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Oxygen sensitivity of erbium-doped AlN films probed by site selective spectroscopy

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Abstract

In the aim of better understand the influence of oxygen on the luminescent properties of Er:AlN films, two samples synthesized by radiofrequency reactive magnetron sputtering, have been analysed by site-selective spectroscopy around 1.55 μm and compared to a reference aluminosilicate sample. The erbium content in the films was estimated to 3.3 at.% and oxygen content ranges from 6.2 at.% to 58.6 at.% (determination by EPMA). Line narrowing study was performed for values 6.2 at.% and 22.5 at.%. Both films were annealed at 1075 K for 1 h. Site-selective spectroscopy was carried out using a Ti:sapphire laser light with typical linewidth of 2 GHz tuned around 980 nm as the excitation source. The samples were cooled down to 1.5 K in a liquid-helium bath cryostat and their $^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ luminescence was detected using a high-sensitivity germanium-cooled detector. It appears that the site distribution of the Er:AlN samples is not continuous as in classical aluminosilicate glass but presents a rupture that suggests the existence of two kinds of sites for erbium: oxygen site and nitrogen site. These observations can easily be interpreted within the framework of the nephelauxetic effect that explains a shift of the site distribution to the longer wavelengths with an increase of boundings bonding covalency.
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1. Introduction

There is, in the scientific community, a permanent interest for rare-earth-doped semiconductors due to the possibility they offer to provide thin-film electro-luminescent devices in the visible and also in the optical telecommunication range. As an example, erbium-doped semiconductors have been grown and good capabilities have been reported for GaN or nanocrystalline silicon [1,2]. In the case of erbium, it has been shown that wide band gap materials are required to improve luminescence intensity at room temperature [3]. Therefore, AlN (gap equal to 6.2 eV) is a good candidate for

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erbium doping and luminescent properties of er-
bium-doped AlN at room temperature have
already been reported [4,5]. Moreover, erbium-
doped AlN films have been proposed as optical
sensors to evaluate wear and corrosion in coated
mechanical components [6]. However, it has been
shown that luminescence intensity and spectral
profile is very dependent of synthesis conditions
and post-deposition treatments.

In the aim of better understand the influence of
synthesis process on luminescent properties, this
paper investigates more accurately the influence of
oxygen on the luminescent properties of Er:AlN
films by site-selective spectroscopy around 1.55 µm
[7,8]. Two samples synthesized by magnetron RF
sputtering under different oxygen pressures have
been analysed and compared to a reference alu-
minosilicate sample. It appears a strong sensitivity
of the site distribution of erbium dopants de-
pending on the oxygen content. More precisely, it
is shown that the site distribution is not continu-
ous as in the case of the aluminosilicate sample
and can be related to the existence of oxygen and
nitrogen environments for erbium sites.

2. Experimental

The Er:AlN samples studied in this work were
films deposited on Si substrates using radiofre-
quency reactive magnetron sputtering from a
99.99% pure Al target. The deposition system has
already been described elsewhere [6]. All deposi-
tions were achieved with a discharge power of 600
W ($\varnothing$ of the target $= 100$ mm), a total pressure of
0.74 Pa and a relative nitrogen pressure (PN2/
PTot) equal to 0.5. The oxygen content in the films
was varied by using a precision valve to introduce
a controlled leak of air in the deposition chamber.
In this way, thin films with an oxygen content
ranging from 6.2 to 58.8 at.%, as measured by
electron probe microanalysis (EPMA), were de-
posited. The incorporation of erbium in the AlN
films was achieved by partially covering the alu-
minium target with an adapted number of small
metallic erbium pieces. The erbium concentration
can be adjusted by modifying the Er/Al area ratio
on the target or on the position of erbium pieces

compared to the magnetron ring. The erbium
concentration in the samples was estimated to 3.3
at.% by EPMA. Annealing of the films was carried
out at 1075 K in a quartz tube, previously evacu-
ated down to an ultimate vacuum pressure of less
than 3×10^{-3} Pa, for 1 h in a dynamic hydroge-
nated argon atmosphere.

