## Hybrid cavity polaritons in a ZnO-perovskite microcavity

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We realize a Fabry-Perot hybrid microcavity containing an association of a ZnO thin layer and of a layer of the two-dimensional layered perovskite 5-methyl-2-furanmethanamonium lead bromide (MFMPB). From angle-resolved reflectivity experiments performed at low temperature of 5 K, we show that this hybrid cavity works in the strong-coupling regime and that the lower, middle, and upper polariton branches are observed. We show that the middle polariton branch (MPB) contains a significant component of the cavity photon and both of the two exciton species.

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# I. INTRODUCTION

Since the first experimental demonstration by Weisbuch et al.<sup>1</sup> in 1992, vertical semiconductor microcavities working in the strong-coupling regime have been intensively studied.<sup>2,3</sup> The great interest arisen by this field is partly due to the fact that it can lead to a new kind of coherent light source: the polariton laser.<sup>4</sup> Its working principle is to create and maintain a Bose-Einstein condensate of polaritons in the lowest energy state of the lower polariton branch (LPB). Coherent light is then emitted outside the microcavity because of the spontaneous radiative decay of polaritons constituting the condensate. As they do not require an electronic population inversion, polariton lasers are expected to present lower thresholds than conventional lasers.<sup>5</sup> Some of the theoretical expectations have recently been confirmed by several experimental realizations based on CdTe,<sup>6</sup> GaAs,<sup>7-10</sup> GaN,<sup>11,12</sup> and also on anthracene,<sup>13</sup> an organic material.

The key point to obtain polariton lasing is the initialization of the polariton condensate, which can be reached only if polaritons can relax from the exciton reservoir (lower polariton branch, high- $k_{//}$  values) to the LPB lowest state ( $k_{//} = 0$ ) before their photon parts escape out of the cavity. Since the buildup of the condensate results from a competition between polariton relaxation and polariton lifetime, either the polariton lifetime or the polariton relaxation rate (or both) must be increased. This can be done by working at positive detuning,<sup>14</sup> by performing parametric scattering at the magic angle,<sup>15</sup> or, most commonly, by increasing the cavity quality factor,<sup>10</sup> which dictates in our current situation the polariton lifetime. However, in some cases, particularly in the case of cavities containing organic materials, there are technological difficulties preventing the achievement of sufficiently high quality factors. In the theoretical work of Agranovich *et al.*,<sup>16</sup> another solution to create a very efficient relaxation channel for the polaritons to the lowest energy states of the LPB is proposed: the realization of a hybrid strongly coupled cavity, containing two kinds of materials, an inorganic semiconductor and an organic material, in which both excitons are coupled to the same photon mode. New eigenstates thus exist that are a linear combination of the cavity photon mode and the two excitonic states and that are called the lower, middle, and upper polariton branches (LPB, MPB, UPB, respectively). The two materials are chosen such as, for high  $k_{//}$ , the LPB branch dispersion tends toward the organic material dispersion and the MPB branch dispersion tends toward the inorganic material dispersion. Because the organic materials present a much higher oscillator strength than the inorganic materials one, it is expected that the MPB is relatively flat, allowing an efficient relaxation of the polaritons from the inorganic excitons reservoir assisted by acoustical phonons. While as the polaritons relax to the small  $k_{//}$  of the MPB, the organic exciton part of the MPB increases, and an additional relaxation channel for inorganic excitons, assisted by optical phonons emitted in the organic material, is predicted. Exciton-phonon coupling being generally strong in organic materials, it is thought that the relaxation time of the polaritons can be decreased by at least a factor of 10 and that the phonon relaxation bottleneck usually seen in semiconductor microcavities can thus be bypassed.

