Chapter 16 Organic-Inorganic Hybrid Perovskite Solar Cells

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Abstract Quite high efficiencies exceeding 20% have been realized in solar cells incorporating organic-inorganic hybrid perovskites (APbX_3), which have a unique structure with a center cation [$\text{A} = \text{CH}_3\text{NH}_3^+$, $\text{HC}(\text{NH}_2)_2^+$] located within a PbX_3^- cage ($\text{X} = \text{I}, \text{Br}, \text{Cl}$). Superior characteristics of hybrid perovskite solar cells can be understood from the nature of optical transitions and the efficient carrier collection in the device. From these points of view, this chapter provides details on optical properties of various hybrid perovskite materials and carrier dynamics in the solar cells. In particular, based on the first-principles analyses of different perovskite materials, we present universal rules that allow the unified interpretation of the optical absorption phenomenon in APbX_3 perovskites. The external quantum efficiency (EQE) analysis further reveals that high short-circuit current densities ($>20 \text{ mA/cm}^2$) observed in the perovskite solar cells originate from electric-field-assisted carrier collection and the suppressed optical losses in the devices. Although hybrid perovskites have quite favorable characteristics for solar cells, these materials exhibit rather intense phase change upon exposure to humid air. In this chapter, the degradation process of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in humid air, characterized by applying ellipsometry technique, is further presented and discussed.

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16.1 Introduction

Research into organic-inorganic hybrid perovskite solar cells is progressing rapidly and quite remarkable conversion efficiencies exceeding 20% have already been realized by using hybrid perovskite light absorbers [1-4]. The operation of a hybrid perovskite solar cell was first demonstrated by Kojima et al. using methylammonium lead iodide (MAPbI_3 , $\text{CH}_3\text{NH}_3\text{PbI}_3$) in 2009 [5]. Although the conversion efficiency of this solar cell was 3.8%, later the efficiency was improved to 10.9% in 2012 [6], leading to drastic expansion of the researches on hybrid perovskite photovoltaic devices [7-14].

In the last few years, formamidinium lead iodide [FAPbI_3 , $\text{HC}(\text{NH}_2)_2\text{PbI}_3$], which exhibits higher thermal stability, has been applied to solar cells as an alternative hybrid perovskite material [1-4,15-17]. However, this perovskite is intrinsically unstable and a cubic FAPbI_3 crystal ($\alpha\text{-FAPbI}_3$) shows a gradual phase transformation into a transparent $\delta\text{-FAPbI}_3$ phase having a one-dimensional crystal structure [18,19]. Quite fortunately, FAPbI_3 -based perovskites can be stabilized by including a small amount of MA^+ and Cs^+ and, as a result, a variety of hybrid perovskites (APbX_3) consisting of mixed center cations ($\text{A} = \text{MA}^+$, FA^+ , Cs^+) with different PbX_3^- cages ($\text{X} = \text{I}$, Br) have been developed [1-4,20-24]. To date, quite high conversion efficiencies over 20% have been demonstrated in $(\text{FA},\text{MA})\text{Pb}(\text{I},\text{Br})_3$ and $(\text{FA},\text{MA},\text{Cs})\text{Pb}(\text{I},\text{Br})_3$ solar cells [1-4].

Figure 16.1 shows basic crystal structures of MAPbI_3 and FAPbI_3 hybrid perovskites: (a) MAPbI_3 (pseudocubic), (b) MAPbI_3 (tetragonal) and (c) $\alpha\text{-FAPbI}_3$ (pseudocubic). These crystal structures represent the optimized crystal structures obtained from the density functional theory (DFT) calculation using the Perdew-Burke-Ernzerhof (PBE) scheme [25] within the cubic [Figs. 16.1(a) and (c)] and tetragonal [Fig. 16.1(b)] bases [26,27]. The arrows indicate the directions of the a , b , and c axes of the unit cells. It can be seen that hybrid perovskite compounds in Fig. 16.1 have a unique combination of the organic A-site center cation with the inorganic cage consisting of PbI_3^- . At room temperature, MAPbI_3 single crystals show a tetragonal structure [9,28,29]. However, the MAPbI_3 crystals become cubic above 57 °C [9]. For FAPbI_3 , there are two different phase structures at room temperature (i.e., $\alpha\text{-FAPbI}_3$ and $\delta\text{-FAPbI}_3$) [15,18,29] of which $\delta\text{-FAPbI}_3$, that will be shown later, is the most stable crystal structure at room temperature [18,19].

In Figs. 16.1(a) and (c), the unit cells have pseudocubic structures with the lattice parameters of $a = 6.306 \text{ \AA}$, $b = 6.291 \text{ \AA}$ and $c = 6.310 \text{ \AA}$ (MAPbI_3) and $a = 6.416 \text{ \AA}$, $b = 6.236 \text{ \AA}$, and $c = 6.353 \text{ \AA}$ ($\alpha\text{-FAPbI}_3$). Thus, the unit cell sizes of MAPbI_3 and $\alpha\text{-FAPbI}_3$ are quite similar. However, a of $\alpha\text{-FAPbI}_3$ is expanded slightly, compared with b and c ,

Fig. 16.1 Crystal structures of MAPbI₃ and FAPbI₃ hybrid perovskites determined by DFT calculations using PBE: (a) MAPbI₃ (pseudocubic) [26], (b) MAPbI₃ (tetragonal) and (c) α -FAPbI₃ (pseudocubic) [27]. The arrows indicate the *a*, *b*, and *c* axes of the pseudocubic unit cells. In (b), the in-plane Pb-I networks are shown by the thin red color.

due to the steric effect of FA⁺, while the lattice parameters are almost the same in MAPbI₃. These values are comparable to the experimental values of $a = 6.259 \text{ \AA}$ (MAPbI₃) [9] and $a = 6.362 \text{ \AA}$ (α -FAPbI₃) [19].

In the DFT-optimized structures obtained assuming 0 K, MA⁺ and FA⁺ interact with I atoms, forming hydrogen bonds expressed by I...H–N, and the orientation and location of the center cation are determined primarily by this hydrogen bonding interaction [19,26,27,30-33]. Nevertheless, it has been confirmed experimentally that, at room temperature, MA⁺ and FA⁺ reorient quite rapidly (0.5-14 ps) inside the Pb-I network [19,34-40]. In Fig. 16.1, on the other hand, the I-Pb-I angle is slightly bent and, in the tetragonal phase, the I-Pb-I bond angle changes rather significantly. It has been

Fig. 16.2 Basic structure of a hybrid perovskite (MAPbI₃) solar cell fabricated by spin coating. In this structure, the MAPbI₃ absorber layer is inserted between the mesoporous (mp)-TiO₂ electron transport layer (ETL) and spiro-OMeTAD hole transport layer (HTL).

reported that the introduction of the large center cation leads to the formation of collinear I-Pb-I bonds, which are closer to 180° [41]. Quite interestingly, the collinear bond formation induces the slight band gap (E_g) reduction [30,41,42], which has been explained by the anti-bonding character of the Pb-I bond [41,42].

Figure 16.2 shows a basic structure of a hybrid perovskite (MAPbI₃) solar cell [6,8,10,12]. This solar cell consists of a glass substrate, SnO₂:F transparent conductive oxide (TCO), TiO₂ electron transport layer (ETL), light absorber (MAPbI₃), spiro-OMeTAD hole transport layer (HTL) and back metal electrode (Au or Ag). The spiro-OMeTAD is an organic compound (see Fig. 9.18 in Vol. 2), which is employed quite commonly in hybrid perovskite solar cells [6,8] and can be formed by spin coating. For the fabrication of the solar cells, commercial glass substrates on which TCO (SnO₂:F) layers are formed (TEC-8 or TEC-15, Pilkington) are used widely (see Chapter 18). On this SnO₂:F/glass substrate, a dense (compact) TiO₂ layer, followed by a porous (mesoporous; mp) TiO₂ layer, is formed prior to the perovskite layer fabrication [6,8]. One quite remarkable feature of hybrid perovskite solar cells is that high efficiency devices can be made by adopting a rather simple solution-based process, combined with low temperature annealing at ~100 °C [6,7,12]. Accordingly, by further developing hybrid perovskite solar cells, low-cost production of large-area solar cell modules could be realized.

Fig. 16.3 (a) Schematic of the laser evaporation process and (b) a scanning electron microscope (SEM) image of the MAPbI₃/ZnO/*c*-Si structure [26].

In this chapter, we will overview the optical characteristics of unique hybrid perovskite compounds and the operational principles of the solar cells (Sections 16.2~16.3, H. Fujiwara, M. Kato, T. Miyadera and M. Chikamatsu). Moreover, this chapter describes spectroscopic ellipsometry (SE) characterization of hybrid perovskite structures based on real-time measurements (Section 16.4, N. J. Podoraza and K. Ghimire). One of the drawbacks of hybrid perovskite solar cells is a rather strong degradation in humid air, and the degradation phenomenon and its mechanism are discussed in Section 16.5 (M. I. Alonso).

16.2 Optical Properties

16.2.1 Optical Constants of Hybrid Perovskites

For MAPbI₃, many inconsistent optical data have been reported [26,43-52] (see Fig. 1.3). However, the disagreement observed among the reported optical constants can primarily be attributed to the influence of roughness component (Chapter 6). Since spectroscopic ellipsometry (SE) is a surface-sensitive technique, the fabrication of samples with smooth surfaces is essential for reliable SE characterization. For the preparation of smooth MAPbI₃ and α -FAPbI₃ layers, a laser evaporation technique shown in Fig. 16.3(a) has been applied [26,53]. In this technique, PbI₂ and MAI (or FAI) source materials are heated by a near-infrared laser, and the evaporation rates of the source materials are controlled precisely by adjusting the pulsed-laser power and

frequency. By using this technique, an ultrasmooth MAPbI₃ layer shown in Fig. 16.3(b) can be formed [26] and, in this sample, a thin ZnO layer is provided to improve film adhesion on a crystalline Si (*c*-Si) substrate. For the suppression of surface roughening and structural non-uniformity in the growth direction, characterization of thin layers [45 nm in Fig. 16.3(b)] is quite effective (Chapter 6). The MAPbI₃ and α -FAPbI₃ layers fabricated by laser evaporation show sharp x-ray diffraction peaks, which are consistent with the perovskite pseudocubic phases, and the formation of secondary PbI₂ phase is negligible [26,27].

Unfortunately, MAPbI₃ [51,54-59] and α -FAPbI₃ [16,21,23,29] exhibit significant degradation in humid air (Section 16.5). Thus, to avoid the air exposure, the samples were transferred from the deposition system to the SE measurement system using a N₂-filled plastic bag. From this procedure, the SE spectra of the pristine MAPbI₃ and α -FAPbI₃ were measured without exposing the samples to humid air at all [26,27], although the high-energy spectra of MAPbI₃ ($E \geq 4.75$ eV) were obtained after the short-time air exposure (~ 20 s) at 40% relative humidity [26].

Moreover, to determine reliable optical constants of hybrid perovskites, the SE analyses have been performed using a global error minimization (GEM) scheme [26,27], in which the dielectric function is determined self-consistently using more than two samples having different layer thicknesses on substrates [60,61] (Section 10.2). In this method, the dielectric function is obtained first from a thin layer and the extracted dielectric function is then applied for the SE analysis of a thicker layer (or layers) under the assumption that the bulk-layer optical properties are independent of the layer thickness. In the actual GEM analyses of the hybrid perovskites, a pair of samples with thicknesses in a range of 45-200 nm have been employed [26,27].

