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Ultraviolet photoconductive detectors based on Ga-doped ZnO films grown by molecular-beam epitaxy

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Abstract

A high-quality Ga-doped ZnO film was epitaxially grown on a *R*-plane sapphire substrate by plasma-assisted molecular-beam epitaxy. Photoconductor devices with Al/Ti Ohmic contacts were fabricated. Photoluminescence and photocurrent measurements were carried out to study the emission and absorption properties of the Ga-doped ZnO film. Both spectra are consistent with each other showing good response in the ultraviolet region and weak response in the green–yellow band. Peak responsivity of 1.68 A/W at 20 V bias for 374 nm light was obtained in the ultraviolet region. Transient response of the device is slow due to the presence of the deep levels.
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Wide bandgap semiconductor ZnO has been intensively studied for its potential applications in the area of ultraviolet (UV) optoelectronics, such as UV detection and UV emission [1–3]. ZnO may also be a prospective alternative for GaN towards these applications due to the advantages of the availability of native substrates and higher exciton binding energy. Undoped ZnO generally has an n-type conduction due to the presence of the dominant native defects such as zinc interstitials (Zn_i), oxygen vacancies (V_o), and hydrogen incorporation, which form donor levels [4,5]. Trivalent elements such as Al, Ga, and In are predominantly used as n-type dopants to precisely control the n-type electrical conductivities of ZnO for optoelectronic device applications [6–8]. In addition, intensive study on n-type doping to increase the electrical conductivity and transmittance of ZnO has already been done for the application as electrodes and protective coatings to other optoelectronic devices [9–12]. Furthermore, optical properties of doped ZnO films have been delineated to a large extent. Nevertheless, reports on in-depth studies of photoelectric properties and device performances are still few. In this paper, we study optical and photoelectric properties of Ga-doped ZnO films and the corresponding photoconductive devices.

ZnO films were grown on $(0\,1\,\bar{1}\,2)$ *R*-plane sapphire substrates by plasma-assisted molecular-beam epitaxy. The sapphire substrate was cleaned in boiling aqua regia solution ($HCL:HNO_3 = 3:1$) for 20 min to remove surface contaminants, which was followed by rinsing in DI water and nitrogen-drying. The substrate was then introduced into growth chamber and thermally cleaned at 800 °C in vacuum for 20 min. An oxygen plasma treatment for 15 min at 720 °C was also carried out to generate an oxygen-terminated surface. A radio-frequency plasma source was used to generate oxygen plasma. Substrate temperature was maintained at 550 °C during growth. Ga-doped ZnO film was grown using effusion cell temperatures of 350 °C and 320 °C for Zn and Ga, respectively. First, an undoped

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ZnO layer of 250 nm was grown as a buffer and annealed at 850 °C for 10 min to improve crystalline quality. Then, 250 nm thick Ga-doped ZnO layer was grown on top of the buffer for photodetector devices. X-ray diffraction (XRD) spectrum shows a strong peak at 57.1° with a full width at half maximum (FWHM) value of 0.39° indicating a high-quality ZnO with an orientation of $(11\bar{2}0)$ (top inset of Fig. 1) [13]. Two peaks related to *R*-plane sapphire substrate also appear around 26° and 53°, corresponding to $(01\bar{1}2)$ and $(02\bar{2}4)$, respectively. Electrical properties of the sample were investigated by Hall effect measurements using van der Pauw configuration that yielded an electron concentration of $1.6\times10^{18}\,cm^{-3}$, resistivity of $0.2\,\Omega\,cm$ and mobility of $18\,cm^2\,V^{-1}\,S^{-1}$ at room temperature.

Photoconductive detector devices were fabricated using conventional photolithography techniques. Ohmic contacts of size $150\,\mu m\times2000\,\mu m$ with 100 μm interspacing were patterned on the sample by depositing 20 nm/250 nm thick Ti/Al metal, using e-beam evaporation and standard lift-off techniques. The cross-sectional device structure is illustrated as the bottom inset of Fig. 1. The two arrows indicate the points of probing for device measurements. Annealing was not necessary since as-deposited contacts were already Ohmic. Current–voltage (*I–V*) characteristics were monitored using an Agilent Semiconductor Parameter Analyzer HP4145C and a Signatone probe station. The devices were packaged on TO5 cans for measuring photocurrent (PC) spectra. The home-built set-up consists of a 150 W Xe arc lamp (Oriel) as light source, which is followed by a 0.25 m monochromator and a chopper. Chopped light is cast on the device to generate PC, which is amplified by a home-built preamplifier and fed to a lock-in amplifier, from where the signal is recorded.

