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Lateral photovoltage of B-doped ZnO thin films induced by 10.6 μm CO_2 laser

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Abstract
B-doped ZnO thin films were observed to have a lateral laser-induced photovoltaic effect: the saturation value varied very linearly with the 10.6 μm constant laser spot position between the electrodes on the ZnO surface. It was found that the temperature gradient in the direction of electron transfer (along the film surface) due to the laser spot causes this photovoltage signal to be linearly dependent on the position of the laser spot in this isotropic system. This linearity is expected to make ZnO a candidate for position-sensitive photodetectors.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Zinc oxide (ZnO), a II–VI semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV [1, 2], has been widely studied due to its intrinsic properties, which are suitable for potential application in ultraviolet (UV) light emitters or light emitting diodes (LEDs), transparent high power electronics, spin functional devices, solar cells and UV detectors, and as window material for displays [2–8]. With regard to the photoelectric properties of ZnO, UV detectors based on ZnO photoconducting layers [3, 4], metal–semiconductor Schottky barriers [2, 5] and heterojunctions [9] have been reported. For these detectors, the attention was focused mainly on the ultraviolet or visible range. We had reported functional heterojunctions consisting of metallic MgB_2 and n-type ZnO and its photovoltaic effect under a pulsed infrared irradiation at room temperature [10]. Here we show that B-doped ZnO thin films exhibit a lateral laser-induced photovoltage (LPV): the saturation values of this photovoltage vary very linearly with the position of the laser spot under illumination with a constant intensity 10.6 μm radiation from an infrared laser. This property of linear position saturation photovoltage (SPV) is expected to make the ZnO a candidate for position-sensitive photodetectors.

2. Experimental procedure

For the purpose of enhancing its hardness, element B was used as the dopant and the doped ZnO thin films were grown on fused quartz substrates using pulsed-laser deposition with a boron and ZnO mosaic target under an optimal substrate temperature of 550 °C. The film thickness was fixed at 500 nm and the film area was $10 \times 10\,mm^2$. Nanoindentation, transmittance and Hall effect measurements revealed that our B-doped ZnO films had good hardness (12.10 ± 1.00 GPa), relatively high transmittance (mean value >81% in the visible range) and low resistivity ($<3 \times 10^{-3}\,\Omega$ cm) at room temperature [11]. The schematic picture of the experimental set-up for the LPV measurement is shown in the inset of figure 1. The B-doped ZnO thin film surface was irradiated with a small area of 0.5 mm diameter of the 10.6 μm constant intensity laser beam with an energy power density of $0.15\,W\,mm^{-2}$. The lateral

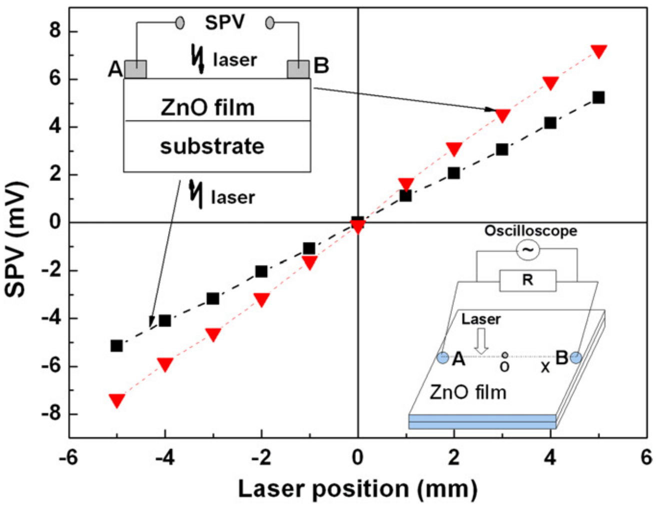

Figure 1. Dependence of the SPV on the position of the laser spot in the x direction when laser spots are irradiated on the ZnO surface and the substrate. The inset displays the schematic set-up for photovoltage measurement.

photovoltage between the indium electrodes was measured and recorded by a 350 MHz sampling oscilloscope terminated into 1 MΩ at ambient temperature. The electrodes were always kept in the dark to prevent the generation of any electrical contact photovoltage.