Infrared room temperature photoluminescence
(PL) was excited by the 980 nm radiation of a CW
Titanium–sapphire laser while the PL signals were
analysed through a 1/4 m monochromator, de-
tected using a liquid-nitrogen cooled Ge detector
and measured by a standard lock-in amplifier.
Two samples have been tested using high-resolu-
tion spectroscopy, namely site-selective spectro-
scopy. In these experiments, a sample is excited
using the Ti:sapphire laser light with typical line-
width of 2 GHz. The wavelength used for the ex-
periment is tuned around 980 nm in accordance
with the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ absorption transition. The
samples were mounted in a liquid-helium bath
cryostat that enables to reach temperature as low
as 1.5 K, the temperature used for all the mea-
surements. Assuming a fast and efficient relaxation
from the $^4I_{11/2}$ (the maximum phonon energy in
AlN being close to 900 cm^{-1} as reported in [8]) the
$^4I_{13/2} \rightarrow {}^4I_{15/2}$ luminescence emitted by the sample
was collected and focused on the entrance slit of
the 1/4 m monochromator. The signal was then
processed as mentioned above. As a reference of
aluminium oxide environment, an aluminosilicate
glass fabricated by MCVD process has also been
examined.

3. Results and discussion

The evolution of the erbium emission band at
room temperature around 1.55 µm, as a function
of oxygen content in the films, is shown in Fig. 1.
As can be observed, the intensity as well as the
profile of the emission at room temperature
changes when the oxygen content increases.
Moreover, a shift of the peak intensity to the
longer wavelengths is observed as the oxygen level
rises (see inset of Fig. 1).

Two Er:AlN films have been tested using site-
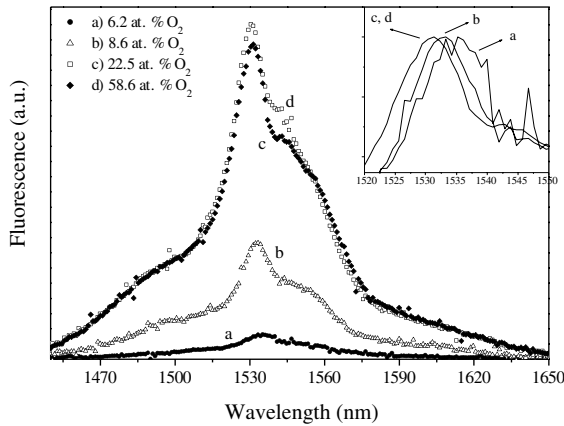selective spectroscopy. The oxygen content of the

Fig. 1. Evolution of the erbium PL emission at room temperature around 1.55 μm as a function of oxygen content in the films. In the inset, an enlargement of the normalized main peak is depicted.

oxygen rich film (which will be referred as the O$^+$ film) was estimated to 22.5 at.% while the oxygen poorer film (which will be referred as the O$^-$ film) presented an oxygen content of 6.2 at.%.

The principle of the fluorescence line narrowing (FLN) experiment is the following: at very low temperature, it is possible to probe the luminescent properties of the erbium ions belonging to different sites using a spectrally narrow laser. Actually, in a crystal and moreover in a glass, the luminescent ions are located in different crystallographic sites characterised by different crystal field electronic environment. Each class of sites possess its own luminescent properties, namely: position of the energy levels, broadening, lifetime... At low temperature, the emission and absorption bands are narrow due to the small homogeneous broadening and the small number of energy levels populated. Using a spectrally narrow laser, it is then possible to selectively excite the ions: each excitation wavelength corresponding to a given class of sites. Because the nonresonant excitation occurs in the $^4I_{9/2}$ $^4I_{11/2}$ excited state, rapid relaxation from this excited state to the emitting state ($^4I_{11/2}$ $^4I_{13/2}$) contributes to a residual broadening. That is the reason why, in all the spectra, measured lines are still broad as compare to resonant fluorescence line narrowing (RFLN) experiment [9]. In the case of our samples, the evolutions of the 1.55 μm emis-

sion spectrum as a function of the excitation wavelength are reported in Figs. 2–4. For all the samples, at shorter excitation wavelength, a broadband emission is obtained, resulting from the nonselective excitation of all the erbium ions. Decreasing the excitation energy (increasing the wavelength), it is then possible to achieve a selective
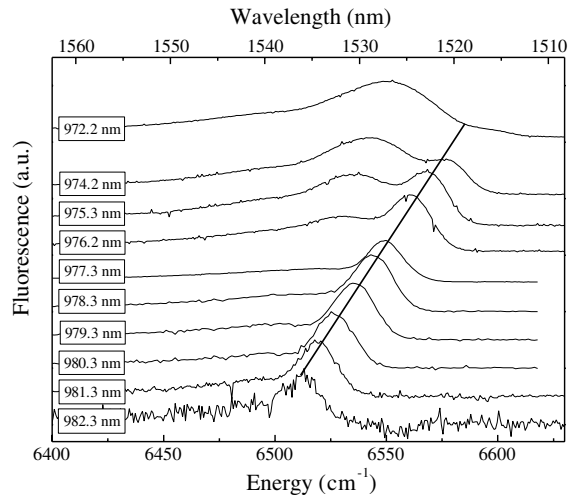

