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Effect of Optical Microcavity on Absorption Behavior of Homo-Tandem Organic Solar Cells *

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The optical microcavity effect of the homo-tandem solar cells is explored utilizing the transfer matrix method. Ultrathin silver can reduce the deadzone effect compared with graphene and PH1000, and leads to a factor of 1.07 enhancement for an electrical field in a metal microcavity. The enhancement is considered to be the fact that strong exciton-photon coupling occurs in the microcavity due to ultrathin Ag. On the basis of the optical enhancement effect, optical behaviors are manipulated by varying the microcavity length. It is confirmed that ultrathin silver can serve as an ideal interconnection layer as the active layer is ∼150 nm thick and the thickness ratio between front and rear active layers lies between 1:1 and 1:2.

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Organic solar cells have intensively attracted a great deal of interest in the past few years.[1−3] At present, over 12% power conversion efficiency (PCE) of organic solar cells (OSCs) has been achieved through material innovation and device optimization.[4] However, due to the small exciton diffusion length and low carriers mobility of organic materials, the dilemma between optical absorption and charge carrier transportation has to be considered carefully.[5,6] The typical ∼100-nm-thick active layer limits overall light absorption enhancement and as a result leads to a low exciton generation rate.[7] The problem can be solved by stacking two or more subcells in series.[8] In particular, the homo-tandem device via stacking the same subcells with the optimized thickness effectively improves light absorption and decreases the collecting distance of charge carriers, alleviating the non-geminate recombination.[9,10] In the tandem structure, two subcells are connected in series through an interconnection layer (ICL). From an optical point of view, an ideal ICL has a high optical transmittance to minimize optical losses, the ability to redistribute the optical field to optimize the current matching between the front and rear subcell. To respond to this need, graphene, metal grids, and conducting polymers are investigated.[11−13] Ultrathin metal films (UMFs) are widely used as ICL, mainly due to a low percolation threshold, continuous film formation and good electric properties.[14] In addition, UMF improves the optical performance in the inverted solar cell due to the microcavity resonance effect and plasmonic excitation.[15] In the silver microcavity device, organic materials have demonstrated they can strongly couple to the surface plasmon of silver films, even in organic microcavities having Q factors as low as 10.[16] As a result of a coherent exchange of energy between an exciton and a resonant photonic mode, the degree of exciton-photon coupling has a significant effect on the optical intensity distribution. Therefore, it has been used to improve the efficiency of light emitting diodes (LEDs) via a redistribution of the optical intensity of the emitting materials. Varying the emitting film thickness, the coupling factor increases from 31% to 48%.[17] Apparently, ultrathin silver enhances the exciton generation rate in an optical microcavity as compared with traditional ICLs. However, the exciton-photon coupling arising from ultrathin silver in OSCs has yet to be analyzed carefully, especially in homo-tandem devices.

In this work, ultrathin silver is utilized as an ICL to construct a UMF optical microcavity. The optical simulations based on the transfer matrix method (TMM) have been performed to compare with the optical performance of the devices based on PH1000 and graphene. Moreover, optical behaviors of a homo-tandem device are tuned by varying the microcavity length. As a result, the optical performance of homo-tandem solar cells is improved significantly by optimizing the optical intensity distribution to enhance the exciton-photon coupling in an ultrathin silver microcavity.

Polymer: fullerene bulk heterojunction (BHJ) consisting of the donor material poly [4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5b'] dithiophene-co-3-fluoro-thieno[3,4-b]thio-phene-2-car-boxylate] (PTB7-Th) and acceptor material [6,6]-phenyl C71-butyricacid methyl ester ($PC_{71}BM$) is utilized.[18,19] The homo-tandem solar cell is configured as glass/Sn:In_2O_3 (ITO, 100 nm)/zinc oxide (ZnO, 30 nm)/front-PTB7-

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Th:$PC_{71}BM$ (varied)/molybdenum oxide (MoO_x, 10 nm)/ICL/ZnO(30 nm)/rear-PTB7-Th:$PC_{71}BM$ (varied)/MoO_x (10 nm)/silver (100 nm), as illustrated in Fig. 1. In this configuration, the device consists of two subcells, connected by a layer of ultrathin Ag. If the UMF microcavity mode is appropriate to the exciton energy, the strong-coupling regime should survive to much higher excitation density, and thus the polariton lasing might be expected.[20] Usually, enhanced coherence lengths of excitons lead to ballistic transportation, which may enhance the efficiency of OSCs. However, due to the inherent disorder in conjugated polymers, coherence lengths are limited to only 1–2 nm, as deduced from steady-state photoluminescence (PL) measurements.[21] The UMF microcavity gives rise to pronounced vibronic progressions in absorption. Vibronic coupling increases the effective mass of the exciton. As a result, the optical distribution in a microcavity strongly depends on the optical properties of the UMF microcavity. As is expected, it is of significance to optimize the composition and size of the microcavity to control the exciton generation in the homo-tandem solar cell.

