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Monolithic organic-oxide microcavities fabricated by low-temperature electron-beam evaporation

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We report on monolithic symmetric vertical microcavities formed by depositing dielectric-distributed Bragg reflectors (DBRs) by reactive electron-beam evaporation at low temperature (T). The DBRs consist of alternating TiO_x and SiO_x layers with a refractive index contrast of about 0.55 in the visible range. The DBRs, consisting of a very few index-contrast pairs, exhibit high peak reflectivity (93%) around 590 nm with a full width at half maximum of about 160 nm. The excellent compatibility of thin low- T reactive electron-beam evaporated films with a thicker cavity medium comprised of molecular organic compound, and prepared either in a single growth-run, or *ex situ*, opens the way for novel symmetric vertical-emitting resonators and monolithic photo- and electroluminescent microcavities. © 2005 American Vacuum Society.
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I. INTRODUCTION

The optical quality of distributed Bragg reflectors (DBRs) dramatically affects the performances of surface-emitting or transmitting optoelectronic devices, such as sensors,¹ microcavity light-emitting diodes (μLEDs),² and vertical-cavity lasers (VCSELs).^{3,4} For example, semiconductor heterostructures ensure high reflectivity and can be doped to yield conductive mirrors. However, these heterostructures exhibit small refractive index-contrasts, hence a large number of layers are generally needed to achieve high reflectivity. Use of dielectric materials overcomes this drawback, and yields highly reflective mirrors in structures consisting of only a few pairs of alternating layers.

Nevertheless, the high temperature (T) needed for reactive growth processes⁵ limits the integration of such DBRs with an organic cavity layer in the fabrication of μLEDs and VCSELs, despite the excellent luminescence and optical-gain performances that can be exhibited by conjugated molecules.^{6,7} So far, symmetric organic microcavities have been fabricated mainly by sandwiching the active layer between two preformed dielectric mirrors.⁸ Fabrication of symmetric microcavity monoliths instead requires the deposition of the top DBR onto the organic layer. Unfortunately, the high T of the deposition process causes: (i) the loss of adhesion of the organic compound, when heated above its softening temperature; and (ii) the strong deterioration of the optical properties of the light emitting molecules, especially in the oxygen atmosphere⁹ employed for the reactive-oxide growth. In fact, oxygen is known to be responsible for extensive luminescence quenching in organic molecules, as a results of carbonyl ($\text{C}=\text{O}$) formation at the vinyl group site in poly-(phenylenevinylene) compounds.⁹ Such quenching of the luminescence, I , has been effectively explained in terms

of excitonic diffusion towards oxygen-induced defects, which can be described by a simple diffusional model

$$I(t) \cong I_0 t^{1/2} \exp\left(-\frac{t}{\tau_d}\right)^{1/3} \exp\left(-\frac{t}{\tau_0}\right), \quad (1)$$

where t is the time, τ_d and τ_0 are the exciton diffusion and characteristic lifetime, respectively, and I_0 is a constant.⁹

To date, only a few studies have reported on the fabrication of DBRs by alternative low- T approaches.^{10–12} In this work, we demonstrate a monolithic organic vertical microcavity that is formed entirely by reactive electron-beam evaporation of a few pairs of TiO_x and SiO_x thin films at low temperature (20–70 °C). Such DBRs exhibit a reflectivity higher than 93% at 590 nm, and a stop-band with a full width at half maximum (FWHM) of about 160 nm. For comparison, TiO_x and SiO_x layers were also grown at 260 °C (the standard growth temperature for such materials) and their optical and morphological characteristics were compared to the films fabricated at low temperature. The microcavity was tuned between 575 and 590 nm by controlling the thickness of the cavity layer. This technique enables the fabrication of high-performance organic-optical and electrical microcavity devices in a single high-vacuum deposition process.

