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# Fabrication of highly efficient $TiO_2/Ag/TiO_2$ multilayer transparent conducting electrode with N ion implantation for optoelectronic applications

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ABSTRACT

Fabrication of highly conductive and transparent $TiO_2/Ag/TiO_2$ (referred hereafter as TAT) multilayer films with nitrogen implantation is reported. In the present work, TAT films were fabricated with a total thickness of 100 nm by sputtering on glass substrates at room temperature. The as-deposited films were implanted with 40 keV N ions for different fluences ($1\times10^{14}$, $5\times10^{14}$, $1\times10^{15}$, $5\times10^{15}$ and $1\times10^{16}$ ions/cm$^2$). The objective of this study was to investigate the effect of $N^+$ implantation on the optical and electrical properties of TAT multilayer films. X-ray diffraction of TAT films shows an amorphous $TiO_2$ film with a crystalline peak assigned to Ag (111) diffraction plane. The surface morphology studied by atomic force microscopy (AFM) and field emission scanning electron microscope (FESEM) revealed smooth and uniform top layer of the sandwich structure. The surface roughness of pristine film was 1.7 nm which increases to 2.34 nm on implantation for $1\times10^{14}$ ions/cm$^2$ fluence. Beyond this fluence, the roughness decreases. The oxide/metal/oxide structure exhibits an average transmittance ~80% for pristine and ~70% for the implanted film at fluence of $1\times10^{16}$ ions/cm$^2$ in the visible region. The electrical resistivity of the pristine sample was obtained as $2.04\times10^{-4}$ Ω cm which is minimized to $9.62\times10^{-5}$ Ω cm at highest fluence. Sheet resistance of TAT films decreased from 20.4 to 9.62 Ω/□ with an increase in fluence. Electrical and optical parameters such as carrier concentration, carrier mobility, absorption coefficient, band gap, refractive index and extinction coefficient have been calculated for the pristine and implanted films to assess the performance of films. The TAT multilayer film with fluence of $1\times10^{16}$ ions/cm$^2$ showed maximum Haacke figure of merit (FOM) of $5.7\times10^{-3}$ Ω$^{-1}$. X-ray photoelectron spectroscopy (XPS) analysis of N 1s and Ti 2p spectra revealed that substitutional implantation of nitrogen into the $TiO_2$ lattice added new electronic states just above the valence band which is responsible for the narrowing of band gap resulting in the enhancement in electrical conductivity. This study reports that fabrication of multilayer transparent conducting electrode with nitrogen implantation that exhibits superior electrical and optical properties and hence can be an alternative to indium tin oxide (ITO) for futuristic TCE applications in optoelectronic devices.

## 1. Introduction

Transparent conducting electrode (TCE) is a key component in any optoelectronic device including solar cells, flat panel displays, light emitting diodes (LED) [1,2] etc. A good TCE should exhibit low resistivity and high transparency in the visible region of the electromagnetic spectrum [3,4]. Indium tin oxide has been widely used as TCE due to its high conductivity, high transparency and ease of deposition. However, In is high-cost material due to its increasing demand and natural scarcity. Doped single layers and multilayers of $TiO_2$ with metal embedded between the two oxide layers have emerged as TCE with comparable optical and electrical properties for flat panel displays, LEDs and solar cells [5–7]. In addition, $TiO_2$ is a potential semiconductor material with technological importance because of high refractive index (2.7), wide band gap (~3.2 eV), high transmittance (~95%) in the visible region and high mechanical and chemical stability [8–10]. Doped metal oxides like Nb-doped $TiO_2$ (NTO) [11], Al-doped ZnO (AZO) [12], and F doped-$SnO_2$ (FTO) [13] have been commonly used as TCE in optoelectronic devices. In addition, electrical conductivity has been further increased by sandwiching a thin metal (M) film

