Defect density and dielectric constant in perovskite solar cells

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We report on measurement of dielectric constant, mid-gap defect density, Urbach energy of tail states in CH$_3$NH$_3$PbI$_3$Cl$_{1-x}$ perovskite solar cells. Midgap defect densities were estimated by measuring capacitance vs. frequency at different temperatures and show two peaks, one at 0.66 eV below the conduction band and one at 0.24 eV below the conduction band. The attempt to escape frequency is in the range of $2 \times 10^{11}$/s. Quantum efficiency data indicate a bandgap of 1.58 eV. Urbach energies of valence and conduction band are estimated to be $\sim16$ and $\sim18$ meV. Measurement of saturation capacitance indicates that the relative dielectric constant is $\sim18$.

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Perovskite solar cells based on methyl amine lead iodide-chloride (MAX3) system are a new and exciting technology for solar energy conversion. High solar conversion efficiencies have been obtained in this material system, with efficiencies exceeding 17% having been reported. This material, which is poly-crystalline, is remarkable in that it shows very high absorption coefficients, characteristic of organic dyes, and yet has a relatively small exciton binding energy of $\sim(55 \pm 20)$ meV, thereby assuring that electrons and holes separate out by thermal decomposition. For all practical purposes, the material behaves as an inorganic semiconductor with relatively large diffusion lengths approaching 1 $\mu$m for both carriers. For device optimization, one needs to know fundamental properties such as defect densities in the material, tail state densities, and Urbach energies of tail states.

We used two types of device structures for our measurements: a p-i-n cell and a n-i-p cell. The intermediate base layer is designated i because it is not intentionally doped even though, in general, it is n-type. The p-i-n device was deposited on ITO substrates coated with PEDOT:PSS (Poly (3,4-ethylene dioxythiophene) Polystyrene sulfonate), and light entering the cell from the p side. The n-i-p structure consisted of the normally used TiO$_2$/perovskite/p-heterojunction/gold structure, with TiO$_2$ deposited on FTO (Fluorine-doped Tin Oxide), and light entering the n side first. See Fig. 1 for a schematic diagram of the two structures. For p-i-n cell, a PEDOT:PSS layer was spin coated onto ITO substrates, followed by annealing at 110°C. Then, the perovskite layer was deposited on top of PEDOT:PSS using a single solvent method. The films were then annealed at 90°C for 90 min until perovskite forms. For the n-i-p cell, TiO$_2$ was deposited on FTO using the method described by Chen et al., followed by vapour deposition of lead iodide and methylammonium iodide. The hole-transporting layer was formed by spin-coating a layer of P3HT (Poly-3-Hexyl Thiophene) from solution, and the device was completed by thermally evaporating 80 nm of circular gold contacts.

The illuminated I-V curve for the two types of cells is shown in Fig. 2. The p-i-n cell has a power conversion efficiency of $\sim$12% and the n-i-p cell $\sim$15%. The thickness of the perovskite i layer for the p-i-n cell was $\sim$160 nm and for n-i-p cell $\sim$460 nm. The corresponding quantum efficiency (QE) curves are shown in Fig. 3(a), and they show QE extending out to 800 nm. One can calculate the bandgap by plotting $[\text{QE}]^2$ vs. photon energy E, and the intercept gives the bandgap. The chart in Fig. 3(b) shows a bandgap of 1.58 eV.

Subgap quantum efficiency was also measured in these devices, and the curve for a n-i-p cell is shown in Fig. 4. The data show a fall off below $\sim$1.65 eV, with an exponential tail below $\sim$1.6 eV indicating the presence of tail states. The Urbach energy for valence band states is 16 meV. The data below 1.5 eV indicate the presence of midgap states. Assuming the usual value for the density of conduction band states in inorganic semiconductors to be $\sim10^{21}$/cm$^3$, the midgap state density is found to be in the range of $\sim$few $\times 10^{14}$/cm$^3$, in good agreement with the capacitance data which are discussed later.

