Thickness dependence of the Amplified Spontaneous Emission threshold and operational stability of in poly(9,9-dioctylfluorene) active waveguides operating in air

M. Anni [1] , A. Perulli [2] , and G. Monti[2]

[1]Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, Italy

[2]Dipartimento di Ingegneria dell' Innovazione, Università del Salento, Italy

In the frame of developing new active materials for laser and light amplifier application large interest has been devoted in the last decades to organic conjugated polymers. In particular it has been demonstrated that Amplified Spontaneous Emission (ASE) is a widely diffused process as it has been observed in several classes of luminescent polymers, thus stimulating the development of laser prototypes with different active materials and resonator geometry [1]. To date the best performances, in terms of low threshold, are obtained in waveguide configuration combining the large amplification due to the light propagation for several millimeters within the active film, and the efficient lasing feedback coming from periodic modulation of the dielectric constant in distributed feedback lasers. Despite the strong dependence of the waveguiding properties of the active films on its thickness, the active film thickness variation has been to date mainly used to tune the ASE peak wavelength while the thickness effects on the ASE threshold have been to date investigated only in few cases, finding a decrease of the ASE threshold as the active film thickness increases. Moreover the ASE intensity operational lifetime in light amplifying organic waveguides has been studied only in few recent cases, despite its evident importance for applications, while its thickness dependence has not been investigated to date.

In the present study we show the main results of the investigation of the thickness dependence of the ASE threshold and operational lifetime in air-poly(9,9-dioctylfluorene)(PF8)-glass asymmetric active waveguides. The complete work can be found in [2].

The active films were realized by spin coating on a glass substrate of PF8 toluene solutions with 10 different concentrations from about 4 10^{-5} M to about 3 10^{-4} M, leading to thickness from about 35 nm to about 660 nm. The samples were pumped by a Nitrogen laser (337 nm) delivering 3 ns pulses with a repetition rate of 10 Hz and a maximum pulse energy of 155μJ, focused in a 6.6 mm $\times$ 100 μm rectangular stripe by a cylindrical lens. In order to minimize the photoluminescence (PL) intensity fluctuations due to laser instabilities all the PL spectra have been acquired by accumulating the signal due to 10 laser pulses. The PL was collected from the sample edge, dispersed by a TRIAX 320 monochromator with a 150 ll/mm diffraction grating and detected by a Peltier cooled Si- Charge Coupled Device (CCD). The spectral resolution was about 2 nm. All the measurements were at room temperature in air. The ASE intensity decay dynamic measurements have been performed in air, by measuring the sample emission spectrum every 5 seconds for 15 minutes, at an excitation density of 2.2 mJcm^{-2}.

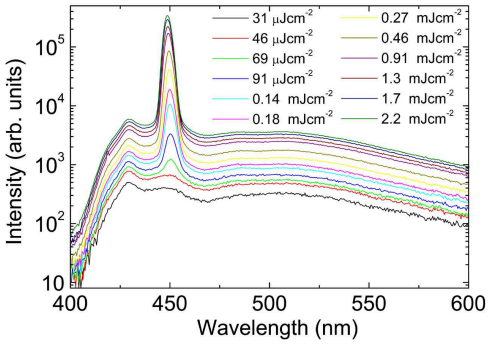

Figure 1. Excitation density dependence of the PL spectra of 230 nm thick sample.

The emission spectra of all the investigated samples (see Fig. 1 for the 230 nm thick sample) show the typical features of the PF8 glassy phase PL, with a 0-0 line at about 429 nm, followed by vibronic replicas at about 450 nm and 480 nm. As the incident excitation density increases a clear line narrowing of the 0-1 vibronic band, due to ASE, is observed for all the sam-

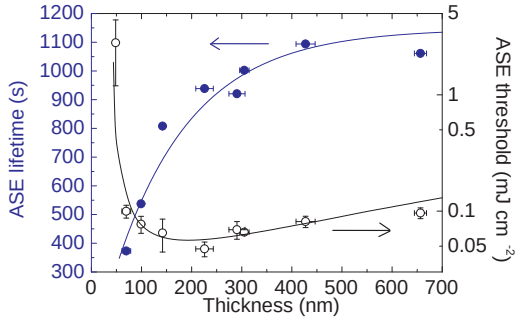

Figure 2. Thickness dependence of the ASE lifetime (full dots) and of the ASE threshold (empty dots). The line across the lifetime data is a guide for the eyes, while the line across the threshold data is the best fit curves with Equation 1.