Fig. 2. Evolution of the $^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ emission spectrum at 1.5 K as a function of excitation wavelength for the aluminosilicate glass.
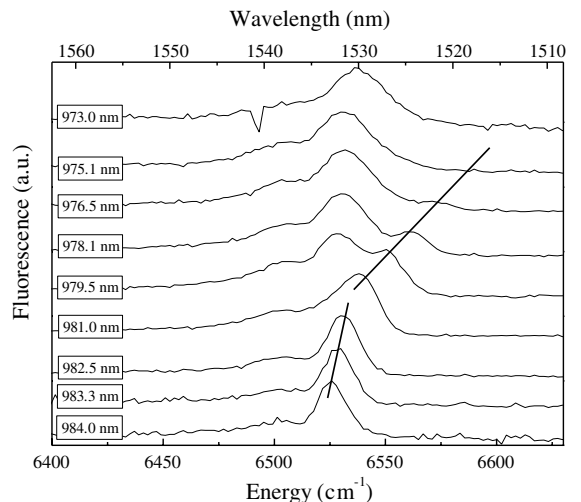
Fig. 3. Evolution of the $^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ emission spectrum at 1.5 K as a function of excitation wavelength for the O$^+$ film.
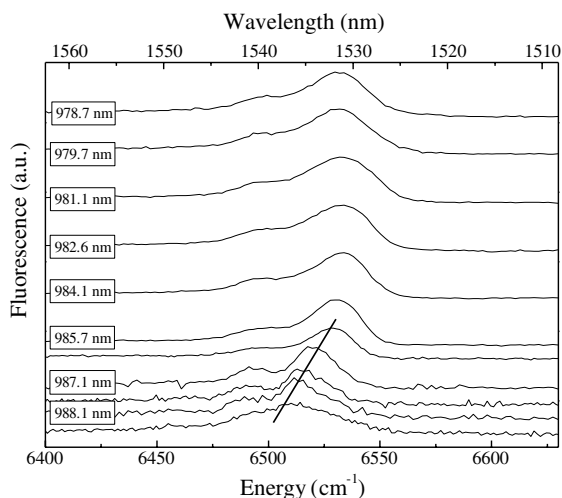
Fig. 4. Evolution of the $^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ emission spectrum at 1.5 K as a function of excitation wavelength for O$^-$ film.

Fig. 5. Maximum intensity of the selective excitation emission as a function of the excitation energy for the aluminosilicate glass, the O$^+$ film and the O$^-$ film.

excitation characterised by a sharp emission band of which the position varies with the excitation wavelength: it is attributed to the zero-phonon transition of the probed class of sites (transition between the bottom Stark levels of the two energy manifold involved). At longer wavelength, no more ions are excited and no signal is detected. The spectral range over which the zero-phonon transition is recorded gives information about the site distribution of the erbium ions in the studied matrix: the larger this spectral range, the more inhomogeneous is the environment of the erbium ions.

As it appears in Fig. 2, the aluminosilicate glass exhibits a continuous site distribution extending from roughly 972 to 982 nm (around 100 cm^{-1}). The energy of the maximum PL intensity of the selective excitation emission varies linearly with excitation energy (see Fig. 5). This is interpreted as an evidence for a unique kind of environment for erbium ions that is slightly modified from one ion to another. It can be related to the Gaussian profile of the site distribution already pointed out by RFLN [10].

