
Proc. XXXVII International School of Semiconducting Compounds, Jaszowiec 2008

Ultraviolet Detectors Based on ZnO:N Thin Films with Different Contact Structures

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Al/ZnO:N/Al and Ni/ZnO:N/Al diode photodetectors fabricated by dc magnetron sputtering of ZnO:N films on *p*-Si substrates are studied. The photocurrent-to-dark current ratio equal to 250 at $\lambda = 390$ nm and the time constant of photoresponse about 10 μ s for Al/ZnO:N/Al structures with 4 μ m interdigital spacing was achieved. The Ni/ZnO:N/Al diode structure has the rectification ratio $\approx 10^2$ at bias 1 V, the maximal responsivity about 0.1 A/W is observed at 365 nm, and the measured time constant of photoresponse is about 100 ns.

PACS numbers: 81.05.Dz, 81.15.Cd, 85.60.Dw, 72.40.+w

1. Introduction

Ultraviolet (UV) detectors have attracted great interest during recent years, due to their applications such as missile warning systems, solar astronomy, high temperature flame detection, precise measurement of UV radiation effect on human body, ozone layer monitoring, etc. [1–3].

ZnO is a direct wide band gap ($E_g = 3.4$ eV) semiconductor material which can be used for UV photon detection. ZnO has optical and electrical properties similar to GaN. Nevertheless, it possesses such preferences as relative cheapness, non-toxicity, advantages in technology and resistance to radiation damage.

Recently, many publications have appeared in literature devoted to creation of ZnO based photoresistors and Schottky photodiodes for UV spectrum region. For the photoresistors it is easy to obtain higher photoresponsivity. Also the amplifying equipment is not necessary and the measuring system is simple and cheap. However, its photoresponsivity has a nonlinear behavior with incident power, poor UV/visible contrast, and persistent photoconductivity response. Furthermore, the photoresponse time of photoconductive detector is usually longer than other types of detectors [4].

In Ref. [5] photoconductive detectors based on ZnO thin films were obtained. These detectors were sensitive to UV radiation, but had a large photoresponse time due to O₂ adsorption-desorption processes from surface. Authors of Ref. [6] demonstrated that doping by nitrogen improves properties of ZnO detectors such as time constant up to microseconds. According to the early report, doping by nitrogen increases photoresponsivity of ZnO based detectors and decreases time constant due to acceleration of adsorption-desorption processes of molecules O₂ and C from surface of ZnO:N thin film [7].

The purpose of this work is creation of photoresistor and diode structure on the basis of ZnO, doped by nitrogen (ZnO:N), and research of their electric and photoelectric characteristics. We report on the epitaxial growth of *c*-preferred oriented ZnO films, doped by nitrogen as acceptor impurity (ZnO:N), on *p*-Si (1 0 0) substrate by dc magnetron sputtering in nitrogen plasma, as well as the fabrication and characterization of photoconductive Al–ZnO–Al metal–semiconductor–metal (MSM) structure and Ni/ZnO:N/Al diode as UV radiation detectors.

2. Experimental procedure

2.1. Sample preparation

ZnO:N thin films were deposited on *p*-Si (1 0 0) substrate by dc magnetron sputtering in nitrogen plasma. All ZnO films (undoped and N doped) were deposited by magnetron sputtering using ZnO sintered target slightly doped by Al. Dc magnetron sputtering was carried out in vacuum chamber with total gas pressure 4 mTorr at magnetron power 1200 W. ZnO samples without nitrogen were deposited in Ar gas ambient. N-doped ZnO films were deposited by sputtering ZnO target in N₂/Ar (10/1) gases ambient. Target–substrate distance was 3 cm. For all depositions growth temperature T_s was 25°C. The thickness of the layers was about 100 nm.

Al/ZnO:N/Al interdigital transducer (IDT) MSM structures were formed using standard lift-off lithography. Before formation of IDT structure by Al (300 nm) deposition, the surface was cleaned in O₂ plasma during 5 min. Al electrodes were

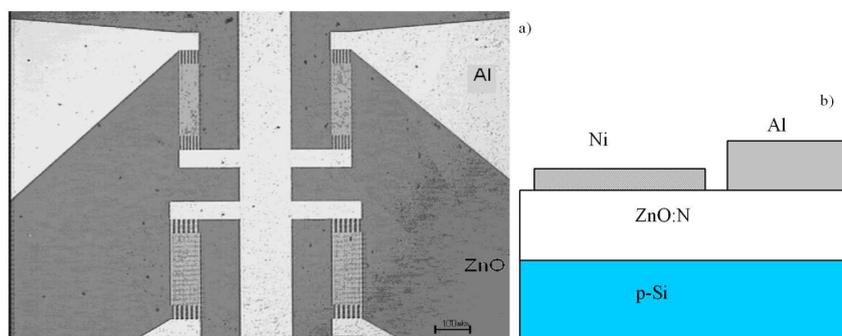


Fig. 1. (a) SEM picture of ZnO:N UV detector with MSM structure. The Al fingers are 580 μm long, 4 and 6 μm wide and have an interelectrode spacing of 4 and 6 μm , respectively; (b) schematic image of surface-barrier Ni/ZnO:N/Al diodes.