II. EXPERIMENT

Corning glass substrates ($10 \times 10 \text{ mm}^2$) were carefully cleaned with acetone, then dried under a nitrogen flow and fixed onto the rotating sample holder of a Temescal Super-source 2 electron-beam gun system at a distance of about 35 cm from the oxide sources. The chamber was evacuated to a base pressure of $1\text{--}2 \times 10^{-6}$ mbar. The electron-beam source operated at 9 kV with a constant deposition rate of about 2.0 Å s^{-1} , and film thickness was monitored by a quartz gold-coated crystal microbalance. The films were deposited from 99.9% purity TiO_2 pellets and SiO_2 disks (Ley-

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FIG. 1. Surface morphology of the samples: TiO_x^{HT} (a), TiO_x^{LT} (b), SiO_x^{HT} (c), and SiO_x^{LT} (d). HT and LT indicate high and low T deposition, respectively.

bold, Germany) at a working pressure of 2.4×10^{-4} mbar. A controlled oxygen atmosphere was provided by a gas inlet through a precision needle valve positioned a few centimeters from the samples. SiO_x and TiO_x films were deposited both by heating the chamber at 260°C using a halogen lamp (SiO_x^{HT} and TiO_x^{HT} samples) and at ambient T , under conditions where the only chamber heating was induced by the switched-on electronic gun (SiO_x^{LT} and TiO_x^{LT} samples).

In the low- T process, the starting temperature of the chamber was 25°C . An increase of $1\text{--}2^\circ\text{C}$ per layer was observed during deposition. The bottom mirror of our vertical microcavity was composed of 5.5 pairs of (≈ 75 nm thick) TiO_x and (≈ 105 nm thick) SiO_x layers. In this study, the microcavities were fabricated both *ex situ* by spin casting a polymethyl-methacrylate-chloroform solution on the bottom DBR with a rotation speed between 2000 and 3000 rpm, and *in situ*, by direct evaporation of low-molecular-mass organic molecules. The top reflector, comprised of 4.5 periods of $\text{TiO}_x/\text{SiO}_x$ layers was then evaporated on the cavity layer at low T . Measurements of the normal incidence transmission of single layers, DBRs, and microcavities were performed by a double-beam UV-VIS-NIR Cary 500 spectrophotometer (Varian, Australia). For modelling and fitting the experimental transmission data, we used a transfer-matrix

software for the optical design and analysis of thin films (TfCalc 3.5, from Spectra Inc., OR).

III. RESULTS AND DISCUSSION

Among the possible growth methods, reactive electron-beam evaporation is a powerful technique to prepare films of good quality and controlled thickness and stoichiometry with high reproducibility.^{5,13} The surface morphology of our deposited layers, imaged by atomic-force microscopy (AFM), is displayed in Fig. 1. The corresponding root-mean-square (rms) roughness and the grain-size distribution are reported in Table I. All the deposited films exhibit very smooth surfaces, ranging from about 1 to 3 nm. In particular, the SiO_x samples do not show significant variations at different evaporation temperatures. In contrast, the TiO_x films deposited at 260°C exhibit smaller surface grains and a higher packing density with respect to the TiO_x film deposited at low temperature (TiO_x^{LT}). Indeed, at high T the mobility and reactivity of the species involved in the decomposition of the TiO_2 source are increased, thus promoting surface flatness.

The transmission spectra of the low- T films are shown in Fig. 2. They were fitted by the transfer matrix model,¹⁴ tak-

TABLE I. Surface morphology characteristics, refractive indexes, and Cauchy parameters [Eq. (2)] of the evaporated compounds. The errors on the fitting parameters are smaller than the last reported digit.

Sample	T (°C)	rms (nm)	Grain width (nm)	Grain height (nm)	n (580 nm)	A	B (nm ²)	C (nm ⁴)
SiO _x ^{HT}	260	1.6	35–101	1.6–10.0	1.43	1.395	2.003×10^4	-1.999×10^9
SiO _x ^{HT}	<70	2.0	27–113	3.5–9.7	1.42	1.401	1.556×10^4	-3.034×10^9
TiO _x ^{HT}	260	2.1	15–55	2.8–12.7	2.19	2.140	2.529×10^3	6.772×10^9
TiO _x ^{LT}	<70	3.1	35–63	3.6–9.7	1.98	1.862	4.048×10^4	2.942×10^8

ing into account the wavelength dependence of the refractive index, n , given by the Cauchy dispersion formula,¹⁵

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}, \quad (2)$$

where A , B , and C are fitting parameters (values reported in Table I). We found that higher deposition temperatures lead to higher values of the refractive index of the TiO_x films, which is consistent with the morphological observation of a higher packing density. However, little appreciable change in n is observed for the SiO_x layers evaporated at low and at high T in [Figs. 3(a) and Table I].

