Polymer microcavities by room temperature electron-beam evaporation of TiO_x and SiO_x

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Abstract

We report on monolithic symmetric vertical microcavities exploiting two $\text{TiO}_x/\text{SiO}_x$ distributed Bragg reflectors (DBRs), realized by means of electron-beam evaporation. The whole nanofabrication process is carried out without heating the chamber atmosphere, thus allowing the direct evaporation of the top dielectric mirror onto the organic layer previously spin-cast on the bottom DBR stack. The high adhesion to the substrate, the possibility of employing active media of low softness temperature, and the absence of any degradation of the emission properties of the organic compound opens the way for novel vertical emitting resonators and monolithic photo- and electroluminescent microcavities. Our mirrors exhibit a stop-band reflectivity higher than 95% and a spectral width of more than 170 nm.

Keywords: Polymeric microcavities; Organic microcavity; Photoluminescence; Multilayer structures.

1. Introduction

Organic conjugated materials are suitable for a wide range of applications ranging from telecommunications to optical interconnects, high-density data storage, displays and sensors, by virtue of their intrinsic structural flexibility, ease of processing and low-cost device fabrication, and excellent optical performances. A number of organic compounds including conjugated polymers, low-molar-mass molecules, and even single crystals, have been indeed employed to realize light emitting devices (LEDs) [1]. In addition, many organics were found to exhibit optical gain over a broad spectral range [2], and they have been therefore employed in the realization of laser devices [3] by different classes of resonators, including external cavities [4], distributed feedback devices [5], planar microcavities [6] and vertical cavity surface emitting lasers based on integrated multilayer microcavity structures. These devices consist of an organic layer deposited by casting or evaporation between two high reflecting mirrors.

So far, organic microcavities have been mainly fabricated by using a distributed Bragg reflector (DBR)

[7] on one side of the cavity and a metal mirror on the other side, or by sandwiching the organic active layer between two pre-realized dielectric mirrors. These architectures are made necessary by the methods employed to realize the DBRs, which generally use high temperatures ($> 250^\circ\text{C}$), whereas very few studies have been to date reported about alternative low temperature approaches [8]. In fact, the top mirror can not be easily evaporated at high temperature on the organic layer previously deposited onto the bottom mirror, since: (i) the possible presence of oxygen in the process atmosphere can heavily deteriorate the luminescence performances of conjugated compounds upon heating [9], and (ii) the long heating interval needed to achieve a high reflective mirror often causes an irreversible loss of adhesion between the organics layer, driven above its softness temperature, and the bottom reflector.

In this work, we report on monolithic symmetric organic microcavities fabricated by a non-invasive, novel low temperature electron-beam evaporation of both the dielectric mirrors. Our devices were realized by spin-coating the organic compound onto the bottom $\text{TiO}_x/\text{SiO}_x$ mirror, and subsequently directly depositing the top mirror onto the organic layer in high-vacuum atmosphere. The conjugated polymer-based microcavities operate at wavelength (634 nm) equal to the optical cavity length of the device. This fabrication technique offers the unique

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Fig. 1 Molecular structure of MEH-PPV (a) and scheme of the sample characterised by angle-resolved PL measurements through the top-deposited DBR (b).

Fig. 2 AFM three dimensional view of the TiO_x surface of the top cavity mirror.

possibility of realizing high-performance molecular optoelectronic devices in a continuous high-vacuum deposition process, so it can be a strategic approach for the industrial massive production of encapsulated microcavity-based LEDs.

2. Experimental

Corning glass substrates ($10 \times 10 \text{ mm}^2$) were carefully cleaned in acetone and then dried under a nitrogen flow and fixed on the rotating sample holder of a Temescal Supersource 2 electron-beam gun system, at a distance of about 35 cm from the oxide sources. The chamber was evacuated by a turbomolecular drag pump, providing a base pressure of $1\text{--}2 \times 10^{-6}$ mbar. The films were deposited in an oxygen atmosphere using 99.9% purity TiO_2 tablets and SiO_2 disks (Leybold, Germany) as source materials.