sputtered by electron beam evaporation (Fig. 1a). In Ni/ZnO:N/Al diode structure the rectifying ultrathin Ni (20 nm) contact to ZnO:N film was formed by vacuum thermal evaporation (VTE). Before formation of Ni contact, the surface of ZnO:N film was cleaned in Ar plasma during 5 min. After that we deposited Al (200 nm) electrode using VTE (Fig. 1b). For investigation of semiconductor-metal interface quality and nitrogen impurity effect, we also deposited non-doped ZnO thin films on *p*-Si (1 0 0) substrate and fabricated the same contact structures to them.

2.2. Sample characterization

The structural properties were measured by X-ray diffraction (XRD) using a Siemens D5000 diffractometer, utilizing Cu K_{α} radiation ($\lambda = 0.1542$ nm). The photoluminescence (PL) properties were studied by femtosecond Ti:sapphire laser (37 mW, 170 fs, 76 MHz). The surface morphology was examined by atomic force microscopy (AFM — Veeco Digital Instruments Nanoscope 3100) in tapping mode. The electrical measurements were carried out using Keithley 2700/Module 7700. Spectral photoresponse measurements were performed using KGM-70 lamp in combination with monochromator MDR-4. The precision silicon photodetector (FD286) was used to control the optical power on the detector. The photoresponse speed of the detector was also measured. The signal from a 100 Ω load resistor was recorded by oscilloscope with a time resolution better than 1 ns, using 9 V bias voltage.

3. Results and discussion

Figure 2 shows the XRD pattern of ZnO thin film prepared by dc magnetron sputtering. Only the (002) diffraction peak of ZnO at 33.98° with the full width at half maximum (FWHM) of 0.4° could be found. Therefore, it is obvious that the film has preferred orientation along *c*-axis. The diffraction peak at 32.95° belongs

to Si substrate. The magnitude of this peak indicates that thickness of ZnO:N film is small. Figure 3 shows AFM images of the ZnO:N films. ZnO films doped by nitrogen are of polycrystalline nature with characteristic grain size diameter 58 ± 15 nm and surface root mean square roughness 5.2 nm. The XRD spectra of ZnO films demonstrates only the reflection peaks peculiar to ZnO wurzite structure which is in coincidence with atomic force microscopy analysis.

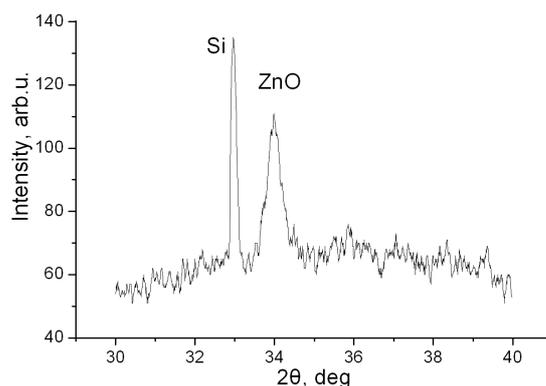


Fig. 2. XRD θ - 2θ spectra of a ZnO:N/*p*-Si film.

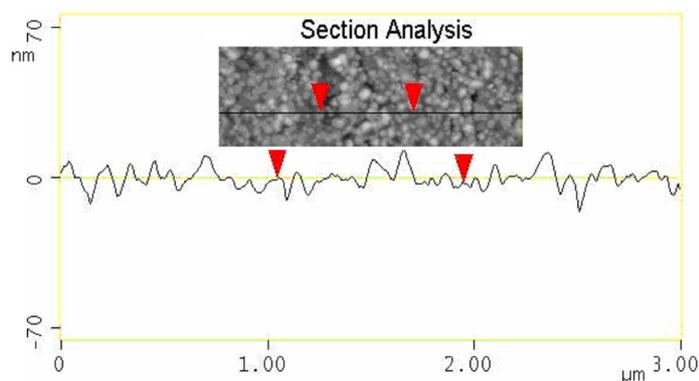


Fig. 3. AFM images of a ZnO:N/*p*-Si film.

