three distinct peaks: (100), (002), and (101) which were similar to those of pure ZnO, whereby both results agree with the standard Wurtzite structure (JCPDS file No. 05-0664). No other phases have been detected, which indicates that all indium ions blend in the crystal lattice of bulk ZnO. The grain sizes were calculated using the Scherer formula,

\[ D = k\lambda/\beta \cos \theta \]  

(4)

where \( \beta \) is the full width at half maximum of the peak corresponding to plane (0 0 2), k is the so-called shape factor which usually takes a value of about 0.9, and \( \theta \) is the angle obtained from 2\( \theta \)corresponding to maximum intensity peak in the XRD pattern. The peak position and resolution were determined using the Gaussian peak fitting method. Standard deviation for all calculation was lower than 0.5 nm. Our IZO NCs blue curve showed the domain size of around 10 nm. Our IZO NCs red curve indicated the domain size of 5 nm. XRD results clearly show the increasing Zn(St)2 : SA ratio and the increasing reaction temperature facilitated larger NCs. In our work, by controlling the Zn(St)2 : SA ratio and reaction temperature, the size of NCs can be controlled.

The FE-SEM graph of the representative NCs on silicon substrate is summarized in Supplementary information, Figure S1. The butylamine-capped IZO nanocrystals (denoted as BA-IZO NCs) were synthesized by ligand exchanging the stearic acid capped IZO nanocrystals (denoted as SA-IZO NCs) with butylamine (see the Experimental section).

The Fourier-transform infrared (FTIR) spectra of BA-IZO NCs (red spectrum) and spectra of SA-IZO NCs (blue spectrum) are shown in Figure 2. In Figure 2, the absorption peaks in the range of 2800-3000 cm\(^{-1}\) and 477 cm\(^{-1}\) coincide with the spectrum signals for C-H and Zn-O, respectively. The COO- asymmetric vibration band was presented at 1546-1402 cm\(^{-1}\). The alcohol group did not bind to the surface of the nanocrystals as a ligand, carboxylic groups (COO-) were found that mainly covered the IZO surface (Scheme 1). In addition, BA-IZO NCs spectra featured a significant peak in the range of 3484 cm\(^{-1}\) and 1455 cm\(^{-1}\), confirming the presence of the N-H group. The vibration band of the C-N group made an appearance at 1065 cm\(^{-1}\). In comparison, the obviously reduced intensity for the C-H and COO- groups and the Zn-O bonding in the red spectrum demonstrated that the SA ligand was partially replaced by the BA ligand.

The surface structure of SA-IZO NCs and BA-IZO NCs 5 nm was investigated using proton \(^1\)H-NMR (Figure 3). By combining the NMR results, the surface structure was clearly depicted. In the \(^1\)H-NMR spectra of the SA-IZO NCs (Fig. 3(a)), the corresponding proton was observed at 3.42 ppm (a) for (-CH\(_2\)-) near the carboxylic group and 1.41 ppm and 0.99 ppm were detected for the (-CH\(_2\)-) and (-CH\(_3\)) in the alkyl chain (b-c), respectively. The integral ratio of b:c is around 10:13:1 (Supplementary information, Figure S2a). The SA-IZO NCs surface was covered with stearic acid. The \(^1\)H-NMR spectra of BA-IZO NCs (Fig. 3(b)), at 3.49 ppm
were noted to have (-CH$_2$-) (a); specifically, 2.02 ppm (I) was noted for (-CH$_2$-) in the butylamine group. The ligand-exchange percentage was confirmed to be around 75% (detail explanation in Supplementary Information, Fig. S2b). The asterisk indicates the peak deriving from solvent Toluene-$d_8$ (2.08, 697, 7.01, and 7.09 ppm), CDCl$_3$ (7.26 ppm), and residual 2-propanol (4.04 ppm). From the proton $^1$H-NMR we determined that the stearic acid remained on the IZO NCs.

The thermal gravimetric analysis of BA-IZO NCs 5 nm showed that, when heated in air up to 200 °C, the decomposition of water and the BA ligand occurred. The partial ligand exchange with the SA ligand remains on the surface of the IZO NCs, showing that the decomposition was completed at ~382 °C (Fig. 4). Beyond 500 °C, no detectable weight loss was observed.

