Shallow nitrogen ion implantation: Evolution of chemical state and defect structure in titanium

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ABSTRACT

Evolution of chemical states and defect structure in titanium during low energy nitrogen ion implantation by Plasma Immersion Ion Implantation (PIII) process is studied. The underlying process of chemical state evolution is investigated using secondary ion mass spectrometry and X-ray photoelectron spectroscopy. The implantation induced defect structure evolution as a function of dose is elucidated using variable energy positron annihilation Doppler broadening spectroscopy (PAS) and the results were corroborated with chemical state. Formation of 3 layers of defect state was modeled to fit PAS results.

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1. Introduction

Defect creation and doping offer tremendous potential to generate attractive properties in materials [1–3]. With the growing interest on development of thin film nanostructures by PE-CVD, ion mixing and implantation, it is imperative to understand the evolution of defect structure and chemical species formation across thin regions of materials with potential applications in the field of nanotribology, electronics, sensor and energy, where modified and/or buried layers are used to obtain certain characteristic properties [4–6]. Since, Plasma Immersion Ion Implantation (PIII) is known for high dose ion implantation, its utility lies in surface modification aspects of such materials. PIII combines several useful (reactive and non-line of sight) features of both plasma enhanced chemical vapor deposition (PECVD) and conventional beam line ion implantation, with superior productivity [7–9]. Hence, PIII has been used for several engineering applications [10–15]. However, its potential application for shallow ion implantation is not explored much.

Titanium and its oxide, nitride and oxy-nitride derivatives exhibit several attractive properties [16,17]. Similarly, band gap of titanium oxide can be tuned by doping with nitrogen [18]. TiN is commercially used for hard coating applications due to its excellent hardness (VHN-2400). Hence, the process of nitrogen incorporation in Ti or TiO_2 is important. Assessments based on conventional thermodynamic and growth kinetic considerations have predicted the formation of TiN and/or TiO_xN_y during nitrogen Plasma Immersion Ion Implantation of Titanium [19,20]. However, such theories have been found to be inadequate at nanometer regime [21]. Additionally, the initial interest in PIII was built upon surface modification of materials for metallurgical applications, where change in chemistry of the surface is considered important. In fact, reactive shallow ion implantation introduces a complex state of interaction in between defects and different chemical states across a thin region. As a result, the evolving chemical state and defect structure significantly influences characteristic properties of materials, particularly when the region under consideration is very small. Hence, the process of shallow nitrogen ion implantation of Titanium warrants a detailed investigation of the chemical state and defect structure using complimentary analytical techniques.

In this paper, we attempt to understand various issues pertaining to the evolution of defect structure and chemical state across the thickness of a thin layer of titanium during shallow nitrogen ion implantation by PIII process. The chemical state information was obtained from secondary ion mass spectroscopy (SIMS) and X-ray photo-electron spectroscopy (XPS). The defect structure evolution was analyzed using variable energy positron annihilation Doppler broadening spectroscopy (PAS) and the results were corroborated with chemical state evolution.

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2. Experimental details

The schematic of the PIII system used in specimen preparation is shown in Fig. 1. A radio frequency (R F) generator (Huttinger, PFG 600 RF) was connected to a spiral antenna for the excitation and sustenance of homogeneous plasma of the process gas at a low power (75 W) and pressure $\sim 8 \times 10^{-3}$ mbar. Metallographically polished high pure titanium (99.9%) specimens were surface cleaned (using Ar + H$_2$ plasma) for 10 min by 1 kV pulsed bias (1.5 kHz) inside the chamber. Subsequently, implantation was carried out using high pure nitrogen (99.89%) such that positive nitrogen ions in the evolving sheath bombard the specimen surface at normal incidence when the specimen is biased to a negative pulsed DC voltage of 10.5 kV (100 Hz with 45 µs ON time). Though no external heating was provided, a temperature less than 100 °C was estimated for this process. Two specimens were implanted with nitrogen ions for 45 min (S1 $\sim 0.6 \times 10^{17}$ atoms/cm^2) & 90 min (S2 $\sim 1.2 \times 10^{17}$ atoms/cm^2) under the above conditions to ensure TiN formation [22]. The voltage and current output from the pulsed dc source were monitored using a digital oscilloscope (Agilent DSO 5012A) to keep control over the ionic current. The instantaneous pulse rise time was measured to be of the order of $\sim$1.5 µs. However, a mono-energetic distribution of ion energy was assumed for the purpose of estimating the range and defects using SRIM code. The RF plasma constitute N$^+$ and N$_2^+$ ions, radicals and neutrals; and N$^+$ ions acquire the highest energy to have an implantation peak at around 22 nm. Hence, actual concentrations of nitrogen and nitrogen containing chemical species were determined ex-situ using depth resolved XPS analysis as discussed later.

The PIII processed specimens, S1 & S2 were analyzed using Cameca IMS4F-Secondary Ion Mass Spectrometer (SIMS), to get the depth profiles of the elements in the specimen, using 10 nA of 4.5 keV Cs$^+$ primary ion beam rastered over a square area of size 150 µm × 150 µm. The secondary ions were collected from a circular area of 63 µm diameter at the center of the sputtered area as a function of sputtering time. The sputtering time was calibrated to sputtered depth by measuring the depth of the sputter crater formed using a Dektak surface profilometer, model 6 M.