Figure 16.4 shows an example of GEM analysis performed for MAPbI₃ [26]. In this case, two samples with MAPbI₃ layer thicknesses of 45 nm [Fig. 16.3(b)] and 85 nm were used and two sets of ellipsometry spectra were obtained from these samples [i.e., $(\psi, \Delta)_{45\text{nm}}$ and $(\psi, \Delta)_{85\text{nm}}$]. For this SE analysis, an optical model shown in Fig. 16.4(a) has been assumed. The interface and SiO₂ layers correspond to the surface roughness of the ZnO layer and the native oxide of the *c*-Si substrate, respectively. The ZnO surface roughness can be characterized from the SE analysis of a ZnO/SiO₂/*c*-Si structure (see Section 18.3.2). The optical properties of the surface roughness layer are calculated as a 50:50 vol.% mixture of the bulk layer and voids by applying the Bruggeman effective-medium approximation (EMA) [60,61] (see Sections 3.4.2 and 6.1), while a 50:50 vol.% mixture of MAPbI₃ and ZnO is assumed for the interface layer.

Figure 16.4(b) shows experimental SE spectra of $(\psi, \Delta)_{85\text{nm}}$ and the solid lines

Fig. 16.4 (a) Optical model and (b) (ψ, Δ) ellipsometry spectra for a MAPbI₃ (85 nm)/ZnO (50 nm)/SiO₂ (2 nm)/c-Si structure [26]. The solid lines show the fitting result calculated using the MAPbI₃ dielectric function extracted from the thinner layer (45 nm). In (a), the layer thicknesses determined from the SE analysis of (b) are shown. In (b), the SE measurement was carried out in a N₂ environment without exposing the sample to air at an angle of incidence of 75°.

represent the fitting result calculated using the MAPbI₃ dielectric function extracted from $(\psi, \Delta)_{45\text{nm}}$ [26]. The calculated spectra show excellent fitting to the experimental spectra, confirming the validity of the analysis. The layer thicknesses determined from the SE analysis of Fig. 16.4(b) are also summarized in Fig. 16.4(a). In the subsequent analysis, the final dielectric function is extracted from $(\psi, \Delta)_{45\text{nm}}$ by adjusting the MAPbI₃ bulk layer thickness slightly since the ϵ_2 values obtained from the above analysis show very small negative values ($\epsilon_2 \sim -0.05$) at $E < E_g$. In particular, the bulk layer thickness is increased slightly (~5% of total thickness) so that the ϵ_2 values at $E < E_g$ become completely zero. Such minor adjustment is often necessary due to the imperfection of samples. It should be noted that the surface-roughness layer thickness of 2.9 ± 0.1 nm obtained from the SE analysis of $(\psi, \Delta)_{45\text{nm}}$, shows reasonable agreement with the root-mean-square roughness of 4.6 nm observed in AFM. Thus, the overall ellipsometry analysis can be justified by comparing the roughness values characterized from SE and AFM [Fig. 6.1(b)]. It has been confirmed that thermal annealing (80 °C for

Fig. 16.5 (a) ϵ_2 spectra and (b) α spectra of MAPbX_3 ($X = \text{I, Br, Cl}$) and $\alpha\text{-FAPbI}_3$. The reported optical data of MAPbI_3 [26], $\alpha\text{-FAPbI}_3$ [27], MAPbBr_3 [52], and MAPbCl_3 [52] are shown. The results of $\alpha\text{-FAPbI}_3$ and MAPbI_3 were obtained from the GEM analyses of polycrystalline layers, whereas those of MAPbBr_3 and MAPbCl_3 were extracted from the single crystals.

45 min) of a MAPbI_3 sample does not change the SE result significantly, while annealing at a higher temperature (100 °C for 45 min) leads to PbI_2 formation by the MAI desorption [26].

Figure 16.5 summarizes (a) the ϵ_2 spectra and (b) the α spectra of MAPbX_3 and $\alpha\text{-FAPbI}_3$. The optical functions of MAPbI_3 [26] and $\alpha\text{-FAPbI}_3$ [27] have been determined from the GEM analyses of the laser-evaporated layers (i.e., Fig. 16.4 for MAPbI_3), whereas those of MAPbBr_3 and MAPbCl_3 have been obtained from the SE analyses of the single crystals [52]. The complete optical data of these materials are also shown in Chapter 10 (Vol. 2). In Fig. 16.5(a), when the X-site halogen atom is changed, the whole dielectric function shifts toward higher energy with the gradual reduction of the ϵ_2 amplitude for the lighter halogen atom. In this case, a high-energy transition peak observed at 3.24 eV in MAPbI_3 splits into two peaks in MAPbBr_3 and MAPbCl_3 . The sharp absorption peaks of MAPbBr_3 and MAPbCl_3 , observed near the E_g regions, originate from excitonic transitions [62] and the excitonic peaks become more pronounced in MAPbCl_3 .

Quite interestingly, the ϵ_2 amplitude of $\alpha\text{-FAPbI}_3$ is roughly half of that of MAPbI_3 at $E < 3$ eV, even though the overall ϵ_2 -spectral shape is independent of the center cation.

Accordingly, the replacement of the A-site cation has a large influence on the absorption strength. In fact, the α values of α -FAPbI₃ are notably smaller than those of MAPbI₃ and, at 1.7 eV, α of α -FAPbI₃ is half of that of MAPbI₃ [Fig. 16.5(b)]. The lower light absorption observed in α -FAPbI₃ explains why thicker absorber layers (~500 nm) are generally necessary for FAPbI₃-based perovskite solar cells [1-4], compared with MAPbI₃ solar cells (typically ~300 nm) [7]. The low α values observed in α -FAPbI₃ have also been confirmed based on external quantum efficiency (EQE) analysis of a α -FAPbI₃ solar cell [27]. The results of Fig. 16.5 show clearly that the A-site cation (MA⁺ and FA⁺) modifies the oscillator strength of the optical transition (or ϵ_2 amplitude), while the X-site halogen atom determines the transition energy.

Often, high conversion efficiencies demonstrated in MAPbI₃ solar cells are attributed to quite high α in MAPbI₃ [13,63,64]. Nevertheless, many α values reported earlier for MAPbI₃ have been overestimated seriously due to the influence of surface roughness (see Fig. 1.3 and Chapter 6), and the actual α values of MAPbI₃ in Fig. 16.5(b) are comparable to those of CuInGaSe₂, GaAs, and CdTe absorbers (Fig. 1.6). In other words, the α values of α -FAPbI₃ are lower than major solar-cell materials. Since hybrid perovskite layers fabricated by spin-coating processes are generally thin (< 1 μ m), the optical confinement is of significant importance particularly in FAPbI₃-based solar cells (see also Section 16.3).

Figure 16.6 summarizes (a) the dielectric functions and (b) the α spectra of hybrid-perovskite secondary phases including PbI₂ [26], MAI [26] and δ -FAPbI₃ [27], together with those of MAPbI₃ and α -FAPbI₃ in Fig. 16.5. As confirmed from Fig. 16.6, PbI₂ exhibits ϵ_2 peaks at 2.51, 2.97, 3.26, 3.90, and 4.33 eV, where the rather sharp peak at 2.51 eV has been attributed to an excitonic transition [65,66]. On the other hand, the visible light absorption in MAI and δ -FAPbI₃ is quite weak.

Figure 16.7 presents the critical point (CP) analyses of (a) MAPbI₃ [26] and (b) α -FAPbI₃ [27] dielectric functions. As described in Section 4.3.1, the CP analysis is used commonly to determine the optical transition energies and E_g accurately. For the CP analyses of MAPbI₃ in Fig. 16.7(a) and α -FAPbI₃ in Fig. 16.7(b), a procedure described in Section 10.3.2 has been employed. Briefly, in this CP analysis, the second-derivative spectra calculated from the modeled dielectric functions (Chapter 10 in Vol. 2) are employed to suppress the spectral noise and the theoretical fitting to these spectra is then carried out. The open circles in Figs. 16.7(a) and (b) show the $d^2\epsilon_1/dE^2$ spectrum obtained from the modeled dielectric functions, while the solid lines represent the fitting results calculated from Eqs. (10.2) and (10.3). From the CP analysis, E_0 (E_g) of MAPbI₃ is found to be 1.61 ± 0.01 eV, while the peak transition energies in the high

Fig. 16.6 (a) ϵ_2 spectra and (b) α spectra of hybrid-perovskite secondary phases including PbI_2 [26], MAI [26] and $\delta\text{-FAPbI}_3$ [27], together with those of MAPbI_3 and $\alpha\text{-FAPbI}_3$ in Fig. 16.5.

energy region are determined to be $E_1 = 2.53 \pm 0.01$ eV and $E_2 = 3.24 \pm 0.01$ eV [26]. The CP analysis of $\alpha\text{-FAPbI}_3$ has been implemented assuming only three transitions at $E \leq 3.5$ eV, which results in the CP energies of 1.55 ± 0.01 eV, 2.48 ± 0.01 eV, and 3.04 ± 0.01 eV [27]. The CP energy of 1.55 ± 0.01 eV corresponds to E_g of $\alpha\text{-FAPbI}_3$. Thus, E_g of $\alpha\text{-FAPbI}_3$ changes only slightly, if compared with MAPbI_3 .

On the other hand, E_g can be analyzed more conveniently using a $(\alpha E)^2$ - E plot. In Fig. 16.7(c), an example of this E_g analysis, performed for the α spectrum of MAPbI_3 , is shown [26]. In this analysis, the E_g value is determined from the intercept, but the analysis implemented using different $(\alpha E)^2$ regions gives different E_g values. Thus, the reliability of this analysis is rather low. Moreover, when the effect of surface roughness is underestimated in SE analyses, E_g is also underestimated (see Fig. 1.3). Accordingly, slightly smaller E_g values reported for MAPbI_3 (1.50-1.61 eV in Refs. [10,12,16,29,54,67]) and $\alpha\text{-FAPbI}_3$ (1.43-1.53 eV in Refs. [4,15-17,21,29,68]) could be interpreted by (i) the uncertainty in the E_g analysis and (ii) the contribution of surface roughness.

In Fig. 16.7(d), from the α spectrum of MAPbI_3 and $\alpha\text{-FAPbI}_3$, the Urbach energy (E_U) is further determined assuming $\alpha \propto \exp(E/E_U)$ [i.e., $\ln(\alpha) \propto E/E_U$]. The E_U values

Fig. 16.7 Critical point (CP) analyses of (a) MAPbI₃ [26] and (b) α -FAPbI₃ [27] dielectric functions, together with (c) E_g analysis for MAPbI₃ using the $(\alpha E)^2$ - E plot [26] and (d) analysis of the Urbach energy (E_U) assuming $\ln(\alpha) \propto E/E_U$. In the CP analyses of (a) and (b), the open circles denote the experimental data and the solid lines represent the theoretical fittings. From the CP analyses, E_g values are determined to be 1.61 ± 0.01 eV (MAPbI₃) and 1.55 ± 0.01 eV (α -FAPbI₃). These E_g values correspond to the transition energies of E_0 . In (c), the E_g analysis results for two different $(\alpha E)^2$ regions are shown, which result in different E_g values. The open circles show the experimental data and the solid lines represent the linear fitting results.

of MAPbI₃ and α -FAPbI₃ estimated from this simple analysis are 14 meV [26] and 16 meV [27], respectively, confirming the sharp absorption onset near E_g in hybrid perovskites [45].

In Fig. 16.8, the crystal structures and α spectra of δ -FAPbI₃, MAPbI₃·H₂O and orthorhombic CsPbI₃ (δ -CsPbI₃) are shown. The crystal structure of δ -FAPbI₃ in Fig. 16.8(a) is derived from the DFT calculation, while the reported crystal structures of MAPbI₃·H₂O [69] and δ -CsPbI₃ [29] are shown in Figs. 16.8(b) and (c), respectively.