XPS analysis for the 5 nm and 10 nm BA-IZO NCs films cured at 350-600 °C was performed in order to investigate their chemical composition according to the curing temperature. In Figure 5(a), the overall trend is that a higher temperature promotes the 5 nm and 10 nm oxidation of IZO NCs thin films. The concentration ratio of zinc/indium in both cases was calculated and it was confirmed that a 6 molar percentage of indium was doped in the zinc oxide structure. As the curing temperature increased, atomic concentration of the carbon due to the organic capping groups on the IZO NCs surface decreased, signifying oxidation of the IZO NCs thin films. The XPS spectra exhibited peaks of the Zn 2p$_{3/2}$ core level with a binding energy of 1021.4 eV and the In 3d$_{5/2}$ core level with a binding energy of 444.2 eV (Supplementary Information, Fig. S3) was associated with Zn and In in the completely oxidized state. The C 1s peak shows the two-peak C 1s binding energy at 284.6 eV and 288.3 eV (Supplementary information, Fig. S4). The O 1s peaks were charge-calibrated by positioning the C 1s peak to 284.6 eV of the BA-IZO NCs 5 nm and 10 nm thin films. The deconvolution of the XPS spectra for O 1s shows the presence of two peaks as presented in Supplementary Information, Figure S5. The dominated peak OZnO centered at 529.9 eV was concerned with O$^{2-}$ ions in the oxygen of the hexagonal Wurtzite structure. The Ov peak at 531.4 eV reflected oxygen vacancies in structure.

In order to investigate electron transport properties in a thin film solid, we compared the current-voltage (I-V) characteristic of 5 nm BA-IZO NCs annealed at 350 °C, 400 °C, 500 °C, and 600 °C. The I-V curve was obtained using metal-insulator-metal (MIM) devices, where the thin films of BA-IZO NCs cured at different temperatures act as the insulator layer and the low-resistivity silicon wafer and
aluminum act as the back and top electrodes, respectively. The results are shown in Figure 6. All samples were measured at room temperature. Transport measurement at room temperature exhibited a non-ohmic and non-symmetric I-V characteristic for positive and negative bias value for BA-IZO thin film cured at 500 °C and 600 °C. Slight asymmetries, such as the non-linear I-V measurement, were observed with BA-IZO NCs films cured at 350 °C and 400 °C, which showed the threshold voltage (Vth) characteristic of the Coulomb blockade of transport. The Coulomb blockade of electron transport occurs if two conditions are fulfilled. First, the tunneling rate must be sufficiently small: \( \Gamma \ll k_B T / h \), which showed insulating behavior. Second, the electrostatic charging energy for transporting an electron to another nanocrystal must be sufficiently large: \( e^2 / C > k_B T \) (C was the capacitance of nanocrystal). It is thus clear that the electronic coupling between the IZO NCs was relatively weak (Table 1); therefore, the Coulomb blockade should occur if the charging energy is larger than \( k_B T \). We can therefore see a decrease in the current around zero bias with the sample cured at 300 °C and 400 °C, called a Coulomb blockade. In contrast, the sample cured at a high temperature (cured at 500 °C and 600 °C) the electron transport was observed to be better, due to the decomposition of ligand capping at high temperature, indicating that the charging energy is smaller than \( k_B T \).

The bottom-gate and top contact TFT were constructed in a SiO2 substrate and a vacuum deposited thin film Al metal, respectively, as a gate electrode, source and drain electrode. An SEM image shows the cross section of the representative TFT device, source and drain electrode. An SEM image shows the cross section of the representative TFT device and SEM image of the cross-section of a representative TFT device. TFT performance, (b) butylamine-capped IZO NCs of 5 nm; (c) butylamine-capped IZO NCs of 10 nm.

The TFT performance was measured in an ambient environment. All devices showed the n-type characteristic. Figures 7(b) and 7(c) show the transfer curves of the BA-IZO NCs 5 nm and 10 nm films, respectively, which were cured at different temperatures of 350 °C, 400 °C, 500 °C, and 600 °C with a patterned BA-IZO NCs active layer. For both BA-IZO NCs sizes of 10 nm and 5 nm, the highest mobility was observed with the samples cured at 600 °C, \( \mu = 0.13 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1} \), and \( \mu = 0.6 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) along with a good Ion/off. Interestingly, the increasing mobility was obtained with a reduction in the particle size of BA-IZO NCs (Figure 8(a)). Table 1 summarizes the electron properties of our samples, including mobility \( \mu \), Ion/off, \( V_{th} \), the degree of electronic coupling \( V(\mu eV) \), and tunneling rate \( \Gamma(s^{-1}) \). V and \( \Gamma \) between the orbital of adjacent nanocrystals in the film can be obtained by measuring the electron mobility \( \mu \) and by using Eq. (3), whereby s is the length over which an electron is transferred in one tunneling event. By using quantum chemical calculation with the Gaussian program, we determined \( s = 0.51 \, \text{nm} \), which is suitable for the length of the BA ligand. We found that \( \Gamma \) was considerably smaller than the tunneling rate \( k_B T / h \), which marks the onset of coherence.