In the past, hybridization between different excitons has been demonstrated in microcavities containing two sets of GaAs quantum wells of different thicknesses,<sup>17</sup> containing two different molecular dyes,<sup>18</sup> or containing a molecule dye and a molecular cristal.<sup>19</sup> To our knowledge, we present here the first hybrid microcavity applying the ideas of Agranovich et al. As the inorganic material, we have chosen ZnO semiconductor.<sup>14</sup> ZnO microcavities working in the strong-coupling regime have been recently realized  $^{20-2\bar{2}}$  and ZnO excitons are very robust since they present an exciton binding energy of 60 meV.<sup>23</sup> As the organic material, we propose a semiconducting molecular crystal belonging to the family of the two-dimensional layered  $[R - (CH_2)_n - NH_3]_2 PbX_4$  perovskites where X is a halogen (I, Br, or Cl), n is the length of the alkyl chain and Ris an organic group.<sup>24-28</sup> This kind of material presents all the properties cited above to allow an efficient relaxation channel in the configuration proposed by Agranovich et al. When deposited by spin coating, the perovskite layer is composed of PbBr<sub>6</sub><sup>2-</sup> inorganic layers that alternate with organic layers. The electronic structure of such self-organized perovskites is analogous to multiquantum well structures in which the inorganic layers form wells having a width of several angstroms, while the organic layers act as barriers having a width of 1 nm. Due to the small width of the quantum wells and to the large difference between the dielectric constants of the organic and inorganic layers, exciton binding energy in perosvkite molecular crystals is of the order of several 100 meV,<sup>24,29</sup> and strong oscillator strengths have been measured:  $4 \times 10^{13}$  cm<sup>-2</sup> for  $[C_6H_5 - (CH_2)_2 - NH_3]_2PbI_4$ ,<sup>27</sup> which is one order of magnitude higher than in conventional inorganic quantum wells. Additionally, we have shown in Ref. 29 that the exciton-phonon interaction is strong, more than one order of magnitude higher than in GaAs quantum wells. Finally, a very important advantage of the perovskite materials is their great flexibility: the spectral position of the exciton can be tailored by substituting different halides X,<sup>25</sup> or by changing the organic part of the molecule.<sup>26</sup> To realize the structure proposed by Agranovich et al., we have synthesized a perovskite whose exciton energy lies under the ZnO exciton energy: MFMPbBr<sub>4</sub>, where MFM is an abbreviation for 5-methyl-2-furanmethanamonium. The absorption spectrum of this molecule, called in the following MFMPB, is shown in Fig. 1.

#### II. ZnO-PEROVSKITE MICROCAVITY

Figure 2 exhibits a sketch of the realized hybrid microcavity. The bottom mirror is constituted by 7 AlN (44.8 nm)/Al<sub>0.2</sub>Ga<sub>0.8</sub>N (39.3 nm) Bragg pairs deposited by molecular-beam epitaxy (MBE) on a silicon substrate. A 44-nm ZnO layer is then deposited by MBE on this mirror. To be sure that the only coupling between the ZnO layer and the perovskite layer is mediated by the cavity photon and that the Förster short-range dipole-dipole interactions are negligible, the perovskite layer and the ZnO layer are separated by a 97-nm silicon oxide layer deposited by PECVD (plasma-enhanced chemical vapor deposition). A 40-nm thin film of MFMPB perovskite layer is then spin coated on top of this silicon oxide layer, using a 5 wt % solution of MFMHBr and PbBr2 dissolved in stoichiometric amounts in N,N-dimethylformamide. Before closing the cavity with a 15-nm-thick Al layer produced by electron beam, a capping layer of 20-nm silicon nitride is deposited by PECVD in order to protect the perovskite layer



FIG. 1. Optical density spectrum of a 40-nm-thick MFMPB layer deposited by spin coating on a glass substrate. Inset shows the chemical structure of the 5-methyl-2-furanmethanamonium ion (MFM).

against the too high temperature of the Al evaporation process and in order to place the perovskite under a maximum of the electric field. The electric-field distribution of the cavity mode is simulated using a transfer matrix model and is shown in Fig. 2. A maximum of the field is seen inside the perovskite layer and on the edge of the ZnO layer. As a consequence, there is a significant field amplitude inside both layers and an effective coupling between the photon mode and the two excitonic modes can be expected.

