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Ion and Electron Beam Induced Luminescence of Rare Earth Doped YAG Crystals

G. Gawlik*, J. Sarnecki, I. Jóźwik, J. Jagielski and M. Pawłowska

Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warszawa, Poland

The aim of this work was the evaluation of ion-beam induced luminescence for the characterization of luminescent oxide materials containing rare earth elements. The yttrium aluminium garnet epilayers doped with Nd, Pr, Ho, and Tm atoms were used. The ion-beam induced luminescence spectra were excited using 100 keV H_2^+ ion beam and were recorded in the wavelengths ranging from 300 nm up to 1000 nm. The separate parts of the surface of the same samples were used for ion-beam induced luminescence and cathodoluminescence experiments. Cathodoluminescence spectra have been recorded in the range from 370 nm up to 850 nm at 20 keV e-beam in scanning electron microscope equipped with a grating spectrometer coupled with a photomultiplier. The observed narrow ion-beam induced luminescence lines can be ascribed to the well known radiative transitions in the rare-earth ions in the YAG crystals. The cathodoluminescence spectra reveal essentially the same emission lines as ion-beam induced luminescence. The decrease of the ion-beam induced luminescence lines intensity has been observed under the increasing ion fluences. The ion-beam induced luminescence may be used for characterization of transparent luminescent materials as an alternative method for cathodoluminescence and can be especially useful for observation of ion-beam damage formation in crystals.

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1. Introduction

Recently the growing interest of the ion-beam induced luminescence (IBIL) method used for material characterization is observed. The ion induced luminescence can be directly applied for characterization of scintillating materials [1]. The luminescent signal can also be used for the "*in situ*" control of the target damage induced by the ion implantation [2]. Very high sensitivity of luminescent methods makes ionoluminescence suitable for detection of some impurities such as transition metals and rare earth (RE) elements [2]. Because of high sensitivity on impurity detection the IBIL can also be employed for the identification of art materials like jewels, paints, metals, ceramics of similar composition but of different provenience [3].

The aim of this work was the evaluation of capabilities of ionoluminescence method for the characterization of luminescent oxide materials containing RE elements for optoelectronic applications.

2. Experiment

IBIL of RE elements doped yttrium aluminium garnet (YAG) epilayers has been measured under hydrogen ion beam irradiation. The YAG epilayers were grown on the YAG single crystal substrates. The YAG epilayers were doped with Nd, Pr, Ho, and Tm atoms during liquid phase epitaxy (LPE) growth. Ionoluminescence was excited using the molecular 100 keV H_2^+ ion beam with the ion current density ranging from 1 μ A/cm^2 up to 5 μA/cm^2. The IBIL spectra in the wavelength range from 300 nm up to 1000 nm with the resolution of 1 nm were recorded using a minispectrometer equipped with a CCD detector end fiber optic waveguide. The fiber optic waveguide was directed perpendicularly to the ion beam direction. The samples were placed in the ion implanter target chamber at the angle of 45° with respect to the ion beam and to the fiber optic waveguide. Collection time for one IBIL spectrum was set from 1 s up to 10 s depending on total brightness of the emitted light. The IBIL spectra have been recorded at the increasing hydrogen ion fluences so that the first spectrum was recorded at about 2×10^{13} cm^{-2} and the last one at about 2×10^{16} cm^{-2}. The first IBIL spectrum for each sample was recorded at the very beginning of the irradiation.

The same samples were used for the IBIL and cathodoluminescence (CL) experiments. The virgin part of the sample surface was exposed to the electron beam for CL excitation. CL spectra have been recorded in the range from 370 nm up to 850 nm at 20 keV e-beam in scanning electron microscope (SEM) equipped with a fiber optic waveguide guiding the light to a grating spectrometer coupled with a photomultiplier.

* corresponding author; e-mail: grzegorz.gawlik@itme.edu.pl

3. Results and discussion

Each of the RE doped YAG crystals used in the experiments exhibits bright luminescence of different colors when exposed to hydrogen ion irradiation. Under hydrogen ion beam Tm doped YAG emits blue light, Ho doped YAG emits green light, Pr:YAG looks reddish, and Nd:YAG emits light of mixed green-blue color. Intensity of emitted light decreased with the increasing hydrogen ion fluence without visible changes of the emitted color.

