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Doping Induced Modifications In Physico-Chemical Properties Of Zno Thin Films

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Abstract
This paper describes the effect of doping on the physicochemical properties of ZnO thin films synthesized by using successive ionic layer absorption and reaction (SILAR) method at room temperature over glass substrate. Proportional doping of Al, Cu, and Ag carried by in situ deposition method over ZnO materials. These as deposited and doped thin films are characterized for X-ray diffraction (XRD) which infers about ZnO being wurtzite in nature while doping shows decrement in crystallite size with suppression of peaks corresponding to ZnO and formation of composite thin films. Observation of peas at 1373cm-1 in Raman spectra confirms the ZnO material while on doping rising of peaks at 1288, 1362 and 1841cm-1 with increase in intensity shows formation of different compositions. The energy dispersive X-ray analysis (EDAX) shows elemental composition variation upon doping in ZnO thin films. Surface morphology when observed using atomic force microscopy (AFM) reveals the surface topography modifications with observation of conversion of granular structure of ZnO into leaf like shape with doping of Al, Ag and Cu as observed form scanning electron microscopy (SEM). From the observed result it can be inferred that the doping may create significant variations into the physicochemical properties of ZnO thin films.
Keywords: *ZnO films, Nanoparticles, Doping, Leaf structure, potential properties*

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I. Introduction

Zinc oxide being II-VI group compound possessing potential properties which make it suitable for applications into different electronic gadgets. ZnO is used as an additive in numerous materials and products including cosmetics, food supplements, rubbers, plastics, ceramics, glass, cement, lubricants, paints, sunscreens, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants and semiconductors, although it occurs naturally as the mineral Zincite, but in most cases Zinc Oxide is produced synthetically in laboratories [1, 2]. The piezoelectric and pyroelectric properties of ZnO mean that it can be used as a sensor, converter, energy generator and photo catalyst in hydrogen production [3-5]. It has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spintronic [5-7].

Zinc oxide is used in semiconductor gas sensors for detecting airborne compounds such as hydrogen sulphide, nitrogen dioxide, and volatile organic compounds. ZnO is a semiconductor that becomes n-doped by adsorption of reducing compounds, which reduces the detected electrical resistance through the device, in a manner similar to the widely used tin oxide semiconductor gas sensors [6-8]. It is formed into nanostructures such as thin films, nanoparticles, Nano pillars or nanowires in order to provide large surface area for interaction with gasses. The sensors are made selective for specific gasses by doping or surface-attaching materials such as catalytic noble metals [9-12]. These ZnO thin films when used for sensing the gases the phenomenon considered in most the experiments are conductivity based hence in tailoring the conductivity it is necessary to dope these materials with suitable elements, hence considering this as the prime objective we have tried to study the effect of doping on physicochemical properties of ZnO thin films [13-15]. The native doping of the semiconductor due to oxygen vacancies or zinc interstitials is n-type. ZnO is a relatively soft material with approximate hardness of 4.5 on the Mohs scale [16-18].

From the literature it is observed that the ZnO thin films can be deposited using different techniques like magnetron sputtering [19], chemical vapour deposition [20], pulsed-laser deposition [21], sol–gel process, etc. [22-24] etc. while the large area homogenous thin films can be when deposited using chemical route like SILAR it may results in formation of perfect elemental composition as expected [25-27].

Hence considering the synthesis and application point of view, we have deposited the ZnO thin films using ssuccessive ionic layer absorption and reaction (SILAR) method at room temperature over glass substrate and tried to study the effect of doping over the physicochemical properties by doping transition metals Aluminium (Al), Copper (Cu) and Silver (Ag) [28-30].

