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ZnO Diode Fabricated by Excimer-Laser Doping

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A ZnO diode was fabricated by using a laser-doping technique to form a *p*-type ZnO layer on an *n*-type ZnO substrate. A zinc-phosphide compound, used as a phosphorous source, was deposited on the ZnO wafer and subjected to excimer-laser pulses. The current–voltage characteristics showed a diode characteristic between the phosphorous-doped *p*-layer and the *n*-type substrate. Moreover, light emission, with a band-edge component, was observed by forward current injection at 110 K. © *2000 American Institute of Physics.* [S0003-6951(00)02722-4]

ZnO has been investigated as a green fluorescent material for many years.[1,2] Recently, ZnO has also been studied as a short-wavelength light-emitting material[3,4] because it has a direct 300 K band gap of 3.37 eV. However, there are no reports of $p-n$ ZnO diode formation because it is difficult to obtain *p*-type ZnO. We have attempted to create *p*-type ZnO by excimer-laser doping of a bulk, *n*-type ZnO wafer, grown by the hydrothermal method.[5] We have earlier reported the use of laser doping to create p^+-ZnSe ($5\times10^{19}\,\mathrm{cm}^3$, Hall concentration)[6,7] and have also fabricated $p-i-n$ CdTe γ-ray detectors.[8,9] In the present study, we have obtained a diode current–voltage ($I-V$) characteristic, and have observed electroluminescence by current injection. For the ZnO diode, the laser doping procedure is as follows:

(1) A 35-nm-thick zinc-phosphide (Zn_3P_2) film, as a phosphorous (P) source, is deposited on the ZnO wafer by conventional vacuum evaporation.
(2) The ZnO wafer and Zn_3P_2 film are then exposed to KrF excimer-laser radiation in an ambient of high-pressure nitrogen or oxygen in order to avoid abrasion or reevaporation from the sample surface. The ultraviolet excimer laser is thought to decompose the Zn_3P_2 into Zn and P atoms, and then provide heat energy to make these atoms diffuse into the ZnO. Then, we believe that a P-doped ZnO layer is formed through the replacement of O atoms by P atoms.

Single-crystal ZnO wafers, which were grown by the hydrothermal method,[5] were used as the substrate material. The initial Zn_3P_2 film thickness was 35 nm, and the KrF excimer laser had a wavelength of 248 nm, a pulse width of 20 ns, and a power density of 150 $\mathrm{mJ/cm}^2$. The irradiation chamber contained either nitrogen or oxygen at a pressure of 4 atm(4.1×10^5 Pa).

Three different types of samples and processing, listed in Table I, were examined in this investigation. The type I and II preparations had no dopant, but were designed to determine the influence of the laser irradiation alone on the ZnO surface. The type III processing, on the other hand, involved the Zn_3P_2 dopant material. Surface changes in the type I and II samples were studied by photoluminescence (PL) and surface $I-V$ measurements. The $I-V$ and electroluminescence measurements on the type III sample were carried out by conventional methods.

Figure 1 shows the laser-induced change in the PL spectrum of a high-resistivity ZnO substrate (1 $\mathrm{k}\Omega\,\mathrm{cm}$); the PL was excited by a He–Cd laser at 110 K. The untreated ZnO wafer has only a band-edge-emission peak, appearing at about 370 nm [Fig. 1(a)]. As shown in Fig. 1(b) for the type I sample, the band-edge peak decreases and a new broad peak appears at about 500 nm after laser irradiation in a nitrogen environment. The decrease of the band-edge intensity probably results from a deterioration of the crystallinity of the ZnO surface, due to the laser irradiation. On the other hand, as shown Fig. 1(c) for the type II sample, no new peaks appear in the 500 nm region, and the intensity of the band-edge emission does not change after excimer-laser irradiation in high-pressure oxygen. These results suggest that the peak around 500 nm is due to oxygen vacancies[10] formed by the high-temperature excimer-laser radiation, and that the high-pressure oxygen environment suppresses the formation of oxygen vacancies at the ZnO surface. The surface resistivity was not changed after excimer-laser irradiation in high-pressure oxygen, but was drastically reduced, evidently through donor formation, when irradiated in a high-pressure nitrogen ambient. This result can be explained by the expected donor nature of oxygen vacancies in ZnO, and the suppression of such vacancies by annealing in an oxygen environment.

The $I-V$ characteristics of the ZnO diode fabricated using a low-resistivity (0.2 $\Omega\,\mathrm{cm}$) substrate (type III sample) are shown in Fig. 2. The electrodes were placed between the P-doped ZnO layer and the *n*-type ZnO substrate. These

TABLE I. Samples and processing employed in this study.

