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NTO/Ag/NTO multilayer transparent conducting electrodes for photovoltaic applications tuned by low energy ion implantation

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ABSTRACT

Multilayer structures with optimized Nb (3.7 at.%) doped TiO_2 (NTO) having the layers as NTO/Ag/NTO (NAN) were fabricated to obtain high optical transmittance and low electrical resistivity which could be a suitable replacement of the conventional transparent conducting electrodes used in the energy conversion and optoelectronics devices. These optimized pristine films of NAN layers were deposited by sputtering and implanted with 40 keV N^+ ions with fluences ranging from 1×10^{14} to 1×10^{16} ions/cm^2. The N^+ ion implantation leads to the improvement in the electrical conductivity of NAN films, confirmed by the Hall measurement. The resistivity of pristine film is 9.6×10^{-5} Ω cm which decreases to 5.5×10^{-5} Ω cm after ion implantation for the N^+ ion fluence of 1×10^{16} ions/cm^2. Electrical transport properties were studied in the temperature range of 80–340 K, and the results show stable behavior of films. This substitutional doping causes narrowing of band gap and improvement in the electrical conductivity. The optimized NAN multilayer films show a low sheet resistance of 6.9 Ω/□ and a high transmittance of ~81% for the 1×10^{16} ions/cm^2 fluence. The Haacke figure of merit (FOM) of 18×10^{-3} Ω^{-1} was obtained for the highest fluence (1×10^{16} ions/cm^2). The X-ray photoemission spectroscopy study of the implanted samples revealed substitution of Ti by Nb in NTO film and appearance of Ti^{3+} state. The work function of pristine NAN films, measured using ultravoilet photoemission spectroscopy (UPS) was found to 4.63 eV, which matches with the work function of active layer of photovoltaic cell. On implantation, the O ions are replaced by N^+ ions. These results indicate that the NAN films with N^+ ion implantation are suitable for potential transparent conducting electrode (TCE) applications in photovoltaics due to their high transmittance, low electrical resistivity and compatibility for growth of further layers.

1. Introduction

Transparent conducting electrodes (TCE) having high transmittance and low electrical resistance are an important component in light conversion applications such as photovoltaic cell, smart windows and light emitting diodes (LEDs) and they are used in touch-panel screen and flat-panel displays as well, and hence have a huge market (Kim et al., 2013; Sharma et al., 2016a; Sibin et al., 2017). TCE an essential component in solar cell technologies acts as a front electrode in both inorganic solar cells (CdTe) (Green, 2007) and organic solar cells (Günes et al., 2007). Having large use and crucial role in optoelectronic devices; the TCE should posses the low electrical resistivity and high optical transmittance over a wide optical range. Since the photovoltaic is a large area application therefore a durable and cost effective TCE is required. As transparent conductors (TCs) are a significant component in all electrical and optically activated devices so there is need of high quality and low cost TC. Moreover, the TCs need a low electrical resistivity to produce a low voltage drop through the conductor surface. TCs are widely used in smart windows (Sun et al., 2017) and solar thermal collectors (Colangelo et al., 2016). In smart windows, the purpose of TC is to transmit maximum light and to control the solar heat gain. Meanwhile, in solar thermal collectors it allows solar radiation to collector and stops the heat loss. Although, Indium doped Tin oxide (ITO) is the most widely used TCE in optoelectronic devices, it shows some feasibility problems such as, scarcity of In, high deposition temperature, and low mechanical stability etc (Kumar and Zhou, 2010). This has led to researchers investigating several alternatives – doped metal oxides viz. Nb:TiO_2 (Singh et al., 2017a), Al:ZnO (Ayadi et al., 2014), carbon nanostructures viz. carbon nanotubes (Hecht et al., 2011), graphene (Bae et al., 2009), and their components, conducting