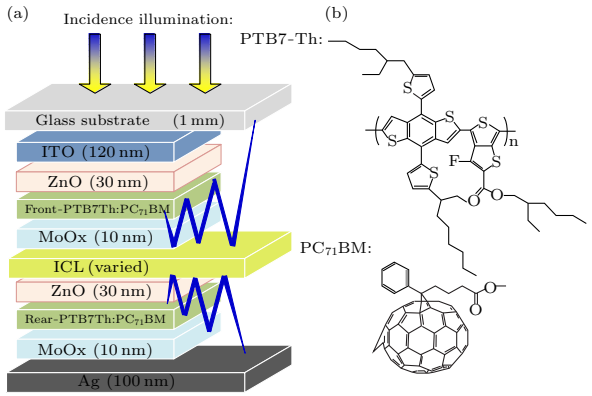

Fig. 1. (a) Schematic drawing of a homo-tandem solar cell. (b) Molecular structures of PTB7-Th and $PC_{71}BM$.

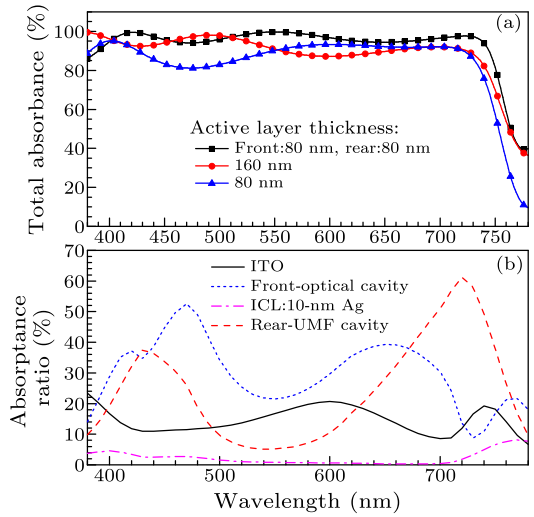

Fig. 2. (a) Total absorbance comparison between the homo-tandem solar cell with 10-nm-thick Ag and single-junction solar cell with different thick active layers. (b) Absorbance ratio of several layers for the homo-tandem solar cell.

Complex refractive indices of ITO, PEDOT: PSS, MoO_x, ZnO, Ag and PTB7-Th:$PC_{71}BM$ are taken from the literature for calculations.[22–24] The enhancement associated with the optical microcavity effect is investigated by increasing the total active layer. The cell consists of a weak optical microcavity configured by ITO and ICL, and a strong UMF microcavity by UMF silver and thick Ag electrode. The UMF microcavity exerts significant effects on the optical performance of the cell. According to the work of Lidzey *et al.*, the Rabi splitting energy of microcavity, $\hbar\Omega$, is proportional to $(f/n_c^2 L_{\text{eff}})^{1/2}$, where f is the effective exciton oscillator strength per unit area of microcavity materials, n_c is the refractive index in the microcavity, and L_{eff} is the effective length.[25] As a result, coupling efficiency enhancement is expected by optimizing microcavity length and refractive index to promote the generation rate of excitons in the microcavity. As UMF silver is assumed to be 10 nm, optical absorbance of the cells is calculated by utilizing TMM. Compared with the single-junction solar cell in Fig. 2, there is no doubt that an increased active layer thickness leads to an optical enhancement in the whole visible spectrum for the homo-tandem solar cell. In the UMF microcavity, optical absorbance of the active layer is higher at longer wavelengths, compared with that of traditional solar cells. Therefore, it is expected that a high exciton generation rate will appear in the UMF microcavity. In the electrical view, it is convenient to keep amount balance of exciton generation on the bilateral of UMF, thus the short circuit current J_{SC} of the homo-tandem solar cell is promoted.

In the optical microcavity, two reflective layers form a high-finesse optical microcavity, in which the transmitted light-wave oscillates, thus the photons bounce between ICL and the bottom layers. The refractive index of ICL determines the coupling efficiency of the exciton-photon in the microcavity. Here graphene and PH1000 are the alternative for ultrathin silver as ICLs with zero and non-zero extinction coefficient in the homo-tandem solar cell, respectively. The optical characteristics of cells with different cavities are compared together. To fully understand the behavior, the microcavity resonance effect should be taken into consideration.[26] Under normal illumination, a portion of incident light is reflected away from the microcavity, and the remaining light makes round trips between two reflective layers. The multiple reflections form a stable optical resonance field. The optical resonant condition for the light with a given wavelength λ can be described as[15]

$$\sum_i n_i d_i + \frac{\lambda}{4\pi}(\psi_1 + \psi_2) = \frac{m\lambda}{2}, \tag{1}$$

where n_i and d_i are the refractive index and thickness of the active layers, ψ_1 and ψ_2 are the phase change upon reflection from the ICL and the thick Ag electrode, respectively, and m is a positive integer. As mentioned above, if d_i is comparable to L_{eff}, the strong coupling efficiency occurs.