We also studied photoluminescence of as-grown ZnO and ZnO doped N films by femtosecond Ti:sapphire laser at room temperatures. No photoluminescence was observed for all ZnO/*p*-Si films. It is related to low crystalline and optic quality of ZnO and ZnO:N thin films due to their low thickness.

Shown in Fig. 4 are the I - V characteristics of the fabricated Al/ZnO:N/Al IDT structure (a) and Ni/ZnO:N/Al diodes (b). The linear dependence of I - V curve from the Al/ZnO:N/Al structure clearly indicates the ohmic behavior of the

Al contact to ZnO:N film. On the other hand, the rectified $I-V$ curve of the Ni-ZnO contact confirms junction formation between Ni and n -type ZnO doped by N. In this paper we will consider only $4\ \mu\text{m}$ Al/ZnO:N/Al IDT structures because $I-V$ characteristics, spectral photoresponses and time constants of $4\ \mu\text{m}$ and $6\ \mu\text{m}$ Al/ZnO:N/Al IDT structures have similar behavior.

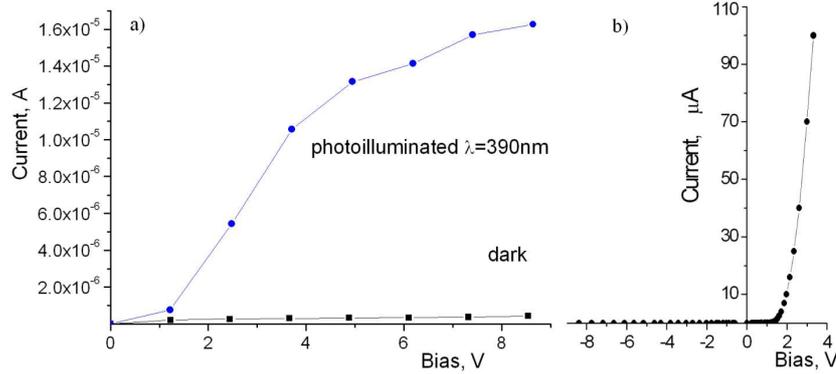


Fig. 4. $I-V$ characteristics of the fabricated Al/ZnO:N/Al IDT structure (a) and Ni/ZnO:N/Al diode (b).

We achieved a photocurrent-to-dark current ratio about 250 for $4\ \mu\text{m}$ and $6\ \mu\text{m}$ Al/ZnO:N/Al IDT structures peaked at around 390 nm. Under 3 V bias, the measured average dark current for Al/ZnO:N/Al structure is 350 nA (Fig. 4a). This is much smaller compared with Ref. [8]. The low dark current is desirable to enhance the detector's signal-to-noise (S/N) ratio since the shot noise, which exceeds the Johnson and $1/f$ noise if the operating frequency is not too low, is proportional to dark current [9]. Furthermore, it should be noted that the light current did not linearly increase above 5 V applied bias, indicating the sweep-out effect up to this bias [10].

Ni/ZnO:N/Al diode structure has high rectification ratio about 10^2 at bias 1 V (Fig. 4b). The $I-V$ characteristics for a Schottky diode is expressed by [11]:

$$J = J_0 \left[\exp \left(\frac{eV}{nkT} \right) - 1 \right],$$

where $J_0 = AT^2 \exp(\Phi_B/kT)$ is the saturation current density according to thermionic emission theory, n — ideality factor, k — the Boltzmann constant, T — the absolute temperature, A — effective Richardson coefficient, and Φ_B — the barrier height. The ideality factor was calculated by $I-V$ curve fitting (Fig. 4b) and value of $n = 7$ was obtained.

The spectral photoresponse of Al/ZnO:N/Al IDT structure (biased at 2 V) is shown in Fig. 5a. The maximum of photoresponsivity peaked at around 380 nm. In this case the fabricated detectors are sensitive to visible irradiation because of

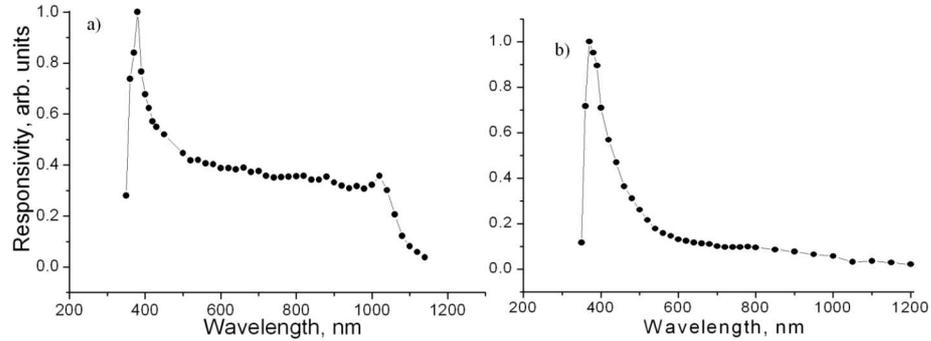


Fig. 5. Spectral photoresponse of the ZnO:N photodetectors: (a) Al/ZnO:N/Al IDT structure (biased at 2 V) and (b) Ni/ZnO:N/Al diode (biased at -1 V).