All recorded IBIL spectra are rich in emission lines from NIR up to UV spectral range (Fig. 1). The observed narrow IBIL lines can be ascribed to the well known radiative transitions in RE ions in the YAG crystals. For example the transitions of IBIL lines for 0.5%Ho:YAG are displayed in Fig. 2. In this case a broad band emission can be observed besides the narrow lines characteristic of transitions in Ho^{3+} ions (Fig. 1).

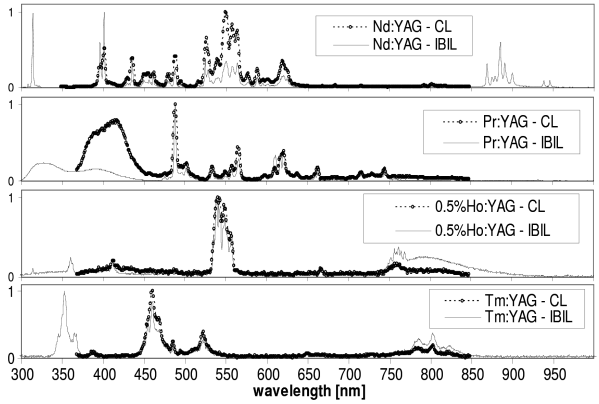

Fig. 1. IBIL and CL spectra (normalized) of YAG crystals doped with the RE elements: Nd, Pr, Ho, Tm. IBIL spectra — solid lines, CL spectra — dashed lines.

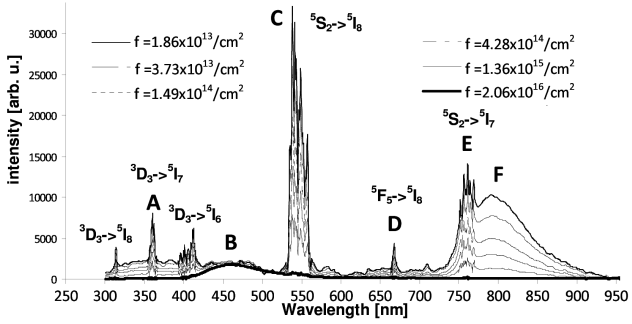

Fig. 2. Changes of 0.5%Ho:YAG IBIL spectra with increasing hydrogen ion fluence ranging from $1.86 \times 10^{13}/\mathrm{cm}^2$ up to $2.06 \times 10^{16}/\mathrm{cm}^2$.

In order to assess the usefulness of IBIL spectra for the analysis of luminescence properties of RE doped YAG crystals the same samples were analyzed using cathodoluminescence, which is a well established experimental technique and may serve the purpose of a reference method. The CL spectra reveal essentially the same emission lines as IBIL, including the broad band emission lines observed for 0.5%Ho:YAG. However, it should be noted that relative intensities of the IBIL and CL lines are slightly different.

The IBIL spectra for 0.5%Ho:YAG were recorded at different hydrogen ion fluences with the constant hydrogen ion beam current 3 μA/cm^2. The spectra recording time was progressively increased from 1 s up to 10 s to compensate for the light brightness reduction with the increasing ion fluence. One may note different degradation rates of the IBIL emission lines. The degradation rates of most Ho^{3+}-related lines are very similar, however those of broad band emission lines are different. The degradation of the emission band with the maximum at 790 nm is higher than that of Ho^{3+}-related IBIL lines. On the other hand, the degradation rate of the emission band with the maximum centered at 460 nm seems to be insensitive to the ion fluence (Fig. 3). The nature of this center is unclear, but it should be pointed out that the fluence insensitive ionoluminescent broad band was also observed by Manfredotti et al. in the synthetic diamond [4].

