MEASUREMENT OF CHARGE CARRIER MOBILITY IN PEROVSKITE NANOWIRE FILMS BY PHOTO-CELIV METHOD

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Abstract. In this paper the holes’ mobility for the configuration FTO/TiO2/CH3NH3PbI3/Spiro-MeOTAD/Au was measured for the first time by the Photo-CELIV method. The TiO2 dense film was deposited by reactive sputtering at room temperature on FTO glass substrates. High crystalized perovskite films were deposited from solutions in one step by spin coating. Spiro-MeOTAD molecular glass was used as holes transporting layer. The highest holes’ mobility from TiO2 thin film through the perovskite and Spiro MeOTAD film to the top gold electrode was of order 8.5×10⁻⁷ cm²/Vs.

Key words: perovskites, holes’ mobility, photo-CELIV, solar cells, titanium oxide, CH3NH3PbI3.

1. INTRODUCTION

The organic-inorganic perovskite solar cells have attracted much attention during the last five years and became the most promising material for the new generation of solar cells [1–5]. In particular, the organic-inorganic halide perovskites have several features such as: long charge carrier lifetime, long diffusion length and ambipolar charge transport capability, which made them very attractive materials for solar cells. Also their facile synthesis directly on the substrate at low temperature made them very suitable for applications on plastics substrates. Within the last six years the efficiencies of a typical solar cell: FTO/TiO2 dense/TiO2 mes/Perovskite/HTM/Au rapidly increased from 4% to 21%.

However, despite the extremely fast progress, the materials’ electronic properties that are crucial to the photovoltaic performance are relatively little understood. It is still under debate whether the photo-generated charges have an excitonic or a free-carrier character. Also, it is not completely clear how the charge carriers’ mobility of the active layer influences the overall performance and the origin of the high efficiencies of perovskite-based solar cell devices. Moreover the results strongly depend on the preparation method, the purity of the material and the film treatment, which can result to uncontrolled morphological variations and poor reproducibility of photovoltaic performance.

The theoretical calculations of mobility of charge carriers in hybrid perovskite, using the density functional theory including van der Waals interaction and the Boltzmann theory for diffusive transport in the relaxation time approximation, indicate that the mobility of electrons in MAPI perovskite crystals ranges from 5 to 10 cm²V⁻¹s⁻¹ and that for holes within 1–5 cm²V⁻¹s⁻¹, where the variations depend on the crystal structure investigated and the level of doping [6]. In the case of devices, the perovskite films are composed of microcrystals, or nanowires, hence the experimental values of mobility of charge carriers in perovskites films may differ from theoretical calculation by many orders of magnitude. On the other side the charge carrier’s mobility in the Spiro-Me-O-TaD holes transporter layer is much lower, which can globally conduct to a lower charge carrier’s mobility through the whole device multilayer structure.
In this paper we investigate the mobility of holes through the interface CH$_3$NH$_3$PbI$_3$/Spiro-MeOTAD by using the Photo-generated Charge Extraction by Linearly Increasing Voltage (Photo-CELIV) method. Photo-CELIV is a new and powerful technique for studying charge transport physics, particularly in disordered systems such as organic semiconductors [7]. We considered here the multi-layer structure based on methyl-ammonium lead-iodide perovskite: FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$/Spiro-MeOTAD/Au.

The TiO$_2$ film may be deposited by different methods such as spin coating [8–9], spray pyrolysis [10–13], and PLD [14–16]. Different from the most common studied system using MAPI perovskite, in this study the TiO$_2$ dense film was deposited by sputtering and not by spray pyrolysis. The advantage of sputtering method comparing to spray pyrolysis is the very high reproducibility and deposition at room temperature. There is no need to heat the substrate FTO/glass films. In our previous studies [17–33] we have demonstrated that heating of transparent conducting electrodes at more than 300 °C conduct to irreversible changes of the electrical properties.

