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Ultraviolet photoresponse properties of zinc oxide on type IIb diamond heterojunction

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ABSTRACT

Heterojunctions between ZnO and diamond are difficult to synthesize due to doping problems. In this work, a successful heterojunction that is sensitive to ultraviolet (UV) light has been fabricated using sputtered ZnO thin film on type IIb diamond, where boron activation at room temperature is possible at low concentrations. Current–voltage measurements show a p–n characteristic with significant UV photoresponse properties. The threshold voltage under UV illumination is decreased by 0.4 V, which can be predicted using a theoretical model.

1. Introduction

Zinc oxide (ZnO) and diamond are materials with wide energy band gaps of ~3.3 and 5.5 eV, respectively, and are thus attractive for opto-electronic applications. It is widely known that as-grown or undoped ZnO typically exhibits n-type conductivity. Although the source of free electrons contributing to n-type conductivity has not been conclusively identified it is usually attributed to zinc interstitials, oxygen vacancies, hydrogen or even incorporated electronegative hydrogen carbonates [1–3]. Due to the compensation effect of a large n-type carrier concentration, p-type ZnO is extremely difficult to synthesize. Similarly, diamond rarely exhibits n-type conductivity and the doping process in diamond is difficult to achieve due to its compact lattice, allowing diffusion of species smaller than or comparable to carbon at reasonable temperature [4]. However, p-type conductivity is known to occur for type IIb diamond, in which boron is the dominant impurity at a concentration below 1 ppm. In principle, ZnO can thus be combined with type IIb diamond to make a p–n heterojunction. An added advantage is mechanical and chemical stability as well as the high thermal conductivity of diamond (22 W cm^{-1} K^{-1}), which is very useful in high temperature device applications. Despite this interesting possibility, ZnO on diamond heterojunction is difficult to synthesize as one of the crucial factors that could determine successful fabrication of the ZnO on diamond heterojunction is the level of effective boron doping in diamond. Due to the small lattice constant of diamond, most doping elements would lead to severe distortions of the unit cell and are difficult to be incorporated. Only boron has been found to be suitable as an acceptor or donor, capable of forming a miniband, lowering activation energy and enabling ohmic contacts by tunnelling. The activation energy of boron is $\Delta E_A = 0.37$ eV and boron activation at room temperature can be obtained although full activation is unlikely. It is believed that boron activation is possible either at low concentrations, when the Fermi level crosses the acceptor level, or at high concentrations, when the miniband starts to overlap with the valence band [5]. At low boron concentrations, reasonable carrier activation can be obtained for doping level of 10^{13} cm^{-3} [5]. Interestingly, no rectifying behavior is usually achieved for high levels of boron doping but current rectification has been observed for heterojunctions where diamond has been doped with residual boron [6]. Doping diamond with residual boron is a difficult task with uncertain results. Type IIb diamond, which is semiconducting by nature, has a low concentration of boron and could thus be used as a p-type material without the need for intentional doping with residual boron. Moreover, this material has been used in previous efforts to fabricate a bipolar transistor with some success [7]. In this work, we report the fabrication of a heterojunction using as-grown ZnO on type IIb diamond and its ultraviolet (UV) photoresponse properties.

2. Experimental details

Type IIb natural diamond measuring $2.5 \times 2.5 \times 0.5$ mm^3 was used in this work. The as-received diamond was cleaned using ethanol, acetone as well as deionized water sequentially in an ultrasonic bath and dried using pure nitrogen gas. No attempt was made to determine the concentration of boron inclusion in the

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type IIb diamond but a concentration below 1 ppm of boron or an estimated density of 10^{17} cm^{-3} has been known to cause p-type conductivity [8]. The surface of the diamond was partially sputtered with a thin film of ZnO (~500 nm) using a pure ZnO target in a pure argon atmosphere.

Current–voltage (*I*–*V*) measurements were performed in the dark and under UV illumination at room temperature using a Keithley *I*–*V* measurement system. UV measurements were done under a 6 W UV lamp (λ=372 nm) while the distance between the lamp and the sample was 10 cm. X-ray photoelectron spectra were recorded using monochromatised Al Kα (1486.7 eV) X-ray radiation while micro-Raman spectroscopy and X-ray diffraction measurements were done using a Renishaw RN 1000 model and a PANalytical X'pert PRO high resolution X-ray diffractometer system, respectively. An argon ion line at 514.5 nm was used as the excitation source for Raman measurements, while the XRD measurements were performed with a fixed copper anode operating at 40 kV and 30 mA. The X-ray diffraction data were collected using Cu Kα radiation.

3. Results and discussion

Fig. 1(a) shows the Raman spectrum of the type IIb diamond. The low concentration of below 1 ppm of boron can be inferred from Raman measurements, where the 1332.3 cm^{-1} diamond peak (FWHM=4.5 cm^{-1}) was Lorentzian symmetric. Boron concentration was thus believed to be below the threshold of $\sim 2\times10^{20}$ cm^{-3}, the so-called Mott density, which corresponds to the onset of metallic conductivity [8–10]. A concentration above the threshold value will result in an asymmetric peak shape or the so-called Fano-like lineshape, which is caused by a quantum mechanical interference between the zone-centre Raman active optical phonon and the continuum of electronic states induced by the dopant [10]. Fig. 1(b) shows the X-ray excited Auger electron B KLL peak at the kinetic energy range ~176–184 eV, which is within the range observed for the presence of boron [11].