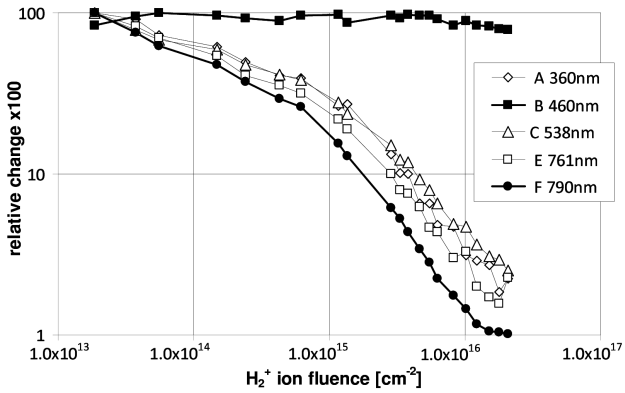

Fig. 3. Degradation of IBIL spectral lines with increasing hydrogen ion fluence. The lines indicated as A, B, C, E, and F are referred to the spectral lines in Fig. 2. Photon count numbers at line's maxima were used for estimation of IBIL lines degradation.

Most Ho^{3+}-related IBIL emission lines decay in a similar way. The experimental data may be fitted using a simple relation (Fig. 4):

$$N = C\,[A/(A + b\phi)]\,, \tag{1}$$

where N is the observed light intensity, ϕ — the hydrogen ion fluence, A — the initial concentration of effectively observed luminescent centers, b — the number of nonradiative recombination centers created by one hydrogen ion, C — the constant.

The above model was constructed under the assumption that the implanted hydrogen ion creates a given number of nonradiative recombination centers and does not influence the properties of radiative recombination

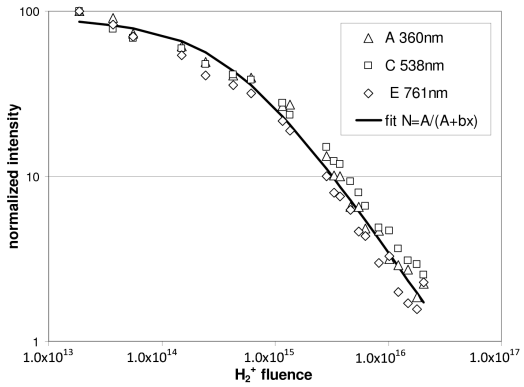

Fig. 4. Fit to experimental data using Eq. (1). The experimental points indicated as A, C and E are referred to the spectral lines indicated in Fig. 2. Photon count numbers at line's maxima were used for estimation of IBIL lines degradation.

centers related to the RE ion in YAG. The observed IBIL signal degradation is thus caused by the competition between the stable radiative transitions and the ion beam induced fluence dependent nonradiative transitions.

It is possible to fit the experimental data by using Eq. (1) with two assumptions: (i) that A is equal to the Ho concentration in the crystal ($A = 2.4 \times 10^{15}$ cm^{-2}) and (ii) that one H_2^+ ion creates 6 nonradiative transition centers (Fig. 4). Such estimation gives the largest number of nonradiative transition centers created by one incident proton (3 nonradiative centers per one proton). The number of nonradiative centers created by one proton may be actually lower because some nonradiative centers may exist already in the non-radiative Ho:YAG crystal. Hence A may be lower than atomic Ho concentration and consequently, b may be proportionally smaller than 6.

Both A and b values are arithmetically coupled, therefore the determination of an actual number of the recombination centers generated by one proton requires independent experiments.

4. Conclusions

Irradiation with hydrogen ions of RE doped YAG crystals generates strong light emission. The IBIL spectra consist of well known radiative transitions characteristic of RE ions in YAG. The information provided by IBIL may be competitive for material characterization by the cathodoluminescence method. First of all IBIL experiments can be carried out "*in situ*" in the ion implanter target chamber during the implantation process. Degradation of IBIL signal with the ion fluence gives estimation of the largest possible number of nonradiative centers created by one implanted ion (proton). The experiments point also to a significantly stronger IBIL signal when compared to the CL one making experiments easier and much faster.

Summing up, the ionoluminescence may be used for characterization of transparent luminescent materials as an alternative method for cathodoluminescence. This method can be especially useful for ion-beam damage formation in crystals. However, determination of the nature of observed nonradiative centers requires additional material characterization using independent methods.

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