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Highly spectrum-selective near-band-edge ultraviolet photodiode based on indium oxide with dipole-forbidden bandgap transition

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ABSTRACT

We reported a highly spectrum-selective ultraviolet photodiode based on In_2O_3 with dipole-forbidden bandgap transition. The near-band-edge ultraviolet emission and absorption were observed in the hybrid In_2O_3 films with the In_2O_3 nanocrystals embedded into the amorphous In_2O_3 matrix, indicating that the dipole-forbidden rule of bulk In_2O_3 is broken. The hybrid In_2O_3 film was deposited on the p-GaN/sapphire wafer to form an In_2O_3/p-GaN heterojunction photodiode. The photodiode showed an obvious rectifying behavior in a current–voltage measurement and a narrow-band ultraviolet photoresponse at the near-band-edge region under back-illumination conditions. Electronic structure calculations based on the first-principles method demonstrate that the breaking of dipole-forbidden transition rule is derived from the surface states of In_2O_3 nanocrystals. Our results suggest that tailoring the In_2O_3 nanocrystalline structure is an effective route to achieving novel optical properties and applying these properties to the ultraviolet optoelectronic field.

1. Introduction

Wide-bandgap oxides have attracted much attention due to their excellent properties and functionalities [1–13]. Among these oxides, indium oxide (In_2O_3) is extensively applied in the fields of solar cells, liquid crystal displays and photovoltaic devices, due to its outstanding properties of combining high transparency in the visible-spectrum range with high electrical conductivity [14–21]. Owing to the dipole-forbidden nature of the band-edge quantum states of In_2O_3, there exists an energy difference between the fundamental bandgap of ~2.9 eV and the optical bandgap of ~3.8 eV [22–24]. The symmetry properties of the conduction-band minimum (CBM) and valence-band maximum (VBM) states of the In_2O_3 prohibit the near-band-edge (NBE) transition, involving the process of light emission and absorption. Therefore, it is commonly believed that In_2O_3 is not a suitable light emitter and absorber in the NBE region (near the fundamental bandgap energy), which hinders its potential application in the ultraviolet (UV) optoelectronic field, such as photodiodes (PDs) and light-emitting diodes (LEDs). Nevertheless, recent research suggests that the dipole-forbidden rule can be broken and the strong NBE UV emission was observed in the nanostructural In_2O_3 [25–28]. Therefore, In_2O_3 nanoengineering is a suitable route to break dipole-forbidden rule and realize UV emission/absorption at the NBE region, which can be used to fabricate high-efficiency UV light emitting and detecting devices.

In this paper, we fabricated the hybrid In_2O_3 films with the In_2O_3 nanocrystals embedded into the amorphous matrix. Photoluminescence (PL) and optical absorption properties of the hybrid In_2O_3 films were investigated in detail. The hybrid In_2O_3 film was deposited on p-GaN to form a heterojunction photodiode. A narrow-band UV photoresponse at the NBE region under back-illumination conditions was observed. The physical mechanism of the breaking of dipole-forbidden rule in the In_2O_3 nanocrystals is also discussed in detail through first-principles calculations.

2. Experimental and first-principles calculations details

The In_2O_3 thin films were deposited on the quartz substrates at room temperature using pure argon (Ar) as the working gas by

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radio frequency (rf) magnetron sputtering method. Commercial available high-purity In_2O_3 target (purity > 99.99%) with stoichiometric proportion was used in our experiments. The vacuum chamber was evacuated to a base pressure of 10^{-4} Pa before the film deposition and the sputtering pressure was controlled to 0.1 Pa. In order to wipe off impurities on the surface of the In_2O_3 target, the target was pre-sputtered by Ar gas for 10 min before the In_2O_3 layer was deposited on the substrate. The growth process of the In_2O_3 layer lasted for one hour. The as-grown In_2O_3 film was annealed at 400 °C in air for 30 min in a horizontal quartz tube furnace. For the preparation of In_2O_3-based heterojunction photodiode, the In_2O_3 layer was first deposited on the commercial available p-type GaN/sapphire wafer at room temperature and then was annealed at 400 °C in air. The Ni/Au electrodes were deposited through a shadow mask on the p-type GaN layer and served as the p-type electrode. The indium metal was sintered on the In_2O_3 layer and served as the n-type electrode.

The crystal structure characterizations were performed by using X-ray diffraction (XRD) with Cu Kα radiation of 1.5406 Å. The surface morphologies and compositions were characterized and recorded using a field-emission scanning electron microscope (FESEM) with an energy dispersive X-ray spectrum (EDS) analyzer. A high-resolution transmission electron microscope (HRTEM) was used to examine the crystalline structure of the hybrid In_2O_3 thin films. The optical absorption spectra were recorded using an UV–vis–near-IR spectrophotometer. The PL measurements were performed using a He–Cd laser with a 325 nm line as the excitation source. The current–voltage curves were measured at room temperature in order to further verify the formation of the p–n heterojunction. The spectral response of the In_2O_3-based heterojunction photodiode was recorded using the 150 W Xe lamp, monochromator, chopper and lock-in amplifier. The illumination light is shed onto the heterojunction from the p-GaN side.