The optical properties of such dielectric layers are strongly dependent on the deposition method.¹³ In particular, when TiO₂ is evaporated, it decomposes into suboxides and free oxygen. For this reason, an oxygen atmosphere and high temperature in the chamber (usually more than 250 °C) are often employed, in order to force the evaporant to recombine reactively with the oxygen in the deposition chamber, thus restoring the stoichiometric composition associated with colorless titanium dioxide.⁵ Higher packing densities, and hence larger values of n , are also induced by such growth

conditions.¹⁶ According to previous investigations involving resonant elastic scattering of α -particles¹⁷ on films deposited by electron-beam evaporation at high T , refractive indexes in the range 2.2–2.3 have been obtained by using a relatively high-oxygen partial pressure during growth. This approach yields a high stoichiometric content of oxygen in the TiO_x compound.

In our study, we have chosen to work with an oxygen partial pressure (2.4×10^{-4} mbar) for which deposition of

FIG. 2. Transmission spectra of single dielectric layers evaporated at low temperature, TiO_x^{LT} (a) and SiO_x^{HT} (b). The transfer matrix fitting curves (solid lines) are superimposed to experimental data (empty dots). The achieved thickness is of about 180 and 210 nm for the TiO_x^{LT} and the SiO_x^{LT} layer, respectively.

FIG. 3. (a) Refractive index vs wavelength of TiO_x (full squares and empty squares) and SiO_x (full circles and empty circles) growth, respectively, at 260 °C and at room temperature. (b) Transmission spectra of the DBR mirrors realized by alternating 5.5 couples of TiO_x/SiO_x evaporated at low T . Circles: experimental data. Solid curve: theoretical prediction.

FIG. 4. Transmission spectra of the organic μ -cavities with two cavity layers of thickness 395 nm (a) and 415 nm (b). Inset of (b): Schematic structure of the device.

titanium dioxide (TiO_2) is expected to occur at high T , although chemical-sensitive techniques, would be required to assess the exact stoichiometric composition of the deposited TiO_x^{HT} . It is well established that both amorphous and crystalline phases often coexist in TiO_2 films.^{18,19} In particular, the rutile polymorph is the thermodynamically stable state and the anatase crystalline phase is achieved with T up to 800 °C,¹⁹ whereas the amorphous state is favored at low T (<200 °C).²⁰ The bond flexibility and the variable stoichiometry of Ti films determine a free-energy landscape that strongly favors the formation of an amorphous state.¹⁸ The low values of n , measured in our TiO_x^{LT} samples, indicate that the TiO_x compound deposited at low T is likely in the amorphous state.

Our DBRs, comprised of 5.5 $\text{TiO}_x^{\text{LT}}/\text{SiO}_x^{\text{LT}}$ pairs, exhibit transmission values as large as 93% around 590 nm, and a stop-band with FWHM of about 160 nm [dotted curve in Fig. 3(b)]. In spite of the relatively low n of TiO_x^{LT} , the refractive index contrast achieved between the compounds evaporated at low T is large enough to fabricate efficient broadband DBRs in the visible spectral range. The transmission spectrum [continuous line in Fig. 3(b)] calculated by using the refractive index of the TiO_x^{LT} and SiO_x^{LT} films determined by measurements on single layers, reproduces quite well the experimental data [dots in Fig. 3(b)]. This demonstrates the very precise thickness control and the good reproducibility of the low- T electron-beam deposition process.

