The effect of the air environment and prolonged illumination on conductivity and photoconductivity of organic-inorganic perovskite CH$_3$NH$_3$PbI$_3$ films

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Abstract. A significant effect of the environment (vacuum, air) on the results of measurements of CH$_3$NH$_3$PbI$_3$ films conductivity and photoconductivity is shown. It was found that prolonged illumination with white light does not change the value of CH$_3$NH$_3$PbI$_3$ interband photoconductivity (hν > 1.6 eV), but leads to a metastable increase in the photoconductivity near the quantum energy hν ≈ 1.2 eV. This indicates a photoinduced creation or filling of nonrecombination localized states, located at an energy distance of 1.2 eV from the transport level of nonequilibrium charge carriers.

1. Introduction

Organic–inorganic hybrid perovskites or organometal halide perovskites have received attention in recent years due to the possibility to use them for creating cheap solar cells on flexible substrates with a high conversion efficiency of light rising to over 25.2%. A serious problem associated with the use of perovskites for creating photovoltaic structures is the change of their parameters under external influences. The aging of photovoltaic structures in a humid or in an oxygen atmosphere leads to degradation of their parameters [1]. Prolonged illumination of the structures also reduces the efficiency of light conversion by these structures. Illumination in a humid atmosphere or in the presence of oxygen significantly increases the degradation [1, 2, 3].

It should be noted that the results of studies presented in the literature contradict one another in a number of cases. In particular, according to ref. [4], only holding in an oxygen atmosphere, or only lighting in a vacuum, does not lead to a change in the parameters of the structures. Illumination in an oxygen atmosphere causes degradation of the material [4]. But at present there is no unambiguous point of view on the metastability of photoinduced changes in the parameters of photovoltaic
structures [1, 5, 6], as well as on the nature of the change in the concentration of defects caused by illumination.

It should be noted that, mainly, photoinduced degradation studies were carried out on photovoltaic structures based on MAPI [7–10]. That made it difficult to determine the role of the active perovskite layer in the change of photovoltaic structure parameters. The photoinduced change of the MAPI films parameters has been studied to a much lesser degree and the results of various works in a number of cases do not agree with each other. Therefore, it is of interest to investigate the effect of air environment and prolonged illumination of MAPI films on photoconductivity and conductivity that determine the efficiency of using of hybrid perovskites for the creation of solar cells [11].

2. Experimental

In this paper, the conductivity and photoconductivity of the perovskite films based on MAPI were investigated. 600 nm thick CH₃NH₃PbI₃ films were formed on glass substrate with deposited aluminum or gold contacts. Perovskite thin film was deposited by the one-step method. The investigated film has a microcrystalline structure. The measurements of dark conductivity (σ_d) and photoconductivity (Δσ_ph = σ_ph - σ_d, where σ_ph is the conductivity under illumination) were carried out both in air and in vacuum (at a residual pressure of 10⁻³ Pa). The films were annealed in vacuum for the 5 minutes at the temperature of 100 °C before all measurements. Photoinduced changes of the MAPI films parameters were investigated after illumination them by the white light of an incandescent lamp through a heat filter with an intensity of 40 mW cm⁻² for 1 hour at room temperature. The illumination was carried out both in vacuum and in air.

To avoid unintended sample degradation and/or undesired heating, the Raman measurements were taken using laser excitation power of 10⁻⁵ W (λ_exc = 514 nm, Horiba Labram Evolution). The curve deconvolution of Raman spectra using Gaussian curves has been performed by OriginPro v.9 with R² of at least 0.998.

3. Results and discussion

The performed studies showed that the effect of the air atmosphere is the main factor determining the measured conductivity of the films (10⁻⁶–10⁻⁷ Ohm⁻¹ cm⁻¹) at the room temperature. Temperature annealing results in a decrease of the measured conductivity of the film. This may be due to the removal the moisture or oxygen from the surface or from the volume of the film. Exposure of an air atmosphere on the film annealed in vacuum leads to an increase in its conductivity.

The performed investigations have shown that the environment also influences on the MAPI photoconductivity and its spectral dependence. Figure 1 shows spectral dependencies of the photoconductivity normalized to the number of incident photons (Δσ_ph/N = Δσ_ph/N) of annealed MAPbI₃ films measured in vacuum and in air. The obtained dependences have the typical shape for perovskites photoconductivity spectra with an exponential region (Urbach's tail) in the region of photon energies smaller than the band gap (hν<1.6 eV) and a weak change in the photoconductivity in the region of high photon energies. It should be noted that the observation of a certain maximum in the region of the edge of the photoconductivity and, apparently, associated with the excitons, depends on the intensity of the light used for recording the spectrums.

It can be seen from the figure 1, that for a similar shape of the Δσ_ph spectral dependences, the photoconductivity measured in vacuum is smaller than one measured in air. The similarity of the curves of photoconductivity spectral dependences measured in vacuum and in air indicates that, apparently, environmental conditions does not cause a change in the spectral dependence of optical transitions determining Δσ_ph, but leads to a change in the lifetime of charge carriers. The obtained result seems to be unexpected, since, according to ref. [12], the injection of oxygen from air in MAPI should lead to the appearance of deep recombination states on the surface of the film or on the boundaries of the grains. It also was noted the significant role of oxygen injected into the MAPI film.
from the atmosphere in processes that lead to a change in the physical parameters of this material [2, 12, 13].