First-principles calculations of the electronic structures were carried out using the density functional theory (DFT) as implemented in the Vienna ab-initio simulation package (VASP) code with the projector augmented wave (PAW) potentials [29,30]. The generalized gradient approximation (GGA) to the exchange-correlation functional was used. The cutoff energy for the plane-wave basis set is 500 eV. For the indium atoms, d states were treated as valence states. For the bulk In_2O_3, a 40-atom supercell with bixbyite structure was used in the calculations on the band structures and optical properties. To integrate over the Brillouin zone (BZ), a $2 \times 2 \times 2$k-point mesh was used. An In_2O_3 quantum dot (QD) with a diameter of 1.5 nm, including 55 indium and 84 oxygen atoms, is cut from the bixbyite bulk In_2O_3.

3. Results and discussion

Fig. 1a shows the typical XRD patterns of as-grown and 400 °C annealed In_2O_3 films deposited on quartz substrates. No diffraction peak is observed for the as-grown In_2O_3 film, indicating an amorphous structure. For the 400 °C annealed In_2O_3 film, there exist weak diffraction peaks and the matching of observed 2θ values with the standard In_2O_3 diffraction data confirms that the annealed film is crystallized with a cubic structure. To further check the crystal structure after being annealed, we performed the TEM measurement. The TEM image of the In_2O_3 film after being annealed is shown in Fig. 1b. It can be seen that the In_2O_3 nanocrystals are embedded in the amorphous matrix, indicating a hybrid In_2O_3 nanocrystals/amorphous film. The nanocrystal size is estimated to be several nanometers. The surface and cross-sectional SEM images of the annealed In_2O_3 thin film are shown in Fig. 1c and d, respectively. It is observed that the film is compact with a thickness of ~1.2 μm. In addition, we also examined the proportion of indium and oxygen elements using EDS analyzer. The indium and oxygen compositions are 41.28 at% and 58.72 at% for the as-grown film, as well as 41.12 at% and 58.88 at% for the annealed film, respectively, suggesting that the stoichiometric proportions of indium and oxygen elements of the films are slightly larger than 2:3.

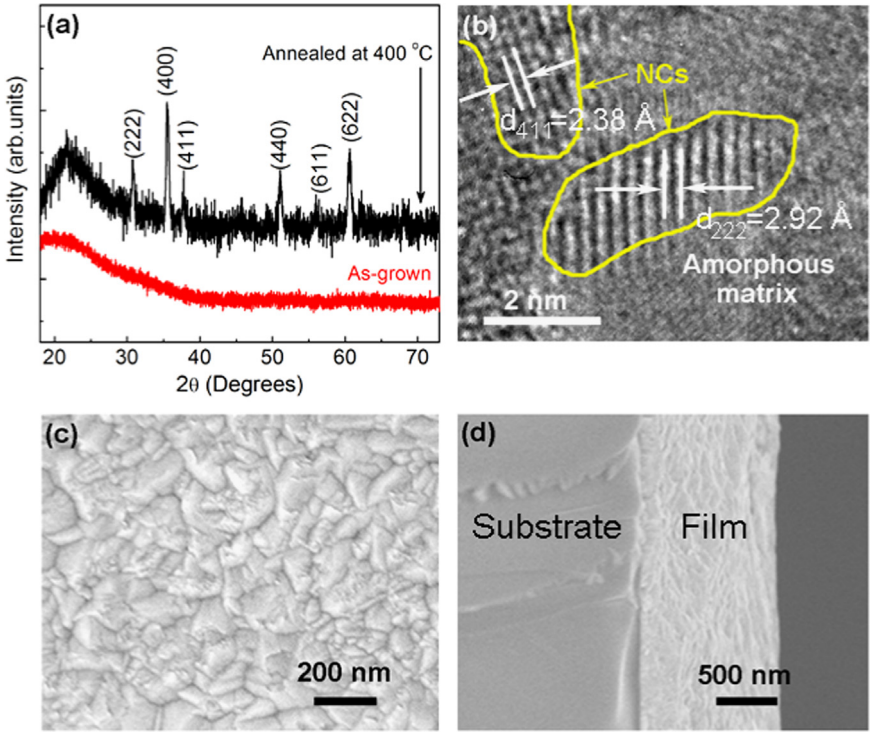

Fig. 1. (a) XRD patterns of the as-grown and 400 °C annealed In_2O_3 thin films grown on quartz substrates. (b) TEM image, (c) surface and (d) cross-sectional SEM images of the annealed In_2O_3 thin film.