II. Experimental

In the present work ZnO doped with Copper (Cu) silver (Ag) and aluminium (Al) are synthesis by Advanced Successive ionic layer absorption and reaction (SILAR) Deposition Method which has several advantages over other methods like chemical bath deposition (CBD), Electrochemical and Sol-Gel Method [1-5]. The variety of methods for ZnO production, such as vapour deposition, precipitation in water solution, hydrothermal synthesis, the sol-gel process, precipitation from microemulsions and mechanochemical processes, makes it possible to obtain products with particles differing in shape, size and spatial structure [30-32]. The basic reactants used for ZnO are Zinc Nitrate (Zn(NO3)2) and ammonium persulphate (APS) as source of Zinc while distilled water used as source of Oxygen. Zinc Nitrate Solution (Zn(NO3)2) were purchased from Sigma-Aldrich (C4H5N, M.W. 67.09) reagent grade was distilled prior to use. Analytical grade ammonium per-sulphate (APS) was used as oxidizing agent. Deposition carried over the ultrasonically cleaned glass substrate. Doping performed using Copper (Cu) silver (Ag) and aluminium (Al) solution for 0.1 M. For that we take 5 ml of Cu, Al or Ag solution and 95 ml ZnO Solution mix it and star it for 20 min [33-35]. The sequential merging of substrate into different beakers of reactants leads in formation of ZnO and doped thin films over the substrate surface.

III. Result And Discussion

X-ray diffraction study (XRD)

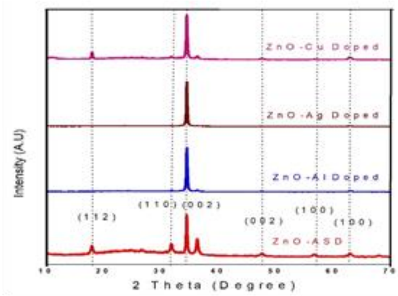

Fig. 1: XRD pattern of as deposited and Al, Ag and Cu doped ZnO thin films

From figure 1, the X-ray diffraction study confirms that, as deposited ZnO peak positions indicate the formation of hexagonal wurtzite crystal structure with most preferred orientations (112), (110), (002), (002) and (100), which are in very good agreement with the standard JCPDS (N0-36-1451) [36-38]. While upon doping it is observed that, the ZnO peaks expect (002) are suppressed, this may be attributed to the fact that the interstretial oxygen vacancy may have been fulfilled with the dopent element, with no successive evidence of rising any significant peaks for it. From the figure it is clearly seen that no secondary phase are observed, hence it is evident that no characteristic peaks of impurities are obtained [39, 40].

Raman Spectroscopy Analysis

Raman Spectroscopy is a non-destructive chemical analysis technique which provides detailed information about chemical structure, phase and molecular interactions, Raman spectrum being based upon interaction of light with the chemical bonds within a material, the characteristic bond stretching of the materials with different wavelength can be understood. From fig. 2.

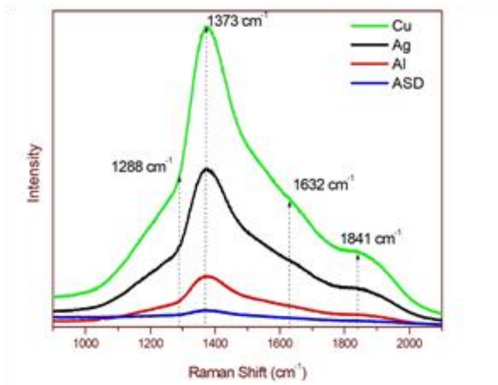

Fig. 2: Raman spectra of as deposited and Al, Ag and Cu doped ZnO thin films.

From fig. peak observed at 1373cm-1 corresponds for 1LO transitions in ZnO materials, while rising of new shoulder peaks and kinks at 1288 cm-1, 1632 cm-1 and 1841 cm-1 reveals modification after doping with Al, Ag and Cu in ZnO materials corresponding to 1TO and 2LO vibrations. The observation of increment in peak intensity and rising of kink and shoulders can be clearly at large proportion into Cu thin films [41, 42].

Energy-dispersive X-ray spectroscopy (EDAX)

Energy dispersive X-ray spectroscopy analysis (EDAX) used for elemental analysis or chemical characterization of the as deposited and doped ZnO thin films. The elemental composition as observed from the EDAX is observed to be similar as has been used for the synthesis methods [43, 44]. The equal proportion of elemental contribution of Zn, O and doped elements Al, Ag and Cu are observed as represented into Fig 3 (a), (b), (c) and (d) respectively.

Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) image of As-deposited films with a surface roughness of 3.90 nm, while variation into the grain size and surface roughness is observed upon doping.

