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Defects induced broad spectral photoresponse of PVT-grown bulk AlN crystals

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ABSTRACT

Aluminum nitride (AlN) is a wide bandgap semiconductor with promising application prospect in deep ultraviolet optoelectronic devices. Here, bulk AlN crystals in millimeter size were grown using an improved physical vapor transport technique. Schottky diodes based on these crystals demonstrated good photoresponse to a broad spectral range from 261 nm to 1064 nm. The photoresponse is attributed to the defects induced midgap energy states. The device demonstrated a photo responsivity up to 3.7 AW^{-1} at 360 nm with bias voltage of −10 V. This research paves a new way for broad spectral photodetectors.

AlN crystal has a wide direct electronic energy band up to 6 eV. Besides, it has outstanding physical properties including high melting point, high thermal conductivity, and high breakdown voltage. Therefore, intense research efforts have been devoted to AlN to study its application in laser diodes (LDs), deep-ultraviolet photodetectors (DUV-PD), and deep-ultraviolet light-emitting diodes (DUV-LEDs) over the past several decades [1–5]. Early in 2006, Yoshitaka et al. had developed an AlN PIN homojunction LED with an emission wavelength of 210 nm [6]. In 2015, Wei Zheng et al. employed AlN micro/nanowire to fabricate a fast speed photodetector with a good photoresponse performance in vacuum-ultraviolet (VUV) spectrum [7].

Compared with thin films or nano-structures, the research on bulk AlN crystal in terms of its application in optoelectronics devices is inadequate. One important reason is that the crystal defects are inevitable with current crystal growth techniques. The defects can induce midgap energy states in the band gap, which will affect the photoexcitation and emission properties, hinder the band edge transitions, and thus degrade AlN crystals' performance in DUV optoelectronic devices. The most common lattice defects in bulk AlN crystal are vacancy defects including N vacancies "V_N" and Al vacancies "V_{Al}", and oxygen substitutional defect, "O_N". Furthermore, it has been reported that O_N and V_{Al} can constitute O_N-V_{Al} complexes with several different energy states [8]. It is easy to understand that these defects induced energy states in AlN can induce violet and visible emission, which is of lower energy than the band edge emission. The broad emission feature of AlN crystals is getting rising attentions and has been well studied [9]. As comparison, the defects induced broad spectral photoresponse ability of AlN crystals has been less noticed, and there are seldom works reported so far. In fact, the research on materials with broad spectral photoresponse properties is always a hotspot in energy and sensing fields with applications including photovoltaics, photocatalysis and photodetection [10,11]. In this work, bulk AlN crystals were grown by physical vapor transport (PVT) method. Two terminals devices were fabricated based on these crystals. By use of laser sources with emissions spread over from DUV to Near-infrared (NIR), the photoresponse behavior of these devices were studied. Bulk AlN crystals here demonstrated a promising application prospect in broadband photodetectors.

The bulk AlN crystals were grown by PVT method. In the PVT process, a powder or polycrystalline AlN source was sublimated in a cylindrical crucible in a nitrogen atmosphere with pressure of several hundred millibars. Sublimated AlN vapor transported across a temperature gradient from the source reservoir to the recrystallization tungsten (W) substrate [12]. Temperature gradient distribution from material source to the recrystallization zone is a vital parameter in the growth process in terms of crystal size and quality. To realize more precise control in the crystals grown process, a novel furnace with two heaters was applied in this work [13]. These two heaters acted on sublimation and recrystalline regions independently. Therefore, the temperature gradient could be deliberately designed to improve the crystal growth process. Specifically, the optimized procedure is to hold a temperature around 2250 °C for 6 h with nitrogen pressure of 900 Torr at the grown stage.