Fig. 16.8 Crystal structures of (a) δ -FAPbI₃, (b) MAPbI₃·H₂O and (c) δ -CsPbI₃ and (d) their α spectra. The DFT-derived crystal structure (δ -FAPbI₃) and reported crystal structures of MAPbI₃·H₂O [69] and δ -CsPbI₃ [29] are shown. All the crystals have similar one-dimensional crystal structures. In this figure, the α spectra reported for δ -FAPbI₃ [27], MAPbI₃·H₂O [51] and δ -CsPbI₃ [70] are summarized. The α spectrum of δ -FAPbI₃ is shifted by $5 \times 10^5 \text{ cm}^{-1}$ for clarity.

All the crystal phases have one-dimensional crystal structures consisting of PbI₆ octahedra, although the crystal structure of δ -FAPbI₃ is slightly different from the other two. It should be noted that, at room temperature, δ -FAPbI₃ and δ -CsPbI₃ are the most stable phases of FAPbI₃ and CsPbI₃ [22]. On the other hand, it has been confirmed that the MAPbI₃·H₂O phase is formed by the exposure of MAPbI₃ to humid air [51] (Section 16.5).

It can be seen from Fig. 16.8(d) that the reported α spectra of MAPbI₃·H₂O [51] and δ -CsPbI₃ [70] are quite similar to that of δ -FAPbI₃. In fact, all these materials show similar absorption peaks at $E = 3.0$ - 3.3 eV with weak shoulder peaks at 3.6 - 3.8 eV. The sharp peak at 3.1 eV in MAPbI₃·H₂O has been attributed to the excitonic transition [51]. The DFT calculations confirmed that the interaction between the neighboring PbI₆ octahedrons contributes to reduce E_g and, as a result, E_g of MAPbI₃ with three-dimensional PbI₆ structure is much smaller, compared with two-dimensional PbI₂ and one-dimensional MAPbI₃·H₂O crystals [59].

16.2.2 Optical Transitions in Hybrid Perovskites

To understand the light absorption in hybrid perovskite crystals, the optical transition analyses have been implemented using DFT. In particular, the dielectric functions of MAPbI₃, MAPbBr₃ and α -FAPbI₃ can be reproduced quite well assuming simple pseudocubic structures based on DFT within PBE [26,27]. Moreover, universal rules that allow the unified interpretation of the light absorption in APbX₃-type perovskites have been established [27]. In this section, these results obtained from the DFT analyses are introduced.

Figure 16.9 summarizes the DFT-derived crystal structures of (a) MAPbI₃ [26], (b) α -FAPbI₃ [27] and (c) MAPbBr₃ [27], and corresponding DFT dielectric functions of (d) MAPbI₃ [26], (e) α -FAPbI₃ [27] and (f) MAPbBr₃ [27]. The crystal structures of MAPbI₃ and α -FAPbI₃ in Fig. 16.9 are identical to those shown in Fig. 16.1. The arrows indicate the a , b , and c axes of the unit cells. In the optimized structures, the C–N bonds of MA⁺ in MAPbI₃ and MAPbBr₃ are aligned to be almost parallel to the a axis, whereas the N–C–N plane of FA⁺ in α -FAPbI₃ is parallel to the a - b plane (or the line connecting two N atoms of FA⁺ is parallel to the a axis). The orientation of FA⁺ in α -FAPbI₃ [Fig. 16.9(b)] is consistent with the experimental result [19].

In Figs. 16.9(d)-(f), the experimental dielectric functions shown in Fig. 16.5 (open circles) are compared with the DFT-derived dielectric functions (solid lines). The theoretical dielectric functions have been obtained assuming the different polarization states with directions parallel to the a , b and c axes in Figs. 16.9(a)-(c), and the arrows indicated in Figs. 16.9(d)-(f) represent the transition (CP) energies in the Brillouin zone described below. For MAPbBr₃, however, all the calculated spectra have been shifted toward higher energy by 0.22 eV to match the DFT result with the experimental result. The DFT calculations show that all the perovskite compounds have highly anisotropic optical characteristics. In the case of MAPbI₃, for example, the dielectric function for

Fig. 16.9 Pseudocubic crystal structures of (a) MAPbI₃, (b) α-FAPbI₃ and (c) MAPbBr₃ obtained from the DFT calculations, and ε₂ spectra of (d) MAPbI₃, (e) α-FAPbI₃ and (f) MAPbBr₃, obtained from the experiments (open circles) and DFT calculations (solid lines). In (a)-(c), the arrows indicate the *a*, *b*, and *c* axes of the unit cells. In (d)-(f), the experimental results correspond to those shown in Fig. 16.5, and ε_a, ε_b and ε_c represent the ε₂ spectra calculated assuming the light polarization along the *a*, *b*, and *c* axes in (a)-(c), respectively. On the ε₂ spectra, the transition energies determined by the DFT analyses (see Fig. 16.10) are indicated. In (f), the DFT spectra of MAPbBr₃ have been shifted toward higher energy by 0.22 eV to obtain better matching with the experimental spectrum. The experimental and DFT data are taken from Ref. [26] (MAPbI₃) and Ref. [27] (α-FAPbI₃ and MAPbBr₃).

the a axis polarization (ε_a) is quite different to those for the b and c axes (ε_b and ε_c), and similar trends can be confirmed for MAPbBr₃. It can be seen that the overall shapes of ε_b and ε_c obtained for MAPbI₃ and MAPbBr₃ show remarkable agreement with those of the experimental spectra. In the case of α -FAPbI₃, the ε_2 spectra for the a and b axes (ε_a and ε_b) exhibit different shapes from that for the c axis (ε_c), and the shape of ε_c agrees well with the experimental dielectric function.

In Figs. 16.9(d)-(f), the CP energies (E_{0-3}) of MAPbI₃, MAPbBr₃ and α -FAPbI₃, deduced from the DFT calculations, show excellent agreement with the experimental results, and all the fine absorption features observed experimentally in these perovskites are reproduced quite well. However, the band-edge excitonic transition observed in MAPbBr₃ at 2.4 eV is not reproduced in the calculation result as the DFT calculations in Fig. 16.9 have been performed without incorporating electron-hole interactions (or exciton formation). Consequently, the calculated ε_2 becomes lower than the experimental ε_2 near the E_g region. In contrast, excellent matching is observed between the experimental and DFT spectra for MAPbI₃ and α -FAPbI₃, confirming that the contribution of excitons in the light absorption process is negligible in these materials [26,27]. Non-excitonic nature of MAPbI₃ has already been confirmed and discussed quite extensively [47,71,72].

Figure 16.10 shows the band structure and the density of states (DOS) of (a) MAPbI₃ [26] and (b) α -FAPbI₃ [27], calculated from the pseudocubic structures of Figs. 16.9(a) and (b), respectively. For the band structures, the corresponding Brillouin zone is shown in the inset and the partial DOS of each material is also shown. The V_j and C_j in these figures denote the j th valence and conduction bands from the valence band maximum (VBM) and the conduction band minimum (CBM), respectively. In both MAPbI₃ and α -FAPbI₃, V_1 consists of the Pb 6s and I 5p states, whereas C_1 is dominated by Pb 6p [9,26,64,73,74], as confirmed from the corresponding partial DOS. The band structures of MAPbI₃ and α -FAPbI₃ are quite similar, but α -FAPbI₃ has an additional conduction band at ~2.9 eV due to the π -state of the sp^2 C atom in FA⁺. The insets of Fig. 16.10(a) also show the charge density profiles of MAPbI₃ for the designated energy regions of $E = 1.4 \sim 1.6$ eV (CBM), $E = -0.2 \sim 0.0$ eV (VBM), and $E = -0.6 \sim -0.4$ eV. Because of the antibonding nature of Pb-I [75], the charge densities near VBM are localized on the Pb (6s) and I (5p), while the charge density near CBM is dominated by Pb 6p. In the band structures of Fig. 16.10, the energy positions of M_{1-3} and those of X_{1-3} differ slightly because the assumed cubic crystal is distorted and the resulting reciprocal lattices ($a^* = 2\pi/a$, $b^* = 2\pi/b$, $c^* = 2\pi/c$) are different. In particular, the α -FAPbI₃ unit cell is distorted largely due to the steric effect of FA⁺ and the energy differences of M_{1-3}

Fig. 16.10 Band structure and DOS of (a) MAPbI₃ [26] and (b) α -FAPbI₃ [27] pseudocubic crystals. In (a) and (b), V_j and C_j denote the j th valence and conduction bands from VBM and CBM, respectively, and the partial DOS distributions are also indicated. The optical transitions determined by the polarization-dependent DFT analyses are indicated by arrows and the energy positions of these transitions are shown in Fig. 16.9. The inset of (a) shows the high symmetry points in the Brillouin zone defined by the reciprocal lattices ($a^* = 2\pi/a$, $b^* = 2\pi/b$, $c^* = 2\pi/c$) of the assumed pseudocubic structure and the charge density profiles for the designated energy regions of $E = -0.2 \sim 0.0$ eV (VBM), $E = 1.4 \sim 1.6$ eV (CBM) and $E = -0.6 \sim -0.4$ eV.

Fig. 16.11 (a) Energy separation between the conduction and valence bands ($E_C - E_V$) in MAPbI₃ and (b) contributions of various interband transitions to the ϵ_2 spectrum of MAPbI₃. In (a), V_jC_1 ($j \leq 4$) denote the interband transitions of $V_j \rightarrow C_1$ in Fig. 16.10(a). In (b), the ϵ_2 contributions of V_jC_1 for the b axis (i.e., ϵ_b) are shown, and the amplitude of the ϵ_2 spectrum for the V_1C_1 transition is reduced to half for clarity. The data reported in Ref. [77] are shown.

and X_{1-3} are larger in α -FAPbI₃ than in MAPbI₃.

The arrows in Figs. 16.10(a) and (b) represent the interband transitions that occur at high symmetry points in the pseudocubic Brillouin zone. These optical transitions have been characterized by calculating the dielectric response of each interband transition by DFT [26,27], as described below. The energy positions of the arrows in Figs. 16.9(d)-(f) correspond to the interband transition energies obtained from the corresponding band structures. In the case of MAPbI₃, however, the E_2 transition consists of three components and each component is labeled using the subscript of a , b or c . It can be seen that MAPbI₃ [9,26,64] and α -FAPbI₃ [27,76] are direct transition semiconductors with the E_0 (E_g) transition at the R point (cubic symmetry) and other hybrid perovskites also show direct gaps [27,76]. The transition energies of E_{0-3} obtained from the band structures show remarkable agreement with the experimental values, as confirmed from Fig. 16.9(d)-(f).

Figure 16.11 shows the optical transition analysis performed for MAPbI₃ [77]. In this analysis, the energy separation between the conduction and valence bands ($E_C - E_V$) is calculated first for each interband transition of $V_j \rightarrow C_k$. In Fig. 16.11(a), the calculated

results for V_jC_1 ($j \leq 4$) of Fig. 16.10(a) are shown, where V_jC_1 denote the transition of $V_j \rightarrow C_1$. The ϵ_2 contributions induced by the V_jC_1 transitions are calculated further [Fig. 16.11(b)] and are compared with the energy separations in Fig. 16.11(a). From this procedure, the optical transitions at high symmetry points that satisfy van Hove singularities [78] in $\mathbf{k}$ space (i.e., $\nabla_{\mathbf{k}} [E_C(\mathbf{k}) - E_V(\mathbf{k})] = 0$) have been determined. It can be seen from Fig. 16.11(b) that the optical transition in the visible region is dominated by the V_1C_1 transition. In Fig. 16.11(b), the ϵ_2 contributions for the b -axis component [i.e., ϵ_b in Fig. 16.9(d)] are shown and, in this case, only the transitions at the R , M_1 , M_2 , and X_2 points are allowed (i.e., b^* component of the Brillouin zone). From these assumptions, the CP energies observed in the ϵ_2 spectrum of MAPbI₃ are assigned to the interband transitions of V_1C_1 at the R (E_0 transition), M_2 (E_1 transition) and X_2 ($E_{2,a}$ transition) points. Moreover, the ϵ_2 peaks for the V_2C_1 and V_4C_1 transitions are attributed to the transitions of V_4C_1 at the M_1 point ($E_{2,b}$ transition) and V_2C_1 at the X_2 point ($E_{2,c}$ transition). The CP energies observed in Fig. 16.11(a), however, deviate slightly from the exact peak positions confirmed in the calculated ϵ_2 spectra and thus slight ambiguity remains. Similar optical transition analyses have been made for α -FAPbI₃ and MAPbBr₃ [27].