Figure 4 shows two transmission spectra of a complete vertical microcavity. We emphasize that the evaporation of a

top dielectric mirror onto a previously deposited organic layer can be carried out only at low- T , because heating the polymer compound above its softening temperature could cause a significant loss of adhesion and consequent catastrophic detachment from the substrate. This issue deserves to be discussed further. Even though microscopic origin of the glass transition phenomenon in amorphous organic materials is still an open issue, it is well established that, upon increasing temperature, both the structural relaxation time, τ , and the viscosity, η , of polymers undergo a sudden decrease, due to the drastic increase of the mobility of the large molecules in the liquid. The temperature dependence of the relaxation time and of the viscosity is usually well described by the Vogel-Fulcher-Tamman law (VFT),²¹

$$\tau(T) = \tau_0 \exp[DT_0/(T - T_0)], \quad (3)$$

where τ_0 is the relaxation time at very high temperatures, D is referred to as the strength parameter, and T_0 is the temperature at which the divergence of the relaxation time is predicted. This is, for example the working principle of mechanical lithography, such as nanoimprinting and soft molding,^{22,23} on polymeric compounds. During the film evaporation process, the organic film faces down, so that heating above the glass-transition temperature (T_g) would cause an irreversible gravity-induced loss of adhesion. High- T processes would be possible, but only for intervals shorter than the characteristic structural rearrangement time of the employed organics. However, this is very unlikely, since above T_g one has τ on the order of 10^2 s or smaller, whereas the slow evaporation rates, needed for depositing smooth dielectrics, requires times ranging from many minutes to hours for achieving a complete DBR.

The resonant modes of our microcavities, resulting from two different cavity layer thicknesses (395 and 415 nm), can be clearly seen at about (a) 576 nm and (b) 590 nm, respectively. The shift of the cavity wavelength mode ($\Delta\lambda = 14$ nm) induced by the change, Δd , of thickness of the resonant layer, indicates that the device operates in the fourth order, namely,

$$m = 2n\Delta d/\Delta\lambda \cong 4, \quad (4)$$

and that the optical cavity length is equal to $L = 2\lambda/n$. In addition, the FWHM of the resonant modes, $\Delta\lambda_m$, is about 15 nm, corresponding to a cavity quality factor, $Q = \lambda/\Delta\lambda_m \approx 40$. This would correspond to cavity internal losses per pass of about 10%. This is comparable to losses obtained by state-of-the-art organic lasers employing external resonators.⁷ Moreover, since the transmission losses in the region are less than 7% [Fig. 3(b)], this allows one to estimate that about 3% of the energy stored in the microcavity is dissipated per pass because of film scattering and local non-perfect alignment of the evaporated DBRs with respect to the microcavity axis.

These are of course critical issues, particularly in the fabrication of organic-based surface-emitting lasers. In particular, using microcavity architectures requires high optical-gain materials, that are able to compensate for losses as result of

very thin active layers. The gain values reported to date for some organic-luminescent systems, such as Alq₃:DCM blends, methyl-substituted ladder-type poly(paraphenylene), and polyfluorenes and polythiophenes,^{8,24} are of the order of 10² cm⁻¹. Therefore, strongly reflecting mirrors and smooth surfaces that minimize interface scattering are very desirable for fabricating organic VCSELs. In addition, the possibility of carrying out the deposition of the top DBR at low temperatures allows full exploitation of the wide chemical flexibility afforded by using conjugated molecules. The glass-transition temperatures of these molecules are usually between 100 and 200 °C.

IV. CONCLUSION

In conclusion, we reported on the fabrication of vertical microcavity monoliths formed by reactive electron-beam evaporation at low temperature. The reflectors were made by alternating TiO_x and SiO_x layers with a refractive-index contrast of about 0.55 in the visible range. The DBR exhibits high peak reflectivity (93%) and a stop-band width of about 160 nm. We carried out the entire fabrication process without heating the deposition chamber, which allowed the direct evaporation of the top dielectric mirror onto the organic layer previously spin-cast on the bottom DBR stack. Novel vertical-emitting photo- and electroluminescent microcavities can be built either in a single growth-run, or *ex situ*. This opens the way for the possible use of active media of low softening temperature in monolithic devices with superior optical performance.

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