Angle-resolved reflectivity measurements of the hybrid microcavity are performed using a xenon lamp as the excitation source, between 5° and 70°, at low temperature 5 K. Figure 3 shows a series of reflectivity spectra at 5 K for several incident angles  $\theta$  and for transverse electric (TE) polarization (the spectra obtained with the transverse magnetic polarization are similar). Three dips, whose energy position, intensity, and linewidth are angle dependent, can be observed. A first anticrossing between the cavity photon and the MFMPB exciton can be observed at 20°, a second anticrossing between



FIG. 2. (Color online) Intensity of the electric field superimposed on the sketch of the studied microcavity.



FIG. 3. (Color online) Angle-resolved reflectivity measurements from the ZnO/MFMPB hybrid microcavity performed at 5 K for transverse electric (TE) polarization. The dashed lines are guides to the eyes. The inset shows an enlargement of the dip corresponding to the lower energy polariton for an angle of  $45^{\circ}$ .

the cavity photon and the ZnO exciton is observed around 50°. The energy of the three minima observed in Fig. 3 are reported in Fig. 4 as a function of  $k_{//} = (E/hc)\sin\theta$ , the in-plane wave vector. Note that the lower energy polariton seems to be split in two dips from 40°: one dip that lies at the energy of the MFMPB exciton, and another dip that moves to higher energies. This last dip is due to the strong coupling between the Bragg mode and the MFMPB exciton, similarly to what was observed in ZnO bulklike microcavities.<sup>20,30</sup>

In Fig. 4, the dispersion curves of the uncoupled ZnO and MFMPB excitons and cavity photon modes are reported, with the ZnO and MFMPB excitons being considered dispersionless. The solid lines, called LPB, MPB, and UPB for lower, middle, and upper polariton branches, are fitted from a quasiparticle model with three different levels, describing the interaction of the two excitons with the photon mode:

$$H = \begin{pmatrix} E_{cav} & V_{MFMPB} & V_{ZnO} \\ V_{MFMPB} & E_{MFMPB} & 0 \\ V_{ZnO} & 0 & E_{ZnO} \end{pmatrix}.$$
 (1)

 $E_{ZnO}$  is the energy of the ZnO exciton, fixed at the value,  $E_{ZnO} = 3.375 \text{ eV}, E_{MFMPB}$  is the energy of the perovskite



FIG. 4. (Color online) Cavity-polariton dispersion curves as a function of the in-plane wave vector. The squares are experimental data extracted from the reflectivity spectra shown in Fig. 3. The continuous lines (LPB, MPB, and UPB) are fits from three-level system resolution, only the full square being taken into account. The open squares correspond to the strong coupling between the Bragg mode and the MFMPB exciton as explained in the text and are not included in the fit. The uncoupled excitons (ZnO and MFMPB) and cavity dispersion curves are also presented (dotted lines). The inset shows the Hopfield coefficients of the middle polaritonic branch versus in-plane wave vector.

