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The recovery of radiation damages in ZnO introduced by combinatorial ion implantation techniques

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We have developed two ion implantation systems for producing the combinatorial library. One is the moving mask system. Another is the new scanning system that can make continuous dose variation. These techniques were applied for searching the new luminescence property of ZnO. The series of the combinatorial ion implantation experiments indicated that the luminescence resulted from the recovery by the annealing was mainly observed at the wavelength of 525 nm.

Key words: Combinatorial chemistry, Ion implantation, radiation damages, photoluminescence.

1. INTRODUCTION

The ion implantation technique plays an important role in the field of semiconductors, and it has also been applied to several materials. It is also a useful and powerful way of doping of several impurities in these materials. Ion implantation loaded with a mask system at the end station has very recently been developed as an instrument for material research [1], and has already been applied in a few studies [2, 3]. This approach is helpful and useful in scientific and technological fields for the following reasons. The first is the high repeatability of ion implantation, and the second is that the dose library of the implants in the substrate makes it possible to suppress unintentional factors after several sample treatments. We very recently developed a scanning system for the ion beam to create a continuous dose in the substrate [4].

We selected zinc oxide (ZnO) because of its many applications [5-11]. One of these is that it is well known as a luminescence material in field emission displays (FEDs) under irradiation by a low-energy electron beam [7, 10, 11]. There have been different theories on the origin of green emission when this occurs; one has been the transition from shallow donors to the deep acceptor [12, 13] while another has been a singly-charged oxygen vacancy [14-16]. A green emission centered at 525 nm has usually been detected in implanted ZnO samples annealed at 750 - 950 °C for several hours in air [17]. Generally, the implanted materials exhibit complex phenomena depending on annealing conditions such as temperature, time, and atmosphere. The behavior of the implanted materials is related to the damages introduced by ion implantation. To examine the effect of damages, the inert gas is ideal species. This paper discusses applications of new systems that have been developed for ion implantation, which allow studies on the recovery of ZnO implanted with Ar.

2. EXPERIMENTALS

C-axis oriented ZnO thin film was synthesized through electron cyclotron resonance (ECR; Astex, AX-4300) assisted chemical vapor deposition (CVD) on Si and Al_2O_3 substrates. The reaction chamber containing the ECR source was pumped with a turbo-molecular pump to $2x10^{-8}$ Torr. The Zn source was zinc acetylacetonate ($Zn(CH_3COCHCOCH_3)_2$: $Zn(acac)_2$), which was vaporized at 70-95℃ and transferred to the reaction chamber at an Ar gas flow. The gas containing the $Zn(acac)_2$ vapor was blown out to the substrate from a ring injector. The ZnO sample had a columnar morphology. The thickness of ZnO thin film was 200 nm.

After thin-film deposition, several ions were implanted at room temperature, using a mask and the new scanning systems we developed [4].

The implanted ZnO thin film was annealed at 800 °C for 3 h in ambient air. We then measured the room-temperature photoluminescence spectrum (RT-PL; BIO-RAD, rpm 2000). The excitation source was a He-Cd laser (325 nm), which made it possible to obtain a PL spectral map with a lateral resolution of 100 μm.

3.RESULTS and DISCUSSION

Figure 1a shows the typical RT-PL spectrum of the implanted ZnO thin film. This sample is the annealed ZnO thin film after Mn implantation. One emission centered at 525nm is observed, and same result was reported in the previous study [17]. Figure 1b indicates the comparison with the ZnO thin films deposited on Si and Al_2O_3 substrates. These films were annealed at 800℃ for 3h before RT-PL measurements. On the ZnO/ Al_2O_3, the spectrum indicates the emission in the visible region centered at 527nm. The emission in the visible region emission is usually observed in ZnO. The feature of the spectrum obtained in ZnO/Al_2O_3 is very similar with that in Fig. 1 (a). Because of this feature, it is difficult to detect the effect of the ion implantation in the RT-PL spectrum. In order to solve above problem, the growth condition of ZnO thin film is optimized. The result is shown in Fig. 1 (b). The RT-PL spectrum of ZnO/Si indicates the band-edge emission after the annealing, and there is no evidence of

the visible region emission. This is good property for studying the optical property.