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between these two dielectric (D) layers to form a DMD multilayer. Among metals, Ag is a good candidate because it exhibits low resistance and high transmittance (as a very thin layer) in the visible region, so Ag ( < 20 nm thick) [14] is commonly used as the interlayer in DMD multilayers. Many advantages of the metal embedded multilayer structure have been reported over the single layer TCO [15,16]. Researchers have been investigating various multilayers employing the Ag layer as a middle layer with different oxides such as $SnO_2$/Ag/$SnO_2$ [17,18], $SnO_x$/Au/$SnO_x$ [19], ZnO/Ag/ZnO [20], AZO/Ag/AZO [21], ITO/Ag/ITO [22] and $TiO_2$/Ag/$TiO_2$ [23] exhibiting low resistance and high transmittance in the visible region. Kim et al. [24] investigated the effect of Ag layer thickness on electrical and optical properties of $TiO_2$/Ag/$TiO_2$. Authors found highest transmittance of 86.3–97% at 591 nm for different Ag thicknesses, and sheet resistance slightly decreasing from 6.17 to 2.27 Ω/sq with increase in the Ag layer thickness. Dhar et al. [25] deposited $TiO_2$/Ag/$TiO_2$ by sputtering on the flexible substrate; Ag thickness was varied between 5 and 13 nm. It was reported that Ag layer became contiguous as it approaches the critical thickness of 9.5 nm and multilayer with Ag thickness 9.5 nm had the best figure of merit, $6.14\times10^{-4}$ $\Omega^{-1}$. Many other researchers [26,27] have also investigated the properties of the $TiO_2$/Ag/$TiO_2$ multilayer thin films. Tin dioxide based multilayer $SnO_2$/Ag/$SnO_2$ films studied by Yu et al. [28] as a function of Ag thickness varied between 0 and 9 nm showed an average transmittance of > 83%, sheet resistance of 9.61 Ω/sq and highest figure of merit ($1.6\times10^{-2}$ $\Omega^{-1}$) for the $SnO_2$ (25 nm)/Ag (5 nm)/$SnO_2$ (25 nm) tri-layer film.

Ion doping is a unique method to restore the vacant oxygen sites in a $TiO_2$ lattice, and N-ion was taken as a particular choice [29]. It was reported that ion-doped $TiO_2$ causes band bending due to an alteration in electron concentration via charge transfer between a dopant and conduction band or valence band [30]. In N-doped $TiO_2$, new energy states are introduced above the valence band of the $TiO_2$, by increasing the electron density [31]. According to Asahi et al. [29] doping of N into $TiO_2$ contributes to band gap narrowing to provide visible-light response. Many research groups [29,32,33] have analyzed the N 1s XPS spectra and found that the peak at 396 was assigned to atomic β-N and substitutional N doping. Peaks at 400 and 402 eV are attributed to molecularly chemisorbed (γ-$N_2$) and organic impurities [34]. Jangheum et al. [35] reported smoothing of Cu film on N doping as indicated by surface morphological study using AFM & SEM.

In this work, we have fabricated $TiO_2$/Ag/$TiO_2$ multilayer films by sputtering and the pristine films were implanted by the $N^+$ 40 keV ions of various fluence. The thickness of upper and lower $TiO_2$ layer was kept constant at ~45 nm, and that of embedded Ag layer was taken ~9 nm to form a continuous layer, necessary for good electrical conduction.