The two Er:AlN samples present very different behaviours. The site distribution for O$^+$ is discontinuous, as can be observed in Fig. 3, and the energy of the maximum PL intensity of the selective excitation emission shows a change of slope
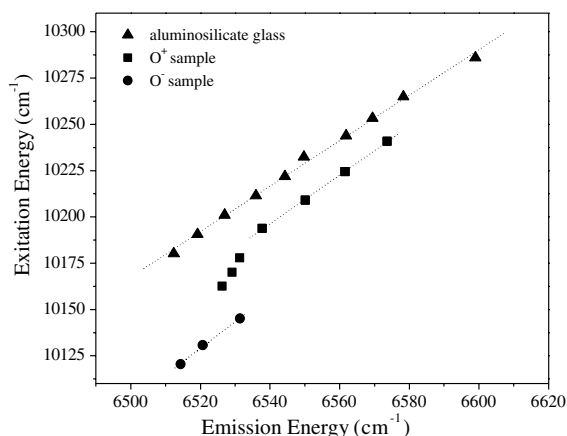
near 10180 cm^{-1} excitation energy (see Fig. 5). For this sample, the site distribution can be divided in two contributions, that suggesting the existence of two kinds of sites. The spectral spreading of this site distribution (around 80 cm^{-1}) is reduced compared to aluminosilicate glass and is globally shifted towards longer wavelengths. In opposite to sample O$^+$, the site distribution for sample O$^-$ do not present any discontinuity as can be observed in Fig. 4. As was observed for the aluminosilicate glass, the energy of the maximum PL intensity of the selective excitation emission for the O$^-$ sample varies linearly with excitation energy (see Fig. 5). However, the site distribution for this sample seems very reduced (25 cm^{-1}) and strongly shifted to longer wavelengths.

Due to the presence of both nitrogen and oxygen in the AlN films, it is reasonable to interpret the two sites distributions observed in O$^+$ as being related to Er–O and Er–N environments. Taking into account the covalency of the bondings and its influence on the energy gap between manifolds (nephelauxetic effect [11]) the oxygen site corresponds to the first part of the site distribution (973.04 → 981 nm). It is interesting to note that the spectral range covered by this first site distribution is similar to that of the reference sample. This suggests that it is related to Er–O–Al environment. The "nitrogen" site would then correspond to the second part of the site distribution at longer

wavelength which agrees the covalent nature of the Er–N bonding. It is surprising that this rupture of the site distribution is not observed in the O^- sample. In this sample, it seems that only the nitrogen site is detected with a small site distribution extending from 985.7 to 988.1 nm. However, this film contains around 6.2 at.% of oxygen and the corresponding site distribution at shorter wavelengths was then expected.

4. Conclusions

The aim of this paper was to analyse the environment of erbium ions in AlN films using non-resonant site-selective spectroscopy. Two samples with different oxygen contents have been studied and an influence of oxygen concentration on the site distribution has been observed. It appears that the site distribution is not continuous as in classical aluminosilicate glass but presents a rupture that suggests the existence of two kinds of sites for erbium: "oxygen" site and "nitrogen" site. These observations can easily be interpreted within the framework of the nephelauxetic effect which explains the shift of the site distribution to the longer wavelengths in accordance with an increase of the bonding covalency. It would be further interesting to have access to the crystal field splitting and to the homogeneous broadening of such covalent erbium environment.

References

[1] J.M. Zavada, M. Thaik, U. Hommerich, J.D. McKenzie, C.R. Abernathy, S.J. Pearton, R.G. Wilson, J. Alloys Compds. 300 (2000) 207.

[2] M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, K. Yamamoto, Appl. Phys. Lett. 71 (1997) 1198.

[3] P.N. Favennec, H. L'Haridon, D. Moutonnet, Y.L. Guillo, Electron. Lett. 25 (1989) 718.

[4] R.G. Wilson, R.N. Schwartz, C.R. Abernathy, S.J. Pearton, N. Newman, M. Rubin, T. Fu, J.M. Zavada, Appl. Phys. Lett. 65 (1994) 992.

[5] K. Gurumurugan, H. Chen, G.R. Harp, W.M. Jadwisienczak, H.J. Lozykowski, Appl. Phys. Lett. 74 (1999) 3008.

[6] J.C. Oliveira, A. Cavaleiro, M.T. Vieira, Surf. Coatings Technol. 132 (2000) 99.

[7] M. Kuball, Surf. Interface Anal. 31 (10) (2001) 987.

[8] F. Auzel, 1st Franco-Israeli Workshop, Jerusalem, December 1988 (published in SPIE, 1182 (1989) p. 59).

[9] R.M. MacFarlane, R.M. Shelby, J. Luminescence 36 (1987) 179.

[10] L. Bigot, A.M. Jurdyc, B. Jacquier, D. Bayart, L. Gasca, Phys. Rev. B 66 (2002).

[11] R. Reisfeld, C.K. Jorgensen, in: Lasers and Excited States of Rare Earths, Springer-Verlag, 1977.