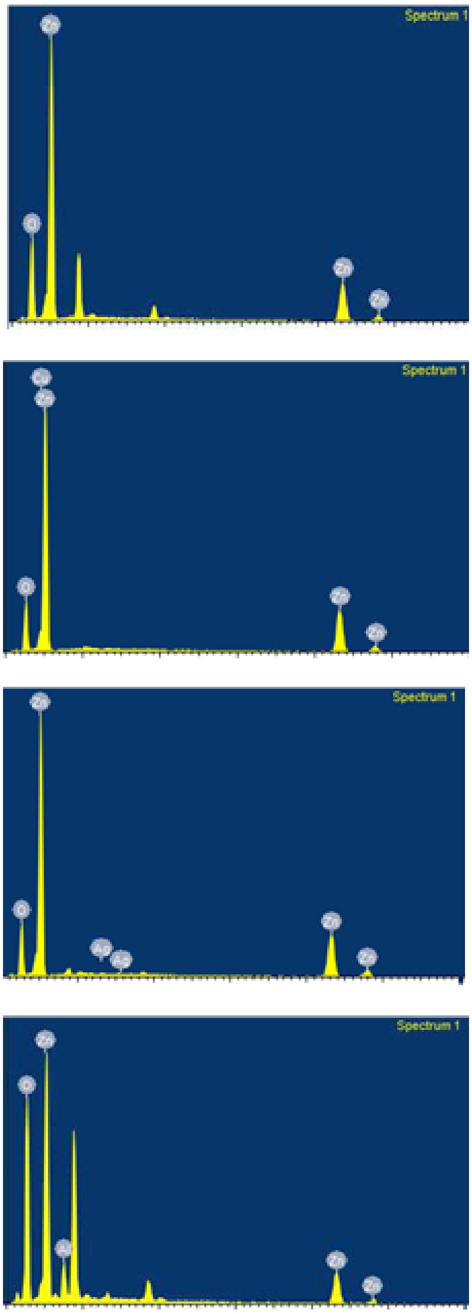

Fig. 3 EDAX spectra of as deposited and Al, Ag and Cu doped ZnO thin films.

The as deposited thin films of ZnO revealed rough surface with multiple ridges while on doping the surface is observed to level with aspect ratio variations from 68, 146, 153 and 133 in as deposited, Al, Ag and Cu respectively as observed from Fig 4 (a), (b), (c) and (d) respectively.