We next measured the deep defects using capacitance(C)-frequency (f) techniques at various temperatures. In this

![FIG. 1. Schematic diagrams of n-i-p and p-i-n perovskite solar cells.](image-url)
method, as the frequency decreases, deeper traps participate in capacitance, and hence, capacitance increases. Walter et al.\textsuperscript{19} showed that the defect density at a given energy is proportional to $f \times \frac{dC}{df}$. They also show that distinct peaks arise in $[f \times \frac{dC}{df}]$ vs. frequency data when the measurements are done at different temperatures. These peaks arise because the emission rate from a trap responding at a given frequency depends very strongly on the energy of the trap and the measurement temperature. The emission rate for a given trap position is given by\textsuperscript{22}

$$e_n = N_c \langle v_{th} \rangle \sigma_n \exp\left(\frac{-E_T}{kT}\right),$$

(1)

where $N_c$ is the effective conduction band density of states, $\langle v_{th} \rangle$ is the RMS thermal velocity of electrons, $\sigma_n$ is the capture cross section, $E_T$ is the trap activation energy, $k$ is the Boltzmann constant, and $T$ is the temperature. Equation (1) is an Arrhenius equation, in which the emission rate is heavily dependent on the trap depth, the sample temperature and the pre-exponential factor $N_c \langle v_{th} \rangle \sigma_n$. It is this prefactor that is commonly known as “the attempt to escape frequency” ($v_{th}$)\textsuperscript{19} and its measurement is essential if trapping dynamics are to be accurately described.

From Eq. (1), a plot of $\ln(e_n)$ ($e_n$ being the measurement frequency at which the peak occurs) vs. $1/kT$ will yield a value for the trap energy. Then, knowing the activation energy, one can calculate the attempt to escape frequency form the peaked $[f \times \frac{dC}{df}]$ curve. When making a plot vs. $1/kT$, one must be mindful of the fact that $N_c \approx T^{3/2}$,\textsuperscript{25} and

FIG. 2. Illuminated I-V curves of n-i-p (a) and p-i-n (b) cells measured using solar simulator. The conversion efficiencies are 11% for p-i-n cell and 14% for n-i-p cell.

FIG. 3. Quantum efficiency (QE) vs. wavelength data (panel a) and $(\text{QE} \times E)^2$ vs. photon energy $E$ data in (panel b) for both n-i-p and p-i-n cells. The intercept on the energy axis in (b) indicates a bandgap of 1.58 eV for both types of cells.

FIG. 4. Subgap QE data for the n-i-p cell showing an Urbach energy of 16meV for valence band edge, and defect states extending to mid-gap region.

FIG. 5. Capacitance(C) vs. frequency(f) data, drawn as $(C \times \frac{dC}{df})$ vs. frequency, for the n-i-p cell taken at various temperatures. The peaks correspond to attempt to escape frequencies at different temperatures. There are two distinct curves, a main set of curves corresponding to a major defect and a second curve shown in the inset indicating the presence of secondary peak in defect density.
Therefore, one must plot \( \ln \left( \frac{e_n}{T^2} \right) \) vs. \( \frac{1}{kT} \), and then the slope gives a value for trap energy \( E_T \).

In Fig. 5, we show the experimental data for \( \frac{f \times dC}{df} \) vs. frequency, measured at various temperatures. The inset in the figure shows that the data indicate that there is a secondary peak related to a trap at a different energy in addition to the main peak.

The trap energy plot deduced from the data of Fig. 5 are shown in Fig. 6, and the slope indicates trap energies of 0.66 eV below the conduction band and 0.24 eV below the conduction band. The attempt-to-escape frequency \( \nu_0 \) calculated from the peaks for the dominant trap is \( \sim 2 \times 10^{11}/s \), in the usual range for inorganic solids.25,27,28 The defect density deduced from C-f plots at room temperature is plotted in Fig. 7(a) as a function of energy and shows a major peak at around 0.65 eV below conduction band, with a peak value of \( 3 \times 10^{19}/cm^3 \cdot eV \), in good agreement with the value estimated from the subgap QE data. The sharp decrease in density at low energies probably corresponds to tail states near the conduction band with Urbach energy of \( \sim 18 \) meV. The defect density, when plotted on a linear plot, shows an excellent Gaussian shape, centered at 0.65 eV, as shown in Fig. 7(b).

Capacitance measurement also provide a value for the relative dielectric constant of the perovskite. In Fig. 8, we plot the capacitance measured at low frequency where all traps respond vs. applied voltage. The saturation value for the capacitance indicates that the depletion layer has spread to the back doped contact layer. We independently measured the physical thickness of the i-layer in the perovskite n-i-p cell. By comparing the saturation capacitance, whose value is given by \( \varepsilon \frac{A}{t} \), where \( t \) is the thickness, \( A \) the area and \( \varepsilon \) the dielectric constant, we determine that the relative dielectric constant is \( \sim 18 \). This result is in agreement with values derived from first-principle calculations for CH_3NH_3PbI_3 by Brivio et al.29

In summary, we have measured the deep defect densities, attempt-to-escape frequency Urbach energies, and relative dielectric constant in high quality Pb-halide based perovskite devices.

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7\( v_0 \) is \( \sim T^{1/2} \).26
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