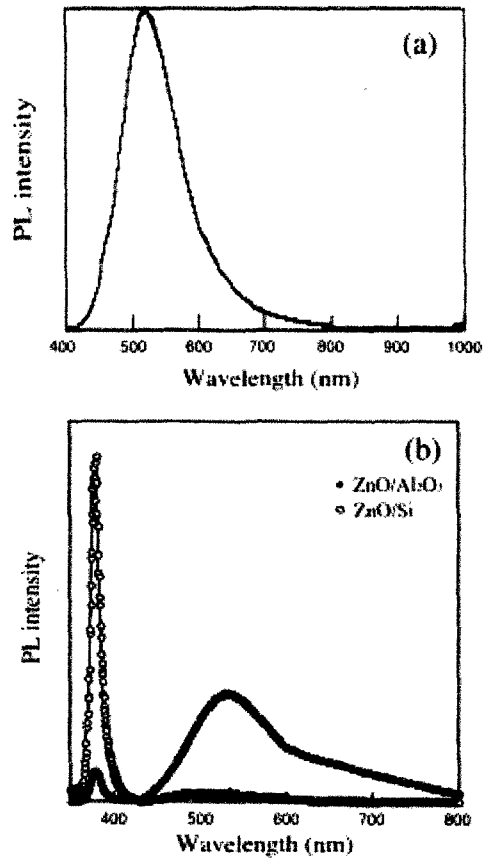

Fig. 1. RT-PL spectra of several ZnO thin films. Typical spectrum of implanted ZnO annealed at 800℃ for 3h in Fig. 1 (a). This sample was implanted with Mn (120keV, $1x10^{15}$ ions/cm^2). (b) shows the spectra of ZnO/ Al_2O_3 and ZnO/Si. These were annealed at 800℃ for 3h.

In order to study the effect of the implanted damage, Ar ions were implanted (accelerating voltage of 80 keV) at room temperature, using a mask and the new scanning systems we developed [4]. The projection range of Ar was 47.5 nm from TRIM calculations [18] and Ar ions were implanted in the ZnO thin film from this range. The Ar dose in ZnO thin film is in Fig. 2a and this was controlled sequentially by a mask system in the vertical direction. It was also controlled by a scanning system in the horizontal direction. The Ar dose created by the scanning system varied by a factor of 2. Figure 2b shows the band-edge emission spectra between A and B in Fig. 1a. These spectra were obtained in steps of 1mm. The intensity decreases gradually with the increase in Ar dose in the horizontal direction. The intensity from the $1x10^{12}$ ions/cm^2 area is smaller than that from the $2x10^{12}$ ions/cm^2, by a factor of about 2. From the results, we concluded that the band-edge emission of ZnO is extinguished by Ar implantation. These results have been identified as a feature of room-temperature ion implantation in ZnO [17]. The reduced emission properties in the as-implanted sample are attributable to the fact that the defects induced by Ar implantation behave as non-radiative recombination centers, because defects such as point defects,

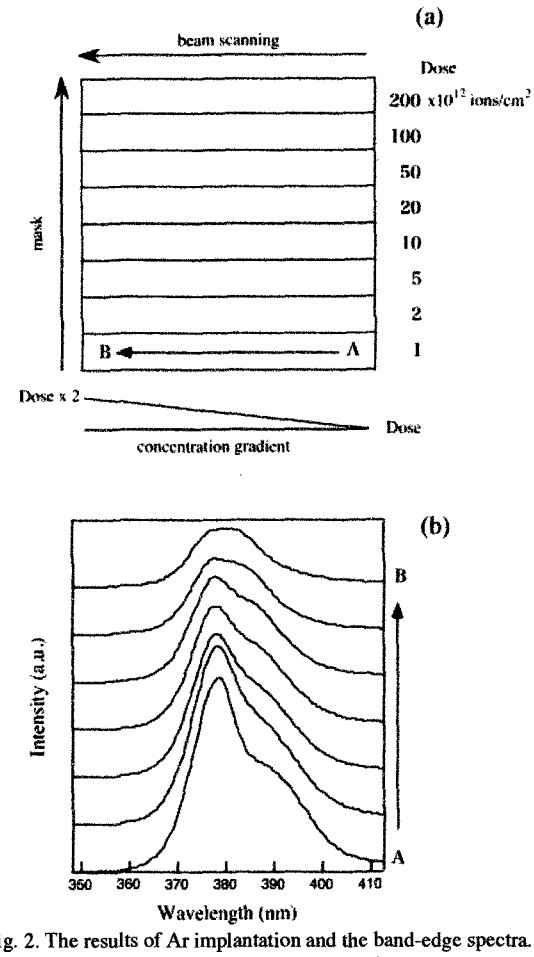

Fig. 2. The results of Ar implantation and the band-edge spectra. (a) illustrated the Ar dose distribution in the substrate. (b) indicated the band-edge spectra.

dislocations, and dangling bond behave as non-radiative centers [19].