The above DFT analysis and partial DOS in Fig. 16.10 indicate that direct semiconductor-type transitions occur within the PbI₃⁻ component in MAPbI₃ and α -FAPbI₃ in the visible region ($E < 4$ eV), supporting the efficient carrier generation in these semiconductors [26,27,77]. By applying the self-consistent GW (sc GW) approximation, the optical transition analyses of MAPbX₃ have been performed and slightly different assignments have been proposed for MAPbI₃ [52]. It should be emphasized that the DFT-derived dielectric function changes rather significantly depending on calculation (approximation) method. As examples, Fig. 16.12 compares the α spectra of (a) MAPbI₃ and (b) α -FAPbI₃ calculated by DFT using different approximations. In these figures, the α values in linear and logarithmic scales are summarized. For MAPbI₃, the DFT calculation results obtained within PBE [26], the GW approximation [30], and the sc GW approximation [52] are shown. In the GW and sc GW calculations, the effect of the spin-orbit coupling (SOC) [79] has been taken into account. For the GW -SOC results [30], however, only relative α values have been reported, and the absolute α values are deduced by assuming that the α values at 3.0 eV are identical to those of the PBE results. All the DFT calculations reproduce E_g of MAPbI₃ successfully, as discussed previously [52,73,80-82]. In general, E_g is underestimated seriously in PBE [83]. For hybrid perovskites, however, the E_g values calculated by PBE agree quite well with the experimental values, which has been

Fig. 16.12 α spectra of (a) MAPbI₃ and (b) α -FAPbI₃ calculated by DFT using different approximations: PBE (MAPbI₃ [26] and α -FAPbI₃ [27]), GW approximation with SOC [30], and self-consistent GW (scGW) approximation with SOC [52]. In (a) and (b), the α values in linear and logarithmic scales are shown. The absolute α values of the GW (SOC) results [30] are deduced by assuming that the α values at 3.0 eV are identical to those of the PBE results.

attributed to the cancellation of errors in the DFT calculations [52,73,79]. On the other hand, if the SOC interaction is not considered in the GW and scGW, the E_g values are overestimated seriously [52,80-82].

The scGW approximation is generally accepted as the most advanced DFT calculation method. However, the transition energies of the α spectrum obtained from the scGW-SOC occur at higher energies and the absolute α values are much smaller, compared with the experimental result. In the GW-SOC results of MAPbI₃ and α -FAPbI₃, small peaks appear near E_g and the absorption features near the fundamental

band edge are not reproduced well. As known widely [30,52,79-81], when the DFT calculations are implemented by incorporating SOC, all the bands split into two bands and the band structure becomes slightly indirect (or pseudo-direct). Thus, the α peak observed in the GW-SOC results could be attributed to the SOC effect. It has been confirmed that the SOC-induced band splitting near the fundamental gap is quite sensitive to the orientation and position of the A-site cation [84-86].

In contrast, the absolute α values and peak energies, deduced from the PBE calculations, show excellent agreement with the experimental spectra, although E_g of α -FAPbI₃ is underestimated. At least at this stage, therefore, the PBE calculations provide the best matching with the experimental data. Moreover, the PBE results reproduce the experimental tail-state absorption quite well with similar Urbach energies ($E_U \sim 15$ meV). This is rather surprising as the DFT spectra are obtained assuming a perfect crystal structure with no phonon interaction (0 K). Accordingly, the room-temperature optical spectra of the hybrid perovskites, obtained from the experiments, exhibit ideal sharp absorption feature with quite suppressed tail-state absorption.

16.2.3 Universal Rules for Light Absorption in APbX₃ Perovskites

The large α reduction induced by the replacement of MA⁺ with FA⁺ in APbI₃ (Fig. 16.5) and the strong optical anisotropy confirmed in the DFT calculations (Fig. 16.9) are found to originate from the strong interaction of the A-site cation with the X-site halogen atom [27]. In particular, the visible light absorption in APbX₃ varies rather significantly depending on the A-site cation species. Here, we discuss the optical absorption phenomena in hybrid perovskites based on more detailed DFT analyses using PBE [27].

Figure 16.13 represents the charge density profiles of (a) α -FAPbI₃, (b) MAPbI₃ and (c) CsPbI₃ in the energy region of $-0.6 \sim -0.4$ eV from VBM ($E = 0$ eV). In this figure, the charge density indicated by the colors decreases with the order of red > yellow > green > blue with red being the highest. These results have been obtained from the DFT-optimized structures (see Fig. 16.9 for MAPbI₃ and α -FAPbI₃). The charge density of MAPbI₃ has already been shown in the inset of Fig. 16.10(a).

The charge densities of the selected energy region ($-0.6 \sim -0.4$ eV) correspond to the valence electron states that involve in the E_1 transition in MAPbI₃ (2.46 eV) and the E_2 transition in α -FAPbI₃ (2.34 eV), as confirmed from the V_1 energy positions at the M points in Fig. 16.10. Here, the valence charge states at the M points are considered

Fig. 16.13 Charge density profiles of (a) α -FAPbI₃, (b) MAPbI₃ and (c) CsPbI₃ in the energy region of $-0.6 \sim -0.4$ eV from VBM ($E = 0$ eV). These profiles represent the valence charge densities for the E_2 transition (α -FAPbI₃) and the E_1 transition (MAPbI₃ and CsPbI₃) at the M point (V_1C_1). The charge density decreases with the order of red > yellow > green > blue with red being the highest. The arrows show the a , b , and c axes of the unit cells, and the valence charges of the I atoms along the a , b , and c axes are indicated as $Q_{I,a}$, $Q_{I,b}$ and $Q_{I,c}$, respectively. For α -FAPbI₃ and MAPbI₃, the data reported in Ref. [27] are shown.

specifically, as the visible light absorption at ~ 2 eV in the hybrid perovskites is characterized by the interband transitions near the M point (V_1C_1). Since the transition probability is determined by the interaction of incoming polarized light with the valence state [see Eq. (4.2)], the optical absorption can be studied more directly based on the valence electron (wave function) in the corresponding energy range. Although the conduction states are also important in determining the transition probability, the effect of the Pb-derived conduction bands is treated as a constant contribution in this analysis.

In Fig. 16.13, the charge density profiles of APbI₃ in the same energy region ($-0.6 \sim -0.4$ eV) are shown, but the distribution of the I-5*p* charge densities varies significantly depending on the cation species. More specifically, the I-5*p* valence electron of α -FAPbI₃ concentrates on the I atoms along the a and b axes, and the valence charges of these I atoms ($Q_{I,a}$ and $Q_{I,b}$, respectively) are far larger than that of the c axis direction ($Q_{I,c}$). In the case of MAPbI₃, the valence charge distribution is more uniform, even though $Q_{I,a}$ is larger than $Q_{I,b}$ and $Q_{I,c}$, while quite homogeneous charge distribution ($Q_{I,a} \sim Q_{I,b} \sim Q_{I,c}$) can be seen for CsPbI₃.

It has been confirmed that the distribution of $Q_{I,a-c}$ is modified strongly by the hydrogen bonding interaction expressed by $I(\delta^-) \cdots H(\delta^+) - N(\delta^-)$ [27], where δ^+ and δ^- denote the positive and negative partial charges, respectively, and the magnitude of δ is determined mainly by the electronegativity. In particular, the hydrogen bondings of $I \cdots H - N$, indicated by the dotted lines in Fig. 16.13(a) and (b), lead to the reduction of the N-I distance [26,33]. In the case of MAPbI₃, for example, the N atom position of MA^+ is located more closely to the b - c plane due to the hydrogen bondings formed with the I atoms in the b and c axis directions. The result of Fig. 16.13 shows clearly that the distribution of $Q_{I,a-c}$ is governed primarily by the N-I distance and $Q_{I,a-c}$ decreases significantly when the N-I distance is smaller. This electrostatic interaction between the N and I atoms, referred to as the anti-coupling effect hereafter, plays a critical role for the interpretation of the visible light absorption in hybrid perovskites. In α -FAPbI₃, the intense anti-coupling effect leads to the significant reduction of $Q_{I,c}$ due to the short distance between the I (c axis) and N atoms. As a result, the valence charge of I 5*p* concentrates on the a - b plane. In MAPbI₃, smaller $Q_{I,b}$ and $Q_{I,c}$, compared with $Q_{I,a}$, can also be interpreted by the strong anti-coupling interaction as the N-I distance is shorter for the I atoms on the b and c axes. In contrast, the anti-coupling interaction is negligible in CsPbI₃ due to the lack of the hydrogen bonding.

The highly anisotropic optical transitions at the M point, observed in the DFT results of Fig. 16.9, can be understood based on the above anti-coupling effect. In the case of α -FAPbI₃, for example, the ε_2 value at 2.34 eV corresponds to the E_2 transition, and ε_b

shows the highest ε_2 value at this energy, while ε_c shows the lowest value [Fig. 16.9(e)]. As confirmed from Fig. 16.13(a), the charge density distribution of $Q_{I,a}$ is oriented along the b axis, increasing the polarizability and the resulting ε_2 value significantly in this direction. Consequently, ε_b of α -FAPbI₃ exhibits the maximum ε_2 value, while very low $Q_{I,c}$ results in very small ε_c . In the case of MAPbI₃, the distribution of $Q_{I,a}$ is aligned along the a axis, leading to the higher ε_a value at 2.46 eV (E_1 transition), compared with ε_b and ε_c [Fig. 16.9(d)]. Moreover, the similar ε_2 values of ε_b and ε_c are consistent with the corresponding charge densities ($Q_{I,b} \sim Q_{I,c}$) shown in Fig. 16.13(b). In contrast, CsPbI₃ shows negligible optical anisotropy because of the uniform charge distribution of $Q_{I,a-c}$. Moreover, when the N atom position of MA⁺ is shifted intentionally and is placed at the center position of the C–N bond in Fig. 16.13(b), the charge density distribution of $-0.6 \sim -0.4$ eV becomes more uniform and the strong anisotropic behavior disappears [27]. Accordingly, the anti-coupling effect is induced primarily by the I···H–N hydrogen bonding interaction.

In Fig. 16.9, among the ε_2 spectra calculated for different light polarizations, the ε_2 spectrum having the lowest ε_2 values in the visible region shows the best match with the experimental data. This result indicates that the visible-light absorption in the actual hybrid perovskites is modified significantly by the strong anti-coupling effect. In other words, although the Pb-derived conduction band (C_1) is independent of the A species, the electronic states of the I atoms are influenced strongly by the hydrogen bonding of the A-site cation.