Type	Dopant source	Environment	Substrate resistivity
I	···	Nitrogen	High
II	···	Oxygen	High
III	Zn_3P_2	Oxygen	Low

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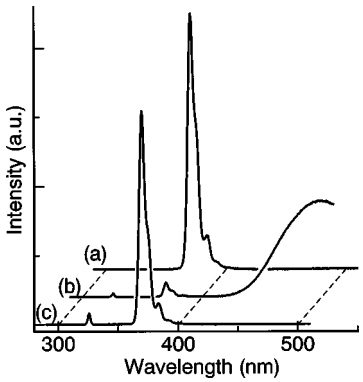

FIG. 1. Photoluminescence spectra from a ZnO wafer: (a) untreated; (b) after excimer-laser irradiation in a high-pressure nitrogen environment (type I); and (c) in a high-pressure oxygen environment (type II). The spectra were excited by a He–Cd laser (325 nm) at 110 K.

characteristics show that a $p-n$ diode can be fabricated. An attempt to prove the p-type nature of the P-doped layer by Hall measurements was not successful. However, the data obtained were confirmed p-type, though the carrier concentrations could not be decided because of their considerable fluctuation. This is considered to be a result of the doped layer being very thin ($\sim$50 nm),[11] and of the very low measurement currents which limit the Hall measurement. The graph in Fig. 2 (see the inset) shows surface $I-V$ characteristics using two gold electrodes on the P-doped layer. For linear dependences of $I-V$ characteristics, the Ohmic contact between the P-doped layer and gold electrode are fairly confirmed. After laser irradiation, the residual Zn_3P_2 layer was not observed from surface analysis, such as Auger electron spectroscopy and x-ray photoelectron spectroscopy.

Figure 3 displays the electroluminescence spectrum and photographs of the light output for a ZnO diode at 110 K. The diode was operated under the following conditions: temperature, 110 K; current density, about 30 A/cm^2 [Fig. 3(a)] or 10 A/cm^2 [Fig. 3(b)]; and bias voltage, 18.4 V [Fig. 3(a)] or 10.1 V [Fig. 3(b)]. The light emission was weak, but a white-violet color was clearly observable. The spectrum, although noisy, includes a peak at about 370–380 nm, attributed to band-edge emission, and a band in the 400–600 nm region.

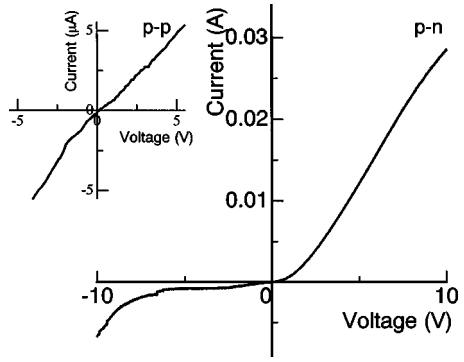

FIG. 2. Current–voltage characteristics for a ZnO diode formed by a P-doped layer on an n-type substrate (type III sample); the substrate had a resistivity of 0.2 Ω cm. The inset shows surface current–voltage characteristics on the P-doped layer measured with two gold electrodes on the surface.

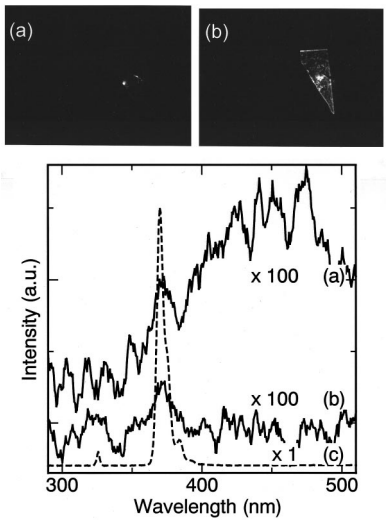

FIG. 3. Photographs of light output and electroluminescence spectra of a ZnO $p-n$ diode operated at 110 K, and (a) 30 A/cm^2 (18.4 V bias) or (b) 10 A/cm^2 (10.1 V bias) of current injection. (c) Photoluminescence spectrum of the same sample, as a reference.

In summary, we have fabricated a ZnO diode by using laser phosphorus doping to form a p-type ZnO layer on an n-type ZnO substrate. A diode $I-V$ characteristic was obtained in this structure, and white-violet electroluminescence was observed at 110 K. The spectrum includes a peak at about 370–380 nm, attributed to band-edge emission, and a broad peak in the region of 400–500 nm, evidently due to defect states.

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