Figure 3a has the intensity map of emissions centered at 515 nm in the visible region. The intensity map reveals the most suitable Ar dose to obtain the maximum emission intensity, which is $1x10^{13}$ ions/cm^2. Spectra in a range of 350 - 800 nm were obtained from lines 1 shown in Fig. 3b. The position of maximum intensity in the spectrum shifts to 505 nm from 512 nm. We need to notice that the spectrum obtained from maximum intensity in the intensity map is spectrum indicated at bottom in Fig. 3b, and the peak position is 512 nm. With increasing Ar dose, the position of maximum intensity in each spectrum shifts to 505 nm from 512 nm with increasing Ar dose.

Previously, green emission had usually been observed in ZnO ceramics, single-crystal, and thin film and this can be explained by different defects. One is the transition between the shallow donor level to the excited state of the deep level [12,13], and another is due to the singly-charged oxygen vacancy [14,15]. The results we obtained from the Ar dose library became an important source of information on the origins of green emission in ZnO. We found that a green emission peak that shifted from 525 to 490 nm could be detected in an Ar dose range of $1x10^{12}$ to $4x10^{13}$ ions/cm^2. It was possible to control the wavelengths of green emissions by Ar implantation. Emission at 525 nm in an area of $1x10^{12}$ ions/cm^2 was also observed in a previous study,

and this characterized the recovery of emission properties in implanted ZnO samples [17]. From the

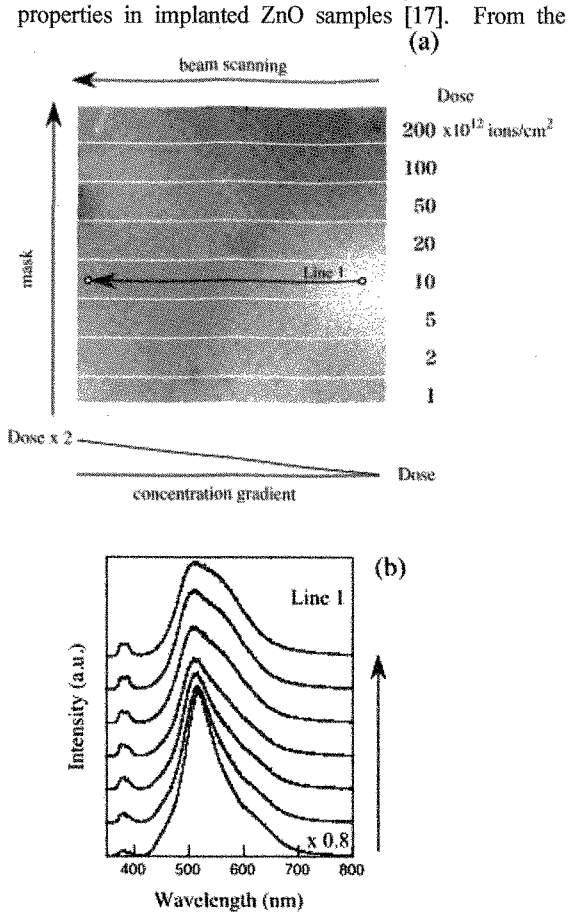

Fig. 3. PL intensity map centered at 515nm and the spectra along the line 1. (a) shows the intensity map and Ar dose. (b) indicates the spectra along the line 1.

above, the damage in the $1x10^{12}$ ions/cm^2 area has already recovered by annealing. The continuous peak shift from 525 to 490 nm indicates the degree of recovery from radiation damage such as native defects related to zinc and oxygen in the ZnO lattice by Ar implantation. The concentration of these defects is proportional to the Ar dose. If peak shift is due to native defects, the degree of reaction to reach a stable state depends on self-diffusion in ZnO. It is known that zinc diffusion is due to an interstitial mechanism, and oxygen diffuses by replacing the vacancy. At 800 °C, the zinc diffusion coefficient is about two orders of magnitude larger than that of oxygen diffusion [20, 21]. The difference in diffusion coefficients means that the oxygen vacancy would like to remain in the ZnO lattice rather than zinc interstitials.

4. CONCLUSIONS.

We optimized the thin film growth condition and developed new combinatorial ion implantation technique. The combination of above two techniques was applied to research the recovery process of the radiation damages in ZnO thin film introduced by Ar implantation. The intensity of band-edge emission continuously decreased with increasing Ar dose. After annealing at 800 °C for 3 h, emission in the visible region was observed. The green emission shifted from 525 to 490 nm in an Ar dose range of $1x10^{12}$ to $4x10^{14}$ ions/cm^2. The maximum intensity was located at 512 nm, and obtained from an area of $1x10^{13}$ ions/cm^2. This indicates that this new system for ion implantation is a powerful method of optimizing optical properties.

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