Fig. 1 shows the *I–V* characteristics of a photoconductor device. Linear dependence confirms Ohmic contact formation. Photoluminescence (PL) characterization was carried out at room temperature on the as-grown sample. A He–Cd laser with an excitation wavelength of 325 nm and a photomultiplier tube were used as the source and detector, respectively. Excited PL emission was measured by using a monochromator, which was aligned normal to the sample surface. Fig. 2a shows PL spectra of the Ga-doped ZnO sample. In the low-temperature PL spectrum of the sample shown as the inset of Fig. 2a, a free exciton bound emission was found at 3.375 eV with a FWHM value of about 20 meV indicating high optical quality of the film [13]. Ga-induced donor-bound excitonic emission (D^oX) was observed at 3.358 eV in the sample from low-temperature PL spectrum along with other Ga-related peaks. In the room-temperature PL spectrum, strong near-band-edge emission is exhibited at 3.262 eV. The dissociation of bound excitons occurs at room temperature resulting in the shift of the free exciton (FE) bound emissions to lower energies. In addition, weak deep-level emissions in the green–yellow band around 2.2 eV were also observed. Fig. 2b shows the corresponding PC spectrum, which was obtained from a fabricated device by applying

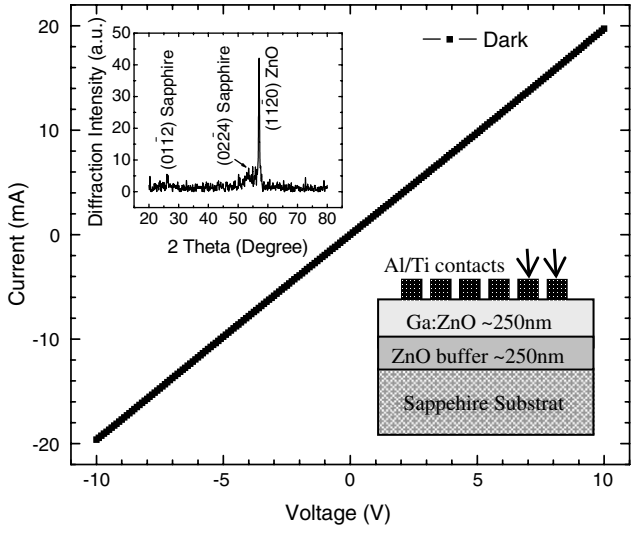

Fig. 1. *I–V* characteristics of the photoconductor obtained in dark. The top inset shows the XRD spectrum of the Ga-doped ZnO film. The lower inset is the cross-sectional illustration of the fabricated device.

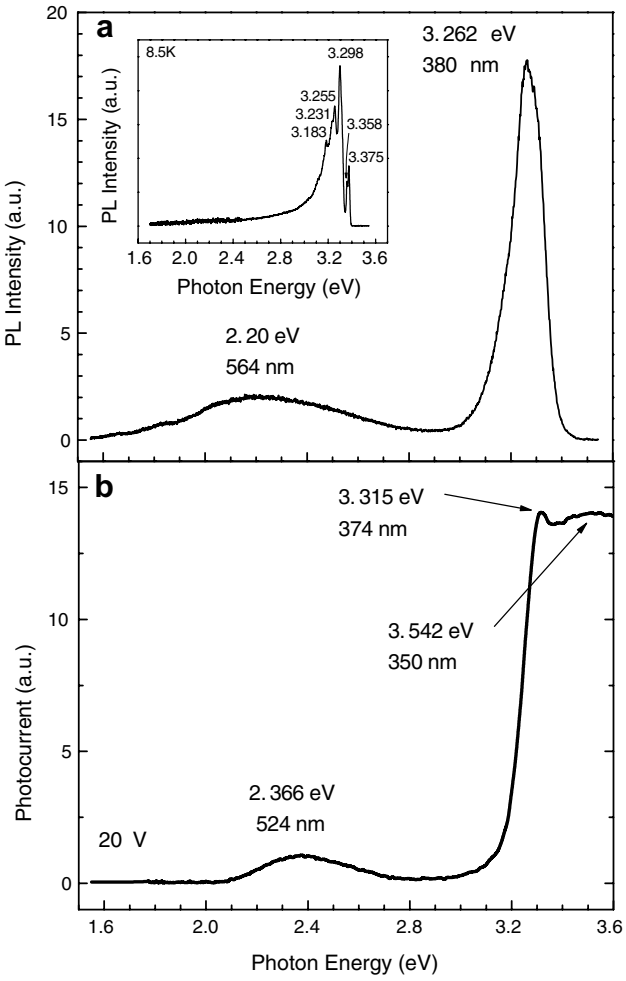

Fig. 2. (a) PL and (b) PC spectra of the Ga-doped ZnO sample at room temperature. Inset in (a) is the low-temperature PL spectrum.

a bias voltage of 20 V. Very good detection was observed in the UV region. The response extends from UVA (400–320 nm) through UVB (320–290 nm) into UVC (220–290 nm) region. A sharp peak at 3.315 eV (374 nm) corresponds to the absorption of the FE. The occurrence of Stokes shift is observed from the blue shift of the FE absorption peak relative to that of the PL emission peak. The presence of the absorption peak related to FE at room temperature is again an indication of the high quality of the ZnO film. The PC signal decreases slightly before exhibiting a broad peak centered around 3.542 eV (350 nm), which is corresponding to the effective band gap of ZnO. Weak absorption around 2.36 eV (~524 nm) is also observed in the PC spectrum. This absorption is consistent with the emission in the PL spectrum, where the deep level emission extends from 530 to 560 nm with a relative peak at 550 nm, which is the green–yellow band. Studies carried out by different groups attribute the origin of this deep level emission to energy transitions related to defects, such as zinc vacancy, lithium impurity, oxygen vacancy, oxygen interstitial, and zinc interstitial [14–18]. Since our samples were grown in Zn-rich condition, we attribute this emission to be related to oxygen vacancies or zinc interstitials, which form deep levels in the forbidden gap of ZnO. These emissions are the result of transitions from conduction band to these deep levels.