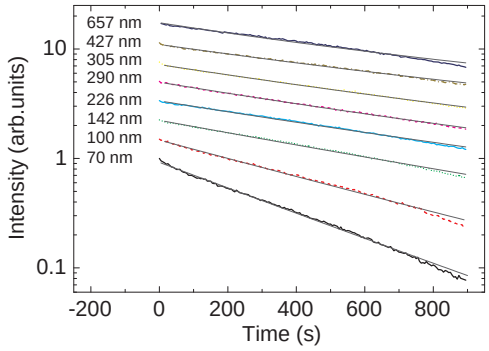

Figure 3. Thickness dependence of the ASE intensity decay in time for an incident excitation density of 2.2 mJcm^{-2}, and best fit curves with our model (gray lines) (the data are scaled for clarity).

ples thicker than about 50 nm for high enough excitation density. The ASE threshold initially decreases (see Fig. 2) in the thickness range 50-230 nm from about 2.8 mJcm^{-2} to 47 μJcm^{-2}, and then progressively increases up to about 100 μJcm^{-2} for a thickness of 660 nm.

The measurements of the ASE intensity stability during operation in air show (see Fig. 3) an exponential ASE intensity decrease with time in all the samples, with a decay time (see Fig. 2) (operational lifetime) increasing with the sample thickness up to 300 nm, and similar for the thickest samples.

In order to determine the origin of our results we started from the understanding of the ASE threshold thickness dependence. As ASE is typically assisted by waveguiding in the active film we modeled the propagating modes at the 0-1 band wavelength in all the samples, by assuming a refractive index n of 1.9 for the PF8 layer and n=1.465 for the glass substrate (measured by spectroscopic ellipsometry). No guided modes are found for PF8 thickness up to 43 nm, in agreement with the observed minimum threshold for ASE. Moreover we conclude that no correlation exists between the observed ASE threshold thickness dependence, and the progressive increase of the number of guided modes [2], indicating that the ASE threshold is mainly dependent on the properties of the first guided mode (TE0).

We continued our analysis by quantifying the TE0 mode confinement(MC) in the active layer, which strongly and monotonically increases with the PF8 thickness (see Fig. 4). This increase improves the stimulated emission, thus increasing the ASE, and decreasing the ASE threshold decrease, thus not explaining the existence of a thickness of minimum threshold.

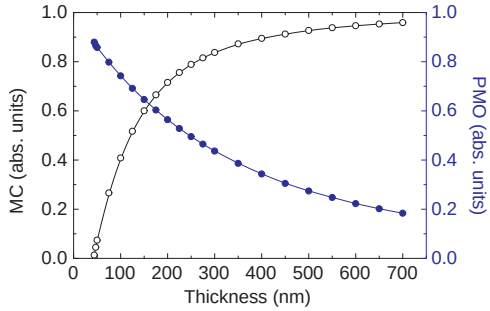

Figure 4. Mode confinement (MC open dots) and pump-mode overlap (PMO full dots) as a function of the waveguide thickness . The lines are guides for the eyes.

In order to understand the origin of the ASE threshold increase above a thickness of 200 nm we observe that, due to PF8 absorption, the pump laser intensity exponentially decreases with the distance from the surface and, as the guided mode electric field maximum is closer to the PF8-glass surface than to the air-PF8 one, a PF8 layer thickness increase leads to a progressive decrease of the spatial overlap between the strongly pumped active layer region and the maximum guided electric field region. A pump laser penetration depth $d_{las} \approx 155nm$ has been estimated from the PF8 absorption spectra.