The obtained bulk AlN crystals were evaluated by X-ray Diffraction (XRD) measurement. Most of the crystals were wurtzite structure, as shown in Fig. 1(a). The diffraction peak at about 36° is indexed as the (0002) diffraction peak of the wurtzite structure. Only (0002) lattice plane could be detected parallel with the substrate, indicating that the

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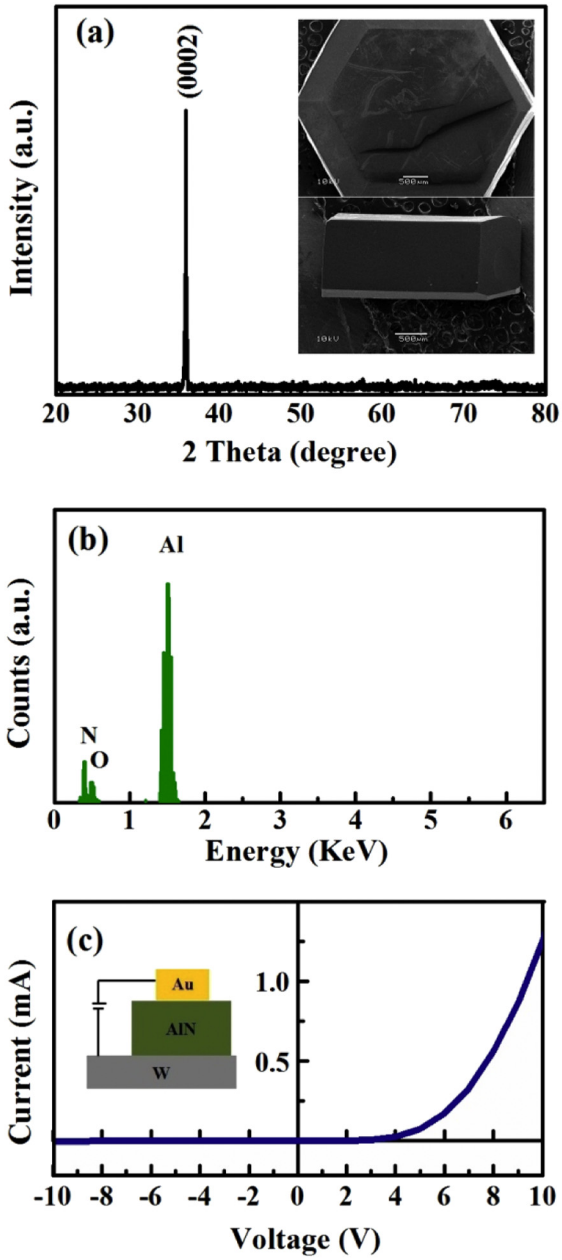

Fig. 1. (a) XRD pattern of the AlN crystals. The insets are the SEM images of the AlN crystals with scale bar of 500 μm. (b) EDS spectrum of AlN crystals. (c) Current-voltage characteristics of AlN based Schottky diode. The inset of (c) is the schematic diagram of diode structure.

sample is a single crystal. The insets in Fig. 1(a) are low magnification SEM images, which show typical wurtzite AlN crystal facades with growth orientations of c-plane (upper inset) and m-plane (bottom inset). In addition, the chemical composition of the AlN crystals was analyzed with energy-dispersive X-ray spectroscopy (EDS) measurement. As shown in Fig. 1(b), the EDS result indicates that there is slight unintentional oxygen doping (~1 at.%) in the crystals.

Bulk AlN crystal based Schottky diodes were fabricated in this work and the current-voltage (*I-V*) characteristics were measured with a DC power supply, as shown in Fig. 1(c). The W substrate, on which the AlN crystals were grown, acted as the cathode in the diode. A gold (Au) pad of 1 mm × 1 mm area was evaporated on the crystal through a shadow mask as the anode. The device has an Au-AlN-W layer stacking sandwich structure. The *I-V* curve shows apparent forward turn-on and reverse cut-off characteristic, which is a typical Schottky diode property [14]. Moreover, six lasers with emission lights of 261 nm, 360 nm, 405 nm, 532 nm, 785 nm, and 1064 nm were used to study the photoresponse of the Schottky device. The measurements were carried out in a glove box at room temperature. The laser output was diverged through an optical fiber, and then illuminated on Au electrode side.