3. Results and discussion

As displayed in the top inset of figure 1, the LPV was obtained through two indium electrodes named A and B located in the middle of the two opposite film sides. The SPV values were plotted as a function of the laser spot position x (along A and B, the coordinate origin O was set at the centre between A and B) on the ZnO surface and substrate, respectively. In the region between the electrodes along the x-axis (shown in the bottom inset of figure 1), whether the laser irradiated on the ZnO surface or the substrate, the SPV varied very linearly with laser position x. Due to the influence of the substrate, the SPV with the laser illumination on ZnO was bigger than that on the substrate at the same position. The open-circuit sensitivities, which means the variation of the output voltage in units of $\mathrm{mV\,W^{-1}\,mm^{-3}}$ for a 1 mm displacement of the spot, were about $10\,\mathrm{mV\,W^{-1}\,mm^{-3}}$ and $7.3\,\mathrm{mV\,W^{-1}\,mm^{-3}}$ for the laser irradiating on the ZnO surface and the substrate, respectively. It is clear that the SPV depends on the position of the spot on the x-axis and undergoes a sign reversal while the laser spot travels from one electrode to the other. The changeover in sign occurs in the middle position ($x = 0$) of the two electrodes. When the light spot is at the centre between A and B, the LPV values are zero due to the diffusion symmetry. If the light position x is positive (negative), the SPV is positive (negative). Furthermore, the signal becomes stronger when the light spot is closer to A or B.

Figure 2 presents the temporal response of the ZnO film to a CO_2 laser with a wavelength of 10.6 μm (an energy power density of $0.15\,\mathrm{W\,mm^{-2}}$) when the light is on and off close to the Aor B indium electrode. It took about 26 s for the photovoltage to reach its saturation value ($\sim$7 mV) from laser on and $\sim$20 s to reach zero from laser off.

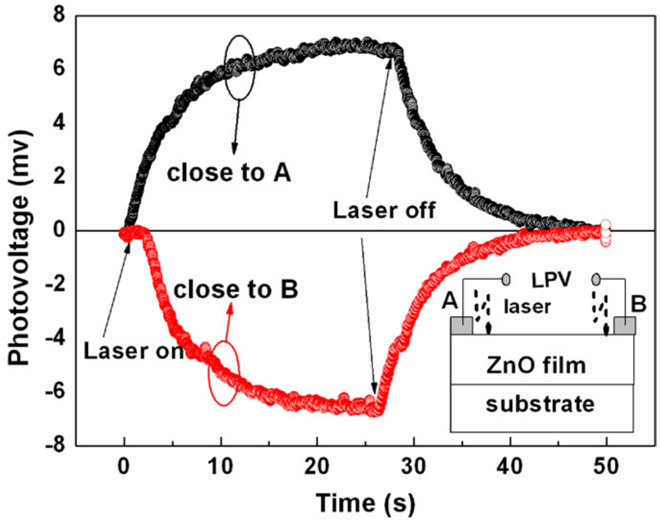

Figure 2. The temporal photovoltaic response of the ZnO film to 10.6 μm constant laser when the light is on and off close to A and B indium electrodes.

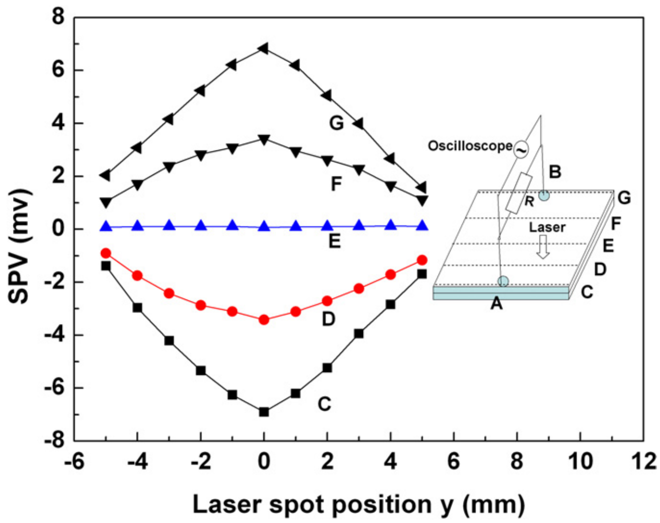

Figure 3. SPV plotted as a function of the laser spot position y along C, D, E, F and G lines on the ZnO surface. The inset shows the scanning line position on the ZnO surface.

For a more detailed investigation of SPV dependence on the laser spot position, the focused laser scanned along the lines named C, D, E, F and G, as shown in the inset of figure 3. A pair of indium electrodes were plotted in the middle of the two opposite sides of the square ZnO film surface. The SPV values, plotted as a function of the laser spot position y along C, D, E, F and G lines on the ZnO surface, are shown in figure 3. It is clear that the SPV still varies linearly with the distance between the electrodes. The SPV values were all zero when the laser spot scans along line E, which is a symmetric line and has equal distance to the two electrodes on the ZnO surface.