We thus quantified the pump-mode overlap (PMO), which is found to be above 0.8 up to a PF8 thickness of about 70 nm, and it progressively decreases down to 0.2 as the thickness increases (see Fig. 4).

The simulated thickness dependence of both MC and PMO has been related to the ASE

threshold by observing that the ASE threshold is reduced both by a MC increase and by a PMO increase. Assuming the same functional dependence of the ASE threshold on both PMO and MC, the simplest decreasing function of both PMO and MC is:

$$ASE_{th} = \frac{A}{PMO \cdot MC} \quad (1)$$

Excellent agreement between the experimental data and the simulated thickness dependence is obtained for A=21.7μJcm^{-2} (see Fig. 2).

The observed increase of the ASE operational lifetime τ_{ASE} with thickness has been explained considering that the PF8 laser exposure in presence of air result both in photo-degradation and in photo-induced absorption, both reducing the waveguide net gain, and thus the ASE intensity. By modeling the ASE decay rate for different excitation regimes (i.e. different depth in the film) and by considering that, as the pump laser intensity decreases with the depth in the active film, the superficial regions of PF8 will be more strongly pumped (thus more strongly emitting), but will also show a quicker ASE decay with time, we determined an analytical expression of the ASE intensity time dynamics as the weighted average of the ASE signals for each depth, weighted by the corresponding exciton density. Excellent agreement is found between the experimental decay dynamics and the best fit curves (see Fig. 3) is obtained.

These results indicate that in thick samples the possible light propagation in film regions far from the air surface, where optical losses are lower (due to lower photo-induced absorption and/or lower photodegradation), is beneficial for the ASE operational lifetime.

Overall our results indicate that a thickness increase of the active layer results in a desirable increase of the ASE operational lifetime, but also in an ASE threshold increase up to a factor of 2, which is evidently negative. In order to determine the existence of an active layer thickness of best compromise between high stability and low threshold we propose a waveguide quality factor defined as:

$$QF = \frac{\tau_{ASE}}{ASE_{th}} \quad (2)$$

Where τ_{ASE} is the ASE intensity decay time obtained by a single exponential fit of the ASE decay dynamics. Our experimental results (see Fig. 5) show that the quality factor increases up to 4 times from 50 nm to about 200 nm, and then decreases for higher thicknesses.

In conclusions we investigated the ASE threshold and operational lifetime thickness dependence

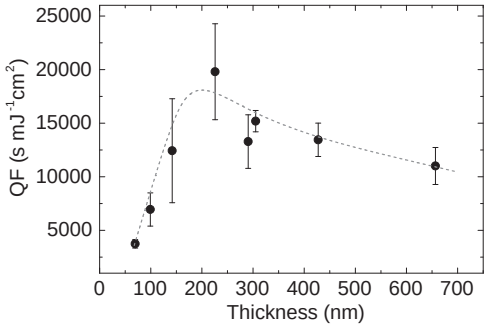

Figure 5. Thickness dependence of the quality factor defined in Equation 2 (the line is a guide for the eyes).

in air-poly(9,9-dioctylfluorene)(PF8)-glass asymmetric active waveguides. Our results show the existence of a minimum ASE threshold thickness, close to the pump laser penetration length in the active film d_{las}. The ASE operational lifetime increases with the active film thicknesses up to $d \approx 2d_{las}$ and then becomes thickness independent. We demonstrated that both effects are related to the non uniform excitation across the active films and that the best compromise between low ASE threshold and high operational lifetime is obtained for $d \approx 2d_{las}$.

As the emission property worsening during laser exposure is a common property of many organic active materials, and as the interaction leading to the photodegradation usually takes place close to the sample surface, we expect that the ASE operational lifetime increase with thickness could be a general property of organic waveguides, and then of general importance in the field of developing organic amplifying devices with high operational lifetime, including DFB lasers that exploit patterned active waveguides.

REFERENCES

1. I. D. W. Samuel and G. A. Turnbull, Chem. Rev. 107 (2007) 1272.
2. M. Anni, A. Perulli, G. Monti, J. Appl. Phys. 111 2012) 093109.