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# High intensity luminescence from pulsed laser annealed europium implanted sapphire

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Sapphire samples ( $\text{Al}_2\text{O}_3$ ) were implanted with 400-keV ions at a dose of  $1 \times 10^{16}$  ions  $\text{cm}^{-2}$ . A comparison was made between furnace annealing and pulsed laser annealing of the implanted samples. Furnace annealing to 1200 °C, followed by excimer laser anneals, resulted in an increase of the cathodoluminescence emission intensity of the implanted europium by a factor of  $\sim 20$ . This enhanced intensity is  $\sim 50$  times that of the signal prior to any form annealing treatment. It is proposed that the laser anneals dissociate Eu related clusters. The Eu 622-nm lifetime reached 1.53 ms compared with an original postimplant value of 0.14 ms. © 1994 American Institute of Physics.

The literature of optical effects resulting from ion beam implantation of insulators is small although it includes examples as diverse as the formation of optical waveguides, waveguide lasers, second-harmonic generation, guided four-wave mixing to production of car mirrors and sunglasses.<sup>1</sup> One topic which has received extensive study in recent years is the attempt to make Er lasers operating at 1.5  $\mu\text{m}$  by direct implantation of the Er ions.<sup>2-4</sup> Independent of the target material there appear to be a number of problems. The first is that the radiation damage quenches the photoluminescence and, hence, lasing action is not possible. Further, in order to anneal out the damage sites, temperatures as high as 1200 °C are required in, for example, sapphire. Such furnace anneals successfully sharpen the line shape for the Er transition and increase the excited state lifetime, but as shown by transmission electron microscopy, also result in a precipitation of Er into either colloids or an oxide phase. Consequently, the overall luminescence efficiency drops by about a factor of 40. Cluster precipitation is most obvious with high Er concentrations, which is unfortunate since one prefers to increase the Er doping to enhance the laser action.

The challenge is thus to dissociate the rare earth clusters into an atomically dispersed state and so increase the overall luminescence efficiency. To this end pulsed laser annealing has been attempted and data are presented here. For experimental convenience the selected ion was Eu, rather than Er, since Eu emits in the red region of the spectrum near 622 nm and the cathodoluminescence equipment was designed for photomultiplier detection. The system was not easily extended into the infrared region for Er signals at 1.54  $\mu\text{m}$ . The change in ion species is not thought to be significant in terms of the annealing response since the behavior of rare earth ions of comparable ionic radius is unlikely to vary greatly. More importantly, as seen from the data presented here, the changes in intensity of the Eu luminescence with furnace annealing are closely similar to those of the Er implants.<sup>2-4</sup>

Laser annealing has been widely and successfully applied to anneal ion implanted semiconductor and metals,<sup>5-8</sup> but the literature for insulator targets is very restricted<sup>9,10</sup> and

has been mainly concerned with laser damage studies.<sup>11,12</sup> Formation of metallic colloids, clusters, or precipitate phases have been reported for many crystalline and glass insulator targets (as reviewed in Ref. 1). In a recent example with ion implanted Ag in glass the colloids were successfully dissociated by pulsed laser annealing.<sup>10</sup> There was, therefore, an expectation that for the rare earth colloids, or precipitates, that a similar dissociation of the clusters might be achieved. The present letter describes the effects of excimer pulsed laser annealing on the cathodoluminescence emission spectra of europium implanted  $\text{Al}_2\text{O}_3$  samples.

The samples used for the annealing studies were implanted with 400 keV ions at a dose of  $1 \times 10^{16}$  atoms  $\text{cm}^{-2}$ . The  $\text{Al}_2\text{O}_3$  sample were tilted by 7° in order to suppress channeling. Thermal treatments have been made by two distinct approaches. The first approach, using standard tube furnaces with temperatures from 100 to 1200 °C, was carried out on an  $\text{Al}_2\text{O}_3$  sample in air for 1 h at each temperature. Since the problem is concerned with colloid or cluster dissociation and formation the speed of cooling may be relevant as dissociated clusters might reform during the cooling cycle. The cooling period was, therefore, relatively fast and ranged from 1 to 10 min, depending on the maximum temperature. The second approach was to use excimer laser pulses. The irradiation were performed in air with an ArF excimer laser [wavelength=193 nm and pulse length=12 ns full width at half-maximum (FWHM)]. The ArF excimer laser for the annealing was partially focused on the sample to yield an energy density between 110 and 190  $\text{mJ cm}^{-2}$ . Energy density fluctuations are about 5%. Several pulses, from 25 to 360, were accumulated in the various areas of the specimen (i.e., 2×3 or 4×4 mm) at a repetition rate of 1 Hz. The data are discussed in terms of three well-defined areas. Data for areas 1 and 2 were for 25 and 100 pulses, respectively, at the 110  $\text{mJ cm}^{-2}$  power level whilst region 3 was for 360 pulses at the higher level of 190  $\text{mJ cm}^{-2}$ . Comparison between the three values is a useful first guide but one must note that the annealing may not be linear with the laser pulse power.

