Photomechanical Modification of ZnS Micro-Crystal to Enhance Electroluminescence by Ultra-Short Pulse Laser Processing

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Abstract

A ZnS micro-crystal was treated by an ultra-short pulse laser and applied to an inorganic electroluminescence (EL) phosphor. We found that the EL emission intensity was increased by the laser-induced photomechanical modification. Pulse duration dependency of the emission enhancement and structural analysis by a scanning electron microscopy indicated that the structural modification was induced inside the ZnS crystal, although a mechanical grinding would induce the structural modification mainly on the crystal surface. The results suggested a new way to enhance emission of inorganic EL devices.
Main text

Recently organic electroluminescence (EL) devices have attracted much attention as an element of next-generation display having flexibility of the screen. On the other hand, inorganic EL devices still possess several advantages such as wide operating temperature range, highly reliability, and high resistance against shock and vibration. The main bottleneck of inorganic EL devices is low efficiency of the light emission.

ZnS crystalline phosphor is a promising material for inorganic EL device [1]. The emission mechanism of the ZnS hetero-crystalline phosphor has been suggested by Fischer in 1963 [2] as presented in Fig. 1(a). When Cu atoms are doped in the ZnS polycrystal with hexagonal and cubic phases, Cu$_2$S needle crystal is produced at the hetero-interface between two crystalline phases [3, 4], and the crystalline complex works as an emission site (Cu$_2$S site) by applying an AC voltage. Thus, increasing the density of the Cu$_2$S site is important to enhance the emission.

Previously, we have applied the modified mechanical grinding technique [5], which is similar procedure established by Ito and co-workers [6], to increase the density of the Cu$_2$S. The method is shown in Fig 1(b). The ZnS micro-crystal with hexagonal phase was mechanically grinded in a mortar to generate mechanical cracks in the crystal (Left-top cartoon of Fig. 1(b)). By annealing the crystal with metallic Cu powder, a large volume of hexagonal phase ZnS was changed to the cubic phase, and the EL emission was increased [7, 8]. This fact suggests that the hetero-interface with the Cu$_2$S site is generated at the
mechanical crack. It is expected that the EL emission can enhance by making the mechanical cracks densely in the ZnS micro-crystal. Here, as an alternative method to generate mechanical cracks inside the ZnS’s micro-crystal, our attention is directed to apply the photomechanical ablation by ultra-short pulse laser to the cracking process [9, 10].

When an intense, infrared ultra-short pulse laser is introduced to an insulating material, optical breakdown is induced inside of the material as a result of effective multiphoton absorption [11]. Since the breakdown (insulator destruction) induces structural destruction, mechanical cracks are generated inside of the material. Simultaneously with such structural destruction, the absorbed light energy is converted to heat, which is attributed to random vibration of the lattice. When a pulse duration is enough shorter than time scale to excitation of the random lattice vibration, the structural destruction would be induced efficiently before heating insulating materials [12].

In this work, the photomechanical ablation by an infrared femtosecond laser was applied to modify the ZnS micro-crystal with hexagonal phase (Left-bottom cartoon of Fig. 1(b)). The crystal was converted to EL phosphor, which is polycrystal consisting of hexagonal and cubic phases and containing Cu$_2$S site, by annealing it with metallic Cu material [2]. The ZnS micro-crystalline powder was sandwiched between two electrodes, and the EL emission was evaluated. The ability was compared with the ZnS micro-crystal modulated by a picosecond laser with same wavelength as the femtosecond one. The pulse duration
effect of the EL emission was discussed with photo-luminescence (PL) and scanning electron microscope (SEM) measurements of these phosphors.

As a starting material, a ZnS powder (Image Tech Inc., average particle diameter: 16 μm,) with wurtzite (hexagonal) structure was prepared. The 0.3 g ZnS powder dispersed in 1 ml anhydrous ethanol was put in a 1 cm square quartz cell, and agitated by a magnetic stirrer. Femtosecond laser pulse train (wavelength: 800 nm, pulse duration: 250 fs, repetition frequency: 1 kHz) from chirped pulse amplified Ti-sapphire laser system (Cyber laser, IFRIT SP-1) was focused at the top (liquid-air interface) of the sample through a 10 cm convex lens (Fig. 2(a)). The pulse irradiation time and the pulse energy were controlled by a mechanical shutter and a gradient neutral density filter which put on the beam line between the laser system and the convex lens. In the experiment using picosecond laser, the pulse duration was tuned to be 2 ps by controlling the chirp pulse compressor after the regenerative amplification. The pulse duration was evaluated by a single shot autocorrelator (Positive light, SSA) with Mach–Zehnder interferometer, whose accuracy is in detection range from 50 fs to 5 ps.