## 2. Experimental details

### 2.1. Sample preparation

$TiO_2$ powder (Alfa-Aesar, 99.99% purity) was used for target preparation. This powder was pressed into 2-in. pellet and then sintered at 1100 °C for 10 h to get better structural stability for film deposition. Commercial Ag target (99.99% purity) was used for Ag layer deposition. Glass substrates of 1×1 $cm^2$ were cleaned using standard cleaning processes. Before deposition, $TiO_2$ and Ag targets were pre-sputtered for 15 min to remove contaminants. RF source for oxide layers and DC source for metal layer deposition were used in TAT structure preparation using sputtering method at 100 W and 16 W with 15 sccm Ar flow, respectively. The $TiO_2$/Ag/$TiO_2$ (45 ± 5 nm/9 ± 2 nm/45 ± 5 nm) structure was sequentially prepared at room temperature on glass substrates. The base pressure of the chamber was ~$5\times10^{-6}$ mbar and working pressure during $TiO_2$ deposition was ~$6\times10^{-3}$ mbar and ~$1.6\times10^{-2}$ mbar for Ag layer. The as-deposited TAT films were implanted with 40 keV $N^+$ ions with fluences of $1\times10^{14}$, $5\times10^{14}$, $1\times10^{15}$, $5\times10^{15}$ and $1\times10^{16}$ ions/$cm^2$ at room temperature using the low energy ion beam facility at the Inter-University Accelerator Centre (IUAC), New Delhi, India. The nuclear energy loss and electronic energy loss values for 40 keV $N^+$ ions were obtained as 20.13 and 13.3 eV/Å respectively; as calculated by the SRIM-2010 software. These values show that entire passage of these ions in the film is dominated by nuclear energy loss. The stopping range of N ions was 60 nm, which is less than the film thickness (100 nm). RBS was performed using 1.7 MV tandem accelerator facility with 2 MeV $He^+$ ions at scattering angle of 165° at IUAC, New Delhi for depth profiling and compositional studies.

### 2.2. Characterization

The crystal structure of the TAT multilayer was investigated by using an X-Ray Diffractometer (Panalytical X-Pert Pro) with CuKα radiation. The morphology and topography of the films were imaged from Nova Nano FE-SEM 450 (FEI) and atomic force microscopy done by Multimode Scanning Probe Microscope (Bruker). Optical transmittance and absorbance were measured using LAMBDA 750 (Perkin Elmer) UV–vis–NIR Spectrophotometer. Carrier concentration, carrier mobility and resistivity of TAT multilayer films were measured by HMS3000, Ecopia using a magnetic field of 0.57 T. Sheet resistance was evaluated using the four-point-probe technique. Composition, valence and chemical states of TAT films were analyzed by the X-ray photoelectron spectroscopy (XPS, Omicron ESCA). For XPS measurement monochromatic Al $K_\alpha$ (1486.7 eV) source with a mean radius of 124 mm was used and monochromatic X-ray resolution as confirmed by FWHM was 0.6 eV. The vacuum pressure of the chamber was ~$4\times10^{-10}$ mbar.

## 3. Results and discussion

### 3.1. Structural properties

The X-ray diffraction (XRD) pattern of the pristine and implanted $TiO_2$/Ag/$TiO_2$ multilayer films for different fluence is shown in Fig. 2. The absence of any peak for $TiO_2$ shows its amorphous behavior which is expected because the deposition was done at room temperature. Peaks at 2θ=38.15°, 44.3°, 64.6° and 77.5°, are assigned to the (111), (200), (220) and (311) planes of Ag (JCPDS No. 04-0783) respectively. After implantation, the intensity of the Ag (111) peak slightly increased with the ion fluences and the full width at half maximum FWHM (β) changed from 0.6605 to 0.5188 and crystallite size increased from 13.3 nm to 16.8 nm as the fluence changed from 0 to $1\times10^{16}$ ions/$cm^2$. Residual stress and lattice constant calculated for pristine and N ion implanted films are shown in Table 1.

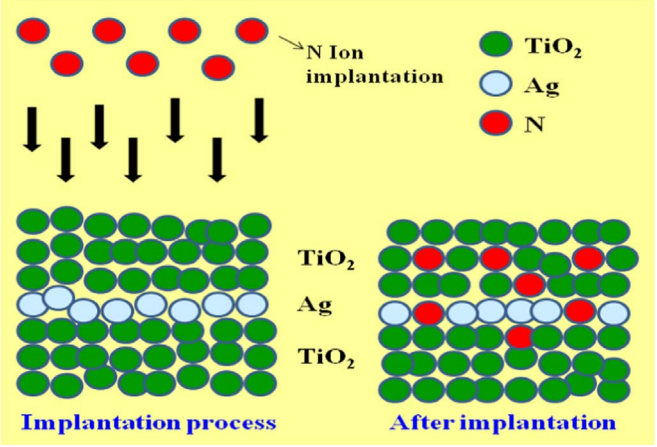


**Fig. 1.** Schematic showing the fabrication of nitrogen ion implanted TAT multilayer film.