Depth analysis of the Eu was made using Rutherford

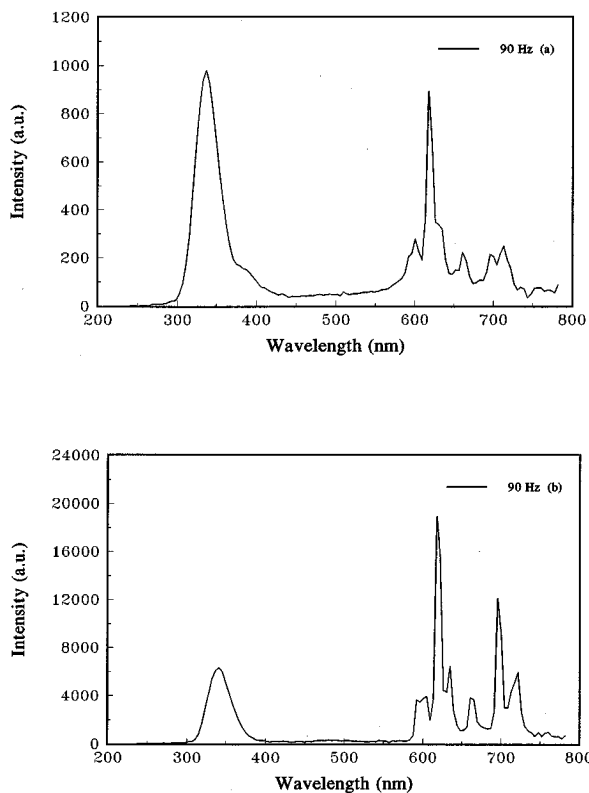


FIG. 1. Examples of the cathodoluminescence spectra from Eu implanted sapphire. (a) after ion implantation and (b) after 1000 °C furnace annealing. The band near 340 nm is from the  $\text{Al}_2\text{O}_3$  and the line near 694 nm from Cr impurities. The main Eu signal is at 622 nm. The lock-in amplifier modulation frequency was 90 Hz.

backscattering spectrometry (RBS) with He ions at 1.89 MeV.

Cathodoluminescence (CL) emission spectra were recorded between 300 and 800 nm for  $\text{Al}_2\text{O}_3:\text{Eu}$  at 293 K with different excitation modulation frequencies. The strongest red emission line from the Eu ions occurs at 622 nm and arises from the transitions from the  $^5D_0$  to  $^7F_2$  levels. Figure 1 displays typical CL spectra taken at room temperature. The broadband emission near 340 nm arises from the sapphire host lattice, the line feature near 694 nm comes from Cr impurities in the host and the remaining line spectra are predominantly from the implanted Eu. Figure 1(a) shows a spectrum after Eu implantation and Fig. 1(b) is after furnace annealing at 1000 °C. Figures 1(a) and 1(b) are presented with different intensity scales and emphasize that after the 1000 °C anneal the overall intensity can be increased by a factor of 20 times for the Eu signal but by different amounts for the Cr impurity and the intrinsic defect emission. Such variations are a function of the anneal temperature. Overall the furnace annealing temperatures ranged from 100 to 1200 °C for the  $\text{Al}_2\text{O}_3$  samples and a graph of the Eu 622-nm CL intensity versus temperature is shown in Fig. 2. It is obvious that the form of the furnace anneal curve closely follows the pattern described earlier for Er implants.<sup>3</sup> Although the luminescence intensity for Eu rose by about 20 times relative to the initial implant signal by annealing to

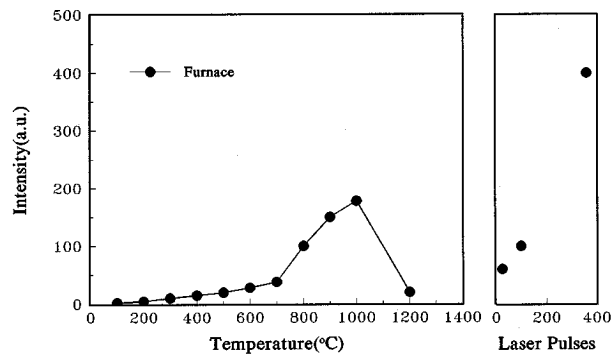


FIG. 2. The 622-nm intensity following isochronal furnace annealing, each of 1 h, and subsequent laser treatments with 25 and 100 pulses at a power level of  $110 \text{ mJ cm}^{-2}$  and 360 pulses at  $190 \text{ mJ cm}^{-2}$ .

