Abstract—Photoelectronic responses of organic-inorganic hybrid perovskite CH$_3$NH$_3$PbI$_3$ on mesoporous TiO$_2$ electrodes are investigated. On the basis of near-band-edge optical absorption and photoluminescence spectra, the bandgap energy and exciton binding energy as a function of temperature are obtained. The exciton binding energy is much smaller than thermal energy at room temperature, which means that most excitons are thermally dissociated and optical processes are determined by the photoexcited electrons and holes. We determined the temperature dependence of exciton binding energy, which changes from ~30 meV at 13 K to 6 meV at 300 K. In addition, the bandgap energy and the exciton binding energy show abrupt changes at 150 K due to structural phase transition. Our fundamental optical studies provide essential information for improving the device performance of solar cells based on halide perovskite semiconductors.

Index Terms—Photoluminescence, Semiconductor devices, Solar energy.

I. INTRODUCTION

Lead halide perovskites, CH$_3$NH$_3$PbX$_3$ [X = Cl, Br, and I], have recently emerged as a promising candidate material for efficient light-energy conversion devices. Although CH$_3$NH$_3$PbX$_3$ itself is a three-dimensional semiconductor, organic-inorganic hybrid lead halide perovskite semiconductors have previously been examined extensively with regards to the unique optical properties of natural lower-dimensional layered perovskite-type compounds [1],[2]. In 2009, Kojima et al. [3] first reported the development of a sensitized solar cell using perovskite CH$_3$NH$_3$PbI$_3$ as a light-harvesting sensitizer with mesoporous TiO$_2$ electrodes and liquid electrolyte. The further breakthrough was the realization of an efficient all-solid-state sensitized solar cell with power conversion efficiency above 10 % based on perovskite CH$_3$NH$_3$PbI$_3$, with the use of the solid-state hole-transporting material Spiro-OMeTAD [4],[5]. With ongoing research, the power conversion efficiency of perovskite-based devices has improved rapidly and is currently at over 19 % [2]-[10], which is much higher than that of conventional dye-sensitized solar cells. More recently, the planar heterojunction-type perovskite solar cell has also been developed [11],[12].

In order to further contribute to the development of increasingly efficient perovskite solar cells, it is necessary to identify the key mechanism that determines the advanced photovoltaic properties of perovskite semiconductors. To date, it has been demonstrated that long carrier diffusion length contributes to the high efficiency of these solar cells [13],[14]. The estimation of diffusion length was conducted using time-resolved photoluminescence (PL) spectroscopy in perovskite thin films, assuming the one-dimensional exciton diffusion model. However, it has not been clarified whether the exciton or free carrier mechanism is an appropriate interpretation of the optical properties. To answer this question, we need to evaluate the exciton binding energy of CH$_3$NH$_3$PbI$_3$. Although several researches have been made to evaluate the exciton binding energy of CH$_3$NH$_3$PbI$_3$ bulk crystals and thin films, the reported literature values are scattered over a wide range [15]-[18], and it still remains under discussion. Therefore, in order to promote an improved understanding of the intrinsic characteristics of perovskite solar cells, it is necessary to reveal fundamental optical properties of perovskite semiconductors and evaluate the exciton binding energy.

In our previous report, we obtained the room-temperature bandgap energy of CH$_3$NH$_3$PbI$_3$ on mesoporous TiO$_2$ electrodes based on their PL, PL excitation, and transient absorption [19]. The combination of these different optical spectroscopy techniques provides detailed information on optical properties [20],[21]. It was found that the PL and PLE spectra have peaks at 1.60 and 1.64 eV, respectively, and we observed a negative TA peak at 1.61 eV due to photobleaching, which usually appears at the bandgap energy of direct bandgap semiconductors. We therefore determined that the direct bandgap energy is 1.61 eV at room temperature.

In this paper, we discuss the optical absorption spectra measured through total optical transmittance (TT) and diffuse reflectance (DR) analyses in a wide temperature range. The...
fabrication process of the perovskite thin films and perovskite-based solar cells used in this study is outlined. The optical absorption spectra of these samples are then obtained and analyzed, taking excitonic effects into consideration, and the temperature dependence of the bandgap energy, the exciton binding energy, and the broadening parameter are determined. Temperature-dependent PL spectra are also measured.

