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Magnetic, structural and optical behavior of cupric oxide layers for solar cells

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ABSTRACT

Room temperature ferromagnetic hysteresis is observed in CuO nano films synthesized through chemical strategy. The room temperature ferromagnetic behavior in CuO is quite a new observation without any doping, annealing or any other post preparation treatments. The observed magnetization value is 0.24 T which is obviously depicted that the nano-scale magnetic properties dependent on the shape and size of nano films. The morphological observations is depicted that the uneven ellipsoidal grains transformed to nano-sheet shaped grains. Atomic force microscopy (AFM) images are also strengthening the observation of shape variations due to bath temperature variation. The surface profile and grain contour images are verified the size and shape variations. Structural variations are precisely predicted by X-ray diffraction patterns and crystallinity of the films is discussed. The growth mechanism of nano sheet formation and physical phenomena are discussed. The luminescence properties variations are observed by photoluminescence (PL) spectroscopy and it has exposed that the bath temperature effects on the CuO films. X-ray photoelectron spectroscopy (XPS) spectra is depicted that Cu $2p_{3/2}$, Cu $2p_{1/2}$ and O_{1s} related peaks at 929.50, 952.80 and 529.38 eV binding energy, respectively. In addition, the optical dielectric dispersion parameters such as effective mass (m_e), optical susceptibility (χ_e), carrier concentration (N), plasma frequency (ω_p), relaxation time (τ) and frequency (f) are also evaluated. Raman scattering spectra revealed the A_g and B_g modes shift at 296 and 628 cm^{-1}.

1. Introduction

The discovery of new fascinating physical phenomena in the modern study of oxide materials is a vital research conception. The high-temperature superconductivity, colossal magnetoresistance, dilute magnetic doping, or multiferroicity were discovered and investigated in transition-metal oxides, demonstrating a prototype class of strappingly correlated electronic systems. This advance was accompanied by massive progress regarding thin film fabrication. The conventional semiconductor technology is approaching fundamental physical limits due to account of decreasing device dimensions. Making use of the spin of the electron as a degree of freedom additional to its charge opened the field of magneto- or spin electronics which is considered a replacement technology [1]. Starting from metal-based devices in the late 1980s, the field of spintronics soon expanded to transition metal oxide [2] and recently even to organic materials [3]. The high quality oxide based thin films and heterostructures are published in the past two decades and it has showed important advances concerning sample eminence. II–VI semiconductor based magnetic semiconductors have been studied for over two decades [2,4,5]. II–VI semiconductor based magnetic semiconductors have been studied for over two decades [6]. Among those systems that exhibit a peculiar magnetic behavior when they are reduced to the nanoscale, nano films of metals occupy an outstanding position. The statement of ferromagnetic-like performance in the surface modified Au, Ag and Cu NPs have attracted much attention, because of their potential in nanotechnology applications in addition to the fundamental physics concepts. It should be stated that the mentioned of ferromagnetism in Cu counterparts an important new proposal to this nanoscale system.

The magnetism and magnetic materials are intimately given the

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prominent role in our daily life. The physicochemical conditions of the deposition conditions determine the dimension of the materials. Cupric oxide (CuO) is an imperative material because of optical band gap energy (1.1–1.5 eV), which is suitable for various devices like lenses and chemical and oil bases [7–10]. CuO is a promising material for the large-scale solar cell application with the theoretical maximum conversion efficiency of ~20%, because of its suitable bandgap (ideal for sunlight absorption), high optical absorption, abundance, and non-toxicity [11–14]. The various techniques are available for the deposition of metal oxide such as successive ionic layer adsorption and reaction (SILAR) [7], sputtering [15], thermal oxidation [16], evaporation [17], molecular beam epitaxy [18], and electrodeposition [19,20], etc. Among them SILAR technique is a promising technique because of its low cost and simple coating process. This low cost and innovative route was first reported by Ristov [21] and our group were previously reported on morphological properties and microstructural studies of cupric oxide thin films [22,23]. In recent times, Punnoose et al. [24] have prepared monoclinic CuO nanocrystals by the sol-gel method. Qin et al. have observed weak ferromagnetism (FM) up to 330 K for small nanograins which is lower than (D <) 10 nm, whereas the magnetic ordering for the CuO grains with D > 10 nm was essentially similar to the antiferromagnetic ordering of bulk CuO [25]. The room-temperature FM in CuO powders and thin films was observed by Qin et al. and they have predicted that the detected FM to be related to oxygen vacancies. Zhang et al. [26] and Wang et al. [27] have reported based on both the experimental and theoretical works that the surface oxygen vacancies of nanostructures play an important role in inducing room-temperature FM. Therefore, we have point out that the surface morphology of a material given the major role to be able to modulate room-temperature FM as a result of different surface areas. The relationship between surface morphology and FM is appreciated to explore in the range nanograins. However, the FM has been still a matter for strong debate, even though various ferromagnetic oxide semiconductors are reported so far. In order to examine the ferromagnetism carefully, several considerations on the evaluation from the experimental side are given. In the present study, we have reported that the FM inclusion in cupric oxide thin films due to the size decrement in grains and elaborate studies on optical properties variations.