Sputtered XCs complexes, where X is any atom from the specimen, provide more quantitative information than what sputtered atomic ions provide [23,24]. The quantification is known to be improved further by including the Cs complexes of clusters also in computing composition [25]. In this line, the most intense Cs complex species ejected from the specimens were identified to be, N Cs, O Cs, Ti Cs, Ti N Cs, Ti O Cs, Ti O$_2$ Cs, N Cs$_2$, O Cs$_2$, Ti Cs$_2$, Ti N Cs$_2$, Ti O Cs$_2$ and Ti O$_2$ Cs$_2$. Since only selected isotopic species can be profiled through depth, the depth profiles of the species, ^{14}N^{133}Cs, ^{16}O^{133}Cs, ^{48}Ti^{133}Cs, ^{46}Ti^{14}N^{133}Cs, ^{50}Ti^{16}O^{133}Cs, ^{48}Ti^{16}O$_2$^{133}Cs$_2$, ^{14}N^{133}Cs$_2$, ^{16}O^{133}Cs, ^{48}Ti^{133}Cs$_2$, ^{46}Ti^{14}N^{133}Cs$_2$, ^{50}Ti^{16}O^{133}Cs$_2$ and ^{48}Ti^{16}O$_2$^{133}Cs$_2$ were acquired. The lower abundant ^{46}Ti^{14}N was chosen instead of the mono-isotopic species ^{48}Ti^{14}N because ^{48}Ti^{14}N and ^{46}Ti^{16}O have the same integral mass. Similarly, ^{50}Ti^{16}O was chosen instead of ^{48}Ti^{16}O to avoid the interference from ^{50}Ti^{14}N. However, the intensities of elemental clusters, which are contributed by all the isotopes, are required for quantitative analysis. The intensity of an elemental cluster is achieved by dividing the intensity of the acquired isotopic cluster by the natural isotopic abundance of that cluster, which is the product of the natural isotopic abundance values of the isotopes in the isotopic cluster. This correction was applied to the intensities of all the acquired species. The number of atoms of Ti, N and O in all the cesium complex species were added together to get the depth profile.

X-ray photo electron spectrometer (XPS)-MECA 2000 was used for analyzing the variation in chemical state due to ion implantation. The specimens were irradiated with Al K-α (1486.6 eV) X-ray and binding energy vs intensity of photoelectrons escaped from the surface ($\sim$3-nm) was deduced. Depth profile of chemical state due to nitrogen ion implantation was obtained by sputtering the surface with Ar$^+$ ions (5 keV). The specimens were sputtered for several (0.5, 1, 2.5, 5, 9, 12, 17, and 20-min) durations and the binding energy data was collected for each (Titanium, Nitrogen and Oxygen) species. However, data analysis was focused to titanium and nitrogen profiles to get depth resolved chemical state information. The sputter yields of the samples were estimated to be slightly above 1 nm per minute. XPS spectra were analyzed using SPECS lab software by considering Shirley type background deduction to decompose and assign the peak energy corresponding to different chemical states of titanium in presence of oxygen and nitrogen.

The specimens were investigated using magnetically guided variable energy positron beam (VEPB) to obtain information about defects [26]. Depth resolved defect information was acquired by varying the bias voltage (0–12 kV) applied to the specimens [27,28]. The 511 keV gamma line produced by the annihilation was recorded using a HPGe detector having a resolution of 1.45 keV at 662 keV gamma line of Cs^{137}. From the line shape of 511 keV gamma, a defect sensitive line shape parameter (S-parameter) is derived. The S-parameter is defined as the ratio of peak counts (511 ± 1 keV) to the total counts in the Doppler broadening curve (511 ± 10 keV). The S vs E (Positron energy) curve was fitted using VEPFIT code [29]. The fitting is achieved by solving the positron diffusion equation by invoking a layered defect structure that traps positrons at different depths inside the specimen. The fraction of positrons (f) annihilated from each layer contribute to the S-parameter and the total contribution from the individual layers can be given as Eq. (1), where suffixes b, s and j represent bulk layer, surface layer and different trapping layers respectively [30]. The variation of S-parameter with respect to depth of pure annealed
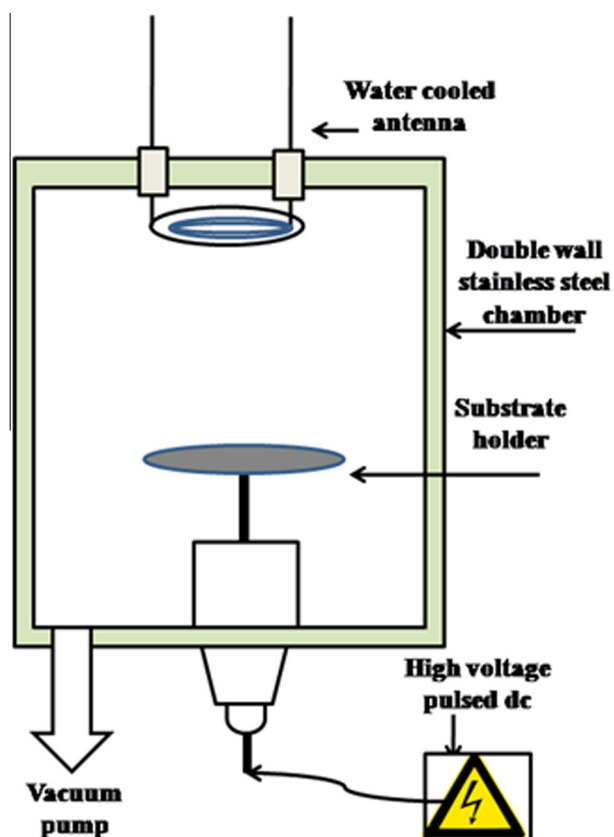

Fig. 1. Schematic of PIII system used for the preparation samples.