Figure 16.14 summarizes the dielectric functions of (a) α -FAPbX₃, (b) MAPbX₃ and (c) CsPbX₃ (X = I, Br, Cl) obtained from DFT calculations [27]. These dielectric functions have been obtained by replacing the A-site cation in identical PbI₃[−], PbBr₃[−] and PbCl₃[−] structures that are deduced from the structural optimization of MAPbX₃. In this figure, however, only the ε_2 spectra of ε_c (α -FAPbX₃) and ε_b (MAPbX₃ and CsPbX₃) are shown, and the bars indicate the energy positions of the E_1 transition at the M_2 point (V_1C_1). It should be noted that, when the PbX₃[−] structures derived from MAPbX₃ are assumed, the energies of the E_1 and E_2 transitions in α -FAPbX₃ become almost identical. It can be seen that the shapes of the ε_2 spectra are similar when the ε_2 spectra of the same X are compared. Nevertheless, the ε_2 amplitude varies systematically with the A-site cation, independent of X, due to the presence of the anti-coupling effect. In particular, the ε_2 value of the E_1 transition, indicated by the bar, increases notably as the hydrogen bonding interaction becomes weaker.

For the variation of the ε_2 amplitude with the A-site cation, more quantitative analyses have been made. Figure 16.15 shows the ε_2 values for the E_1 transitions in

Fig. 16.14 ϵ_2 spectra of (a) α -FAPbX₃, (b) MAPbX₃, and (c) CsPbX₃ (X = I, Br, Cl) calculated from DFT, together with the corresponding ϵ_2 spectra of (d) α -FAPbX₃, (e) MAPbX₃, and (f) CsPbX₃ obtained by applying the sum rule for APbI₃ and APbBr₃. In the figures, only the ϵ_2 spectra for ϵ_c (α -FAPbX₃) and ϵ_b (MAPbX₃ and CsPbX₃) are shown. The bars indicate the energy positions of the E_1 transition at the M_2 point (V_1C_1). The ϵ_2 spectra of (a)-(c) have been obtained by replacing the A-site cation in the identical PbX₃⁻ structures determined from the structural optimization of MAPbX₃. The data reported in Ref. [27] are shown.

APbX₃, which corresponds to the ϵ_2 values indicated by the bars in Figs. 16.14(a)-(c), as a function of the valence charge ratio expressed by Q_X/Q_{Total} [27]. Here, Q_X/Q_{Total}

Fig. 16.15 (a) ϵ_2 values for the E_1 transition at the M_2 point (V_1C_1) in APbX_3 ($A = \text{FA}^+$, MA^+ , NH_4^+ , Cs^+ ; $X = \text{I}, \text{Br}$) as a function of the valence charge ratio expressed by Q_X/Q_{Total} . The Q_X represents the valence charge of the X-site atom along the a , b , and c axes and is calculated by selecting an energy region that corresponds to the E_1 transition at the M_2 point (V_1C_1), whereas Q_{Total} denotes the total charge of APbX_3 in the same energy region. The closed symbol shows the plot for the lowest Q_X/Q_{Total} in each APbX_3 . The data reported in Ref. [27] are shown.

represents the relative magnitude of each X-site valence charge (i.e., $Q_{X,a}$, $Q_{X,b}$ or $Q_{X,c}$) with respect to the total charge of APbX_3 (Q_{Total}). For the calculation of Q_X/Q_{Total} , the energy ranges that correspond to the E_1 transitions have been selected. In Fig. 16.15, the results for ϵ_a , ϵ_b and ϵ_c in each APbX_3 are plotted and the solid lines show the linear fitting results. It can be seen that the ϵ_2 value increases linearly with Q_X/Q_{Total} , confirming the presence of a universal rule for the effect of the A-site cation. As a result, the ϵ_2 value of ϵ_a , ϵ_b or ϵ_c in APbX_3 increases when the corresponding $Q_{X,a}$, $Q_{X,b}$ or $Q_{X,c}$ becomes larger,

The closed symbol in Fig. 16.15 shows the ϵ_2 value for the lowest Q_X/Q_{Total} in each APbX_3 . As we have seen in Fig. 16.9, the experimental ϵ_2 values are reproduced when the strong anti-coupling effect is considered (i.e., the lowest ϵ_2 values in the DFT spectra). Accordingly, the ϵ_2 values of the closed symbols approximate the light absorption strengths in the hybrid perovskites. These ϵ_2 values lead to a straightforward conclusion; the anti-coupling interaction strengthens with increasing number of N atoms

in the center cation. Since FA^+ has two N atoms, a quite large anti-coupling interaction occurs in $\alpha\text{-FAPbX}_3$, which in turn reduces the visible-light absorption significantly, as observed in the experimental α spectra [see Fig. 16.5(b)]. In contrast, Cs^+ is stabilized at the center position of the PbX_3^- cage [Fig. 16.13(c)] and shows the weak anti-coupling effect. Consequently, the visible light absorption increases in the order $\text{FA}^+ < \text{MA}^+ < \text{Cs}^+$.

As confirmed from Fig. 16.9, the experimental ε_2 spectra of $\alpha\text{-FAPbI}_3$, MAPbI_3 and MAPbBr_3 do not match those calculated assuming optical isotropy [i.e., $(\varepsilon_a + \varepsilon_b + \varepsilon_c)/3$] and the overall visible absorption in these perovskites is minimized by the anti-coupling interaction. As mentioned earlier, MA^+ and FA^+ in the PbI_3^- reorient rapidly with a time scale of 0.5–14 ps at room temperature [19,34–40]. In the DFT calculation that assumes 0 K, however, the cation position is fixed completely and the effect of the cation reorientation is neglected. Even in this case, excellent agreement can be seen between the experimental and DFT results. This result supports the fact that the N-I distance is close and the anti-coupling phenomenon persists even at room temperature. In particular, the molecular dynamics (MD) simulations reveal that the orientation of the center cation is not completely random [35–40], and MA^+ and FA^+ are preferentially directed toward the face center position of the cubic structure [36,37,39,40] by maintaining the stable I-H (or I-N) distance even at elevated temperature [36,38,39,40]. Accordingly, the anti-coupling effect observed in the room-temperature optical spectrum can be interpreted by the strong hydrogen bonding effect of MA^+ and FA^+ .

On the other hand, the optical effect of X on the ε_2 spectrum of hybrid perovskites can be modeled according to the sum rule [27], given by the following expression [78]:

$$\int E\varepsilon_2(E)dE = \text{const.} \quad (16.1)$$

When the ε_2 spectrum is shifted toward higher energy by ΔE , the sum rule requires that the ε_2 peak amplitude reduces to $E/(E + \Delta E)$ because $\int E\varepsilon_2(E)dE =$

$\int (E + \Delta E_g)\varepsilon_2(E + \Delta E_g)dE$. As confirmed from Fig. 16.14(a)–(c), with decreasing halogen mass ($\text{I} > \text{Br} > \text{Cl}$), the whole ε_2 spectrum shifts toward higher energy and the ε_2 amplitude decreases. Such spectral changes induced by the X replacement can be expressed by applying Eq. (16.1). Figure 16.14 shows the ε_2 spectra of (d) $\alpha\text{-FAPbX}_3$, (e) MAPbX_3 and (f) CsPbX_3 obtained from the calculations assuming the sum rule [27]. In these results, the ε_2 spectra of APbI_3 and APbBr_3 are shifted so that the E_1 transition energies match those of APbCl_3 . In this case, the amplitude of the shifted ε_2 spectra is

reduced further by applying the sum rule. Under these assumptions, the ε_2 values for the E_1 transition become similar and all the spectra show reasonable overlap in a low energy region (< 3.7 eV). Accordingly, the ε_2 amplitude variation induced by X can simply be interpreted by the change in the transition energy.

16.3 Operating Principles of Hybrid Perovskite Solar Cells

In this section, to understand the working principles of hybrid perovskite solar cells, we will examine the photocarrier generation/collection in MAPbI₃ solar cells based on (i) the internal quantum efficiency (IQE) simulation of a standard solar cell [26], performed by the optical admittance method assuming a perfectly flat structure (Section 2.2 in Vol. 2) and (ii) the characterization of the optical and recombination losses in MAPbI₃ solar cells [87], determined from the EQE analysis using the e-ARC method (Section 2.3 in Vol. 2). These IQE and EQE calculations have been performed using the MAPbI₃ optical constants shown in Fig. 16.5 (see also Fig. 10.2 in Vol. 2).

16.3.1 Optical Simulation of a CH₃NH₃PbI₃ Solar Cell

Figure 16.16(a) shows the IQE and internal absorptance (IA) spectra for a MAPbI₃ solar cell consisting of glass/SnO₂:F (600 nm)/TiO₂ (200 nm)/MAPbI₃ (400 nm)/spiro-OMeTAD (500 nm)/Ag [26]. The IQE and IA spectra can be calculated by $IQE = EQE/(1 - R)$ and $IA = A/(1 - R)$, where R and A represent the reflectance and absorptance of the solar cell structure, respectively. By assuming a perfectly flat structure, the R and EQE spectra can be calculated directly using Eqs. (2.18) in Vol. 2 and (2.26) in Vol. 2, respectively. In the optical simulation of Fig. 16.16(a), the effect of the multiple light reflection/transmission within the glass substrate is neglected (Section 2.2.2 in Vol. 2) and 100% collection efficiency of generated carriers is assumed for the perovskite layer. This simulation result can be reproduced by using the optical constants of glass (Fig. 13.1 in Vol. 2), TiO₂ (Fig. 11.12 in Vol. 2), MAPbI₃ (Fig. 10.2 in Vol. 2), spiro-OMeTAD (Fig. 9.18 in Vol. 2) and Ag (Fig. 12.6 in Vol. 2) summarized in Part II (Vol. 2) of this book. For the SnO₂:F layer [26], however, we assume the Drude parameters of $A_D = 0.919$ eV and $\Gamma = 0.129$ eV, which correspond to $N_{opt} = 1.2 \times 10^{20}$ cm⁻³ and $\mu_{opt} = 49$ cm²/(Vs) (see Section 18.3.4), together with the band-edge Tauc-Lorentz parameters of $A = 44.55$ eV, $C = 12.00$ eV, $E_g = 3.30$ eV and $E_0 = 7.00$ eV [see Eqs. (11.1) in Vol. 2 and (11.2) in Vol. 2]. The above calculation shows that the average R value in the visible region ($\lambda = 400\sim 700$ nm) is $\sim 15\%$ and a strong

Fig. 16.16 (a) IQE spectrum of the MAPbI₃ layer and IA spectra of the component layers in the glass/SnO₂:F (600 nm)/TiO₂ (200 nm)/MAPbI₃ (400 nm)/spiro-OMeTAD (500 nm)/Ag structure [26], (b) normalized partial IQE spectra for the MAPbI₃, and (c) integrated J_{sc} for perovskite solar cells with discrete MAPbI₃ thicknesses from 100 to 1000 nm [26]. In (b), ΔJ_{sc} shows the J_{sc} component generated within the 1-nm-thick MAPbI₃ sublayer, and integrated J_{sc} values relative to the depth from the TiO₂ interface and λ are also shown. The arrows in (b) show the E_g (E_0), E_1 , and E_2 positions. In (c), the solid circles denote the end points of the MAPbI₃ thickness and the dotted line shows the J_{sc} values obtained by varying the MAPbI₃ layer thickness in the solar cell.

interference effect appears in the R and EQE spectra due to the assumed flat structure.

As shown in Fig. 16.16(a), for the $\text{SnO}_2\text{:F}$, the strong light absorption occurs at $E \geq 3.3$ eV ($\lambda \leq 375$ nm) due to the interband transition, whereas the light absorption at $\lambda > 375$ nm indicates the contribution by the free carrier absorption (Chapter 18). The TiO_2 layer shows the interband transition at $\lambda < 385$ nm. Since E_g of spiro-OMeTAD (2.95 eV) is higher than that of MAPbI_3 , the light absorption in this layer is negligible. In addition, the light absorption in the Ag back electrode occurs mainly in the λ region below E_g of MAPbI_3 due to the strong light transmission in this regime. In Fig. 16.16(a), IQE of MAPbI_3 is quite high in a wide λ region of 400–700 nm and the IQE maximum in this range is limited by the free carrier absorption of the $\text{SnO}_2\text{:F}$ layer.