Figure 4 summarizes the spatial distribution of the SPV in the plane of the ZnO surface. The voltage sign reversal is obtained when the spot moves across the centre between the

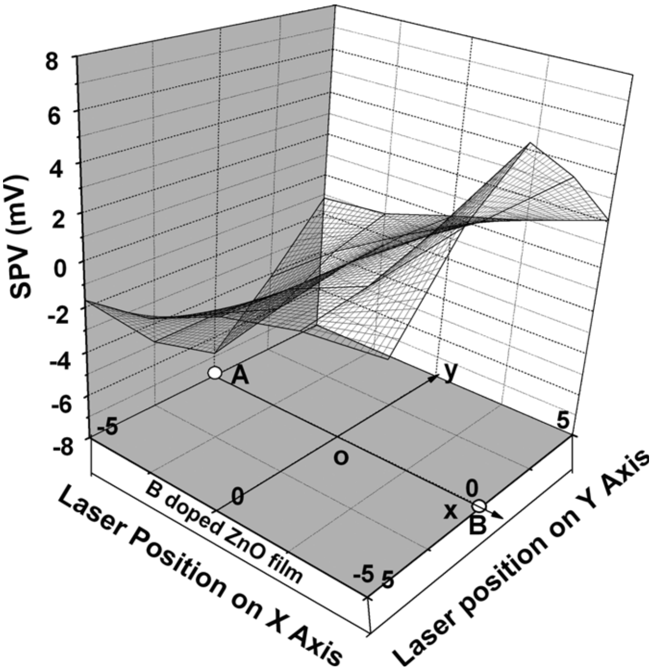

Figure 4. Three-dimensional plot for the SPV as a function of the position of the laser spot.

two contacts A and B. The signal is symmetric on the reflection in a plane normal to the x-axis at $x = 0$.

To understand the mechanism causing the LPV in the B-doped ZnO film, the electrodes were also placed in the middle of another two opposite sides of the ZnO surface and a similar spatial distribution map was obtained, which indicates that the system is isotropic. Hall effect measurement showed that the n-type carrier density of the film was around $2 \times 10^{20}\,cm^{-3}$. The photon energy of the laser pulse with the wavelength of $10.6\,\mu m$ is far below the band gap of ZnO, so the photogenerated carrier effect should be ruled out in the measured voltage. The IR laser is famous for its thermal effect. Because the film is only partially illuminated by the laser beam, a temperature gradient will form between the illuminated and the nonilluminated areas. As the carrier mobility is much higher in the illuminated zone, electrons flow from the illuminated zone to the nonilluminated region. At the same time, transient field is therefore built, as well as the photovoltage. If the distance of the centre of mass of the carrier packet from each electrode is different, then the quantity and time evolution of the collected carriers on the two probe electrodes are different. With time evolution, the nonequilibrium electrons redistribute themselves to accomplish charge transportation equilibrium, which corresponds to the rise time of the photovoltage to its saturation, as shown in the bottom inset of figure 2. Apparently, the temperature gradient at the position of the laser spot in the direction of electron transfer (along the film surface) causes the LPV in this isotropy system, which is called the thermoelectric effect. The ZnO thin films have a tendency to grow with strong (0 0 0 1) preferential orientation on various kinds of substrates, including glass [1]. Our XRD spectra show that the film studied in this paper is c-axis oriented. That means in the surface plane, the film is isotropic, and the thermoelectric effect should be caused by the difference in the carrier mobility between the illuminated and the nonilluminated zones. When the light spot is at the centre between electrodes A and B on the film, the photovoltage is zero due to the diffusion symmetry. If the light spot is close to one electrode, the polarity of the signal from this electrode is negative while the other is positive and vice versa. Based on this effect, we can understand our observed result that there is a monotonic increase in the absolute value of the SPV with the distance between the laser spot and the centre position between the two electrodes. The smaller the distance, the less time the electrons go, and the larger is the SPV measured. Only this diffusion mechanism could explain the irreversible SPV phenomenon we observed. Because our ZnO film is an isotropic system, the temperature gradient along the film surface caused by laser irradiation on the substrate side is the same as that by laser irradiation on the ZnO side. So the value and polarity of the SPV measured in the laser irradiation on the opposite sides of the film are the same as we expected, as shown in figure 1. The slightly larger saturation value of the ZnO film side can be attributed to the surface scattering when the irradiation is on the substrate side. Furthermore, quantitative study on the relationship between SPV and temperature gradient caused by laser illumination is still in progress.

4. Summary

In summary, the B-doped ZnO film has been found to exhibit a laser-induced photovoltaic effect: the SPV shows a high linearity of laser spot position between the electrodes on the ZnO surface. Under laser irradiation, electrons flow in agreement with a gradient between the irradiated and unirradiated regions due to the nonuniformity of irradiation. When electron transfer equilibrium is established, the photovoltage will reach its saturation value. When the laser spot scans along the line between the two electrodes, we can observe a linear increase in the SPV with the distance between the laser spot and the centre position between the two electrodes. This linearity is expected to make ZnO a new type of candidate for position-sensitive photodetectors.

Acknowledgments

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