2. EXPERIMENTAL SETTING

The configuration of studied samples is described in Fig.1. Commercial FTO covered glasses were used as transparent electrodes. A dense titanium oxide (TiO$_2$) film of 30 nm was deposited by reactive sputtering using a metallic titanium target in oxygen atmosphere. Two equimolar solutions of 0.1983 g (1.25 mmole) CH$_3$NH$_3$I at 0.25 ml dry DMF 0.5785 g (1.25 mmole) PbI$_2$ at 25 ml dry DMF, were mixed, just before the spin coating. The CH$_3$NH$_3$I was prepared as follows: 20 ml of a methylamine solution (Ferak 40/ 1.25 mmole) containing 8 g methylamine (257 mmol) was diluted with 80 ml of ethanol. To this solution a Hydroiodic acid solution in water (Merck 57% w/v) was added slowly under stirring until the PH of solution turns to acidic (about 60 ml). The solution was stirred for 2 h at room temperature and evaporated to dryness. The solid was dispersed to anhydrous diethylether and filtrated. It washed copiously with anhydrous diethylether to obtain white crystals. The CH$_3$NH$_3$I crystals were dried at 60 °C in a vacuum oven overnight. The PbI$_2$ was prepared as follows: 3.3 g (10 mmol) of Pb(NO$_3$)$_2$ (Serva anal. Grade) were diluted to 50 ml of distilled water. To this solution, a solution of 3.3 g (20 mmol) of KI (Merck Reag. Ph. Eur.) in 50 ml distilled water was added under stirring, slowly at room temperature. The gold-yellow precipitate was filtered and recrystallized from water to give golden-yellow crystals. The PbI$_2$ crystals were dried at 60 °C in a vacuum oven overnight. The perovskite film was prepared, in one step, by spin coating. The solution was spin on the top of TiO$_2$ dense film at 1 600 RPM during 30 s. For the Hole Transporting Material (HTM) thin films preparation was used the Spiro-MeOTAD purchased from MERCK. A solution of (75 mg in 0.3 ml CB) was spin coat at 3 500 RPM during 20 s. The top gold electrode (of about 40 nm) was deposited by sputtering under vacuum.

The principle of charge carriers’ mobility measurements by Photo-CELIV method is described briefly in Fig. 2.
The method is based on the analysis of the extraction of photo-generated charge carriers current transients when a ramp voltage pulse is applied to a sample with a blocking contact (Fig. 3). The time \( t_{\text{max}} \) corresponding to the maximal current density depends on the mobility of charge carriers (\( \mu \)). The initial slope of the current density transient depends on the bulk conductivity, \( \sigma \), of the sample. The concentration of photo-generated charge carriers \( \Delta n \) or \( \Delta p \) can be estimated by integration of the extracted part of current density transients (above \( j(0) \)). So the carriers’ concentration and the mobility of equilibrium charge carriers may be estimated independently. A short laser pulse (\( \lambda = 532 \) nm) of 250 ms is applied before starting the current density measurement (moment \( t = 0 \) see Fig. 3). This short light pulse will create more charge carriers and we will call \( j_{\text{light}} \) the density of current after the exposure of the sample to this short light pulse. \( j_{\text{dark}} \) is the current density measured in the absence of the light pulse (in dark). The density of photo-generated current, \( j_{\text{photogen}} \) is given by the difference between \( j_{\text{light}} \) and \( j_{\text{dark}} \): \( j_{\text{photogen}} = j_{\text{light}} - j_{\text{dark}} \).

By varying \( A \) – the voltage slope, the best conditions can be achieved to get the initial step \( j(0) \).

In the case of samples with low electrical conductivities, the extracted charge carriers do not significantly affect the electric field inside the samples and the charge carriers mobility can be calculated easily using the following formula:

\[
\tau_{\text{max}} = \sqrt{\frac{2d^2}{3\mu A}}.
\] (1)

If the electrical conductivity of the samples is high, then the mobility can be calculated by the formula:
\[ t_{\text{max}} = \sqrt{\frac{3\tau_\sigma d^2}{\mu A}} \] (2)

Here \( \tau_\sigma \) is Maxwell’s relaxation time. In most of the cases, \( \tau_\sigma \) could be determined from the period of time between the moment of the signal start and the moment when the current density transient reaches the double initial step value: \( 2j(0) \).

In this paper the mobility of holes through the perovskite and Spiro MeOTAD film was determined. The thickness \( (d) \), corresponding to this transversal region (see Fig. 1) was determined by profilometry and was 1.2 \( \mu \text{m} \). The value of \( t_{\text{max}} \) was determined from the graph of photogenerated current density.

3. RESULTS AND DISCUSSIONS

Figure 4b–c depicts the SEM micrographs for the methyammonium-lead triiodine (MAPI) thin films deposited on glass. As one can see the prepared perovskite films presented long crystals (more than 200 \( \mu \text{m} \)). Several studies have established that halide perovskite exhibits unusually long diffusion excitons lengths reaching over 100 nm. This could be explained for the extremely long dimension of these perovskite crystals. Figure 4d presents the SEM micrograph of top Spiro-MeOTAD layer deposited on nanowires perovskite film.

![SEM micrographs](image)

a)  

b)  

c)  

d)  

Fig. 4 – Perovskite nanowire film on glass substrate: a) sample photo; b), c), SEM micrograph of films deposited on glass substrates; d) top view after Spiro-MeOTAD film deposition.