Figure 1. Spectral dependences of MAPI film photoconductivity, normalized to the number of incident photons, measured in the vacuum (1) and in the air (2).

It can be assumed that a larger value of the photoconductivity of MAPI films, measured in air can arise if insertion of oxygen into the investigated film results in the shift of Fermi level in the bandgap. This can lead to a change in the filling of the recombination centres and a decrease in their concentration, which determines the photoconductivity of the MAPI films. An increase in the MAPI photoconductivity in air can occur also if the diffusion of oxygen into the perovskite film will lead to the appearance in the material so-called "sensitizing centres" trapping minority charge carriers.

Let us consider the results of studies of the effect of prolonged illumination on the conductivity and photoconductivity of MAPI films. Prolonged illumination of the samples (for 1 hour), both in vacuum and in the air, practically did not change their dark conductivity. The spectral dependences of the photoconductivity measured in the air also did not change after prolonged illumination of the sample. At the same time prolonged illumination in vacuum results in the difference of spectral dependences of MAPI photoconductivity measured in vacuum before and after light soaking. The results are shown in figure 2.

Figure 2. Spectral dependences of MAPI film photoconductivity, normalized to the number of incident photons, measured before (1) and after (2) prolonged illumination in vacuum. The inset shows spectral dependence of ratio $R = \Delta \sigma_{ph}(B) / \Delta \sigma_{ph}(A)$, where $\Delta \sigma_{ph}(A)$ and $\Delta \sigma_{ph}(B)$ are film photoconductivity before and after prolonged illumination accordingly.
As can be seen in the figure, the photoconductivity of the film does not change in the region of quantum energies corresponding to interband absorption ($h\nu > 1.6$ eV) after preliminary illumination. At the same time, an increase in the photoconductivity in the photon energy range $0.8–1.4$ eV is observed. The staying of the light irradiated samples in the dark for 24 hours resulted in the restoration of their original spectral dependencies of photoconductivity.

The inset in figure 2 shows the spectral dependence of the ratio $R=\Delta\sigma_{ph}(B)/\Delta\sigma_{ph}(A)$, where $\Delta\sigma_{ph}(A)$ and $\Delta\sigma_{ph}(B)$ are the photoconductivity values of the film, measured before and after its preliminary illumination, respectively. The maximum of the ratio $R$ is observed at a photon energy $h\nu \approx 1.2$ eV. The result obtained indicates that prolonged illumination leads either to the creation or filling of localized states located in the MAPI band gap at distance of 1.2 eV from the transport level of non-equilibrium charge carriers. As the increase in the photoconductivity at $h\nu \approx 1.2$ eV is not accompanied by a decrease in the interband photoconductivity, the localized states arising as a result of illumination are not recombination centres and consequently should not lead to degradation of the photovoltaic parameters of solar cells based on MAPI. It may be necessary to apply other techniques to study this effect [14].

Micro-Raman spectroscopy is a well-suited measurement technique to probe organic – inorganic halide perovskite layers locally on the micrometre scale. By using very low excitation laser intensities, we are able to obtain Raman spectra of pristine MAPbI$_3$ layers. After repeatedly measuring of the same sample, we observe structural changes, which we correlate with conductivity and photoconductivity data of the perovskite film.

In figure 3, we plot two typical Raman spectra of freshly prepared non degraded MAPI film (curve 1) and film after illumination when the sample was exposed to the ambient atmosphere for one hour (curve 2).

In the measured spectral region from 70 to 350 cm$^{-1}$, the Raman spectra reveal some distinct bands at $\approx100$, $\approx130$, $\approx160$ and $\approx200$ cm$^{-1}$. We observed these bands systematically in all Raman spectra of pristine and illuminated perovskite films. When the samples were exposed to the ambient atmosphere, the positions of these bands have change slightly and their intensities decreased. The literature data on the bands in the Raman spectrum of MAPI are actually uniform. A decrease in the intensity of the Raman peaks may be due to the fact that the spectra were obtained at geometrically different points of the studied perovskite film.

![Figure 3](image-url) **Figure 3.** Raman spectra measured on a pristine MAPI layer (1) and after illumination to the ambient atmosphere for one hour (2).
Thus, we can conclude that the used irradiation does not lead to MAPI film degradation, and it only causes surface transformations of the film under the influence of moisture, for example. Indeed, the decomposition of MAPbI$_3$ into PbI$_2$ upon temperature and illumination has been widely reported [15], and in fact the Raman feature of the newly formed phase coincides with that of PbI$_2$. In the case of degradation MAPI film becomes more transparent ($E_g \approx 2.4$ eV for PbI$_2$), the penetration depth of the excitation laser and thus the Raman interaction volume increase, leading to an intensity increase of all Raman bands. This is not observed in our experiments, simultaneously, we conclude that the structure of the film locally does not change.

4. Conclusions
The influence of environment and prolonged illumination of MAPI films at room temperature on their conductivity and the spectral dependence of photoconductivity was considered. A significant influence of ambient medium (vacuum, air) on the measurement results of MAPI parameters was found. It was shown that prolonged illumination does not change the interband photoconductivity, but leads to a metastable increase in the photoconductivity near the quantum energy $h\nu \approx 1.2$ eV. The result obtained indicates the photoinduced creation or filling of nonrecombination states located in the band gap of MAPI at an energy distance of 1.2 eV from the transport level of nonequilibrium charge carriers.

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