The electron-beam source operated at 9 KV. The operation current was set to obtain a constant deposition rate (1.5 and 2.0 Å s^{-1} for the TiO_2 the SiO_2 , respectively) which was monitored with a quartz silver coated crystal microbalance. The working pressure was kept constant at 2.4×10^{-4} mbar by a constant pumping speed. A controlled oxygen atmosphere was accomplished by a gas inlet through a precision needle valve positioned at a distance of a few centimetres from the samples. SiO_x and TiO_x films were deposited at low temperature, the only chamber heating being induced by the electronic gun. The bottom mirror of our vertical microcavities, designed to achieve high reflectivity in the red-visible range, was composed of 6.5 pairs of $\text{TiO}_x/\text{SiO}_x$ layers, exhibiting a stop-band reflectivity higher than 95% and a spectral width of more than 170 nm.

The surface morphology and the cross section of the evaporated reflectors were inspected by Atomic Force Microscopy (AFM, NanoScope from Digital Instruments, FL), operating in contact mode under ambient conditions and by scanning electron microscopy (Stereoscan 440 from Leica, Germany). The full dielectric microcavities were realized by spin casting a tetrahydrofuran solution of the prototype conjugated polymer, poly-[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV, refractive index $n \approx 1.8$, molecular weight 300K from

American Dye Source, Canada –molecular structure in Fig. 1a-) onto the bottom DBR. The thickness of the realized polymer film was around 360 nm, measured by a profilometre. Finally, the top reflector (6.5 periods of $\text{TiO}_x/\text{SiO}_x$ couplers) was evaporated on the active layer at low temperature.

Reference samples were also fabricated to evaluate the optical properties of the active material after the evaporation of the top mirror, by directly spin-coating the polymer solution onto a Corning glass substrate, and depositing the top DBR (Fig. 1b). In the same evaporation run, the DBR was also deposited on a Corning substrate for the subsequent optical characterisation. All the stop-bands of our mirrors were determined by transmission measurements, carried out by a Cary 5000 spectrophotometre (Varian, Australia). The photoluminescence (PL) spectra from the reference active layer were collected both before and after the evaporation process by a fiber-coupled charge coupled device (Ocean Optics, FL) and by a Xenon excitation light source (SP spectral products, CT) centred at 480 nm. Finally, PL measurements on the complete microcavity were carried out by collecting the emission in a small solid angle ($\approx 10^{-3}$ rad) around each viewing angle, and angle-resolved reflectance measurements were performed by the Cary spectrophotometre.

3. Results and discussion

The optical and morphological properties of dielectric materials are strongly dependent on the deposition method [10]. Till now, dielectric mirrors fabricated by electron-beam evaporation have been mainly realized in oxygen partial pressure, at chamber temperature higher than 250°C [11]. In fact, when TiO_2 and SiO_2 are evaporated, they usually decompose into sub-oxides and free oxygen, so high temperatures are needed in order to force the evaporants to recombine reactively with the externally supplied oxygen, thus restoring the desired stoichiometric composition. Such growth conditions determine higher packing density, hence larger values of the refractive index, n . However, our studies demonstrated that both TiO_x and SiO_x can be evaporated at low temperature, forming very

Fig. 3 SEM cross-section view of the top cavity mirror

smooth deposited surfaces [12]. In particular, the observed root mean square (rms) roughness is 3.1 and 2.0 nm, respectively, with a grain size distribution comprised between 3.5 and 9.7 nm. Though the n values (≈ 2.0 and 1.4 for TiO_x and SiO_x , respectively) are lower than those of the correspondent layers evaporated at high temperature, the achieved refractive index contrast Δn is about 0.55, which is large enough to fabricate high red reflective broadband DBRs (operating between about 1.6 and 2.1 eV). In addition, the growth temperature and the AFM surface investigation (Fig. 2), which does not show any particular morphological features, indicate that the titanium x -oxide is in its amorphous or polycrystalline state. A Scanning Electron Microscopy (SEM) cross-section image of the 6.5 $\text{TiO}_x/\text{SiO}_x$ DBR, is displayed in Fig. 3. Thin (~ 10 nm) transition layers can be appreciated between adjacent evaporated compounds, indicating the occurrence of interlayer strain/diffusion mechanisms between the two deposited materials.

