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Fabrication of ZnInON/ZnO multi-quantum well solar cells

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ABSTRACT

We report on fabrication and photovoltaic characteristics of solar cells with ZnInON/ZnO multi-quantum wells (MQWs) in the intrinsic layer of p-i-n structure by RF magnetron sputtering. We employed two kinds of p layers: one is p-GaN and the other is p-Si. Under solar simulator light, the short-circuit current (J_{sc}) and the open-circuit voltage (V_{oc}) of the solar cells on p-GaN templates are 1.9 μA/cm^2 and 0.16 V, whereas J_{sc} and V_{oc} are enhanced to 2.5 μA/cm^2 and 0.19 V under simultaneous irradiation of green laser light (532 nm) and the solar simulator light. Solar cells on p-Si substrates do not show such enhancement. A possible origin of the enhancement is a large piezoelectric field generated in strained ZnInON wells coherently grown on p-GaN template.

1. Introduction

Solar cells with low-cost and ultra-high conversion efficiencies, so-called “third generation solar cells”, have attracted attention because of the potential to bring significant reduction in the electricity generation cost [1–5]. In single band gap devices that dominate the current photovoltaic market, choice of the material composing solar cells is a trade-off between maximizing current output with a narrow band gap material and voltage output with a wide band gap material. As a result, the maximum theoretical efficiency is limited to be 30%, which is well known as the Shockley-Queisser limit [6]. One promising way to overcome this limit is employing a tandem structure with several solar cells having different band gap materials. In fact, the reported efficiency of tandem type is high over 40%, being the highest efficiency ever reported for all types of solar cells [7,8]. The tandem solar cells, however, face substantive problems in the current matching between the cells that are connected in series, making further increase in the efficiency challenging. An alternative approach to obtain high efficiency is to use quantum confinement effect in multi-quantum wells (MQWs). In MQW solar cells, consisting of MQWs in the intrinsic layer of p-i-n structure, the output voltage is determined by the quasi-Fermi levels in barrier material with a wide band gap, whereas the output current is dominated by well materials with a narrow band gap. Hence, the output voltage is expected to be larger than that of the cells formed only from the material of the wells [9]. Furthermore, extra absorption of light at longer wavelengths via sub-band transition can enhance the current density output. These advantages of MQW solar cells make their theoretical efficiency over 50 % [10–18].

In this study, we fabricated solar cells with ZnInON based MQWs, taking advantages of the MQW photovoltaic behavior mentioned above. Since the conversion efficiency is highly dependent on the band gap of well layers and barrier layers, materials with tunable band gap is required for maximizing the conversion efficiency. ZnInON semiconductor is a pseudo-binary alloy of wurtzite ZnO and wurtizte InN. Optical measurements revealed that ZnInON has a tunability of the band gap over the entire visible spectrum and a high optical absorption coefficient of 10^5 cm^{-1} [19–21]. Therefore, this compound is a promising candidate for light absorbing MQW materials in solar cells. Compared with other tunable band gap materials such as InGaN, ZnInON have two advantages in terms of the application in MQW solar cells. First, ZnInON can be fabricated by a conventional sputtering, allowing for scaling up to larger substrates with ease. In the case of InGaN, the films are generally grown by utilizing metal-organic chemical vapor deposition method, which makes them of potentially limited use for large-scale demands because of the lack of scalability. Recently, some studies have been therefore directed towards sputtering growth of InGaN. The resultant films, however, turn out to be oxidized due to the residual gases such as oxygen and water vapor that always exists in conventional sputtering chambers [22]. In contrast, because oxygen is one of the main constituents of ZnInON, conventional sputtering chambers can be used for ZnInON deposition. The second advantage is the large piezoelectric constants of ZnInON, which brings low recombination rate of photo-generated carries in QWs because large piezoelectric field generated in QWs separates electron and holes. This large piezoelectric constant of ZnInON owes to the large piezoelectric constant of ZnO (e_{33}: 0.96 C/m^2), which is much larger

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than that of GaN (e_{33}: 0.73 C/m^2). Here, we demonstrate the fabrication of ZnInON/ZnO MQWs and the solar cells with the MQWs in the intrinsic layer of p-i-n structure. The photo-electric properties of the MQWs as well as the photovoltaic properties of the solar cells are evaluated through measurements of current–voltage (*J–V*) characteristics under photo-irradiation.

2. Experimental details

2.1. Fabrication of ZnInON/ZnO MQWs

The structure of ZnInON/ZnO MQWs is shown in Fig. 1(a). Seven or 15 periods of ZnInON(6 nm)/ZnO(10 nm) MQWs were deposited on two types of templates: one is single-crystalline ZnO films prepared on c-plane sapphire substrates, and another is poly-crystalline ZnO films deposited on quartz glass substrates. Here, single-crystalline ZnO templates were prepared by using the nitrogen-mediated crystallization (NMC) method [23–31], which is a method for fabrication of high-quality epitaxial films on large lattice-mismatched substrates. Despite the large lattice mismatch (18%) between ZnO and c-plane sapphire, single-crystalline ZnO films that have atomically flat surface were fabricated by the NMC method. Then, ZnInON well layers and ZnO barrier layers were deposited by RF magnetron sputtering in Ar-O_2-N_2 atmosphere and in Ar-O_2 atmosphere, respectively. The substrate temperature was room one. Finally, InGa electrodes were deposited on the bottom and the top of the ZnO barrier layers to measure *J–V* characteristics.

