Journal of Luminescence 188 (2017) 567–576

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Energy transfer yellow light emitting diodes based on blends of quasi-2D perovskites

Dionysios Papadatos, Anastasia Vassilakopoulou, Ioannis Koutselas*

Materials Science Department, School of Natural Sciences, University of Patras, Patras 26504, Greece

ARTICLE INFO

Keywords:
Low dimensional hybrid organic-inorganic semiconductor
Light emitting diode
Perovskite
Electroluminescence
Excitons

ABSTRACT

The new class of hybrid organic-inorganic semiconductor (HOIS) materials, based on metal halide perovskites, is constantly being pursued for applications such as light emitting diodes (LEDs), solar cells or even single photon emitters, due to their momentous optoelectronic properties. In this work, we present a single layer LED that operates due to energy transfer effects as well as a simple, instant and low cost method for its fabrication. The active LED layer is based on the reaction of zero dimensional $(CH_3NH_3)_4PbI_6$, two dimensional $(F\text{-}C_6H_4CH_2CH_2NH_2)_2PbI_4$ and three dimensional $(CH_3NH_3)PbI_3$ HOIS, which yields a mixture of quasi-two dimensional HOIS and is presented for the first time. The final material manifests simple, yet unique energy transfer effects, while its electroluminescence exhibits excitonic recombination bright yellow light, peaked at 592 nm. Utilizing appropriate mixtures is possible to create films containing such phases that multi-color EL emission is observed, here presented as yellow/green, yellow/red or yellow/red/deep-red. LED device fabricated under ambient air, readily functions at room temperature and low voltages, while the active layer exhibited substantial film continuity with any deposition method.

1. Introduction

Low dimensional (LD) semiconductors is a set of materials where basic research on novel phenomena, due to the enhanced quantum confinement [1,2], has led to the observation of complex phenomena as well as the creation of new types of devices [3,4]. A new class of LD hybrid organic-inorganic semiconductors (HOIS) has been recently introduced, which is cost effective, exhibits useful optoelectronic properties comparable to those of artificially created LD semiconducting systems [5–9], leading also to cost effective novel device fabrication. One of the main attributes of HOIS is the strong dielectric confinement of excitons due to the mixing of organic and inorganic components, leading to the increase of the excitonic binding energy (E_b) and oscillator strength (f_{exc}) [1,2]; therefore, most experiments can be performed at room temperature due to the energetic stability of the inherent direct excitons, while most HOIS based on lead halides are rather stable in air. Since the application of the 3D HOIS $CH_3NH_3PbX_3$ (X= I, Br, Cl) in photovoltaic research [10], numerous scientific works have appeared on HOIS and related devices [11,12]. However, before the important increase of HOIS related scientific reports, HOIS had already been extensively studied [13] and used in devices [14–18], even as room temperature light emitting diodes (LEDs) [19].

Another impressive advantage of the LD HOIS, besides, their self-assembling nature, is that the spectral position of their Optical Absorption (OA) excitonic peaks as well as that of their energy band gap (E_g) can be tuned within the UV–vis spectrum, which is usually affected by simple synthetic path modification [2,14]. A HOIS is usually composed of a metal halide unit network, constituting the semiconducting inorganic part, while an electrooptically inactive amine takes the role of the organic part, where the organic and inorganic parts are periodically positioned in an alternate pattern. HOIS materials synthesized by a broad range of inorganic and organic parameters, have led to various properties, such as tunable absorption in the whole ultraviolet-visible spectra [13], energy transfer phenomena [20,21] or thin film transistor gate materials comparable to amorphous Si [22,23]. Finally, solar cell devices have been formed by three dimensional (3D) and two dimensional (2D) lead halide HOIS [24,25]. By altering the appropriate stoichiometry and synthetic route of both HOIS parts, it is possible to form semiconducting systems with dimensionalities between 3D, 2D, one dimensional (1D) or even zero dimensional (0D) quantum dot like semiconductors [2,26–31]. Furthermore, HOIS where the active part has a dimensionality between 2D and 3D are referred to as quasi-2D semiconductors. The here presented self-assembled quasi-2D HOIS have, when crystalline, a general chemical formula $Z_{n-1}(M\text{-}H)_2Pb_nX_{3n+1}$ where n=1,2,3…, M is an amine [32–35] (M-H stands for the protonated amine), Z refers to CH_3NH_3 (Methylamine-H, abbr. MA-H)