In Fig. 4b we report the normalised PL spectra of the reference sample, before and after the deposition of 6.5 $\text{TiO}_x/\text{SiO}_x$ periods, demonstrating that the emission

Fig. 4 (a): Transmission spectra of the mirror deposited on the reference sample; (b) Normalised PL spectra of the same sample before (empty circles) and after (dotted line) the evaporation of the 6.5 $\text{TiO}_x/\text{SiO}_x$ couples.

properties of the polymer film are largely unchanged by the growth process. We underline that, in order to precisely evaluate the possible changes induced by the deposition on the reference samples, we realized a top DBR having a stop band centred at 1.7 eV (Fig. 4a), i.e. not coinciding with the emission peak of MEH-PPV, thus avoiding a huge forward reflection of the PL and permitting the detection of the signal in our transmission configuration (Fig. 1b). We note that a slight spectral redistribution is appreciable in the transmitted emission after the mirror fabrication, owing to the light travelling through the one-dimensional photonic crystal structure of the top reflector (see the transmittance spectrum of the mirror reported in Fig. 4a). The observed reduction of the collected light at the main emission peak (2.1 eV) by about 20%, is indeed in agreement with the corresponding DBR reflection in the region between 2.0 and 2.2 eV. Therefore, we conclude that the observed variations of the collected spectrum is a consequence of the mirror reflectance, without appreciable damaging induced by the top-deposition process.

Finally, in Fig. 5 we show the PL (empty circles) and the reflectance characteristics (continuous line) of the complete MEH-PPV-based microcavity. The microcavity emission is largely modified with respect to the corresponding (namely, measured at the same collection angle) PL of the bare polymer layer (Fig. 4b). The main PL peak position moves from 2.10 to 2.13 eV, thus being blue-shifted of about 30 meV, and its spectral width (full width half maximum) decreased by more than a factor 3. A second narrow peak is present in the microcavity PL at 2.00 eV, whose spectral width (~ 50 meV) is controlled by the correspondent sharp dip in the reflectance spectra due to the Fabry-Perot cavity mode. According to the resonance condition, $2nd=m\lambda$, where d is the thickness of the cavity layer, nd is the corresponding optical length, and m is an integer, this mode would oscillate at the second order, at a wavelength (634 nm) equal to the optical cavity length of the device [14].

In previous studies, we also demonstrated the direct patterning of MEH-PPV by gentle soft molding procedures [15]. We believe that the combination of non-invasive

Fig. 5. Reflectance spectra (continuous line) and PL spectra (empty circles) of the red symmetric microcavity, collected at 35° . The strong suppression of the reflectivity at energy larger than 2.1 eV is due to the MEH-PPV absorption.

direct mirrors fabrication onto organic films and soft lithographic techniques can be a strategic route for the realization of fully nanostructured, three-dimensionally optically-confined, organic-based optoelectronic devices. In particular, evaporating the top mirror at low temperature is a unique approach to preserve the previously fabricated pattern on the active polymer, which would be irreversibly damaged by heating above the softness temperature of the organic compound.

4. Conclusion

The loss of adhesion and the degradation of the optical-emitting properties of the organic compounds upon increasing temperature make necessary to employ low-temperature fabrication processes for realizing monolithic vertical cavity surface emitting devices. In this paper, we report on conjugated-polymer based monolithic symmetric microcavities realized by an organic-compatible, low-temperature, electron-beam process. The compatibility of this process with the deposition of molecular compounds opens the way for the design and the fabrication of a novel class of organic-based optoelectronics, including monolithic cavities for possible polariton lasing and encapsulated LEDs, integrated arrays of one-dimensional photonic crystal devices, and three-dimensional photonic resonators.

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