The mechanical grinding of the ZnS powder was performed and combined with the femtosecond laser treatment. The 2 g ZnS powder was put in a magnet mortar stirrer (AS ONE Corporation, MMPS-T1) and grinded for 1 hour with a rotation speed of 100 rpm. After the grinding, the powder was dispersed in the anhydrous ethanol and exposed to the femtosecond laser with same procedure mentioned in above.
After the treatment, the ZnS powder was mixed with a metallic copper powder (purity: 4N, Average particle diameter: 1μm, ZnS : Cu = 2000 : 1 (weight ratio)) and annealed [13]. The annealing was performed by increasing the temperature from 23 ℃ to 800 ℃ with a rate of 100 ℃/min and keeping at 800 ℃ for 15 min. The Cu doped ZnS powder was dispersed in a resin consisting of mixture of cyanoethyl pullulan and cyanoethyl polyvinylalcohol (Shin-Etsu Chemical, CR-V and CR-S) and used as a luminescent ink. The ink was deposited on an electrode plate made of indium tin oxide (ITO) by screen printing and covered with a Barium Titanium (IV) Oxide (BaTiO3) dielectric and a carbon electrode (Fig. 2(b)). An EL emission by applying an AC voltage (212 V, 10 kHz) between the electrodes was detected by a photometer (KONICA MINOLTA, LS-110).

The photoluminescence from the ZnS powder after the laser treatment and the annealing was measured by a fluorescence spectrophotometer (JASCO, FP-6500) at room temperature. The excitation wavelength is 335 nm, which is around maximum absorption of the ZnS micro-crystal. The crystal shape after the laser treatment and the annealing was observed by a scanning electron microscope (LEOL, JSM-7400F) and compared with that after mechanical grinding without the laser irradiation.

The laser pulse energy dependence of the EL emission is shown in Fig. 2(c). The intensity of the emission increased with the laser pulse energy. When the laser pulse energy was 0.15 mJ/pulse, the intensity of the emission was about 5.5 times larger than that of the reference sample with the annealing and without the laser treatment (Left bar indicated as
We found obvious enhancement of the EL emission leaded by the femtosecond laser irradiation process.

The laser irradiation time dependence of the EL emission is shown in Fig. 2(d). The intensity increased with the irradiation time. The crystal structure of the ZnS phosphor after the femtosecond laser treatment was checked by XRD spectra as shown in Fig. 2(d). Although the spectral shape before the annealing is same as that of hexagonal phase crystal, specific peaks of the cubic phase crystal was increased after the annealing. Also for the case by the mechanical grinding, similar XRD spectra indicating the crystal phase transition has been confirmed. The behavior agrees with the hypothesis presented in the Fig. 1(b). This result suggests that mixed crystal with major cubic and minor hexagonal phases is induced by the femtosecond laser treatment and the annealing. These results suggest that the twin crystal plane of cubic and hexagonal phases is increased with the irradiation time.

The pulse duration effect on the EL enhancement was evaluated by comparing emission intensities of the ZnS micro-crystal modulated by the femtosecond laser (250 fs) and the picosecond laser (2 ps) respectively. The applied voltage dependence of the EL emission is shown in Fig. 3(a). The emission intensity of the EL device with the picosecond laser treatment (blue line) was almost same as that without laser treatment (black line), although the intensity with the femtosecond laser treatment (red line) was about 5.5 times larger than them. In this experiment, the same laser condition of wavelength (780 nm), pulse repetition
rate (1 kHz), and pulse irradiation time (30 min) was used except for the pulse duration. This result clearly suggests that the pulse duration is one of the important factors to modulate the ZnS micro-crystal.

The PL spectra of the ZnS micro-crystal after the laser treatments and the annealing are shown in Fig. 3(b). The spectral shape after the laser treatment was almost same as that without the laser treatment. The PL spectrum would be attributed to radiative relaxation from defect states originating in Zn vacancy in the ZnS crystal [14-17]. The PL intensity was increased with the laser treatment. This suggests that the defect states generated by the laser treatment and the annealing. The similar behavior was observed for the ZnS crystal after the mechanical grinding. The PL enhancement by the femtosecond laser treatment was higher than that by the picosecond laser treatment, indicating large modification is induced by the femtosecond laser treatment.

The EL intensity was compared with that by the mechanical grinding as shown in Fig 4(a). The EL enhancement by the femtosecond laser treatment (5.5 times of the reference) was smaller than that by the mechanical grinding (7 times of the reference). When the femtosecond laser treatment was performed after the mechanical grinding, the enhancement was better than that by the mechanical grinding (9 times of the reference). We found an additional modification by the femtosecond laser treatment, which is different form that by the mechanical grinding.

The SEM images of the ZnS micro-crystal after the laser treatments were compared with
that after the mechanical grinding (Fig. 4(b)). The crystal shape after the femtosecond (picosecond) laser treatment was almost same as that before the laser irradiation. This indicates that the laser ablation of whole crystal is not induced by the laser irradiation. On the other hand, small debris of the crystal with a size of a few µm was observed after the mechanical grinding, meaning that the mechanical destruction is obviously induced by the grinding.

