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Properties of mixed molybdenum oxide–iridium oxide thin films synthesized by spray pyrolysis

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Abstract

Molybdenum-doped iridium oxide thin films have been deposited onto corning glass- and fluorine-doped tin oxide coated corning glass substrates at 350 °C by using a pneumatic spray pyrolysis technique. An aqueous solution of 0.01 M ammonium molybdate was mixed with 0.01 M iridium trichloride solution in different volume proportions and the resultant solution was used as a precursor solution for spraying. The as-deposited samples were annealed at 600 °C in air medium for 1 h. The structural, electrical and optical properties of as-deposited and annealed Mo-doped iridium oxide were studied and values of room temperature electrical resistivity, and thermoelectric power were estimated. The as-deposited samples with 2% Mo doping exhibit more pronounced electrochromism than other samples, including pristine Ir oxide.

Keywords: Iridium oxide; X-ray diffraction; Spray pyrolysis technique; Thin films; Mo-doped iridium oxide

1. Introduction

Iridium oxide offers promising candidature for many applications such as optical information storage [1], catalyst for O_2 evolution [2], photo electrolysis [3], and electrochromic devices [4]. Due to fast response (~50 ms) and outstanding stability (~10^7 cycles) in liquid electrolyte (e.g. H_2SO_4), iridium oxide plays a pivotal role in electrochromic device [1,4]. Recently many workers are interested in this material in connection with the electrochromism (EC). To the best of our knowledge mixed IrO_x–MoO_3 thin films have not yet been studied.

Ir oxide, anodically colouring material has better optical switching response than MoO_3 cathodically colouring, in proton containing electrolytes. However, MoO_3 is more akin to sensitivity of human eye, which lead to greater apparent colouration efficiency. Ir oxide is not a commonly used EC material, mainly because of the cost factor. We have made an attempt to bring down the cost by doping the film with a cheaper material like MoO_3. Among the various iridium oxide based mixed systems, IrO_2–SnO_2 system appears as a most promising one, as reported by Niwa et al. [5]. The colouration efficiency (CE) remains close to the value of Ir oxide as long as "Sn" content is less than 50%. This indicated that the amount of "Ir" can be replaced to a significant extent by a cheaper material without strongly affecting its electrochromism.

In this paper, we report the influence of molybdenum doping in Ir oxide on its structural, electrical, optical and electrochromic properties. Ir oxide films doped with 2%, 4%, 6% and 8% molybdenum were prepared by adding appropriate quantities of ammonium molybdate into the iridium chloride solution.

2. Experimental

For the deposition of Mo-doped Ir oxide thin films by spray pyrolysis, the precursor solutions were prepared by dissolving iridium chloride ($IrCl_3 \cdot 3H_2O$) and ammonium molybdate powders (AR grade, LOBA 99.5% pure) in doubly distilled water separately. The equimolar (0.01 M) concentrations of

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both the solutions were used. These solutions were mixed together in desired volume proportions prior to the deposition, the homogeneous solution was then sprayed onto corning glass and FTO coated conducting corning glass substrates (10–20 Ω/□). The deposition temperature was kept constant at 350 °C and monitored by a chromel–alumel thermocouple fixed to the hot plate. The pyrolytic decomposition of the precursor solution onto the surface of substrate results in the formation of thin solid films. After many trials the preparative parameters (viz. spray rate, nozzle to substrate distance, quantity of solution sprayed, etc.) were optimized to obtain uniform, pinhole free and adherent films. The films were annealed at 600 °C for 1 h in air. After 1 h the films were carefully preserved in the desiccator and later on used for the characterization. The films deposited onto the corning glass substrates were used for the structural, electrical and optical characterization, where as those deposited onto FTO coated conducting glass substrates were used for electrochromic characterization.

The samples with varied amount of 'Mo', viz. 2%, 4%, 6% and 8% were prepared and represented as ID_2, ID_4, ID_6 and ID_8, respectively. ID_O represents undoped iridium oxide thin films. The corresponding annealed samples are represented as IAD_0, IAD_2, IAD_4, IAD_6 and IAD_8, respectively.

Surface morphology was examined using scanning electron microscope (Cambridge Stereoscan 250 MK-3 unit). For structural determination X-ray diffraction (X-RD) technique with Cu Kα (λ = 1.504 Å) line, Philips X-ray Diffractometer PW 1730 was used. IR spectra were recorded in the wavelength range 1600–4000 cm^{-1}. The two-probe method was employed to study the variation of electrical resistivity in the temperature range 25–275 °C. The area of the film was defined and silver paste was applied to ensure good ohmic contacts. The thermo-emf was measured as a function of temperature in the range 25–275 °C.

The electrochemical cell has been formed by using conventional three-electrode system. The samples deposited onto FTO coated conducting glass substrates were used as working electrodes. Graphite and saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. An aqueous solution of 0.5N H_2SO_4 was used as an electrolyte.

3. Results and discussion

3.1. Formation of mixed molybdenum oxide–iridium oxide thin films

The precursor solution was atomized pneumatically through specially designed glass nozzle, which produces solution spray comprising fine aerosol like droplets. The droplets undergo solvent evaporation, solute condensation and vaporization, while approaching towards substrates. The droplet size was so adjusted by controlling the air and solution flow rate such that the pyrolytic decomposition takes place in the close vicinity of the substrate due to temperature gradient formed between substrate and an atomizer and uniform films are produced.

3.2. Thickness measurement

Thickness of the as-deposited (ID_0–ID_8) and annealed (IAD_0–IAD_8) samples of 4 cm × 2 cm area was measured by gravimetric method. The film thickness is calculated by using relation (1)

$$t = \frac{m}{\rho A} \tag{1}$$

where m is the mass of film deposited on area A and ρ is the bulk density of material. The films thicknesses are given in Table 1. For as-deposited samples, film thickness increases from 0.4 to 1.1 μm with increase in doping concentration of molybdenum oxide in iridium oxide. Thickness of annealed samples varies from 0.37 to 0.92 μm with increase in doping concentration. Thicknesses of post-annealed films were found to be less than that of as-deposited films.

3.3. Surface morphology

The surface morphology of the undoped as-deposited iridium oxide film shows smooth surface while undoped annealed iridium oxide films exhibit 'cracked mud' look. Transition metal oxide layers very often exhibit such features [6–8], which is in principle, favorable for some applications such as O_2 evolution and electrochromism, because it gives rise

Table 1
Values of room temperature resistivity (ρ_{RT}), thermal activation energies (E_a), thermoelectric power (TEP) and optical band gap energies (E_g) for all the samples

Sample	Thickness (μm)	ρ_{RT} (×10 Ω cm)	TEP (μV/°C)	Activation energy, E_a (eV)	$E_{(0)}$ (eV)	γ (meV/K)	E_F (eV)
ID_0	0.4	3.1	4.9	0.075	1.16	3.7	0.03
ID_2	0.52	63	9.1	0.1	1.31	7.1	0.032
ID_4	0.62	43.4	9.3	0.19	2.40	8.5	0.06
ID_6	0.78	6028	9.6	0.15	3.35	11.8	0.10
ID_8	1.1	54900	14.0	0.11	4.47	15.1	0.32
IAD_0	0.37	2.4	2.7	0.12	1.17	1.51	0.4
IAD_2	0.5	12.3	4.0	0.11	1.25	1.76	0.75
IAD_4	0.59	37.2	4.6	0.08	1.6	2.16	0.8
IAD_6	0.75	1150	6.0	0.11	1.63	2.56	0.87
IAD_8	0.92	5370	7.5	0.13	1.6	2.68	0.89