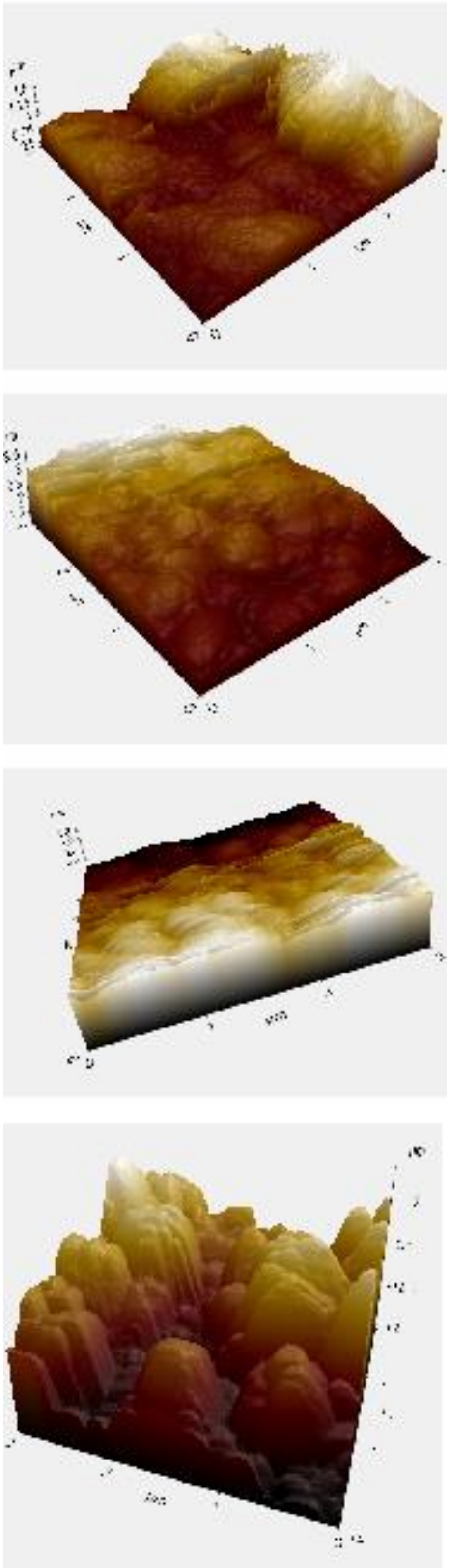

Figure 4. Atomic Force Microscopy (AFM) images as deposited and Al, Ag and Cu doped ZnO thin films.

The suppression of grains can be related to structural updating upon doping with proportionate dopants [45, 46].

Scanning Electron Microscopy (SEM)

Fig. 5 (a), (b), (c) and (d) shows the SEM images of ZnO ASD and Al, Ag and Cu doped thin film at different magnifications.

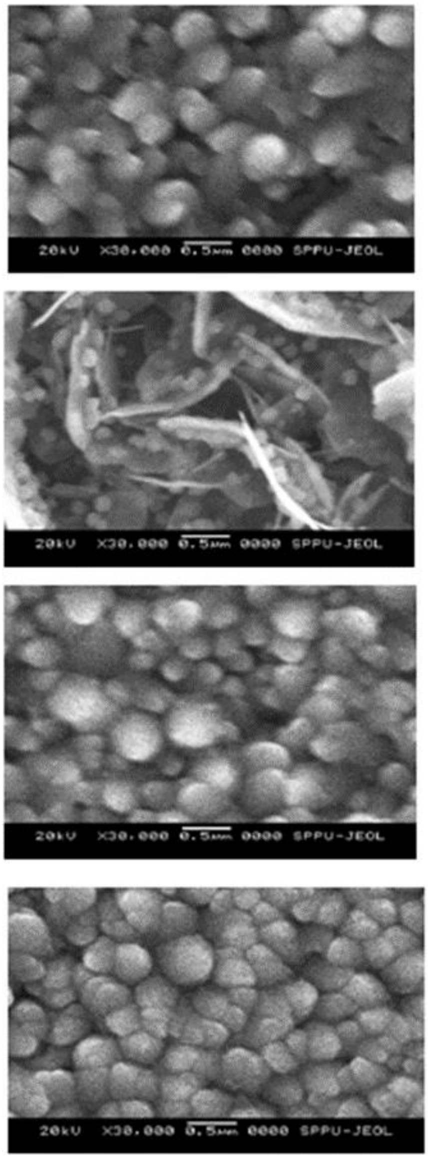

Figure 5. SEM images as deposited and Al, Ag and Cu doped ZnO thin films.

Formation of 3D architecture in Al doped thin films with coalesced nano plates can be clearly seen. The low magnification (Fig. 5 (c)) image confirms the formation of spherical bunches of interconnected ZnO grains. The lower magnified image reveals compact, crack free, smooth, randomly distributed and uniform morphological coverage of ZnO on substrate surface [46]. However, the high magnified image demonstrates the compact packing of grains. It is reported that morphology of doped thin films strongly depends upon nature of anionic oxidizing agents and preparation methods. Image gives a description that these grains are with approximately average size in the range 20–50 nm. The micrograph shows the agglomeration of interconnected grains, the contrast in the SEM image shows that the film has hollow cavities which are highly porous. The porous nature of the ZnO makes it a potential candidate for various surface related applications.

IV. Conclusion

From the above observed results, it can be concluded that the as deposited and Al, Ag and Cu doped ZnO thin films can be successfully grown using the advanced successive ionic layer absorption and reaction (SILAR) at room temperature over glass substrate. The XRD pattern reveals formation of ZnO materials with suppression and modifications in structure upon doping, even the Raman spectra also support the observations made using the XRD analysis. EDAX confirms elemental composition as expected and used for synthesis of the as deposited and doped thin films. The surface morphology studied from the AFM and SEM shows surface modification upon doping, the result related to Al doping as observed from SEM shows growth of nano particles over the plate like structure, which may be very useful while considering the applications in surface based sensors.

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