The enhancement of the EL emission by the femtosecond laser treatment (Fig. 2(c)) means that the number of Cu$_2$S sites was increased by the femtosecond laser treatment. This fact suggests that the number of the mechanical cracks inside Cu$_2$S crystal is increased by the photomechanical modification due to the femtosecond laser optical breakdown as mentioned in the introduction (Fig. 1(b)). The crystal modification process strongly depends on the laser pulse duration. This indicates that the balance between the photomechanical effect and the photothermal effect depends on the pulse duration.

In comparison with that by the mechanical grinding, although the EL enhancement was a little small on the best condition in the present experiment, further enhancement was observed when the femtosecond laser treatment was performed after the mechanical grinding. The further enhancement means that the modification by the femtosecond laser treatment is not same as that by the mechanical grinding. Since the mechanical damage of the crystal surface by the laser irradiation was smaller than that by the mechanical grinding (Fig. 4(b)), the mechanical modification by the laser treatment would be mainly induced
inside crystal. The smaller enhancement for the PL emission than the EL emission also support this hypothesis. In the PL emission detection, only surface of the micro-crystal is excited because the penetration depth of the 335 nm excitation light is less than 100 nm. On the other hand, in the EL emission detection, electric field was applied to whole of the crystal [18]. On the basis of these results, it is suggested that the ZnS phosphor was modified not only on the surface but also inside crystal by both the mechanical grinding and the femtosecond laser treatment, and a synergy enhancement was obtained by the both treatment.

Since the band gap energy of ZnS is 3.7 eV, 800 nm light is transparent to the crystal. It suggests that the optical penetration depth of the femtosecond laser light is much larger than the mean crystal size (about 20 μm). Therefore, the photomechanical effect was occurred not only on the crystal surface but also homogeneously inside the whole crystal. This modification process is different from that by the mechanical grinding, in which the crystal surface would be mainly modified. Further improvement of the femtosecond laser treatment is expected by optimizing laser wavelength, pulse duration, and pulse energy. In this study, the emission intensity was weak for a practical use because optimization of the Cu doping has been insufficient. Optimization of the Cu doping for the laser treatment will be the next step.

The photomechanical modification by the femtosecond laser irradiation was applied to modification of the ZnS micro-crystal for the EL phosphor. We found the EL emission is
enhanced by the treatment, in which crystal was not destructed by the laser irradiation though the crystal was crashed by the mechanical grinding. In addition, further EL enactment was observed when the femtosecond laser treatment was combined with the mechanical grinding. We expect the fine and precise laser treatment opens new potentiality for the application of inorganic EL devices.
References


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Figure captions

**Fig. 1.** (a) Emission mechanism of EL device using ZnS crystal phosphor as band diagram, in which emission is induced in the vicinity of the Cu$_2$S site. (b) Processes to generate of Cu$_2$S site in the ZnS crystal by mechanical grinding (left-top) and laser-induced breakdown (left-bottom).

**Fig. 2.** (a) Schematic diagram of femtosecond laser irradiation to ZnS micro-crystal dispersed in ethanol solution. (b) Device structure using ZnS micro-crystal phosphor. (c, d) Pulse energy (c) and laser irradiation time (d) dependences of EL emission when the ZnS micro-crystal was modified by the femtosecond laser irradiation. The laser irradiation time in (c) was fixed to 30 min. The laser pulse energy in (d) was fixed to 0.1 mJ/pulse. The left bar indicated as “Ref” is Cu-doped ZnS micro-crystal with the annealing and without the laser irradiation. (e) XRD spectra of ZnS phosphor modified by the femtosecond laser irradiation (Pulse energy: 0.15 mJ/pulse, Laser irradiation time: 30 min.) (red lines). XRD peaks of hexagonal and cubic phases of ZnS crystal are indicated as black bars.

**Fig. 3.** Comparisons of EL emission as AC voltage dependence (a) and PL emission spectra (b) of the ZnS micro-crystal modified by the femtosecond (red line) and picosecond (blue line) laser irradiations, in which laser pulses with energy of 0.15 mJ/pulse were focused for 30 min. The black lines are dependences of the crystal without the laser irradiation.
Fig. 4. (a) EL emission of ZnS crystal phosphor modified by mechanical grinding and/or femtosecond laser irradiation (Pulse energy: 0.15 mJ/pulse, Laser irradiation time: 30 min.). “Ref” is Cu-doped ZnS micro-crystal only with the annealing. (b) SEM images of ZnS micro-crystals before the laser irradiation (1), after femtosecond (2) and picosecond (3) laser irradiations, and after mechanical grinding (4). In the laser irradiation experiments indicated in (2) and (3), laser pulses with energy of 0.15 mJ/pulse were focused for 30 min. Scale bars are 10 µm.
Figure 1
Figure 2

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