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Synthesis of Nanocrystalline Iridium oxide Thin Films via Green Chemistry By Sol-gel method

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ABSTRACT

IrO_2 thin films were deposited by green chemistry sol-gel method on conducting glass using 5% anhydrous iridium chloride sol. XRD patterns show polycrystalline nature with rutile structure preferential orientation along [110] plane. SEM shows the uniform deposition of nanowires with dimension from 10-25 nm and 1–2 mm long. PL studies shows shift in the excitonic peak as compared to the bulk IrO_2 optical spectra. Raman spectra have the stretching and bending vibration modes of IrO2 at 615 and 458 cm -1 respectively. The films thickness were in the range of 180 - 230 nm. pH sensor showed very good sensing performance in sensitivity response repeatedly and reversibly between – 52.4 mV/pH and – 52.8 mV/pH in the pH range between 1 to 12 at 300K with response time about 15 sec

Keywords- NC IrO_2 ,sol gel method , XRD ,SEM , Raman Spectra

INTRODUCTION

The electrically conducting IrO_2 belongs to the family of transition-metal dioxide compounds with a rutile structure .Oxides of iridium have electronic conductivities due to slightly non stoichiometric composition[1]. Generally, these oxides show particular point defect structures such as oxygen deficiency or cation interstititials and a corresponding deviation of the ideal oxidation state of the predominant metal .The attractive properties of IrO_2 have been extensively studied for several applications, such as durable electrode materials for chlorine or oxygen evolution, optical switching layers in electrochromic displays, microsensors for gas detection and as a thin film electrode in ferroelectric capacitors for nonvolatile memories[2] .Due to their high chemical stability and high aspect ratio, IrO_2 nanorods (NRs) have been found to be a candidate material for vacuum microelectronic devices .Iridium oxides have advantages over conventional glass electrodes and other metal oxide electrodes were shown to have good stablilty over a wide pH range ,even at high temperatures upto 250°C,at high pressure with fast response time even in non aqueous solutions[3].

AIM OF PRESENT WORK

The synthesis and characterization of IrO_2 nanocrystalline (NC) thin films deposited on glass substrate with different annealing temperature .The relative intensities of the observed Raman features were studied by analyzing the Raman-active modes in the tetragonal rutile structure for the different planes of the NCs. The red shift and asymmetric broadening of Raman line shapes were analyzed using a modified spatial correlation (MSC) model and attributed to both size and residual stress effects [7-8].The results demonstrate the possibility of utilizing experimental RS together with the MSC model analysis as a structural and residual stress characterization technique for NCs.

1.EXPERIMENTAL DETAILS

Iridium oxide nanocrystalline thin films were deposited on glass substrate via green chemistry sol-gel process by using iridium oxide precursor[4-5]. Sigma Aldrich Iridium oxide was taken and Shimla mirch pulp was mixed with Ethanol in ice bath chamber. It was stirred for 5to 6 hours with different concentration .The films were annealed at 250 °C, 300 °C, 350 °C and 400 °C for one hour to obtain desired rutile structure. The films were characterized by XRD, SEM and FT Raman spectroscpy techniques[6].

$2IrCl_3 + 3H_2O \rightarrow Ir_2O_3 + 6HCl$

2.RESULTS & DISCUSSIONS

2.1 Raman Spectra

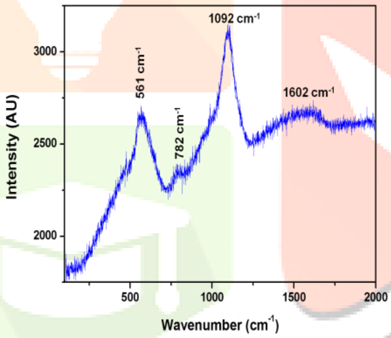

Fig.2.1 Raman Spectra of IrO_2 Thin Film Annealed at 300°C. Raman modes, identified as :-**Eg-** 561. cm^{-1},**B2g-**728.1 cm^{-1}**, A1g-** 752.2 cm^{-1}

The wavelength dependence of optical absorptance spectra of IrO_2 thin films deposited on glass substrate by sol-gel dip coating process derived from different iridium chloride concentrations at room temperature in 200 nm to 800 nm region studies have been made. The band gaps of these films are determined by means of a graphical method using Tauc equation from the absorption coefficient calculated from the absorptance data as shown in Fig.2.1. The band gap was found to be 2.87 eV, i.e. comparable with the bulk IrO_2. With the increase of iridium concentration, minor variations are observed. These absorptance measurements provide evidence for the good crystallinity of IrO_2 deposited thin Films.