1000 °C there was a rapid fall by a factor of about 8 for the higher temperature anneal. This decline is noticeably less than for the earlier Er examples.

With the Er data<sup>3</sup> one saw a steady rise in lifetime with furnace annealing without any alteration after 1000 °C and a parallel situation occurred here for the Eu. Lifetime values were recorded for the 622-nm Eu line as 0.14 ms for the as-implanted sample. After annealing at 800, 1000, and 1200 °C the lifetimes increased to 0.82, 1.44, and 1.35 ms, respectively.

Laser pulse annealings were applied on the same sample after annealing at 1200 °C. After the laser annealing the intensity of the cathodoluminescence emission lines coming from  $\text{Eu}^{3+}$  was increased significantly. For instance, the CL emission line at 622 nm was increased by a factor of 3.5 whereas the broadband in the blue region (340 nm) was increased by a factor of 3. Laser pulse annealings were applied to the  $\text{Al}_2\text{O}_3$  sample three times. Laser annealing changes the relative intensity of the intrinsic band, the Cr impurity and the Eu implanted signals. In each case this is consistent with dissociation of Eu complexes which provides isolated Eu ions that are able to luminesce. The difference in behavior following the three pulsed laser anneals is typified by Fig. 3 in which the relative intensities of the signals are compared after each laser treatment with the zeroth-order signal which was for the sample after the 1200 °C furnace anneal. Since the laser anneal experiments were initial trials they do not represent a detailed analysis of the potential of the pulsed laser treatments, however they clearly indicate enhancement of the luminescence signals and, additionally, the data of Figs. 2 and 3 suggest that further enhancement may be possible. The most important aspect of the data is that the Eu signal increases  $\sim 20$ -fold with respect to the final furnace anneal and  $\sim 50$ -fold compared with the original as-implanted signal.

Subsequent to the furnace anneals laser annealing made small changes in the lifetime and the value rose to 1.53 ms after the third treatment.

Rutherford backscattering spectrometry showed that the europium implanted sapphire had a Eu depth concentration with the expected near Gaussian profile. Analysis of the data

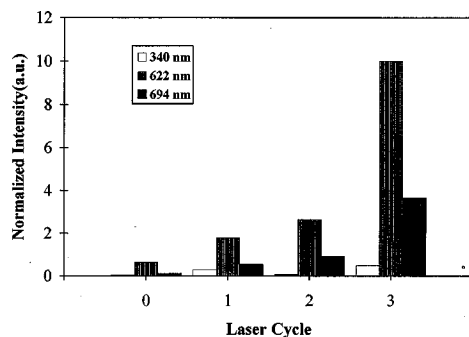


FIG. 3. The relative signal intensities at 340, 622, and 694 nm after 1200 °C furnace annealing (cycle 0) and the three subsequent laser anneals (1,2,3).

gave the projected ion range value of 69 nm, with a FWHM of 50.6 nm. Of particular significance is that there is no noticeable diffusion as a result of either the thermal or the laser annealing. This is the same result as reported for the furnace annealed Er implants and the new data emphasize that laser annealing has not been accompanied by any long-range diffusion.

The data presented here confirm that furnace annealing can significantly alter the state of dispersion of rare earth ions after they have been implanted into sapphire. As for earlier Er data the excited state lifetime can be improved, but unfortunately the high-temperature furnace annealing allows both damage reduction and rare earth precipitation into non-radiative clusters. Destruction of such clusters is feasible by

the rapid thermal heating and quenching which ensues when the material is annealed with short laser pulses. The improvements exceed those reached by furnace annealing by at least a factor of 20 and further experiments are in progress to ascertain the maximum enhancement that is possible. It should be noted that the data are for relatively high implant doses of Eu, which favor cluster generation, so this underlines the favorable result obtained by the laser pulse annealing. Overall the data suggest that, contrary to earlier reports, laser action may be achievable using rare earth ion implanted active ions followed by laser pulse annealing.

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