* Corresponding author.
E-mail address: ikouts@upatras.gr (I. Koutselas).

http://dx.doi.org/10.1016/j.jlumin.2017.04.067
Received 15 October 2016; Received in revised form 12 January 2017; Accepted 30 April 2017
Available online 03 May 2017

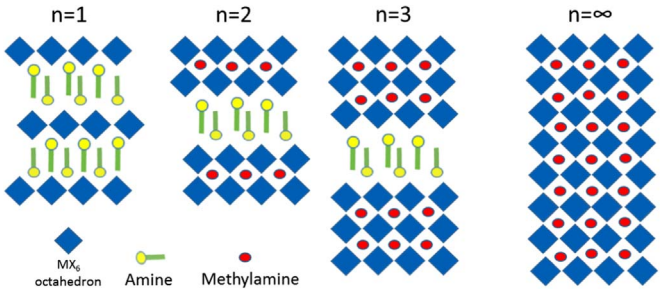

Fig. 1. Schematic representation of the layered structure for the crystalline $(CH_3NH_3)_{n\text{-}1}(4FpA\text{-}H)_2Pb_nI_{3\,n+1}$ LD HOIS. Dimensionalities range from 2D (left) to 3D (right), for $n=1,2,3,\ldots,\infty$.

and X refers to I, Br, Cl. The quasi-2D materials have more interesting quantum effects when these are synthesized as multidimensional mixtures, namely the energy transfer effects. As a direct consequence, LEDs and solar cells have been fabricated from such quasi-2D semiconductor materials [36–39].

For example, Fig. 1 shows structural patterns of the quasi-2D HOIS layered materials. When $n=\infty$ (Fig. 1, right) HOIS is equivalent to the 3D material (perovskite), while when $n=1$ the material is strictly 2D (Fig. 1, left). In the latter case, organic cations are separating the active layers, each one being an infinite 2D sheet of edge sharing PbI_6 octahedra with thickness of ca. 6 Å, while layer's thickness is twice the length of the Pb-halogen bond. Inorganic layer's thickness increases linear with dimensionality's increase from 2D to 3D, approximately of ca. $6\times n$ Å, however, layer's stability is supported by interstitial MA-H cations. The energy band gap (E_g) presents a reciprocal behavior of the quasi-2D HOIS dimensionality, thus, E_g decreases as dimensionality increases, until it reaches that of the 3D HOIS. In addition, the excitonic E_b which is dependent on the organic molecule and the actual crystal structure, tends to decrease too [2]. In most cases, single large crystals of a specific crystalline quasi-2D HOIS are difficult to obtain, especially for $n > 3$, and multi-dimensional mixtures are usually the products. OA and Photoluminescence (PL) spectra in such mixtures appear to be composed as a sum of the corresponding spectra of the individual quasi-2D/3D crystalline HOIS [40].

In this work, we report a simple, instant and low cost method for the fabrication of a LED device constructed by a single active layer, composed of 0D, 3D and 2D HOIS blend, where the organic part (M) will be 4-Fluorophenethylamine (4FpA), Z will be Methylamine and X=I. These precursors create a new mixture of various quasi-2D materials, after reacting. This blend containing specific (0D/3D):2D starting molar ratio, manifests simple, yet obvious energy transfer effects [41], as these have been observed in semiconductor materials like $CsPbBr_3$ [42–44], while similar phenomena in LED have been observed in recent publications [45,46]. LED device, presented herein, can function at room temperature, ambient air and low voltages while the EL emission is visible by naked eye. The active layer showed strong film continuity and significant stability in conditions of high humidity. Finally, a set of simple experiments is presented in order to elucidate the exciton energy transfer model and the range of phenomena it can encompass, while for some specific blend ratios multi-color LED is reported, examples being given in the form of yellow/green, yellow/red or yellow/red/deep red.

