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Preparation of nanocrystalline ZnO/Co_xO_y and CNT/Co_xO_y bilayers for photoabsorption potential: XPS and some surface structural characterization

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ABSTRACT

Zinc oxide and carbon nanotubes (CNT) have been separately grown atop cobalt oxide (Co_xO_y) thin film to form bilayer structures. The structures were characterized by some surface probing techniques. Surface morphology shows that particles of the underlying Co_xO_y film are evenly distributed across substrate, its average size increases between 60 and 73 nm with deposition voltage. A transparent layer of ZnO completely laminated the Co_xO_y film in the first set of bilayer sample. Thickness of overgrown CNT on Co_xO_y is about 16 nm. Dispersion of Co_xO_y crystallites along the path of the adsorbed CNT was also observed. Optical studies indicated that both the Co_xO_y film and the ZnO/Co_xO_y bilayers are fairly transparent to visible light. Values of their energy band gap were estimated in the range between 2.0 and 2.14 eV. Photoemission and crystallographic studies revealed possible interaction between particles of Co_xO_y and ZnO films but not with the substrate. The study suggests that both the laminated II-VI bilayer and the CNT enhanced structures could be a recipe for effective charge harvesting and separation in nanostructured photovoltaic devices.

1. Introduction

Development of metal oxide semiconductor materials for various applications in modern technology cannot be overemphasized. Most transition metals such as Cu, Zn, Ti, Mn, Ni, Co, Fe and their oxides perform very suitably in production of some electronic devices for light harvesting and energy storage potentials, heterogeneous catalysis, electrochromism, magnetoresistive and spintronic information storage and so on [1]. While it has been well established that compounds of some metals like Cu, Zn, Ti, etc can enhance photogeneration and good performance in optoelectronic/photovoltaic devices, Co, Mn, Ni and others are beautifully used in production of many compounds including Dilute Magnetic Substances (DMS), gas sensing materials and so on [2–4]. Thus, fabrication of a simple structure that can combine some of these properties effectively and efficiently remains a challenge in the growing R & D. Although, several efforts have been made to produce a robust component from the addition of one or more metals to a compound but the materials behavior or characteristics were sometimes not well addressed. For instance, the addition of cobalt oxide had been reported to improve the specific capacitance of manganese oxide electrode but the corresponding variation in the electrochemical mechanism was not paid attention to [5]. Nam et al., 2011 [6] fabricated copper nanofibre networked cobalt oxide composite electrode to simply enhance the performance of Lithium ions battery. They obtained the sample by sputtering CoO_x thin film on electrospinned Cu nanofibre. Incorporation of conducting metallic nanowires into cobalt oxide materials in an attempt to improving its electrical conductivity has also been studied. Sutanto et al., 2017 [7] have recently reported the influence of cobalt doping on the optical and structural behavior as well as photocatalytic properties of ZnO thin film. Thus, this study focuses on the possibilities of producing a bilayer structure that can tailor the antireflective capability of an overlaying absorber (zinc oxide) to the morphology of a proximate nanostructured compound (cobalt oxide). The authors also considered separately interaction of CNT with nanocrystalline cobalt oxide with the aim of understanding ultrafast dispersion of the nanocrystals within an active site, in a way to appraise photoabsorption and charge separation potentials of the structure. To our knowledge, production of such bilayer structures has not been reported. The simple growth techniques and comprehensive surface studies of the structures are contents of this report.

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2. Experimental section

2.1. Materials synthesis and film deposition

All chemicals used for preparation of electrolytic solution were ACS reagent grade and they were purchased from Sigma-Aldrich. Si wafers (orientation (111), 1 side polished) and ITO coated glass slides (surface resistivity of 15 Ω/sq) were also purchased from Sigma-Aldrich. Platinum foil (99.95% pure) was purchased from Advent Research Materials. Prior to film deposition, electrodes were cleaned in ultrasonic bath for 10 min, rinsed with distilled water and dried with nitrogen flow. Two different growth techniques were employed; electrochemical deposition for oxide films and chemical vapour deposition (CVD) for CNT. From the growths, three types of samples were produced. These are Co_xO_y thin film, ZnO/Co_xO_y bilayer and CNT/Co_xO_y bilayer. Both Co_xO_y thin film and ZnO/Co_xO_y bilayer were electrodeposited on ITO substrate (20 mm × 15 mm × 0.7 mm). The depositions were performed using a home-made two-electrode cell; this cell has some advantages over the conventional three-electrode. These include low cost, low temperature growth, low volume of electrolyte, adjustment of the electrodes, avoidance of supporting electrolyte or catalyst and so on. The precursor for the growth of Co_xO_y film was prepared from the combination of an alkaline and $CoCl_2·5H_2O$ solution. For the first set of samples, 20 ml of 0.05 M of $CoCl_2·5H_2O$ solution was added to 10 ml of 0.02 M of NaOH in a standard flask to form an electrolyte. This electrolyte was fed into the cell and the electrodes (platinum sheet as counter electrode and ITO substrate as growth/working electrode) held firmly to the holders were connected to a power supply and a digital multimeter to attain stabilized power with sensitive current and voltage modes. A potential of −0.96 V was applied at the anode for 20 min to yield a uniformly distributed Co_xO_y thin layer on the ITO glass. This sample was tagged C11. In a similar way, 15 ml of 0.05 M of $CoCl_2·5H_2O$ solution was added to 5 ml of 0.01 M of KOH to form another electrolyte. This electrolyte was used to deposit the second Co_xO_y sample called D2 on ITO with a potential of −0.86 V in 20 min. For the second set of samples, the already deposited films (C11 and D2) were used as substrates onto which thin layer of ZnO was separately grown from 0.2 M of $Zn(NO_3)_2·6H_2O$ electrolyte. In this case, the growth voltage and time were (1.20 V) and 12 min each. With respect to these substrate-films, the ZnO grown on film C11 was called ZC11 bilayer and the one obtained on film D2 was named ZD2 bilayer. After each stage of deposition, the samples were rinsed with distilled water and dried briefly in an open furnace at 115 °C. Experimental conditions are stated in Table 1. The third set of the samples was obtained in two different ways: first, another Co_xO_y thin film was freshly deposited on Si (111) wafer (20 mm × 20 mm × 0.5 mm) following the same procedure that produced sample D2. After rinsing and drying, it was loaded into an ultra high vacuum (UHV) chamber and annealed briefly at 350 °C. It was then mounted as substrate onto which CNT were grown following a procedure already reported in another work [8]. Prior to deposition, the chamber was pumped to high vacuum (10^{-6} mbar) with substrate temperature at 680 °C. Hydrogen gas was briefly injected into the chamber until the pressure rose to 10^{-1} mbar. The presence of hydrogen gas led to reduction of any adsorbed oxygen molecule at the sample's surface. After this treatment, the chamber was pumped again to 10^{-6} mbar. Acetylene gas (C_2H_2) was then injected to the chamber at a pressure of 10 mbar for 5 min for the growth of CNT onto the substrate (Co_xO_y thin film). The resulting structure was tagged CNT/Co_xO_y bilayer.