II. SAMPLES AND EXPERIMENTAL SETUP

Perovskite thin films were fabricated on mesoporous TiO₂ electrodes using the two-step method [8]. The porous TiO₂ layer was deposited on the glass substrate through spin coating using a TiO₂ paste. The porous TiO₂ films were infiltrated with PbI₂ (99.999%, Sigma-Aldrich) through the spin-coating of a PbI₂ solution in N,N-dimethylformamide in an argon-filled glove box. After maintaining a temperature of 70 °C for 30 min to allow the material to dry, the films were dipped in a solution of CH₃NH₃I in 2-propanol and then rinsed with 2-propanol. We then conducted optical measurements on these samples. Perovskite-based photovoltaic cells were also fabricated by attaching hole-transporting material and gold electrode to the Perovskite-based photovoltaic cells were also fabricated by attaching hole-transporting material and gold electrode to the Perovskite-based photovoltaic cells used in this study. The CH₃NH₃PbI₃ layer was formed on the mesoporous TiO₂ electrode.

Fig. 1. Schematic illustration of the perovskite solar cells and samples. Optical measurements were performed on the sample without hole transporting material and gold electrode. The CH₃NH₃PbI₃ layer was formed on the mesoporous TiO₂ electrode.

III. RESULTS AND DISCUSSION

We confirmed that the solar cell with the produced CH₃NH₃PbI₃ works well, particularly with regards to power-conversion efficiency. Fig. 2 shows the solar-cell performance of our perovskite-based solar cell. We estimated the power conversion efficiency under AM 1.5 conditions. It shows high open-circuit voltage (V_OC = 0.98 V), short-circuit current (J_SC = 19.1 mA/cm²), and fill-factor (FF = 0.68). The power-conversion efficiency was 12.7%.

To evaluate the optical properties of CH₃NH₃PbI₃, we conducted optical absorption measurements as shown in Fig. 3. While DR measurement of perovskite solar cells has been conducted previously [5],[6],[19], we also carried out total transmittance (TT) measurement to achieve a more accurate optical absorption spectrum. For comparison, the DR spectrum is normalized and offset, and it was found that the TT and DR spectra were in good agreement with each other. However, the TT spectra had less signal-to-noise ratio compared with the DR measurements. Therefore, the TT spectra were used for analysis of the perovskite solar cell properties at room temperature.

As we have stated previously, CH₃NH₃PbI₃ is a direct-gap semiconductor [19]. Its TT spectrum has no excitonic peaks, suggesting the exciton binding energy is much smaller than the thermal energy at room temperature (~25 meV). However, even in this case, it is known that the near-band-edge optical absorption is modified due to excitonic effects [23]-[25]. According to [23] and [24], the near-band-edge optical absorption spectrum for a dipole-allowed direct-gap semiconductor, taking excitonic effects into consideration, is expressed as

\[ \alpha \propto A \sum_{n=1}^{\infty} \frac{1}{n^3} \delta(E - E_n)/E^2 + \left(\frac{E - E_p}{E_{ph}}\right)^{1/2} e^{-\frac{E}{E_{ph}}} \]

where \( \tau = \frac{\pi}{\delta(E - E_p)/E^2} \) and \( E_{ph} \) is the photon energy, bandgap energy, and exciton binding energy, respectively. \( A \) is a proportionality coefficient that depends on temperature, while \( E_n \) is the exciton resonance energy and typically follows \( E_n = E_g - E_p/n^2 \) where \( n (1, 2, 3 \ldots) \) is the quantum number. The actual absorption spectrum is modified by intrinsic or extrinsic effects such as thermal broadening and
inhomogeneous broadening. To take these broadening effects into account, the optical absorption is convolved by the Gaussian broadening function \( G(E) \), i.e.,
\[
\alpha_r = \int_0^\infty \alpha(E) G(V - E) dV. \tag{2}
\]

We fit the TT spectra using (1) and (2). The fit result is shown in Fig. 3 as a solid curve, which conforms to the experimental data well, and the broadening function is given as a broken curve in the same figure. The obtained best fit parameters were \( E_g = 1.614 \) eV and \( E_b = 6 \) meV, while the broadening Gaussian function width (the broadening parameter), \( w = 75 \) meV. The estimated bandgap energy shows good agreement with our previous report. Note that the broadening parameter is much higher than the thermal energy at room temperature. We are of the view that this originates from the Urbach tail [19].

Based on the exciton binding energy result of 6 meV, we can conclude that the majority of the excitons in CH\(_3\)NH\(_3\)PbI\(_3\) are thermally dissociated at room temperature. However, this exciton binding energy is much smaller than that given by previous reports, which had results in the range of 37 – 50 meV [15]-[17]. Since these values were estimated at low temperatures of approximately 10 K, we propose that the exciton binding energy varies with temperature. It has been reported that CH\(_3\)NH\(_3\)PbI\(_3\) undergoes phase transition at 150 K and 330 K [19],[26] and large modification of optical properties is anticipated near the phase transition temperature [19].