As discussed previously, due to the structural disorder of the organic ligand on the surface of IZO NCs, the charge carrier is located on the localized sites and the tunneling rate...
\( \Gamma \) was very small compared with \( k_B T/h \). Therefore, charge transport does not occur via band conduction, but takes place by the hopping of the charge carrier from one site to another. The rate of hopping of a charge carrier between two sites depends on the overlap of the electronic wave function of these two sites, which allows tunneling from one site to another. In this paper, we make use of the hopping formalism of Miller-Abrahams.\textsuperscript{14,15} Giving the rate of hopping of the charge carrier from site \( i = \{i_x, i_y, i_z\} \) to site \( j = \{j_x, j_y, j_z\} \), \( \Gamma_{ij} \) is then given by
\[
\Gamma_{ij} = \Gamma_o \exp(-\beta|R_{ij}|) \exp\left[ \frac{E_j - E_i}{k_B T} \right], \quad E_j > E_i
\]
\[
\Gamma_{ij} = \Gamma_o \exp(-\beta|R_{ij}|) \exp\left[ \frac{E_j - E_i}{k_B T} \right], \quad E_j < E_i
\]
where \( \Gamma_o \) is an attempt-to-jump frequency, \( \beta = 4\pi/2m\Delta E/h \) (energy barrier, \( \Delta E \) which depends on NC size, the length and molecular structure of interfacial organic groups), \( |R_{ij}| \) is the distance between site \( i \) and \( j \), \( k_B \) is the Boltzman constant, and \( T \) is the Kelvin temperature. The factor \( \exp(-\beta|R_{ij}|) \) is the tunneling probability between sites with equal energy, which is closely related to the extent of electronic coupling of two adjacent nanocrystals (\( i \) and \( j \), here). The factor \( \exp(-(E_j - E_i)/k_BT) \) is the penalty of a charge hopping higher in energy. On the other hand, for jumps to a lower energy, the penalty is absent and this process has the weight 1 instead of the second exponential dependence. In general, the charge carrier preferably hops to a site that has a lower site energy. The hopping rate depends only on the distance between the site and not on the site energy, and is given by \( \exp(-(E_j - E_i)/k_BT) = 1 \) and \( \Gamma_{ij} = \Gamma_o \exp(-\beta|R_{ij}|) \). We imagine that there is a trade-off between hops over a long distance to energetically favorable sites and hops over a short distance to energetically less favorable sites, leading to the phenomenon of variable-range hopping. As the nanocrystal size decreases, the hopping distance (\( |R_{ij}| \)) decrease that enhances the mobility of the IZO NCs. The degree of electronic coupling between NCs in the film can also be obtained from the measured electron mobility \( \mu \), using Einstein-Smoluchowski equation 1 (Table 1). It is known that the electronic coupling could increase or decrease in some nanocrystal diameter ranges when the nanocrystal size increases.\textsuperscript{15} Recently, Sim \textit{et al.} reported the nonmonotonic behavior of electron mobility with the PbSe NCs size.\textsuperscript{13} This behavior was again

**Table 1.** Summary of mobility value \( \mu \), tunneling rate \( \Gamma \), and coupling energy of BA-IZO NCs 5 nm and 10 nm films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature [°C]</th>
<th>Mobility ( \mu ) [cm²V⁻¹s⁻¹]</th>
<th>L_{off}</th>
<th>( V_{th} ) [V]</th>
<th>Tunneling rate ( \Gamma ) [s⁻¹]</th>
<th>Coupling Energy ( V ) [μeV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 nm</td>
<td>300*</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>( 7 \times 10^{-5} )</td>
<td>45</td>
<td>–25</td>
<td>6.58 \times 10⁷</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.04</td>
<td>4.2 \times 10²</td>
<td>–9</td>
<td>3.76 \times 10⁹</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.2</td>
<td>( 6 \times 10³ )</td>
<td>8</td>
<td>1.88 \times 10¹⁰</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.6</td>
<td>( 4 \times 10⁴ )</td>
<td>10</td>
<td>5.64 \times 10¹⁰</td>
<td>233</td>
</tr>
<tr>
<td>10 nm</td>
<td>300*</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>7.50 \times 10⁻⁵</td>
<td>6</td>
<td>–43</td>
<td>1.76 \times 10⁹</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>400</td>
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</tr>
<tr>
<td></td>
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<td>0.08</td>
<td>( 3 \times 10⁴ )</td>
<td>–30</td>
<td>1.88 \times 10⁹</td>
<td>7.78</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.13</td>
<td>( 5.78 \times 10³ )</td>
<td>–25</td>
<td>3.06 \times 10⁹</td>
<td>13</td>
</tr>
</tbody>
</table>