exciton, which is fixed at the value,  $E_{\text{MFMPB}} = 3.2 \text{ eV}$  and  $E_{\text{cav}}$ is the energy of the cavity photon, which is a function of  $k_{//}$ ,  $E_{\text{cav}}(k_{//}) = \sqrt{E_0^2 + c^2 \hbar^2 k_{//}^2 / n_{\text{eff}}^2}$  where  $E_0$  is the cavity mode energy for  $k_{//} = 0$  and  $n_{\text{eff}}$  is the effective index of the cavity. The two parameters,  $V_{ZnO}$  and  $V_{MFMPB}$  are the interaction potentials between the photon and the ZnO and MFMPB excitons, respectively, with the Rabi splittings being proportional to 2V. The eigenvalues obtained using the coupled oscillator model, with fitting parameters,  $E_0 = 3.189 \text{ eV}, n_{\text{eff}} =$ 2.3,  $V_{\text{MFMPB}} = 26 \text{ meV}$ , and,  $V_{\text{ZnO}} = 22 \text{ meV}$  are compared to the measured dispersion curve in Fig. 4 and a good agreement is observed. The Rabi splitting obtained for the strong coupling between ZnO and the cavity photon in the hybrid cavity is inferior to the Rabi splitting of 70 meV obtained in the  $\lambda/4$ ZnO cavity reported in Refs. 30 and 31. First the effective length of the hybrid cavity is much larger than the one of the ZnO containing cavity. Second, the fact, seen in Fig. 2, that the maximum of the field lies at the edge of the ZnO layer rather than at its center accounts for the reduced interaction between the cavity photon and the ZnO exciton. In the same way, the Rabi splitting obtained for the strong coupling between the MFMPB exciton and the cavity photon in the hybrid cavity is smaller than the Rabi splitting usually observed in  $\lambda/2$ cavities containing perovskites  $(C_6H_5 - C_2H_4 - NH_3)_2PbX_4$ (for example, in Ref. 32, a Rabi splitting of 190 meV has been found in a microcavity containing a 50-nm-thin layer of  $(C_6H_5 - C_2H_4 - NH_3)_2PbI_4$  (called PEPI), experiencing a maximum of the electric field). The fact that the effective length is much larger in the hybrid cavity than in the perovskite containing cavity is a first reason. A second reason comes from the value of the oscillator strength in the MFMPB layer: we measure the absorption spectra of a 50-nm-thin layer of PEPI and of a 40-nm-thin layer of MFMPB prepared in the same conditions as the one used during the hybrid cavity realization, and we find that the oscillator strength of the MFMPB layer is 70% smaller than the one of the PEPI layer, thus explaining the order of magnitude of the observed Rabi splitting.

From the calculation of the eigenstates, the weights of the ZnO exciton, MFMPB exciton and photon mode (named Hopfield coefficients) in each polariton branch can be evaluated for different angles. Around 40° the MPB eigenstate is constituted with 4.5% of MFMPB exciton, 11.5% of ZnO exciton, and 84% of cavity photon (inset of Fig. 4). Thus the MPB branch around the angles  $40^{\circ}$  –  $50^{\circ}$  contains a significant component of the cavity photon and both of the exciton species, as expected in the configuration proposed by Agranovich et al. Nevertheless, further developments require for sure a better balance between the cavity photon and the two excitons. This can be achieved by increasing the Rabi splitting between the MFMPB exciton and the cavity photon which, in turn, will flatten the dispersion curve of the MPB. From a practical point of view, this can be done by increasing the thickness of the MFMPB layer in order to increase the oscillator strength of the organic material, or by using another perovskite whose exciton resonance is closer to the ZnO one, for example, mixed perovskites such as  $(C_6H_5 - C_2H_4 - NH_3)_2PbBr_xCl_{4-x}$ .<sup>33</sup>

### **III. CONCLUSION**

In conclusion, we have fabricated and characterized a hybrid ZnO/perovskite optical microcavity operating in the strong-coupling regime and in which the two exciton resonances are coupled via the photonic cavity mode. This kind of structure could offer an alternative route to enhance the relaxation of inorganic excitons from the reservoir to the  $k_{//} = 0$  states of the LPB, allowing to bypass the phonon relaxation bottleneck usually seen in semiconductor microcavities. Realizing such microcavities opens the way to a very flexible design of novel optoelectronic devices, in which the inorganic excitons reservoir can be electrically injected, and potentially working at room temperature, thanks to the large exciton binding energies of ZnO and perovskite materials.

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HYBRID CAVITY POLARITONS IN A ZnO-PEROVSKITE ...

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