Under AM1.5G conditions, J_{sc} of the solar cell is 19.9 mA/cm^2 with a reflection loss of 3.6 mA/cm^2 and parasitic optical losses of 1.3 mA/cm^2 ($\text{SnO}_2\text{:F}$), 0.3 mA/cm^2 (TiO_2), and 0.1 mA/cm^2 (Ag) in the energy region above $E_g = 1.61$ eV (MAPbI_3). When a natural texture is present, the front light reflection is suppressed and J_{sc} of the MAPbI_3 solar cell increases further.

To visualize carrier generation within the MAPbI_3 layer, partial IQE spectra are calculated by dividing the MAPbI_3 layer into 400 sublayers (i.e., 1-nm thick sublayer). In Fig. 16.16(b), the partial IQE calculated for different depths from the interface and wavelengths are shown. These IQE values are normalized relative to the maximum IQE value and, if the partial IQE spectra are integrated, the IQE spectrum of Fig. 16.16(a) can be obtained. The arrows in Fig. 16.16(b) denote the λ positions that correspond to the E_g (E_0), E_1 and E_2 transitions. In the E_2 transition regime, the partial IQE is limited by light absorption in the upper $\text{SnO}_2\text{:F}$ and TiO_2 layers. At $E \geq E_1$, the partial IQE exhibits rapid decay with increasing depth because of strong light absorption within MAPbI_3 . In contrast, in the region of $E_0 \leq E < E_1$, the IQE values are low because of the smaller α values and photocarriers are generated uniformly throughout the entire MAPbI_3 layer with the appearance of the optical interference effect. In this region, the electrons and holes that are generated near the front and rear interfaces, respectively, need to travel through the whole MAPbI_3 layer. Therefore, the high J_{sc} of 20 mA/cm^2 observed experimentally supports the efficient carrier collection within the whole absorber layer.

In Fig. 16.16(b), ΔJ_{sc} shows the J_{sc} component generated within the 1-nm-thick MAPbI_3 sublayer, and the integrated J_{sc} values relative to the depth are also shown. The integrated values obtained for each λ are also indicated. The calculation result of ΔJ_{sc} confirms the intense carrier generation near the TiO_2 interface and J_{sc} increases gradually at larger depth by the carrier collection in the low α region ($E_0 \leq E < E_1$). It

should be emphasized that the contribution of J_{sc} at $\lambda \geq 500$ nm accounts for 73% of the total J_{sc} , confirming that the longer wavelength response is critical to realize a high J_{sc} [47].

Figure 16.16(c) summarizes the change in J_{sc} with MAPbI₃ thickness [26]. The solid lines indicate the integrated J_{sc} estimated from MAPbI₃ layers with discrete thicknesses ranging from 100 to 1000 nm, and the end points are shown by the solid circles. The dotted line in this figure shows the J_{sc} values obtained by changing the MAPbI₃ layer thickness. In Fig. 16.16(c), the difference in J_{sc} observed between the dotted line and the solid line for the 1000 nm thickness indicates the influence of the back-side reflection. When the absorber thickness is 400 nm, for example, the contribution of J_{sc} improved by the back-side reflection is 2.4 mA/cm². Accordingly, the effect of the back-side reflection is relatively large in the hybrid solar cell and the light is absorbed effectively even in the thin layers. The optimum thickness of 400 nm confirmed in Fig. 16.16(c) can therefore be interpreted as a consequence of the optical confinement effect. The enhanced light absorption is particularly necessary for tandem-type solar cells and the EQE simulation of a MAPbI₃ top cell confirms the importance of the strong optical confinement in the long-wavelength regime (Fig. 6.8).

16.3.2 Carrier Loss Mechanisms

The optical and recombination losses in MAPbI₃ solar cells can be evaluated from the EQE analyses using the e-ARC method (Section 2.3 in Vol. 2). The ARC method is a calculation method developed originally for the estimation of the optical losses in submicron-textured solar cells, whereas the extended ARC (e-ARC) method further allows the analysis of the recombination loss. Here, from the recombination losses deduced from the e-ARC analyses [87], carrier recombination dynamics in MAPbI₃ solar cells are discussed.

Figure 16.17 shows the optical models for MAPbI₃ solar cells (a) with an HTL [88] and (b) with no HTL [89], and the corresponding EQE analysis results are shown in (c) and (d), respectively [87]. The solar cell with the HTL has a structure of glass/SnO₂:F/TiO₂/MAPbI₃/polytriarylamine(PTAA)/Au and shows a high efficiency of 17.6 % ($V_{oc} = 1.1$ V, $J_{sc} = 20.5$ mA/cm² and $FF = 0.78$) [88]. This device incorporates the PTAA layer as the HTL and has a simple structure without a mesoporous TiO₂ layer. In the optical model of Fig. 16.17(a), a complicated structure of SnO₂:F/SiO₂/SnO₂/glass (TEC-8, see Fig. 18.25) has been simplified to a SnO₂:F (600

Fig. 16.17 Optical models for MAPbI₃ solar cells (a) with an HTL [88] and (b) with no HTL [89], and the corresponding EQE analysis results for the MAPbI₃ solar cells (c) with the HTL and (d) with no HTL. In (a) and (b), the values represent the layer thicknesses in the optical model, and the thickness of the HTL layer in (a) is assumed to be zero. For the MAPbI₃ layers, the presence of optical dead layers near the TiO₂ interfaces is assumed. In (c) and (d), the EQE analyses are carried out based on the e-ARC method using the carrier collection length (L_C) as a fitting parameter. The calculated EQE spectra are shown by red lines. The hatched-line regions show the EQE losses originating from the front dead layers. The analysis data are taken from Ref. [87].

nm)/glass structure [26] and the layer thicknesses were deduced directly from the SEM images. In the optical model, however, the PTAA layer thickness is assumed to be zero, since the optical constants of the PTAA layer are unknown and the optical effect of the

wide-gap PTAA layer ($E_g \sim 3$ eV) is negligible. For the calculation, the optical constants of $\text{SnO}_2\text{:F}$ (Fig. 11.11. in Vol. 2), TiO_2 (Fig. 11.12 in Vol. 2), MAPbI_3 (Fig. 10.2 in Vol. 2) and Au (Fig. 12.8 in Vol. 2) have been used. In the EQE analyses, the carrier recombination in the $\text{TiO}_2/\text{MAPbI}_3$ interface region is further assumed. This recombination is modeled by simply dividing a MAPbI_3 bulk layer into two layers and treating a thin layer located at the TiO_2 interface as a “dead layer” that allows no carrier extraction [see Fig. 16.17(a)].

In Fig. 16.17(c), the absorptance spectra of the solar-cell component layers calculated using the optical model of Fig. 16.17(a) are shown. The R_{ARC} shows the reflectance deduced from the ARC method, and the R_{ARC} spectrum includes the contribution of light scattering generated in the textured solar cell (see Section 2.2.3 in Vol. 2). In this figure, the yellow-colored region shows the light absorption in the MAPbI_3 , and the hatched-line region corresponds to the EQE loss caused by the front dead layer. The red line indicates the EQE spectrum calculated by e-ARC, from which the carrier collection length (L_C) can be determined. In the EQE analysis using the e-ARC method, the L_C value modeled by $H(\lambda) = 1 - \exp[-\alpha(\lambda)L_C]$ is used as a fitting parameter, where $H(\lambda)$ and $\alpha(\lambda)$ are the carrier collection efficiency and absorption coefficient spectrum of the absorber layer, respectively. In this simple model, L_C shows a meaningful value only when L_C is smaller than the layer thickness and we obtain $L_C = \infty$ when all the carriers are collected (see Fig. 2.14 in Vol. 2). In Fig. 16.17(c), the calculated EQE spectrum shows good agreement with the experimental result (open circles) when the thickness of the dead layer is 4 nm with $L_C = \infty$, indicating that the dominant recombination occurs only near the TiO_2 interface and the carrier loss near the HTL interface is negligible.

On the other hand, the slight disagreement of the calculated EQE, observed at $\lambda = 720\text{--}800$ nm, can be attributed to the calculation errors of R_{ARC} . Specifically, when the layer thickness of solar cells is thin, the interference fringe becomes large and the calculation of R_{ARC} by the ARC method fails near the E_g region where R shows a sharp increase. This problem can be avoided if the experimental R spectrum obtained from an actual solar cell is used in Eq. (2.26) in Vol. 2. In the analysis of Fig. 16.17(c), however, the error in the R_{ARC} calculation affects J_{sc} only slightly (0.4 mA/cm^2).

The solar cell with no HTL shown in Fig. 16.17(b) has a structure of glass/ $\text{SnO}_2\text{:F}$ /compact TiO_2 /mesoporous $\text{TiO}_2\text{-MAPbI}_3/\text{MAPbI}_3/\text{Au}$ [89]. Quite fortunately, the optical response of the mesoporous $\text{TiO}_2\text{-MAPbI}_3$ mixed-phase layer can be expressed as the two separate flat layers of the TiO_2 and MAPbI_3 [26]. In this analysis, the TiO_2 volume fraction within the mesoporous layer is assumed to be 30% (porosity 70%).

Fig. 16.18 Band diagrams proposed for MAPbI₃ solar cells with an HTL (spiro-OMeTAD) and with no HTL [87]. In this figure, L_C represents the carrier collection length determined from the EQE analyses of Fig. 16.17.

Figure 16.17(d) shows the result of the EQE analysis performed for the solar cell with no HTL [87]. It can be seen that the experimental EQE spectrum of this solar cell is quite different, compared with the solar cell with the HTL. In particular, the EQE response in the longer λ region decreases significantly when an HTL is not present [90-93]. The red line in this figure represents the EQE spectrum calculated assuming the carrier recombination in the front and rear interface regions using e-ARC. This EQE analysis reveals that the thickness of the front recombination layer is 10 nm with $L_C = 280$ nm. Thus, the above result confirms that the carrier collection is hindered strongly when the HTL is not present and the effect of the carrier recombination appears primarily as the reduction of the EQE response in the low α region ($\lambda > 600$ nm).

Figure 16.18 shows the band diagrams proposed for MAPbI₃ solar cells (a) with an HTL (spiro-OMeTAD) and (b) with no HTL [87]. It can be seen that, in MAPbI₃ solar cells, the electrons and holes generated within the absorber layer are collected in the front and rear electrodes without any potential barriers [6]. It is generally assumed that the operation of MAPbI₃ solar cells occurs by the formation of a $p-i-n$ type structure [11,94-97], as confirmed by the electron-beam induced current (EBIC) [94,98] and Kelvin probe force microscopy [95] characterizations. However, the carrier type of MAPbI₃ layers is basically n -type, and the Fermi level (E_F) of a standard MAPbI₃ locates more closer to CBM with an electron concentration of $\sim 10^{17}$ cm⁻³ [99]. When

the MAPbI₃ layer shows *n*-type conductivity, the electric field is expected to concentrate at the MAPbI₃(*n*)/HTL(*p*) interface with a weak electric field at the TiO₂(*n*)/MAPbI₃(*n*) interface, as illustrated in Fig. 16.18(a). Thus, the relatively strong front-carrier recombination near the TiO₂ interface can be interpreted by the weaker electric field in this region. In contrast, the carrier recombination in the solar-cell bottom region is suppressed most likely due to the presence of the strong electric field near the HTL. From the above results, the electric-field-assisted carrier collection by the formation of a *p*-*n*⁻-*n* type structure has been proposed for MAPbI₃ solar cells [87]. The rapid degradation of the solar cell characteristics upon air exposure could be attributed, in part, to the elimination of the strong electric field in the rear p-n junction region.