1.1. Film growth and characterizations

Thin films of cupric oxide were grown by double dip SILAR technique using precursor solution bath encompassing 0.03 M copper sulphate and 0.06 M sodium hydroxide (Sigma Aldrich – 99% pure). The precursor bath temperature was varied from 75 °C to 95 °C and effects of bath temperatures were elaborately discussed for CuO thin films. The chemically etched glass substrates were cleaned using alcohol and acetone before using the deposition process. The pre-cleaned glass substrates were immersed in the precursor chemical bath for a known standardized time followed by immersion in hot solution maintained at 75–95 °C for the same time for hydrogenation. The phase one process of solution dip followed by phase two hot solution dipping is repeated for known number of times. The immersion time and number of immersion also varied to elucidate the properties variation of CuO films. Part of the CuO so formed was deposited onto the substrate as a strongly adherent film and the remainder formed as a precipitate. The schematic diagram of SILAR prepared CuO is given in Fig. 1. An X-ray diffractometer system [X'PERT PRO PANalytical, Netherlands] with Cuk$_\alpha$ radiation (λ = 0.1540) nm was used to identify the crystal structure of the films. Surface morphological study was carried out using a scanning electron microscopy (Philips Model XL 30, USA). The surface topology of the films was investigated by atomic force microscopy (Nanoscope E – 3138 J). Optical properties of the samples were analyzed using a UV–Vis–NIR double beam spectrophotometer (HR - 2000, M/S ocean optics, USA). Raman analyses were performed using Princeton Acton SP 2500 instrument through 0.5 focal length grating monochromator with 514.5 nm excitation line from Ar$^+$ laser. X-ray photoelectron spectroscopy (XPS) studies were made by PHI 5000 Versa Probe. The Lakeshore, VSM 7410, vibrating sample magnetometer was used to analyze magnetic properties of nano films.

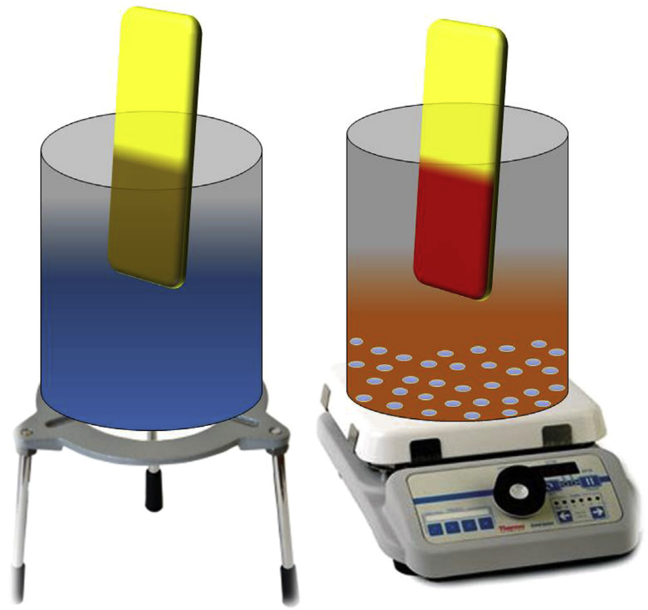

Fig. 1. Schematic representation of CuO formation by dipping method.

2. Results and discussion

2.1. Thickness studies

Fig. 2(a) defines rate of film thickness for SILAR grown CuO film as a function of immersion cycles such as 25, 50, 75 and 100, respectively. Film thickness is assessed against number of immersion cycles at bath temperatures ranging from 75 to 95 °C. The thickness rate linearly increases with increase of immersion cycle and get slowed down after 75 immersions. The rapid growth rate is observed up to 25 immersion cycles and it is exhibited at ~310 nm. The rich and translucent in the beginning of the deposition precursors is noted and it has crooked reddish-brown as escalation of immersion cycle. This is due to the formation of deferred oxides of Cu in the solution to form brown-black CuO. The solutions are substituted with fresh ones in the every 25 immersion cycle. The film growth rate is linearly increased from 25 to 75 immersion cycles and then slowly increased. The maximum value of film thickness is obtained at 540 nm for CuO nano films prepared at bath temperature 95 °C with 100 immersion cycles. Furthermore, variation of film thickness against number of immersion cycles for different deposition time ranging from 5 to 25 s of CuO thin films at bath temperature 95 °C in the supporting information Fig. S1. Progressively the film turns orange, red, brown, etc., due to optical interference under daylight. It is observed from the Fig. S1, film growth rate linearly increases with increase of immersion cycle and