The XRD analysis for the perovskite films deposited on glass, FTO, and TiO\(_2\) films, respectively, are given in Fig. 5.
It was found through powdered X-ray diffraction (XRD) that the methylammonium lead iodide (MAPbI₃) perovskite exists in the cubic Pm3m phase at high temperature above 330 K, below which it undergoes a phase transition to the tetragonal I4/mcm phase and then to the orthorhombic Pnma phase below 170 K [34]. There are no critical differences between the tetragonal and cubic phases, except a slight rotation of PbI₆ octahedra along the c-axis and a small difference in energy. The XRD spectra of the cubic and tetragonal phases are similar with slight differences that consist mainly from splitting of the peaks 100 and 200 of cubic phase to the 002, 110 and 004, 220 of the tetragonal phase, respectively. Moreover two new peaks (211) and (213) appear in the tetragonal phase. The most safe criterion of XRD spectra to distinguish between them is the minor diffraction from the (211) planes at $2\theta \sim 23.5^\circ$.

In our case the presence of a peak at 23.68° in the XRD spectra indicates the presence of the tetragonal I4/mcm phase. The peak at $2\theta = 14.29^\circ$ can be deconvoluted [35] into two peak components at 14.14° and 14.29° attributed to the 002 and 110 diffractions, respectively.

The X-ray diffraction patterns of CH₃NH₃PbI₃ films on different substrates (glass, FTO, and TiO₂) confirm the tetragonal 3D structure and the space group I4/mcm. No peaks of PbI₂ are observed indicating that is no excess of PI₂ and the reaction of perovskite formation was completed. The peaks intensity increase in the case of the deposition of perovskite film on TiO₂ dense films indicating a better crystallisation comparing to films deposited on FTO or glass. The crystallite size influences the transport of charge carriers. A better crystallization and large crystalline size are favourable to a higher transport of charge carriers.

In Fig. 6 is given the current density $J_{\text{light}}$ after laser pulse excitation. From this graph the value of $\tau_\sigma$ could be extracted.

$$J_{\text{light}}(t)$$

$A = 2500 \text{ V/s}$

$J(0)$

$Q(0)$

Fig. 6 – The light current density; $\tau_\sigma$ is Maxwell’s relaxation time.
The value of $t_{\text{max}}$ was determined from the maximum of the photo-generated current (see Fig. 7).

![Fig. 7 – The photo-generated current density.](image)

The form of current density kinetics suggests that the investigated layers were highly conductive. Hence, from the values of $\tau_\sigma$ and $t_{\text{max}}$ the holes mobility $\mu_h$ was calculated according to eq. (2):

$$\mu_h = \frac{3 \tau_\sigma d^2}{A t_{\text{max}}^3}. \quad (3)$$

The obtained values for different slopes of increasing voltage are given in Table 1. This mobility corresponds to the charge transport between the TiO$_2$ interface and top gold contact.

The experimental values of Spiro-OMeTAD, one of the hole transporting material (HTM) with the highest hole mobility, is of about $4 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ [36]. The high reported values of the holes mobility correspond only to theoretical calculation for CH$_3$NH$_3$PbI$_3$ nanocrystals. In practical cases the measured values of mobility of holes are much smaller, of order of $10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ and this could be explained by the disorder and grain boundaries in the case of polycrystalline films, or due to the interfaces between the perovskite nanowires and Spiro-MeOTAD molecular glass material in this case.

### Table 1

<table>
<thead>
<tr>
<th>$U_{\text{max}}$ (V)</th>
<th>$t_{\text{ramp}}$ (s)</th>
<th>ramp $A$ (V/s)</th>
<th>$\tau_\sigma$ (s)</th>
<th>$t_{\text{max}}$ (s)</th>
<th>$\mu_h$ (cm$^2$/Vs)</th>
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<td>5</td>
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<td>2500</td>
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<td>$9.6 \times 10^{-7}$</td>
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<td>5000</td>
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<td>$6.3 \times 10^{-7}$</td>
<td>$8.0 \times 10^{-4}$</td>
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<tr>
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<td>10000</td>
<td>$1.3 \times 10^{-2}$</td>
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<td>$8.5 \times 10^{-4}$</td>
</tr>
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</table>

### 4. CONCLUSIONS

The mobility of holes for the configuration FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$/Spiro-MeOTAD/Au was measured by the Photo-CELIV method. Structural and morphological properties was analysed by X-ray diffraction and Scanning Electron Microscopy. The holes’ mobility was determined by photo-CELIV method using a green laser ($\lambda = 532$ nm). The highest holes’ mobility from TiO$_2$ thin film through the perovskite and Spiro MeOTAD film to the top gold electrode was of order $8.5 \times 10^{-7}$ cm$^2$/Vs. The electrical properties were correlated with the morphological and structural properties of the perovskite film.

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