A novel method for preparing stoichiometric SnO₂ thin films at low temperature

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Tin oxide is a well-known nonstoichiometric material with dual valency. The invariance of stoichiometry is very intriguing. As of today no report is available for preparing perfect stoichiometric tin oxide. Here we report a novel method to prepare stoichiometric tin oxide by modifying the known plasma enhanced chemical vapor deposition technique using SnCl₄·xH₂O as precursor and O₂ as reactant gas at various temperatures from 300 to 800 °C. Tetragonal rutile structure of SnO₂ was found, grown along the [110] direction. X-ray photoelectron spectroscopic measurement showed constant Sn/O ratio. Sn 3d and O 1s were found composed of only Sn⁴⁺ (487.2 eV) and O–Sn⁴⁺ (531.2 eV) with equal peak widths. Raman band intensity (~63 cm⁻¹) was found increasing with temperature, indicating the morphological changes. Sheet resistance of ~0.5 Ω/□ at 300 °C was measured that reduces to ~0.1 Ω/□ at 600 °C. It is found that film stoichiometry remains unaltered, while the structural morphology changes significantly. © 2009 American Institute of Physics. [DOI: 10.1063/1.3115222]

I. INTRODUCTION

Tin oxide is a suitable candidate that finds wide application in the field of sensors, opacifiers, solar cells, etc. Its low cost, chemical stability, and useful electrical properties make it a favorable semiconducting oxide of industrial significance. It belongs to a class of materials that combine high electrical conductivity with optical transparency and thus constitutes an important component for optoelectronic applications. Tin oxide is special in the respect that tin possesses a dual valency preferably attaining an oxidation state of 2⁺ or 4⁺. This dual valency facilitates a variation in the surface oxygen composition.

Different applications require different oxygen deficiency and stoichiometry of SnO₂, e.g., transparent conducting electrode requires uniform stoichiometric films to avoid leakage current, whereas for gas sensors surface and bulk oxygen-related stoichiometric defects are necessary to influence the electronic and electrical properties of a device for better gas sensitivity.¹-⁴ The composition changes at surface would imply significant variations in physical and chemical properties and thus provide a mechanism for tuning these properties.

Therefore, various techniques and methods are invented to prepare SnO₂ films as per the requirement including reactive sputtering, spray pyrolysis, evaporation, sol-gel, pulsed laser deposition, thermal evaporation, and chemical vapor deposition (CVD).¹-⁴ Among these techniques, CVD has meaningful known advantages. The literature survey indicates that the physical properties of the films are strongly dependent on the method and the conditions of the film preparation.

Here we present a novel technique for depositing the stoichiometric SnO₂ thin films using modified plasma enhanced CVD (PECVD) technique with stannic chloride as a precursor and O₂ as a reactant gas. The deposition was carried out on Si (100) substrate from 300 to 800 °C at a rf power of 100 W. Samples were characterized using field emission scanning electron microscopy (FESEM), x-ray diffraction (XRD), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), and micro-Raman spectroscopy. XPS observations indicated that the deposition temperature does not affect the stoichiometry as Sn/O ratio was found constant; Sn 3d and O 1s were found centered at same binding energy value and same full width at half maximum (FWHM) irrespective of the deposition temperature. The fitting data clearly showed that Sn⁴⁺ (487.1 eV) and O–Sn⁴⁺ (531.1 eV) were only detected and the peaks corresponding to other tin valency such as Sn²⁺, Sn⁰, and O–Sn⁴⁺ were not detected, indicating that the stoichiometry of film remains unaltered. The probable reason might be the modified method for in situ heating of the precursor. During the precursor decomposition in oxygen ambient the reactants attain certain level of oxidation. The attained oxidation state remains unchanged due to rf plasma being comparatively at low temperature.

II. EXPERIMENT

Silicon wafers with (100) orientation were used as substrate after cleaning using conventional cleaning process.