To examine this suggestion, we conducted PL and DR measurements in a wide temperature range from 13 K to 300 K, as shown in Fig. 4. For the PL measurements, the excitation photon energy was 1.91 eV. At room temperature, the PL spectrum shows a broad peak at 1.60 eV. According to the estimated bandgap energy of 1.614 eV, there is only a small Stokes shift and, therefore, we hold that the PL origin is the band-to-band radiative recombination of electrons at the conduction band and the holes at the valence band.

We confirmed that the PL spectrum shape is independent of excitation intensity and excitation photon energy under our experimental conditions. This means that the PL processes are independent of photoexcited carrier density. The low-temperature PL spectra are rather complicated: three PL components were observed. With a decrease in temperature, a new PL peak appears at approximately 1.65 eV and two-step optical absorption is observed. This is related to the structural phase transition in the region of this temperature [26]. We believe that the two phases coexist even below the phase transition temperature as, below 50 K, a new PL peak appears at 1.60 eV.

Regarding optical absorption spectra, a broad peak is observed near the band-edge in the optical absorption spectrum at low temperatures (below 50 K). It is our view that this broad peak corresponds to the \( n = 1 \) excitons. The DR spectra were fit using (1) and (2) and, at low temperatures (below 150 K) where two optical absorption edges coexist, we fit the high-energy absorption edge. The fit results are plotted as solid curves in Fig. 4. We obtained the bandgap energy, exciton binding energy, and broadening parameter as best-fit-parameters, which are indicated in Fig. 5. The bandgap energy and broadening parameter show abrupt changes at 150 K, the structural phase transition temperature. It can be seen that the broadening parameter gradually increases with temperatures above 150 K and the exciton binding energy is also temperature-dependent.
At 13 K, the estimated exciton binding energy is 30 meV, which is consistent with the previously reported value [15-17]. It is clear that the exciton binding energy decreases with temperature and a gradual change appears at the phase transition temperature. We hold that the temperature-dependent exciton binding energy can be explained by dielectric permittivity. The dielectric constant of CH3NH3PbI3 should vary with temperature because of the phase transition temperature at 150 K and 330 K, and the exciton binding energy is inversely proportional to the square of the dielectric permittivity. In fact, it has been reported that the dielectric permittivity measured at 90 GHz increases with temperature above 150 K [27]. This trend is consistent with the observed temperature dependence of the exciton binding energy. In addition, it was pointed out that excitons are almost entirely screened at room temperature, yielding free carriers, due to optical phonons and collective rotational motion of the organic cations [28].

Our findings suggest that excitons in CH3NH3PbI3 thin films are not stable at room temperature because of the smaller exciton binding energy (6 meV) than the thermal energy (25 meV), and photoexcited electrons and holes behave as free carriers. This result is consistent with our recent study on time-resolved PL and transient absorption which provides clear evidence that the radiative two-carrier recombination of free electrons and holes determines the optical processes in CH3NH3PbI3 thin films [29].

Comparison with the previous reports should be mentioned. D’Innocenzo et al., recently reported the exciton binding energy of 50 meV that were estimated from the temperature-dependence of exciton linewidth in optical absorption spectra above the phase transition temperature [18]. To estimate the exciton binding energy, they assumed the temperature-independent inhomogeneous linewidth. However, CH3NH3PbI3 thin films show an increase of the bandgap energy with temperature above the phase transition temperature, and this trend is contrary to typical semiconductors, suggesting that material parameters in CH3NH3PbI3 might change with temperature above the phase transition. On the other hand, we evaluated the exciton binding energy using whole spectrum shape near the bandgap energy without such an assumption. Based on these discussions, we believe that our estimation of exciton binding energy better accounts the near-band-edge optical properties of CH3NH3PbI3. It is significant to employ various spectroscopic techniques to reveal the near-band-edge optical and excitonic properties of semiconductors. Through such researches, we can clarify the detailed mechanism for photovoltaic processes in emerging solar-cell materials, lead halide perovskites CH3NH3PbX3 [X = Cl, Br, and I].

IV. CONCLUSION

In conclusion, we have studied the near-band-edge optical spectra of organic-inorganic hybrid perovskite CH3NH3PbI3 on mesoporous TiO2 electrodes by means of TT, DR, and PL measurements. At room temperature, no exciton peaks were observed in the optical absorption spectra. These spectra were then analyzed, taking excitonic effects into account, and an exciton binding energy of 6 meV was obtained. This result is much smaller than that given in previous reports estimated at low temperatures. This indicates that the exciton binding energy is temperature dependent. Further to this, we examined the temperature-dependent DR and PL spectra. At room temperature, almost no Stokes shift was observed. With a decrease in temperature, the exciton binding energy decreases and the PL peak and DR onset energy suddenly show a blue-shift at approximately 150 K, a structural phase transition temperature. We believe that our findings provide the requisite information to develop efficient perovskite solar cells.

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REFERENCES