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polymers (Ha et al., 2004), metallic mesh and nanowires (Park et al., 2014). Although substantial investigations have been carried out on above mentioned transparent electrodes, but each category has problems of its own like high resistivity for conductive polymers and low contact surface area and low transmittance for 3D structure. Of the mostly used metals oxides, viz. TiO_2, ZnO, SnO_2 and WO_3 for the transparent electrode application, TiO_2 is considered as the prime candidate due to its several advantageous characteristics like wide band gap (~3.2 eV), high refractive index (2.7), high transmittance (~95%) in the visible region and good mechanical stability (Hashimoto et al., 2007; Heo et al., 2005). TiO_2 exhibits very good chemical stability, which can be exploited for its use in TCE development (Ellmer, 2012). A very thin layer of Ag (< 10 nm) provides excellent electrical conductivity with low absorbance and sufficient transmittance. The transmittance of this layer can be increased by inserting the metal layer between two oxide layers that reduces the reflection from the Ag surface (Guillén and Herrero, 2011).

Based on the above concept, oxide/metal/oxide (OMO) multilayer structures have emerged as a potential inspiring alternative due to the coexistence of their extraordinary electrical and optical properties. OMO structures not only give improved electrical properties but also exhibit other useful characteristics such as low roughness, good corrosion resistance and high work function. In OMO structure, the researchers have used the metals of Ag, Au and Cu as middle layer (Girtan, 2012; Guillén and Herrero, 2008), and which is primarily responsible for the charge transport activity. The primary goal of inserting metal layer between the two oxides layer is to minimize the reflection effect and increase the transmittance in the visible region and by varying oxide layer thickness the desired maximum transmittance position can also be adjusted. Recently, performance of OMO based structure like ZnO/Ag/ZnO (Sharma et al., 2017), ITO/Ag/ITO (Sibin et al., 2017), SnO_2/Ag/SnO_2 (Liu et al., 2015), TiO_2/Ag/TiO_2 (Singh et al., 2017b), AZO/Ag/AZO (Qi et al., 2013) and ZnO/MWCNT-Ag/ZnO/PET (ZCAZ) (Surbhi et al., 2018) have been reported. Zhu et al. (Zhu et al., 2016) have reported the sputtering current variation effect on the optical and electrical properties of TiO_2/Ag/TiO_2 multilayer TCE sputtered on glass. They have obtained the optimized TAT electrode with sheet resistance of 7.2 Ω/□ and ~91% transmittance with a sputtering current of 0.48 A. Zhao et al. (Zhao and Alford, 2016) studied the effect of TiO_2, Ag layer thickness and deposition rate on the performance of TCE and have observed that thickness of TiO_2 and Ag as 42 nm and 10 nm, respectively gives better results. Kim et al. (Kim et al., 2015) investigated the TiO_2 layer thickness effect on the TiO_2/Ag/TiO_2 multilayer films and reported that TiO_2 (40 nm)/Ag (18.8 nm)/TiO_2 (40 nm) multilayer provides the sheet resistances of 3.9–4.4 Ω/□ and ~95% transmittance at 550 nm wavelength. Dhar and Alford (2013) have reported the critical thickness of Ag layer as ~9 nm to form a continuous film in TiO_2/Ag/TiO_2 multilayer structure for good transport properties. The sputtering method has been extensively used for uniform, stoichiometric and large area deposition and also employed for roll-to-roll deposition of TCO films on glass and plastic substrates, which satisfy industry requirements. The TCE is one of the key components of solar cells and widely used in various type of organic solar cell devices. These TCE have been used in ZnO/Cu_2O based solar cells (Zang, 2018; Zang et al., 2013) and $CH_3NH_3PbI_{3-x}Cl_x$ perovskite solar cells (Zeng et al., 2017).