Fig. 2 shows the current changes of the diode at bias of −5 V under cyclical on-off illuminations of 261 nm, 360 nm, 532 nm and 1064 nm lasers with same irradiance of 50 mW. Notices that these lasers cover a broad spectral region from VUV to IR, but their photon energy are all below the bandgap of AlN crystals (~6.0 eV). There should be no photoelectric response for a perfect AlN crystal theoretically. Nevertheless, it can be clearly seen that the Schottky diode based on present AlN crystals revealed an obvious photoresponse to all the excitation sources. All photoresponses in Fig. 2 are instant, indicating a photoelectric conversion process. This cannot be due to the absorption of band edge absorption, but the defects induced midgap states. With lasers of 360 nm, 532 nm, and 1064 nm, the photocurrent changes sharply, and then reaches to a saturation level. With laser of 261 nm, after the instant increase, the photocurrent continues to increase slowly instead of reaching to saturation. In view of its laggard emerging and slow speed, we speculate that the slow increase may come from a thermal effect. Responsivity (R) is a key figure of merit of photodetectors. It is expressed as $R = \Delta I/PS$, where ΔI is the photocurrent, P the light irradiance, S the area exposed under the light. It can be calculated from Fig. 2 that, with exposure time of about 1 s, the Schottky diode has a max R of 0.36 AW^{-1} at 360 nm, and a minimum R of 0.048 AW^{-1} at 1064 nm.

It is worth noting that all the photocurrents in Fig. 2 show obvious persistent photoconductivity (PPC) effect. Specifically, after the light was turn off, the photocurrents dropped sharply, followed by a long decline tail, and thus take a long time to recover to the initial level. We think the fast drop is due to the recombination of shallow trapped carriers and the slow recover can be attributed to the deep trap states. PPC effect is often observed in other III–V semiconductors and related to metastable traps [15]. For the AlN crystals, the existence of O_N-related *DX* center is generally considered to account for the persistent photoconductivity [16,17].

In general, N/Al vacancies (V_N, V_{Al}), oxygen substitution, and their complexes, have been widely recognized as the origination of defects states in AlN crystals [8,9,18–20]. The existence of those defects induced a battery of energy states in the bandgap of AlN. That's the reason why the present PVT grown AlN crystals are photosensitive to a broad spectral light with photons energy lower than bandgap. To get deeper insight into the relationship between the photoresponse and the energy band structure of AlN crystals, the photoluminescence (PL) property of bulk AlN crystals was characterized with excitation lasers of 193 nm and 261 nm, as shown in Fig. 3(a). With excitation of 193 nm, a near band gap emission has been seen at 205 nm (B1). Besides, there are other two separate emitting bands at violet and yellow spectrum range, with peak centers at around 370 nm (B2) and 650 nm (B3), respectively. These two broad emission bands can also be found in the PL spectrum of 261 nm excitation, but with different intensity. The two broad emission bands have been well studied before [21]. B2 can be attributed to the transitions from conduction band to O_N related states. B3 is ascribed to the transitions from O_N-V_{Al} complexes to valence band [8]. The energy level of O_N related states is about 3.2 eV below conductor band, and O_N-V_{Al} complexes states are about 2.0 eV above valence band. They are consistent with the photon energy of 360 nm and 532 nm, which are 3.4 eV and 2.3 eV, respectively. Moreover, the photo responsivity of the Schottky diode to six different laser sources including 261 nm, 360 nm, 405 nm, 532 nm, 785 nm, and 1046 nm with same irradiance of 50 mW has been measured with bias of −5 V. The relationship between responsivity and exciting photon energy was plotted and shown in Fig. 3(b). The curve has two broad bands near to the B2 and B3 just like the PL spectra. It implies that the broad spectral photoresponse is also due to the defects induced energy states.