Table 1
Growth parameters and thickness of the electrodeposited films.

s/n	Sample	Substrate	Electrolyte	V(V)	Time (mins)	Thickness (nm)
1.	C11 (Co_xO_y)	ITO	$CoCl_2·5H_2O$ + NaOH	− 0.96	20	251.85
2.	D2 (Co_xO_y)	ITO	$CoCl_2·5H_2O$ + KOH	− 0.86	20	218.11
3	ZC11 (ZnO/Co_xO_y)	C11/ITO	$Zn(NO_3)_2·6H_2O$	1.20	12	302.15
4.	ZD2 (ZnO/Co_xO_y)	D2/ITO	$Zn(NO_3)_2·6H_2O$	1.20	12	264.13

2.2. Post deposition annealing and characterization

After the growths, all the samples except the nanotubes were annealed in air at 350 °C for 1 h. The annealing was expected to enhance the film's crystallinity, relative interfacial roughness, layers inter-diffusion and conformity. It could also convert freshly prepared β–Co$(OH)_2$ to pure Co_3O_4 [2]. Thereafter, quality of deposited layers (samples C11, D2 and ZD2) and chemical states of the elemental composition (Co, Zn and O) were studied by X-ray Photoemission Spectroscopy (XPS). XPS spectra were acquired at Micro & Nano-carbon laboratory of Elettra-Sincrotrone Trieste S.C.p.A, using a VG Scientific ESCALAB MK II spectrometer, operating in fixed analyzer energy mode, with pass energy of 20 eV. Non-monochromatized AlKα exciting radiation (1486.6 eV) was used (15 mA emission current and 15 kV anode potential). Binding energy correction due to possible sample charging was applied by assuming the *C 1s* core level line at 284.6 eV. During the experiments, further annealing treatments were carried out under integrated UHV condition. After each spectra count, surfaces of the samples were routinely checked by Low Energy Electron Diffraction (LEED) to ensure any irradiation damage with respect to duration of exposure. Elemental concentration and layer thickness were studied by Rutherford Backscattering Spectroscopy (RBS). Surface microstructure of the samples were investigated by scanning electron microscope (Zeiss supra 40 Gemini column, electron beam energy 5 kV) at CNR-IOM National Laboratory Trieste, crystal structure and particle orientation were studied by X-ray diffraction technique (PANalytical X′pert Pro diffractometer) with CoKα radiation (λ = 1.789 Å). Optical properties were obtained by a dual beam Parkin-Elmer UV/Vis spectrophotometer

3. Result and discussion

3.1. X-ray photoemission spectroscopy (XPS)

Kinetic energy distribution of photoelectrons emitted from specimen materials due to incident monochromatic light can be measured by XPS. Bound electron states in nanocrystalline layers and corresponding buried interfaces are effectively investigated [2,9]. Thus, the chemical states of composition of Co_xO_y nanocrystals and the ZnO overlayer obtained from core-level photoemission studies are presented. The survey spectra of the samples (Fig. 1a) revealed all elemental composition as well as substrate materials. Each XPS peak positioning was estimated at uncertainty of about ± 0.1 eV. According to the survey spectra, no major elemental impurity or contamination due to growth process was found within machine detection limit. *C 1s* line (inset of Fig. 1a) noticeable in all the spectra was derived from adventitious carbon due to exposure to atmosphere. Zn peaks (2p, 3 s, 3p and 3d) are noticed in survey spectra of samples ZC11 and ZD2. Survey spectra of samples C11 and D2 show Co 2p peaks. The Indium (In 3p) signal came from ITO substrate. Examining the Zn 2p region of sample ZD2 in details, the energy difference indicated by spin-orbit splitting of 23.1 eV between Zn $2p_{1/2}$ (1045.2 eV) and $2p_{3/2}$ peaks (1022.1 eV) (see inset of Fig. 1b) allows to identify the deposited layer as ZnO according to literatures [4]. From Co $2p_{1/2}$ (790.5 eV) and Co $2p_{3/2}$ (780.1 eV) of C11 and D2 spectra (Fig. 1b), the spin-orbit splitting of 15.4 eV is in agreement with standard values of CoO in literatures and it is consistent with the presence of mixed Co (II) and Co (III) states [2,4,6,10,11]. The