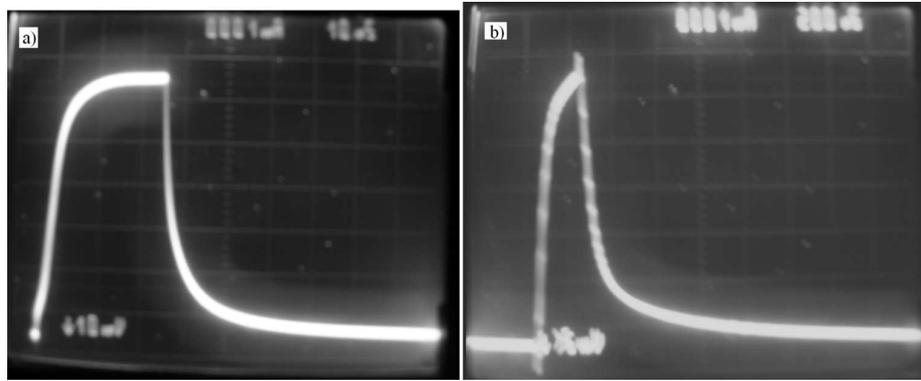


Fig. 6. Temporal response of ZnO:N photodetectors: (a) Al/ZnO:N/Al IDT structure (x scale interval is $10 \mu\text{s}$) and (b) Ni/ZnO:N/Al diode (x scale interval is 200 ns).

short circuit formatted by p -Si substrate, which is sensitive in this spectral region, while ZnO:N film is a window for visible radiation.

The spectral photoresponse of Ni/ZnO:N/Al diodes is shown in Fig. 5b. The maximum of photoresponsivity about 0.1 A/W peaked at around 365 nm . The cut-off at wavelength of 365 nm agrees with the ZnO energy band gap of 3.4 eV . The responsivity decreases at the shorter wavelength range due to decrease in the penetrating depth of the light, resulting in an increase in the surface recombination. The spectrum of responsivity ranged up to 1200 nm due to presence of structural defects in ZnO:N films and photosensitivity of Si substrate to visible radiation.

Figure 6 shows the temporal response of the ZnO:N photodetectors with 9 V bias and 100Ω load resistor. Calculated by exponential function fitting, the time constant of Al/ZnO:N/Al IDT MSM structures was found to be $10 \mu\text{s}$. Also the time constant of Ni/ZnO:N/Al diode was about 100 ns . A large magnitude of time constant for Al/ZnO:N/Al IDT MSM structures can be explained by the oxygen adsorption at the surface and by presence of grain boundaries in polycrystalline

ZnO:N film leading to appearance of trap states. All detectors based on ZnO:N films demonstrated high stability in time.

Photosensitivity of Al/ZnO/Al MSM photodetectors was very low (photocurrent-to-dark current ratio was only 0.05). Also temporal response of the detectors based on undoped ZnO films show a significant larger value of time constant (tens of minutes) than Al/ZnO:N/Al MSM photodetectors. Moreover, resistivity of ZnO films was of order twice lower than nitrogen doped ZnO films. This result testifies that nitrogen incorporates in ZnO film.

We believe that excellent photoelectric characteristics of obtained ZnO:N films is due to positive nitrogen role in suppression of crystal lattice defects in ZnO formed by oxygen vacancies. More advanced experiments are needed to determine nitrogen role in ZnO.

4. Summary

Al/ZnO:N/Al MSM IDT structures and Ni/ZnO:N/Al diode structures were obtained by magnetron sputtering. Photocurrent-to-dark current ratio 250 ($\lambda = 390$ nm) for Al/ZnO:N/Al IDT MSM structures with 4 μm interdigital spacing was achieved. Time constant of photoresponse was about 10 μs . Ni/ZnO:N/Al diode structure has high rectification ratio ($\approx 10^2$ at bias 1 V). The maximal responsivity about 0.1 A/W was achieved at 365 nm. The measured time constant of photoresponse was about 100 ns.

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