Researchers have proposed different methods viz. doping and tracing of impurities in TiO_2, chemical mixing, sol-gel, ion assisted sputtering, ion implantation etc to improve properties of TiO_2. Nb doped TiO_2 has shown enhanced performance as TCE (Hitosugi et al., 2010). A single layer Nb doped TiO_2 (NTO) used as TCE in optoelectronic applications, have shown less working efficiency in terms of electrical conductivity and the films are thicker than the multilayer structure (Tucker et al., 2012). The multilayer structure with Nb doped TiO_2 embedded with metal layer gives higher electrical conductivity with nearly same transmittance while having lower thickness (~80 nm). Ion implantation has been reported as one of the most promising technologies for modification of TiO_2, due to its good process control and restoring of vacant oxygen sites in a TiO_2 lattice (Asahi et al., 2001; Stepanov, 2012). The present work reports the fabrication and characterization of NTO/Ag/NTO multilayer films with varying NTO thickness (25–65 nm) and Ag thickness kept constant at ~9 nm. An optimized thickness for NTO layer was obtained and the structure with NTO/Ag/NTO (35 nm/9 nm/35 nm) shows highest figure of merit (FOM) of $12 \times 10^{-3}\,\Omega^{-1}$. These multilayer films were further implanted with 40 keV N^+ ions to improve the properties with the fluence ranging from 1×10^{14} to 1×10^{16} ions/cm^2. It is seen that doping Nb in TiO_2 and the N^+ ion implantation both contribute in enhancement of electrical conductivity. There is decrement in optical transmittance but the overall FOM has significantly increased to $18 \times 10^{-3}\,\Omega^{-1}$. We have also measured the work function of pristine NAN films using ultravoilet photoemission spectroscopy (UPS). The work function of the TCE is a key factor and have significant impact on the performance of the solar cell because it affects the band alignment of TCE and the next active layer (Po et al., 2011). H.M. Lee et al. (2016) have reported improved power conversion efficiency (3.6%) with MoO_3 graded ITO anodes. Lei et al. (2015) increased the work function of ITO using CuS to gain higher power conversion efficiency (7.4%).

2. Experimental details

Nb powder (Strem Chemicals, 99.9% purity) and TiO_2 powder (Alfa-Aesar, 99.98% purity) were used to fabricate the Nb doped TiO_2 (NTO) sputtering target. These powders were mixed by solid state method and pressed into a 2-in. diameter pellet and then sintered at 1200 °C for 12 h. The first NTO layer of multilayer structure was deposited on corning glass substrate by RF sputtering (120 W) at room temperature. Middle layer of Ag was deposited by DC sputtering (16 W) using silver target (99.98% purity) and the top NTO layer was deposited over the middle Ag layer. Initially vacuum chamber was evacuated to 5×10^{-6} mbar and chamber pressure during deposition was 5×10^{-3} mbar for NTO layer and 1.5×10^{-2} mbar for Ag layer with constant Ar flow at 15 sccm. The distance of target to substrates was 100 mm and deposition rate for NTO and Ag layers were obtained as 1 Å/s and 6 Å/s, respectively. The optimized NTO/Ag/NTO (35 ± 4 nm/9 ± 1 nm/35 ± 4 nm) multilayer structure was consecutively deposited on cleaned glass substrates without a vacuum break. The as-prepared multilayer films were then implanted with 40 keV N^+ ions of fluence ranging from 1×10^{14} ions/cm^2 to 1×10^{16} ions/cm^2 using low energy ion beam facility (LEIBF) at the Inter-University Accelerator Centre (IUAC), New Delhi, India. The thickness of top and bottom NTO layers were varied from 25 nm to 65 nm keeping the same sputtering conditions to find optimized thickness, in terms of maximum FOM.

The electrical properties of pristine and implanted films were measured using ECOPIA-5000 low-temperature Hall Measurement unit using a magnetic field of 0.57 T for temperature range of 80–340 K. The optical transmittance and absorbance were obtained from LAMBDA 750 (Perkin Elmer) UV–Vis-NIR Spectrophotometer with bare glass as a reference in the visible range (300–800 nm) of light. The crystalline properties of pristine and implanted films of NAN structure were probed by X-Ray Diffractometer (Panalytical X-Pert Pro) with CuKα radiation. The morphology of the films was examined by Nova Nano FE-SEM 450 (FEI) and topography was observed by using atomic force microscopy Multimode Scanning Probe Microscope (Bruker). Detailed study of chemical states of elements and the interfacial stability of NAN films were carried out by X-ray photoelectron spectroscopy (XPS, Omicron ESCA). Monochromatic source Al Kα (1486.7 eV) of 124 mm mean radius and X-ray resolution of 0.6 eV and 3×10^{-10} mbar chamber pressure has been used for XPS measurement. The thickness and elemental composition of the films were studied by Rutherford Backscattering (RBS) Spectrometry. These measurements were carried