2.2XRD Pattern

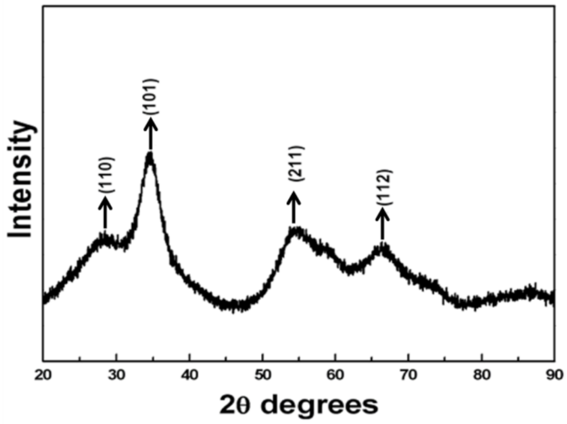

Fig.2.2 The X-ray diffractograms of IrO_2 films prepared at constant deposition time for different substrate temperature.

2.3 PL Spectrum of IrO_2 film

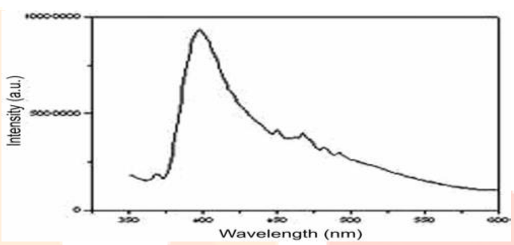

Fig 2.3 - PL spectra of a set of IrO_2 thin films annealed at different temperatures. UV near-band edge emission peak at 385 nm is observed, which originates from the excitonic recombination.

2.4 SEM Images

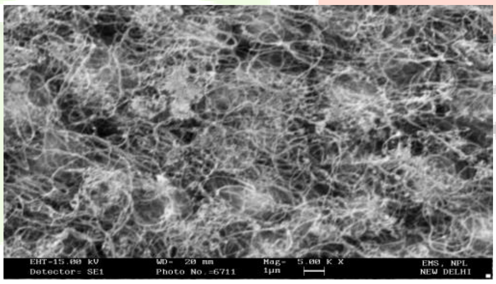

Fig.2.4-Tetragonal IrO2 (JCPDS 15-0870) and 4500C Annealed IrO_2 NC thin film Nanorods -20nm diameter.

The above all samples prepared at different substrate temperatures and solutions of different molarities have been annealed at different temperatures[9] .A temperature controller was used to measure the substrate temperature and to control the resistance heater via a thermo- couple[10-12] . In order to explore influence of the substrate temperature and molarities of solutions,a large number of films were prepared at temperatures ranging from 350 to 500^0C at solutions of 0.005M , 0.01M, 0.02M and 0.03M [13-14].

2.5 IR

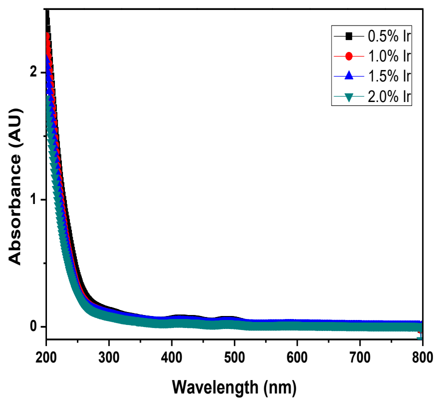

Fig. 2.5: Absorption spectra of IrO_2 dip coated films derived from different Iridium content sol in 200-800 nm region

The fine nanorod porous film network surface morphology of the as-deposited iridium oxide dip coated films are observed in the SEM images Fig.2.5.The films are uniformly deposited over the substrate without any cracks and much agglomeration. The length of nanorods varies from few millimeter to several centimeter range and diameter ~ 25 nm.

CONCLUSION

The nanorods grown by sol-gel process confirms the complete Rutile structure formation at 450°C annealing. The structure and morphology of the film changes with deposition parameters and reaction conditions. Modified SC model is used for explaining the stress induced shift in analyzing the observed Raman features.

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