The responsivity of the same photoconductive device was obtained in the UV region by calibrating the incident power using an UV enhanced Si photodiode (Hamamatsu). Fig. 3 shows the responsivity spectra of the photoconductor device at different bias voltages. The responsivity spectra are almost linear up to 368 nm, after which there is a slight increase in the slope ending in a peak response at 374 nm. The penetration depth of short wavelength light is small that causes only the superficial ZnO layer to participate in the photon absorption, effectively reducing the photoresponse for high-energy illumination. The peak responsivity is about 1.68 A/W at 20 V bias and 0.43 A/W at 5 V. The long wavelength cut-off of the response is determined by absorption edge at 374 nm. The cut-off is sharp and the response drops by an order of magnitude within 16 nm of the absorption edge. The inset of Fig. 3 shows a plot of responsivity against applied bias voltages. A linear increase in responsivity with the increase of bias voltages is observed.

Fig. 4 shows the transient response of the device to UV light illumination at a bias of 10 V. The device was stored in dark for 36 h before characterization. On applying bias voltage, the random movement of carriers is controlled resulting in a dark current close to 19.9 mA. The device was allowed to stabilize and exposed to UV illumination for duration of about 650 s, within which the PC is saturated. Rise time is defined as the time required to reach 90% from 10% of the maximum response value, while the fall time is the time needed to reach 10% from 90% of the maximum response. From Fig. 4, rise time and fall time of about 95 s, and 2068 s are obtained respectively for the photoconductive device. The slow response times are mainly attributed to the deep levels from defects in the epitaxial material. Slow responses were observed from samples with lithium incorporation [15,19] or oxygen deficiency [20,21]. The electrons are trapped during their relaxation in the deep level states, thereby increasing the minority hole carrier lifetime and hence, the response time.

In summary, we have reported optical and photoelectric properties of Ga-doped ZnO films. The static and transient photoresponses of the devices are reported. The highest static response is about 1.68 A/W at 20 V bias for 374 nm light illumination. Slow transient responses, i.e., rise time of 95 s and fall time of 2068 s, were observed due to the presence of deep levels.

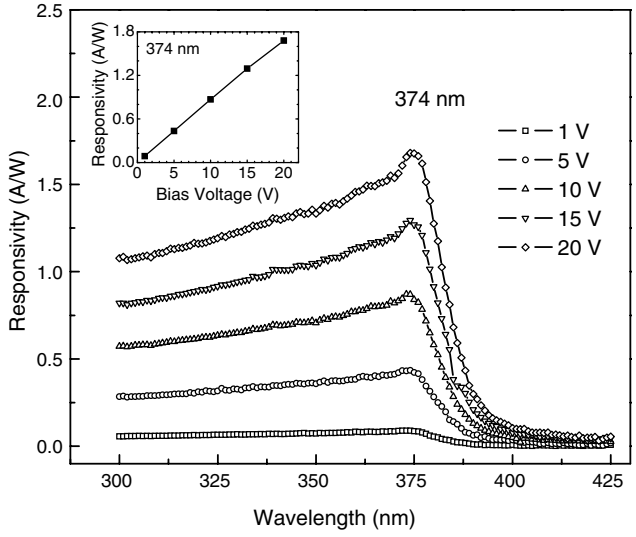

Fig. 3. Responsivity spectra of the Ga-doped ZnO photoconductor at room temperature obtained for different bias voltages. Responsivity against bias voltages is shown as the inset.

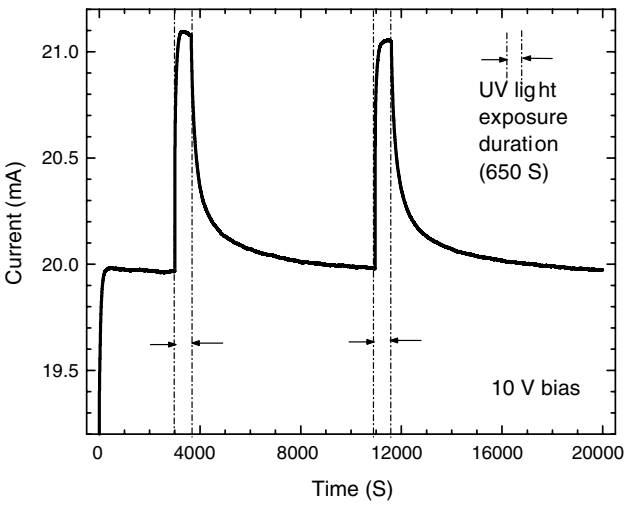

Fig. 4. Transient response of the photoconductor device to UV illumination under 10 V bias.

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