When the HTL is not present, however, the flat-band formation is expected to occur by the absence of the electric field in the bottom region [Fig. 16.18(b)], as evidenced by EBIC [98]. In this device, the photocarrier collection occurs through the carrier diffusion, and the intensified recombination in the rear interface region lowers the EQE response in the longer λ region [87,92]. The lower V_{oc} observed in MAPbI₃ solar cells with no HTL [90-92,100] can be interpreted by the smaller built-in potential.

Earlier DFT studies of MAPbI₃ revealed that mid-gap states are not created by the vacancy/interstitial-type defects in MAPbI₃ [64,101,102], although the formation of complex defects is still possible [103]. Moreover, in the grain boundary region of MAPbI₃, the PbI₂-rich phase having larger E_g is formed, suppressing the carrier recombination in the grain boundary region effectively [104]. In MAPbI₃ solar cells, therefore, the carrier recombination is generally considered to occur in the interface regions. Nevertheless, V_{oc} of MAPbI₃ solar cells varies with the grain size [105], suggesting the possible recombination in the grain boundary region.

Figure 16.19 illustrates the optical and recombination losses in the MAPbI₃ solar cell with an HTL [87], determined from the EQE analysis of Fig. 16.17(c). The numerical values in the figure represent the corresponding current densities in units of mA/cm². The maximum J_{sc} value attainable under AM1.5G conditions is also shown and, from the ratio of output J_{sc} divided by the maximum attainable J_{sc} value, the optical gain of this solar cell is determined to be 70% (18.7 mA/cm²). This particular solar cell shows a large reflection loss (3.2 mA/cm²) due to the lack of an anti-reflection coating and a rather flat layer structure with a thin absorber-layer thickness (~300 nm). The parasitic absorption by the front TCO layer, originating mainly from free carrier absorption, reduces J_{sc} further by 3 mA/cm². The parasitic absorption of the TCO can be reduced largely by employing high-mobility TCO layers (Chapter 19). The recombination loss indicated in this figure corresponds to the interface recombination in the TiO₂ interface

Fig. 16.19 Optical and recombination losses deduced from the EQE analysis performed for the MAPbI₃ solar cell shown in Fig. 16.17(c) [87]. The numerical values represent the corresponding current densities in units of mA/cm². The maximum J_{sc} value attainable under AM1.5G conditions is also indicated. The optical gain shows the ratio of output J_{sc} divided by the maximum attainable J_{sc} value.

region.

It should be emphasized that the MAPbI₃ solar cell shows quite small overall optical losses, compared with other photovoltaic devices including CuInGaSe₂ [Fig. 2.11(b) in Vol. 2], Cu₂ZnSnSe₄ [Fig. 2.15(b) in Vol. 2] and CdTe [Fig. 2.21(b) in Vol. 2] solar cells. In particular, the parasitic absorption within the TiO₂ and HTL layers is negligible and the major optical loss occurs only in the front TCO layer, which can be optimized further. Thus, a quite high conversion efficiency reported for MAPbI₃ solar cells (~20%) can be understood partly by the low parasitic absorption within the solar cell component layers [26].

As a result, the excellent performance of MAPbI₃ hybrid solar cells can be interpreted as being due to a combination of (a) high α values comparable to those of CuInGaSe₂ and CdTe (Fig. 1.6), (b) E_g being close to the optimum value of 1.4 eV (Fig. 1.5 in Vol. 2) and the sharp absorption onset near E_g (low E_U) (Fig. 16.6), which is expected to reduce the open-circuit voltage loss [see Fig. 1.7(b) in Vol. 2] [45], (c) efficient free carrier generation by non-excitonic semiconductor-type transitions within the PbI₃⁻

component in the whole visible region (Fig. 16.9), (d) low levels of carrier recombination by electric-field assisted carrier collection (Figs. 16.17 and 16.18) and (e) the high optical confinement and low parasitic absorption in the solar cells (Figs. 16.16 and 16.19).

16.4 Real Time Spectroscopic Ellipsometry of Thin Film Perovskites

Real time spectroscopic ellipsometry (RTSE) monitoring enables fundamental studies of (i) the growth evolution of both perovskite thin films (MAPbI_3 and related materials) and component materials (PbI_2 and other inorganics, MAI and other organics) as well as (ii) the stability of the resultant films post-deposition. These studies enable detection of phase instabilities and changes in composition and structure occurring either during growth as a function of different deposition conditions or after deposition as a function of external stimuli known to cause perovskite decomposition or phase changes.

There are several methods already employed for perovskite deposition, each with their own region of parameter space yielding optimized materials for devices. Some of these methods are more easily adapted to RTSE monitoring of film growth than others. One case study described here will involve vapor deposition of MAPbI_3 enabled by evaporation of PbI_2 in a MAI vapor rich vacuum chamber. Figure 16.20 shows a schematic of a vacuum chamber outfitted with windows for in situ RTSE measurements during evaporation of PbI_2 , MAI, and other source materials. This evaporation-based approach has multiple utility: (i) PV device quality MAPbI_3 can be made as films and layers in functioning solar cells and (ii) fundamental studies of the component materials MAI and PbI_2 are also enabled. Figure 16.21 shows spectra in ε for component MAI and PbI_2 as obtained from RTSE measurements of their respective component films with analysis using a multiple time point approach to obtain the most average spectra in ε for each film [106,107]. For single component materials like MAI and PbI_2 , multiple time and global sum-of- σ ($\Sigma\sigma$) minimization approaches are suitable for ascertaining ε as well as the time evolution of structural parameters such as bulk layer and surface roughness thickness, as has been detailed for other PV absorber and component materials in other chapters. Spectra in ε for MAPbI_3 shown in Fig. 16.21 has been obtained using a divided spectral range analysis [108] for ellipsometric spectra collected ex situ from a vapor deposited film. This particular sample had relatively high crystalline quality, but a small fraction of PbI_2 also present as confirmed with x-ray diffraction and analysis of ellipsometric spectra using ε for phase-pure solution deposited MAPbI_3 and PbI_2 in a Bruggeman effective medium approximation [107].

Fig. 16.20 Schematic for real time spectroscopic ellipsometry (RTSE) monitoring of MAPbI₃ from multi-source vapor deposition. Adapted from [106].

Fig. 16.21 Reference spectra in ϵ for vapor deposited PbI₂, MAI, and MAPbI₃ used for analysis of RTSE data collected during growth and degradation [107].

Due to the optical contrast between MAI, PbI₂, and MAPbI₃ shown in Fig. 16.21, it is possible to deduce some relative fractional components of each in a phase-segregated multi-component film from ellipsometric spectra. When ellipsometric spectra are collected in situ as a function of time, like RTSE, it is possible to better understand the dynamics of what occurs—namely the appearance or disappearance of particular

components. Two case studies to be investigated here involve monitoring (i) vapor deposition of perovskite films enabled by in situ RTSE measurements and (ii) degradation of a film post-deposition upon exposure to laboratory ambient air. For studies of growth evolution, the deposition system must be adaptable to in situ RTSE via appropriate windows and a clear beam-path. In the case of post-deposition changes in films, all that is required is that a sample be first produced and that the post-deposition environment enables in situ ellipsometry measurements. Here we have applied the simplest post-deposition environment possible, namely leaving the sample exposed to laboratory ambient conditions while mounted upon a spectroscopic ellipsometer.

16.4.1 RTSE during Vapor Deposition

As the first example, consider RTSE measurements collected in situ during thin film vapor deposition using MAI and PbI_2 sources. The intended film composition is predominately polycrystalline MAPbI_3 , possibly with some other components to manipulate the grain boundary chemistry. If not in the appropriate region of deposition parameter space, it is likely to produce significant amounts of phase-segregated $\text{PbI}_2 + \text{MAI}$ instead of the desired perovskite. These phase segregated regions have been observed near the substrate/film and film/ambient interfaces, possibly where interfacial effects impact perovskite stability. The relative amounts of all components may vary with time during deposition. For vapor deposited materials, changes in source-to-substrate throw distance and deposition sequence (simultaneous or alternating source fluxes) can manipulate the final relative amounts of each component. By analyzing vapor deposited films prepared under a variety of conditions, a relatively flexible structural model has been developed to analyze ellipsometric spectra as shown in Fig. 16.22 [106]. The model itself relies on (i) a known substrate, with optical properties and structure most directly obtained from an ellipsometry measurement prior to film deposition, (ii) a substrate-adjacent Bruggeman effective medium approximation (EMA) layer consisting of $\text{PbI}_2 + \text{MAI}$, (iii) a MAPbI_3 layer, (iv) a EMA layer of $\text{PbI}_2 + \text{MAPbI}_3 + \text{void}$, and (v) a surface roughness EMA layer of 0.5 void and 0.5 $\text{PbI}_2 + \text{MAI}$ material fractions. Reference spectra in ϵ shown in Fig. 16.21 are used for the component materials in this structure. To aid in interpretation of the results, individual layer thicknesses and material fractions are combined into effective material thicknesses (d_{eff}) by multiplying each layer thickness (d) by the relative material fraction within that layer (f) such that

Fig. 16.22 Structure model used in analysis of RTSE data collected during vapor deposition and post-deposition degradation. The layered structure for analysis of ellipsometric spectra consists of (i) a known substrate, (ii) a substrate-adjacent Bruggeman effective medium approximation (EMA) layer consisting of PbI_2 + MAI, (iii) a MAPbI_3 layer, (iv) a EMA layer of PbI_2 + MAPbI_3 + void, and (v) a surface roughness EMA layer of 0.5 void and 0.5 PbI_2 + MAI material fractions. The effective material thicknesses of MAPbI_3 , PbI_2 and MAI near the substrate, and surface PbI_2 and MAI are calculated from the sum of the layer thicknesses weighted by the respective material fraction. Adapted from [106,107].

$d_{\text{eff}} = d \times f$. These effective material thicknesses of MAPbI_3 , PbI_2 and MAI near the substrate, and surface PbI_2 and MAI are calculated from the sum of effective material thicknesses of each layer.

Figure 16.23 shows effective thicknesses of the phase segregated PbI_2 and MAI near the film surface and near the substrate as well as the MAPbI_3 component [106]. This particular sample has been made on thermal oxide (250 Å thick) coated crystal silicon with a throw distance of 50 cm and MAI and PbI_2 sources heated to 100 and 300°C, respectively. For the first ~ 10 minutes of the deposition, MAPbI_3 grows with some excess surface PbI_2 . MAPbI_3 thickness increases throughout the deposition, however at 10 minutes of growth effective thicknesses of PbI_2 and MAI near the substrate begin to increase. After ~20 minutes variable amounts of both PbI_2 and MAI appear on the film surface. The appearance of significant amounts of both PbI_2 and MAI near the surface and substrate interfaces implies that moderately thin MAPbI_3 grown under these conditions may not be stable. After sufficient time has passed, ~72 minutes, the

Fig. 16.23 Growth evolution from RTSE in the form of effective material thicknesses of MAPbI₃, PbI₂ and MAI near the substrate, and surface PbI₂ and MAI as functions of time during vapor deposition [106].

near-substrate PbI₂ and MAI effective thicknesses stabilize and the MAPbI₃ thickness deposition rate increases.

To summarize, RTSE analysis of *this deposition* shows three stages: (i) an initial thin MAPbI₃ layer with a slightly lower growth rate from 0-10 minutes, (ii) continued MAPbI₃ growth accompanied by phase segregation of MAI and PbI₂ from 10-72 minutes, and (iii) stabilization of MAI and PbI₂ effective thicknesses and an increase in growth rate for MAPbI₃ from 72 minutes until the end of the deposition. Samples prepared under different deposition conditions have shown immediate appearance of MAI and PbI₂ components with the perovskite, appearance of these components followed by formation of the perovskite, or different behaviors for each component layer. The ability to apply RTSE during vapor deposition shows the possibility of real time monitoring and control of film composition. These types of RTSE measurements have been made both on test substrates for underlying smoothness and structural simplicity (e.g. oxide covered crystal silicon and glass) and in the superstrate PV device configuration on rough SnO₂:F coated glass with an electron selective layer (ESL).