*At 300 °C neither the 5 nm nor the 10 nm BA-IZO NCs film showed TFT characteristic. Note: \( k_BT/h = 5.6 \times 10^{12} \) [s⁻¹]

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Figure 8. (a) Mobility depends on annealing temperature with BA-IZO NCs size of 5 nm (red line) and BA-IZO NCs size of 10 nm (blue line). (b) electronic coupling of BA-IZO NCs films cured at 600 °C (denoted \( V_{IZO NCs} \)) and electronic coupling of PbSe NCs (denoted \( V_{PbSe NCs} \)), size-dependent charging energy of PbSe NCs (denoted \( E_{C PbSe NCs} \)) of ref 15. According to PbSe NCs trend: \textbf{Region 1} on the left indicates the regimes where NC diameter \( d < 6 \) nm, whereas \textbf{Region 2} on the right denotes the regime, where \( d > 6 \) nm.
explained by investigating two main factors, charging energy and electronic coupling energy, which conflict with each other.

Figure 8(b) compares the charging energy and the coupling energy of PbSe NCs from reference 15 and the electronic coupling of our IZO NCs. As for the results with the PbSe NCs case,\textsuperscript{14} in the region 1 where NC diameter (d) is less than 6 nm (d > 6 nm), electron mobility increases monotonically, while it decreases in the region 2 where d is greater than 6 nm (d < 6 nm). The PbSe NCs of the region 1 experiences a significant decrease in the charging energy and a slight ascent in the electronic coupling. The region 2 shows a slight decrease in the charging energy and a noticeable descent in the electronic coupling. We can therefore see that the coupling energy is more decisive than the charging energy for controlling the mobility. Sim \textit{et al.} used the characteristic crossover diameter (NC size) concept to determine the transition point whereby the role of charging energy and electronic coupling energy being responsible for the mobility are changed.\textsuperscript{13} Consequently, the crossover diameter of PbSe NCs was estimated to be 6.1 nm, indicating that, for the case with d > 6 nm, the descent in the electronic coupling was found to deteriorate the electronic mobility.\textsuperscript{13,15} In other words, above the crossover diameter of 6.1 nm, both the electronic coupling energy and charging energy decrease noticeably. This kind of simultaneous decrease was observed for the 5 nm and 10 nm IZO NCs in our experiment, implying that a crossover diameter is certainly less than 5 nm. In order to determine the crossover diameter of the IZO NCs very exactly, the more controlled experiment for the IZO NCs whose diameter is in the range of 2 nm-5 nm are planned in a separate study.

Conclusion

The principal findings in this study are summarized as follows: (i) BA-IZO NCs with butylamine ligand (BA ligand) on the surfaces were synthesized by ligand exchange of SA-IZO NCs with a BA ligand. The ligand exchange percentage, which was determined by nuclear magnetic resonance (NMR) spectroscopy, was around 75\%. (ii) We fabricated IZO NCs films by spin-coating and investigated the influence of annealing temperature and particle size on the characteristics of the thin film transistors (TFTs). The electron mobility increased as the annealing temperature increased, to as high as 0.6 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} with 5 nm NCs film and 0.13 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} with 10 nm NCs film at 600 °C. (iii) Millar-Abrahams hopping formalism was employed to explain the hopping mechanism of our IZO NCs films: nearest variable-range hopping. (iv) The decrease in electron mobility for larger NCs, in our experiment, is due to smaller electronic coupling.

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Supplementary Information. For the FE-SEM of BA-IZO NCs films, the nanocrystal size was a) 5 nm and b) 10 nm, as shown in Fig. S1. The \textsuperscript{1}H-NMR spectra of IZO NCs were capped with stearic acid, as seen in Fig. S2a. The \textsuperscript{1}H-NMR spectra of IZO NCs were capped with butylamine and an explanation is given of calculating the ligand exchange percentage, as shown in Fig. S2b. XPS results of Zn 2p\textsubscript{3}/2 and In 3d\textsubscript{5/2} BA-IZO NC 5nm and 10 nm thin films annealed from 350-600 °C are shown in Fig. S3. C 1s XPS spectra of the BA-IZO NCs 5nm and 10 nm thin films annealed at different temperatures: 350 °C-600 °C, Figure S4. O 1s XPS spectra of BA-IZO NCs 5 nm and 10 nm thin films annealed at different temperature: 350 °C-600 °C, Figure S5.

References