2. Experimental details

2.1. Chemicals

Gallium–indium eutectic (≥99.99% trace metals basis), Methylamine (Meth-40% in water), 4-Fluorophenethylamine (4FpA-99%), Indium tin oxide coated glass (ITO, square surface resistivity 15–25 Ω/sq), Acetonitrile (AcN-CHROMASOLV® Plus ≥99.9%), Hydriodic acid (HI-ACS reagent, ≥47.0%), Lead (II) iodide (PbI_2 − 99.999% trace metals basis), N,N′-Dimethylformamide (DMF-99.8%). All chemicals were obtained from Sigma-Aldrich and used without any further purification. All acid quantities described further in the text will refer to the previously mentioned respective solutions.

2.2. Synthesis

For the blend's synthesis containing 0D and 3D perovskites $(MA\text{-}H)_4PbI_6{\cdot}2H_2O$ and $(MA\text{-}H)PbI_3$, respectively, PbI_2 (1.6 mmol) was dissolved in 5 mL AcN with the addition of 0.170 mL of HI and stirred until an optically clear solution had been obtained. Methylamine (5 mmol) was dissolved as salt by stirring in 5 mL AcN with HI (0.301 mL). These two solutions were slowly mixed under room temperature, and as dried, a black precipitate was formed. Although, the 3D compound can be synthesized by using less methylamine, in this case, the surplus of methylamine leads to simultaneous formation of 3D and 0D crystalline units. The final blend will be denoted as zero and three dimensional (ZTD) semiconductor. A prediction of reaction's products was made using a non-linear fitting function in order to minimize the loss of precursors when these react to form 3D, 0D or other byproducts. This was performed assuming that the reactions have progressively consumed completely every precursor, while the 0D and 3D compounds can be each formed without any preferential choice by nature. We have estimated that the mole fraction of 0D to 3D in the final ZTD compound is 1.43:0.06. Within the same mathematical model low concentration of PbI_2 appears as unreacted which is, however, unobserved in the XRD patterns of ZTD. Therefore, the average molecular weight of the final ZTD material is estimated to be 1090 ± 20 g.

In the case of the 2D perovskite, $(4FpA\text{-}H)_2PbI_4$, PbI_2 (4 mmol) was dissolved in 5 mL AcN and after the addition of 0.425 mL of HI, it was stirred until an optically clear solution was obtained. 4-Fluorophenethylamine (8 mmol) was dissolved as salt by stirring in 5 mL AcN with HI (0.144 mL). These two solutions were slowly mixed under room temperature, yielding a bright orange precipitate. Slow cooling gave rise to red-orange crystals, which have been dried extremely well from solvent. The semiconductor shows strong PL even under room light.

In a typical preparation, the mixed semiconductors where prepared from a 1:1.4 M ratio of the ZTD and 2D precursors. In particular, 30 mg ZTD and 49 mg $(4FpA\text{-}H)_2PbI_4$ were dissolved in 0.300 mL DMF, forming a yellow colored solution. The stirring temperature was set at 40 °C. This specific blend will be referred as BY1. This final mixture is composed out of mainly three phases, as it will be discussed below, the $n=1,2,3$ quasi-2D HOIS; the $n=1$ coincides with the 2D phase. Again, without being able to analytically find the proportions of each phase, we used a nonlinear fitting method to find the best mathematical solution for the chemical reaction products when the above mixture is completely consuming the precursors. The solution for the case described before appears to be for the mole ratio of $2D_{n=1}{:}2D_{n=2}{:}2D_{n=3}{:}2D_{n=4}$:3D to be 2.11:0.29:0.13:0.12:0.08. Even if the mentioned analysis is strictly mathematical, it allows a quantitative pre-determination of the concentration of some of the quasi-2D phases. However, the model cannot discuss the arrangement of these phases, which are mainly nanosized entities. For the cases where twice the molar amount of either ZTD or 2D HOIS was used, similar analysis results are partially portrayed in the experimental OA spectra and more specifically, in the position and intensity of the excitonic absorption peaks. Specifically, when each phase is abundant, a related strong excitonic peak is observed. However, when fast drying or equivalently high heating rates are used, the formation and concentration of each phase is a complex function of the solvent and the temperature, that can only be experimentally determined.

It is stressed that using slightly different ratios of ZTD:2D blends provide similar results for the EL spectra, however, the position of the