16.4.2 RTSE Post-Deposition

As mentioned elsewhere in this chapter, these perovskites may undergo reversible or irreversible changes with temperature variations, applied bias, exposure to moisture and humidity, and under ultraviolet light. In principle, in situ spectroscopic ellipsometry enables monitoring of the changes in optical response and structure for samples prepared by any deposition method if the measurements can be conducted in a suitably controlled environment so that “before” and “after” characteristics are observed. In situ RTSE enables data to be collected during the respective process, whatever it may be. Temperature controlled stages, biased electrical contacts on films, environmental chambers, and unpolarized intense light sources can be readily applied to these kinds of samples. The sample may begin to change immediately upon exposure to laboratory ambient conditions. This exposure to laboratory ambient, nominally room temperature $\sim 20^{\circ}\text{C}$, illuminated, and relative humidity $\sim 50\%$, may cause a MAPbI_3 perovskite to change and decompose into its constituent components PbI_2 and MAI.

In situ RTSE has been performed on a vapor deposited initially predominately MAPbI_3 film prepared on soda lime glass placed on an ellipsometer [107]. Ellipsometric spectra have been collected every 5 minutes for 48 hours. To fit ellipsometric spectra at each measurement time, reference ε from Fig. 16.21 and the structural model from Fig. 16.22 used to describe RTSE of vapor deposition growth have been applied to describe phase segregation and film decomposition. The behavior of the sample post-deposition in ambient laboratory conditions shows similarities to that observed for un-optimized material during growth. Namely, phase segregated MAI and PbI_2 components accumulate near the substrate/film and film/ambient interfaces. Effective material component thicknesses are shown in Fig. 16.24. It is clear that the MAPbI_3 effective thickness decreases with time over the RTSE measurements. This decrease in effective MAPbI_3 thickness occurs with initial increases in the MAI and PbI_2 effective thicknesses near the substrate and surface, implying that phase segregation of the perovskite has occurred. After about 1500-2000 minutes have passed, the amount of MAI and PbI_2 components near the substrate begin to decrease while the PbI_2 near the surface continues to increase and the surface MAI thickness is much lower in magnitude. The sum of all PbI_2 increases with time, MAPbI_3 decreases with time, and MAI first increases then weakly decreases. This indicates that as some of the perovskite is decomposing, the constituents may be reacting.

Fig. 16.24 Effective material thicknesses of MAPbI₃, PbI₂ and MAI near the substrate, and surface PbI₂ and MAI as functions of time during post-deposition exposure in laboratory ambient conditions monitored by RTSE [107].

Fig. 16.25 Mean square error (MSE) as a function of time for fits to RTSE data collected during post-deposition exposure to laboratory ambient conditions, with results in Fig. 16.24 [109].

An interesting observation comes from the quality of the fit over the course of decomposition, represented by the mean square error (MSE) in Fig. 16.25. Reference spectra in ε are used over the full measurement time, however the quality of the fit decreases (MSE increases) at later times. Recent work has shown that changes in the perovskite component optical properties can reduce and stabilize the MSE [109]. A possible explanation for the changes in ε observed may be related to the sum of the effective MAI thicknesses. When considering the density and expected amount of MAI and PbI₂ produced by decomposition of MAPbI₃, the effective thicknesses shown

in Fig. 16.24 imply that some MAI is not accounted in the model. Process parameter dependent phase diagrams for these perovskites [110] indicate that a “stacked perovskite sheet” structure consisting of thin perovskite layers interspaced by MAI exists. This explanation possibly accounts for the missing effective MAI thickness, and the transition from perovskite to stacked perovskite sheet structure could be responsible for the variation in ε needed to reduce MSE of RTSE data fitting at later times during degradation.

16.5 Characterization of Degradation in Hybrid Perovskite Materials

One of the key aspects to achieve the full potential of PV devices based on hybrid perovskites is to control the stability of these materials. Up to date, different fabrication protocols can be followed resulting in different film morphologies which might lead to variable degradation pathways [111]. However, most approaches to produce materials, mainly low-temperature evaporation or solution-based, are apt to result in similar high-performance materials and subsequent devices with rather comparable efficiencies and lifetimes. Several environmental factors such as humidity, heat, and illumination can compromise the stability both of the perovskite materials, in particular MAPbI₃, and of the solar cell devices. The effect of humidity as the main degradation agent has been investigated by SE, and different results have been detected, from reversible hydration to irreversible decomposition of MAPbI₃ [51]. The perovskite structure of MAPbI₃ is depicted in Fig. 16.26(a). Two hydrated MAPbI₃ crystal phases form by water incorporation with either one or two water molecules per formula unit. The monohydrate and dihydrate crystal structures are shown in Fig. 16.26 (b) and (c), respectively.

Fig. 16.26 Crystal structures of the phases related to hydration of MAPbI₃: (a) pristine perovskite phase, (b) MAPbI₃•H₂O (monohydrate), and (c) MAPbI₃•2H₂O (dihydrate).

Fig. 16.27 Dielectric functions determined by ellipsometry of a) MAPbI₃ single crystal and b) MAPbI₃·H₂O monohydrate phase. Data from Ref. [51]. Values of ϵ_2 in the sub-bandgap region are spurious, due to the modelling. Arrows indicate the energies of the main critical points obtained from fits to second derivative spectra.[51,52]

In the seminal work by Leguy et al. [51], solution-processed perovskite films, single crystals and full devices were exposed to high relative humidity (RH) around 75% ($\pm 5\%$). The hydration mechanism was first investigated optically by SE on single crystals of MAPbI₃. The crystals were exposed to a humid ambient with nitrogen as carrier gas at room temperature (21°C). Figure 16.27 shows the dielectric function determined in a crystal before (a) and after 60 h of exposure (b) to the humid ambient. The effect of water was to form a new crystal structure identified by x-ray diffraction as the monohydrate MAPbI₃·H₂O, see Fig. 16.26(b). The initially black MAPbI₃ crystal with band gap ~ 1.6 eV becomes transparent (whitish) in the wet ambient, with a band gap of ~ 3.1 eV.

When subsequently exposed to a dry atmosphere, the crystal instantly starts to convert back to the initial structure, as displayed in Fig. 16.28, with the process ending in the full recovery of the material. The spectra measured both during hydration or dehydration can be well understood by an effective Bruggeman mixture of the two phases, therefore suggesting that water is highly mobile within the perovskite lattice with the transformation occurring more or less homogeneously throughout the sample. Both from diffraction and SE investigations it appears that dehydration is faster than

hydration. However, the time needed for the transformation depends from the initial material condition: the presence of defects such as pores or grain boundaries facilitate water diffusion through the sample. Consequently, the transformation of thin polycrystalline films starts almost instantaneously [51,59] because water penetrates more efficiently within the grains than in compact single crystals. The study on thin films [51] lead to the following equations for the hydration of MAPbI₃:

Eq. (16.2) describes a two-step process in which the crystal structure of MAPbI₃ is first saturated with one water molecule per unit cell, followed by the insertion of a second water molecule upon longer exposure to humidity. Accordingly, the monohydrate is an intermediate product that can be easily converted back to MAPbI₃. However, when the reaction is driven further to the right of the stoichiometric equation (16.2), the formation of the dihydrated crystal phase initiates the decomposition with formation of PbI₂ and release of water ending in an irreversible degradation of the film. In polycrystalline film material the transformation is reversible up to a certain point before any dihydrate formation. Later, both reactions may happen simultaneously at different film locations. For instance, decomposition may appear at grain boundaries while there are still grains of pristine MAPbI₃. In Ref. [51], this situation was detected after a monohydrate content in the film of about 20% was reached. Then, the roughness increased dramatically with formation of needle-like structures which are presumably the dihydrate. Therefore, the exact degradation pathways depend on the sample morphology. Furthermore, temperature and illumination also play a role but the interplay of all causes is not well established yet. A decisive factor is whether water condensation occurs on the surface of the film or not [51,111]. If water condensation is avoided, the process is reversible in films and even in solar cells, where the photovoltaic performance of “degraded” devices was recovered with a simple drying step under a nitrogen stream for a few hours [51].

Fig. 16.28 Ellipsometric spectra presented as pseudo-dielectric functions measured during the back-conversion from a $\text{MAPbI}_3 \cdot \text{H}_2\text{O}$ monohydrate crystal to the pristine MAPbI_3 phase, see Ref. [51]. Dotted lines display the experimental results and solid lines the simulations based on an effective Bruggeman mixture of the two phases and voids. The chosen time intervals represent approximately equidistant volume fractions, i.e., variations of 0.25 in hydrate content upon drying from 1(wet) to 0. The vertical scale corresponds to the uppermost spectrum and the rest are shifted downwards by steps of -2 for clarity.

Shirayama et al. [59] have characterized the degradation processes of ultra-smooth MAPI thin films prepared by a laser evaporation technique. In this study, the exposure of the MAPbI_3 samples to humid air was carried out under ordinary room illumination. They observed that at 75% RH, the surface reaction was quite rapid and the mirror-like surface of the pristine MAPbI_3 layer became whitish within 20 s after the air exposure. Unfortunately, reliable optical characterization of this process was quite difficult due to the extensive developed roughness and further analysis was not made. The authors monitored the film changes at RH of 40%, observing by SEM that even at this relatively low RH value [112], large structural changes in the near-surface region take place after a short exposure. The changes in optical functions are displayed in Fig. 16.29 as pseudo-dielectric imaginary part ϵ_2 . Although SEM

Fig. 16.29 Variation of ϵ_2 reported in Ref. [59] for a MAPbI₃ thin film during exposure to air at 40% RH. The spectra of MAPbI₃ in N₂ and of a PbI₂ film are plotted for reference. The degraded sample spectrum does not change after a thermal annealing at 100°C, indicating its stability.

indicated a much faster surface transformation, changes in the optical properties start to be evident at times beyond 2h. In particular, absorption features that coincide with those of a PbI₂ reference start to appear clearly while the band gap transition at 1.6 eV gradually disappears with the exposure time until at $t \geq 24$ h, the bandgap is located at 2.4 eV, consistent with that of PbI₂. Even if during the initial degradation process ($t \leq 3$ h) the change of the $\langle \epsilon_2 \rangle$ spectrum is rather small, the E₂ peak shows a distinct peak shift which has been related to the formation of the hydrate phase in the surface region. In contrast to the film thickness increase during hydration observed in Ref. [51], at low RH [59] a reduction of the total layer thickness was observed. This was explained by the concurrence of a desorption reaction in addition to the hydration reactions of Eq. (16.2). The thickness reduction occurs according to:

In this study it was emphasized that the time scale of the MAPbI₃ degradation observed at 40% RH (1 day) starts from the surface and is much faster than that reported in earlier studies at similar RH (1 month) without illumination [113]. This correlates quite well with the efficiency loss observed in actual solar cells (1–2 days at 55% RH)

[54]. Accordingly, the degradation of hybrid perovskite solar cells in humid air is most likely caused by the rapid changes near the interfaces that conform the devices. In fact, the contacts performance has been found to degrade faster than the perovskite active layer itself [114].

As a conclusion of these studies, it seems that the degradation processes depend strongly both on the morphology of the samples and on the ambiental conditions, but mainly on the latter. Although humidity is an essential parameter, also temperature and illumination are important degradation agents. Structural studies combined with SE measurements provide insight into the degradation pathways. SE monitoring can be very helpful to follow the changes, allowing to identify the degradation species and to keep track of the thickness and roughness variations associated to these changes.

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