The band gap energy was determined by Tauc plots using optical reflection and transmission data obtained with a UV-visible spectrophotometer (JASCO V-530). The band gap of ZnInON was 3.1 eV, whereas the band gap of ZnO was 3.4 eV. The chemical composition of films was measured with a wavelength dispersive X-ray fluorescence spectrometer (Rigaku ZSX Primus II). The chemical composition ratio of ZnInON films was $(ZnO)_{0.97}(InN)_{0.03}$.

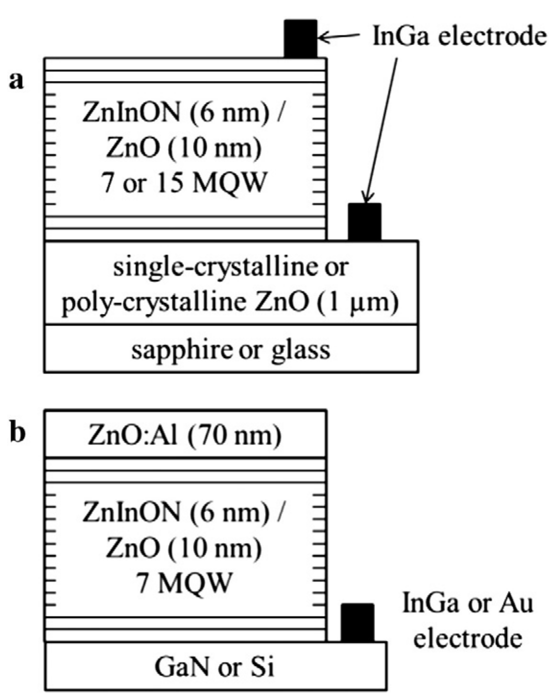

Fig. 1. Schematics of (a) ZnInON/ZnO MQWs structure, (b) solar cells with ZnInON/ZnO MQWs in the intrinsic layer of p-i-n structure.

2.2. Fabrication of ZnInON/ZnO MQW solar cells

The solar cell structure is shown in Fig. 1(b). The MQW solar cells were composed of n-type ZnO:Al (AZO), 7 periods of $(ZnO)_{0.97}(InN)_{0.03}$(6 nm)/ZnO(15 nm) MQWs, and p-type GaN template or p-type Si substrate. It is well known that ZnO exhibits n-type conductivity even without intentional doping, and there is difficulty in obtaining p-type because of self-compensation from native defects along with the deep acceptor levels of the dopants [32]. Therefore, p-type GaN templates, which were commercially available, were used in this study. The crystal structure as well as the band gap of GaN is the same as wurtzite ZnO, and the lattice mismatch between them is significantly small of 1.9%. ZnInON well layers and ZnO barrier layers were deposited by RF magnetron sputtering in Ar-O_2-N_2 atmosphere and in Ar-O_2 atmosphere, respectively. The substrate temperature was room temperature. N-type AZOfilms of 70 nm in thickness were deposited on MQW layers by RF magnetron sputtering in Ar atmosphere. InGa electrodes were deposited on the p-GaN templates, while Au electrodes were deposited on the p-Si substrates by sputtering. No post anneal was performed.

The film thickness was measured by X-ray reflectometry. The crystallinity of ZnInON films was examined by x-ray diffraction (XRD) analysis with a four-circle texture diffractometer (Bruker D8 Discover) using Cu Kα radiation ($\lambda = 0.15418$ nm). *J–V* characteristics were measured under AM 1.5 (100 mW/cm^2) and a diode-pumped-solid-state green laser light (532 nm, 2.15 W/cm^2) irradiation.

3. Results and discussion

3.1. Photo-electrical properties of ZnInON/ZnO MQWs

First, we investigated the photo response of ZnInON/ZnO MQWs. Fig. 2(a) and (b) show *J–V* characteristics of 7-period ZnInON/ZnO MQWs on single-crystalline ZnO template and on poly-crystalline ZnO template, respectively. The linear relationship of the *J–V* characteristics shows that the contact between ZnO and InGa electrodes has ohmic character. The conductivity of the MQWs is enhanced by the irradiation of solar simulator light, indicating the absorption of the light and photo-induced generation of carriers. The photo-to-dark conductivity ratio of the MQWs on single-crystalline and on poly-crystalline ZnO templates are 41.8 and 1237.4, respectively, which demonstrates the high photosensitivity of the ZnInON/ZnO MQWs. We observed that the poly-crystalline ZnO has quite large surface roughness (root mean square roughness (RMS): 13.1 nm), that is, large haze, whereas the single-crystalline ZnO has atomically flat surface of RMS = 0.16 nm. Therefore, the higher current density of MQWs on poly-crystalline ZnO is due to the longer optical path as the result of efficient diffuse light scattering. It should be noted that there is a difference in the photo response between MQWs on single-crystalline ZnO and on poly-crystalline ZnO under irradiation of the solar simulator light together with the green laser light. The conductivity of MQWs on single-crystalline ZnO shows 1.8 times enhancement by superimposing the green laser light, whereas that on poly-crystalline ZnO does not. Since the photon energy of the laser light (2.3 eV) is smaller than the band gap energy of the well layers (3.1 eV), the photo-conductivity enhancement is probably due to the enhanced extraction of photo-generated carriers from the well layers.

The rather low photo-conductivity is brought about by the small thickness of MQWs and the wide band gap of the well layers. Hence, we fabricated a 15-period ZnInON/ZnO MQWs on a single-crystalline ZnO template, aiming to increase the photo-conductivity. The *J–V* characteristic is shown in Fig. 2(c). As expected, the photo-conductivity is increased with increasing the number of period of MQWs from 7 to 15. The photo-to-dark conductivity ratio is high of 54.1. However, the photo-conductivity shows only 1.2 times enhancement by superimposing the green laser light. The reason of this small enhancement will be discussed in the next section.