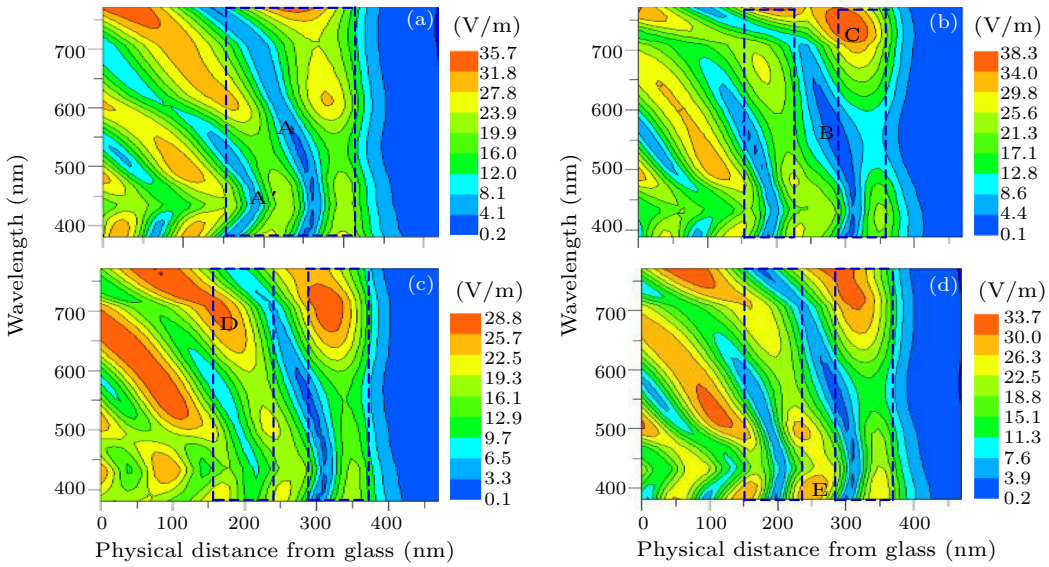

Fig. 3. Total electric field (V/m): (a) the single-junction solar cell with active layer thickness of 160 nm, (b) the homo-tandem solar cell with ultrathin silver microcavity, (c) the homo-tandem solar cell with graphene microcavity, and (d) the homo-tandem solar cell with PH1000 microcavity.

In Fig. 3, the active layer is just plotted in the connective dashed line. The valleys of A and A′ correspond to the minima of optical resonance. The valley, namely the deadzone, as the result of the microcavity resonance effect, adversely hinders the dissociation of exciton and transportation of free charge carriers toward the electrode. According to Eq. (1), the deadzone is unavoidable in the thick-film device. Surface plasmon polaritons (SPPs) from ultrathin silver can guide the parallel propagation of the electromagnetic lightwave, which results in the resonant changes in amplitude and phase in the microcavity. For example, the shift of valley B induced by ultrathin silver is notable in Fig. 3(b), which masterly avoids the occupation of a dead-zone in the active layer of OSCs. What is more, an enhancement factor of 1.07 at point C is also attributed to ultrathin silver. In a UMF microcavity, a several-tens nanometer-thick PTB7-Th:$PC_{71}BM$ provides a convenient system in which a coherent energy exchanges between an exciton and a resonant photonic mode. It demonstrates as a mixing in the energetic dispersions of the microcavity and exciton modes and the formation of the cavity-polaritons, which can be described as a linear mixture of the photon and exciton. Owing to the strong coupling effect, the photons in the UMF microcavity can be efficiently converted into excitons. Concerning graphene, due to its high extinction coefficient as the graphene is thicker than 10 nm, the optical intensity in the microcavity decreases significantly as shown in Fig. 3(c). Similarly, PH1000 is not an ideal ICL either, because its low reflectance leads to an insufficient optical resonance strength in the microcavity as shown in Fig. 3(d). Anyway, the optical enhancement is the result of the optical field redistribution in the homo-tandem solar cell, and reflects a coupling degree of exciton-photon in the ultrathin silver microcavity. To investigate optical absorbance enhancement by the ICLs, the total absorbed photons (TAPs) over visible wavelengths for normal illumination is defined as TAPs $= \int_{380}^{780} A(\lambda)S(\lambda)d\lambda$, where $A(\lambda)$ is the absorption spectrum in the active layer, $S(\lambda)$ is the solar irradiance spectrum, and $A(\lambda)$ is calculated from TMM with the variations of active layer thickness and ICLs. In the homo-tandem solar cell, $A(\lambda)$ is the sum of absorbance spectra of the front and rear subcells.