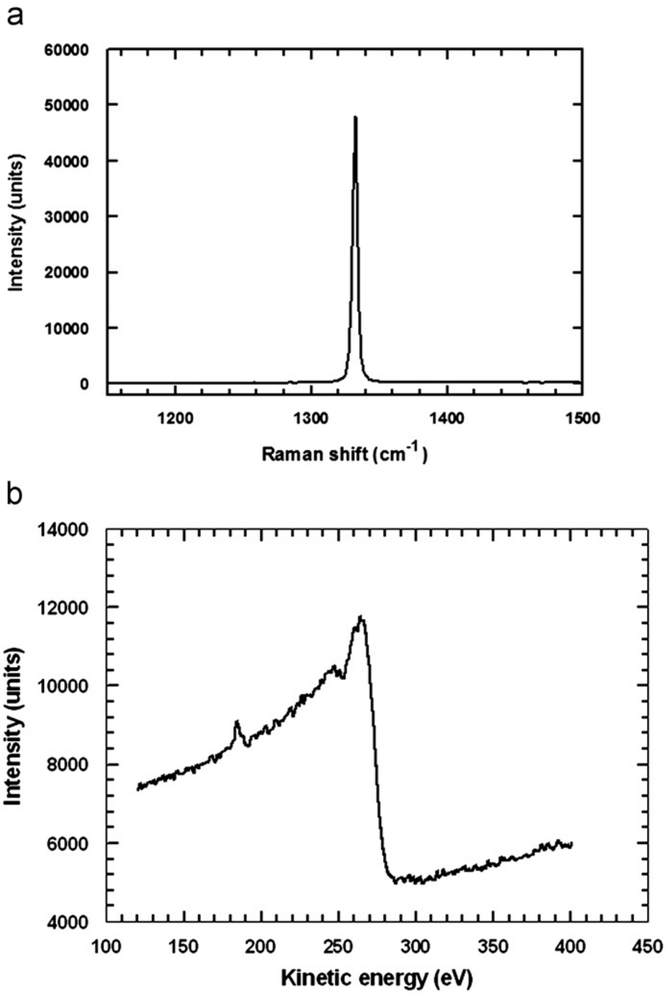

Fig.1. (a) Raman spectrum of type IIb diamond and (b) the B KLL peak of the type IIb diamond, showing the presence of boron.

A schematic diagram of the ZnO on type IIb diamond heterojunction is shown in Fig. 2.

The XRD pattern of the heterojunction shows the ZnO (0 0 2) and the diamond (1 1 1) peaks at 2θ–34.2° and 44.6°, respectively (Fig. 3(a)). The former peak indicates the wurtzite ZnO hexagonal structure with lattice constants a=3.249 Å and c=5.026 Å. The SEM image in Fig. 3(b) shows the typical surface morphology of the continuous crystalline ZnO thin film prepared using d.c. sputtering. No contaminants were detected in the ZnO thin film by EDS analysis. Characterization of the sputtered ZnO thin films showing n-type conductivity had been reported previously [2].

I–*V* measurements of the In and Ni metal contacts are taken to ensure that ohmic contacts are established on the ZnO thin film and type IIb diamond, respectively. The linear dependence of the *I*–*V* characteristics in Fig. 4 indicates that ohmic contacts are fairly established after annealing the contacts in air in a controlled furnace at 600 °C for 3 min.

Fig. 5 shows the *I*–*V* measurements of the ZnO on type IIb diamond heterojunction performed in the dark as well as under UV light. The inset shows the spectrum of the UV lamp. From the *I*–*V* measurements, it is obvious that forward conduction occurs when the applied voltage reaches ~4.0 V for both dark and UV conditions. The diode turn-on can be interpreted as over a small range of voltages rather than occurring abruptly at the threshold voltage. Fig. 6(a) and (b) shows that the threshold voltages under dark and UV conditions are 5.9 and 5.5 V, respectively. The UV illumination results in an increased current flow of an order of magnitude higher. The relatively high voltages are probably due to low ionization of the boron acceptors in diamond. The reverse breakdown voltages for the dark and UV light measurements are −4.6 and −6.6 V (Fig. 6(c) and (d)), respectively. As the reverse bias reaches 10 V, the current for UV illumination is ~135 nA, while only ~22 nA is observed for dark condition.

The change in threshold voltage under UV illumination can be predicted as follows. Since the ZnO on diamond heterojunction deviates from the case of an ideal *I*–*V* characteristic, threshold

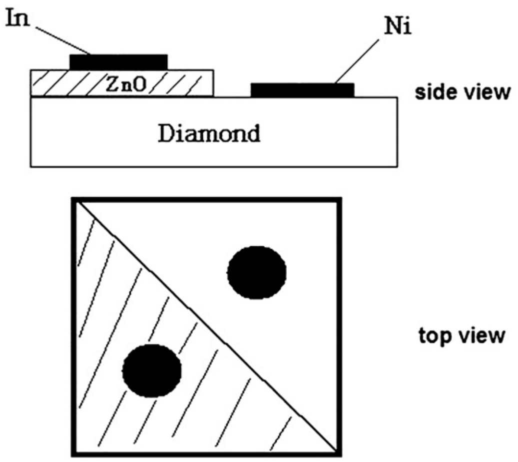

Fig. 2. Schematic diagram of ZnO on type IIb diamond heterojunction.