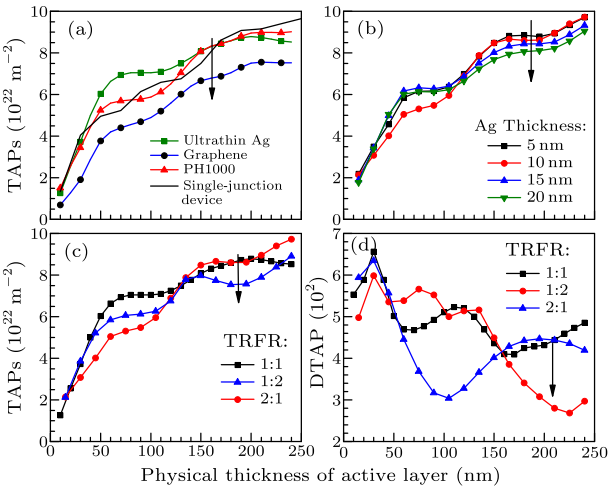

Fig. 4. TAPs as a function of physical thickness of active layer with the variation of: (a) ICL, (b) Ag thickness, and (c) TRFR. (d) DTAPs varies as a function of physical thickness of the active layer for the cells with different TRFRs.

As observed in Fig. 4(a), the TAPs of single-junction and tandem solar cell present absorbance saturation of the active layer, and ultrathin silver improves the optical absorbance as the total active layer thickness increases to be 150 nm. According to the

microcavity resonance theory,[27] a thick ultrathin silver increases the strength of exciton-photon coupling, while reducing the amount of photons entering into the UMF microcavity. To enhance the resonance strength, ultrathin silver used as a mirror with some reflection has to be tailored by varying its thickness. As is illuminated, the TAPs reduce as ultrathin silver thickness increases from 5 to 20 nm as calculated in Fig. 4(b). In the optical view, the enhancement due to light trapping in the microcavity compensates for the weak absorption of the whole sunlight spectrum (380–780 nm), leading to improved light harvesting across the whole absorption region of the homo-tandem solar cell. In the electrical view, it provides a convenient transporting path for a free charge carrier to arrive at the metal electrode. The conductivity of ultrathin silver will decrease significantly if the thickness is below the percolation threshold (∼10 nm) due to the formation of incontinuous islands. As a result, 10 nm is considered to be an optimum thickness as ICL in the homo-tandem solar cell. Concerning PTB7-Th:$PC_{71}BM$, a suggested empirical value of ∼0.3 eV is often taken as the exciton binding energy.[28] If the microcavity length meets with the requirements of the Rabi resonance,[25] the strong coupling of exciton-photon will be expected to promote the exciton generation, although it is usually considered as 100%.[29] As a result, it requires to make clear how the microcavity length affects the optical absorbance of the cell. The TRFR of the active layer is defined as the thickness ratio between the front and rear of active layers. Thus the rear active layer thickness is equivalent to the length of the UMF microcavity. The optical absorbance with variation of TRFR is illustrated in Fig. 4(c). The optical field discontinuity of two subcells induces the mismatch of excitons density of two subcells, which severely decreases J_S. The discontinuity can be roughly defined as the deviation of TAPs (DTAPs), namely the root mean square (RMS) of TAP difference integration of two active layers in the visible spectrum. It is apparent that low DTAPs represent a favorable current continuity of two subcells. As observed in Fig. 4(d), although a value of 2:1 for TRFR leads to an optical enhancement factor of 1.15, DTAPs increase simultaneously. To achieve high optical absorbance, it is required to extend the UMF microcavity length for high optical absorbance. However, the extension results in a low exciton-photon coupling efficiency of an ultrathin silver microcavity. To optimize the microcavity length for more photon harvesting, the interaction mode between microcavity resonance and SPP of the incident light needs to be analyzed in detail. For the UMF silver microcavity device, the experimental results have shown a 7% enhancement of PCE.[11] Based on these, we can confirm that UMF silver serves as an ideal ICL if the active layer is ∼150 nm thick and TRFR lies between 1:1 and 1:2.

In summary, UMF silver utilized as ICL avoids the deadzone effect and increases optical absorbance of homo-tandem solar cells, as compared with graphene and PH1000. Moreover, considering the optical resonance effect and coupling of exciton-photon in an ultrathin silver microcavity, the length of ultrathin silver microcavity is primarily optimized for improving optical absorbance of homo-tandem solar cells. As the active layer is ∼150 nm thick and TRFR lies between 1:1 and 1:2, high optical performance of homo-tandem solar cells can be achieved.

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