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Pure and Noble Metals Doped Nanostructure Tungsten Trioxide Films

G. Adilakshmi[1], A. Sivasankar Reddy[1*], R. Subba Reddy[1], P. Sreedhara Reddy[2], Ch. Seshendra Reddy[3]

[1]*Department of Physics, Vikrama Simhapuri University P.G. Centre, Kavali -524201, A.P., India*
[2]*Department of Physics, Sri Venkateswara University, Tirupati- 517502, A.P., India*
[3]*Department of Polymer science and engineering, Korea National University of Transportation, Chungju, Republic of Korea*
**Corresponding Author: A. Sivasankar Reddy*

ABSTRACT: Pure, silver (Ag) and gold (Au) doped tungsten trioxide (WO_3) nanostructure films were prepared by electron beam evaporation technique on glass substrates. The structural, compositional, surface and optical properties were investigated using XRD, EDS, SEM and UV-Vis-NIR spectrometer. From XRD results, the crystallinity of the films decreased after adding the dopants to WO_3. The surface morphologies were strongly influenced by the dopants. The doped films have rough surface than pure WO_3 films. The optical studies showed that the transmittance and band gap was decreased with dopants. The obtained band gap values for pure,Ag and Au are 3.4, 3.24 and 3.04eV, respectively.

Key words:Electron beam evaporation, Nanostructure, tungsten trioxide, Thin films, Metal doped

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I. INTRODUCTION

Currently nanostructure Tungsten trioxide (WO_3) thin film has been received a growing interest because of their size, different morphologies used in variety applications such as light emitting diodes, smart windows, gas sensors, and photocatalyst [1-3].Introducing of thedopantslike, Ni, Au, Ag, etc., change the structural, electrical, optical and gas sensing properties of WO_3. Tungsten trioxide thin films have been deposited by various physical and chemical deposition methods such as electron beam evaporation, chemical vapor deposition, laser deposition and sputtering[4-7]. Among these, electron beam evaporation techniquesatisfies certain propertiessuch as adherence, stoichiometric, pin hole free, films with good crystallinity at lower substrate temperatures. In this workpure,5% Ag and 5%Au doped WO_3 filmswere prepared by electron beam evaporation technique and studied the physical and chemical properties.

II. EXPERIMENTAL

Pure, 5%Ag and 5%Au doped tungsten oxide thin films were deposited on glass substrates using electron beam evaporation technique. The substrate was well cleaned before introducing into the deposition chamber. A 10mm diameter pure, Ag and Au doped WO_3 pellet (99.9% purity) were used as source targets for evaporation. The WO_3 was first baked in an oven at 473K for 2hours in vacuum before used for evaporation to remove any moisture in the material. The pellets were placed in copper crucibles that was kept in water-cooled copper hearth of the two electron guns for evaporation. A power supplies were employed to heat the tungsten filaments. The substrates were placed normal to the evaporation sources at about 7.5cm distance from the target source. The chamber was evacuated to a base pressure of about $9.6x10^{-4}$Pa and an accelerating voltage of about 45kV was used during evaporation at room temperature.

The crystallographic structure of the films was analysed by XRD (Seifert 3003TT X-ray diffractometer), using Cu Kα radiation (k = 0.1546nm).The microstructure and surface morphology of the films were studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. The chemical composition of the films was analysed by Energy Dispersive Spectroscopy (EDS) attached with SEM. The optical transmittance spectrum in wavelength of recorded 300-900nm was recorded using double beam spectrophotometry.

III. RESULT AND DISCUSSIONS

The XRD patterns of the pure and doped WO_3 nanostructures are shown in Fig.1. The pure films exhibited two prominent peaks corresponding to (120) and (112) reflection planes of WO_3. The observed diffraction peaks can be well indexed to

monoclinic crystal structure of WO_3 (JCPDS card No.043-1035). By adding the dopants to the WO_3, the crystallinity of the films decreased and no Ag and Au phases or/and their oxide phases were observed. It indicates that the metal particles(Ag, Au) incorporated into WO_3 lattice or Ag, Au atoms segregates in nanocrystalline grain boundaries. The diffraction peaks intensity decreases by adding the dopants is may be due to the lattice distortion induced by doped ion into WO_3 crystal [8].The greater radius of dopant atoms cannot replace the W to become a co-dissolved structure but an embedded structure in which exists on the surfaces in the form of atom clusters or nanoparticles [9, 10].

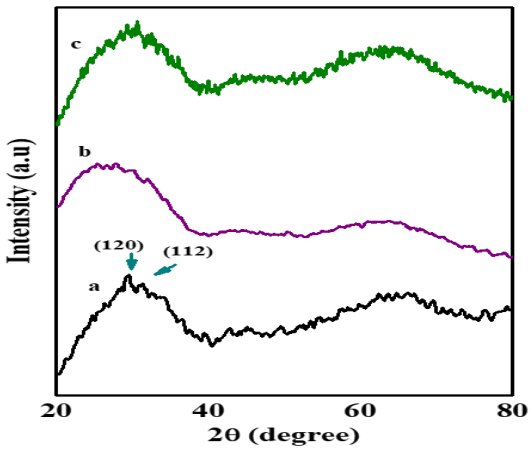

Fig.1. XRD patterns of WO_3 nanostructures (a) pure (b) 5%Ag doped (c)5% Au doped

The EDS results revealed that the films contain W, O, Ag and Au elements only. Fig.2. shows EDS spectra of pure, 5%Ag and 5%Au doped WO_3films.

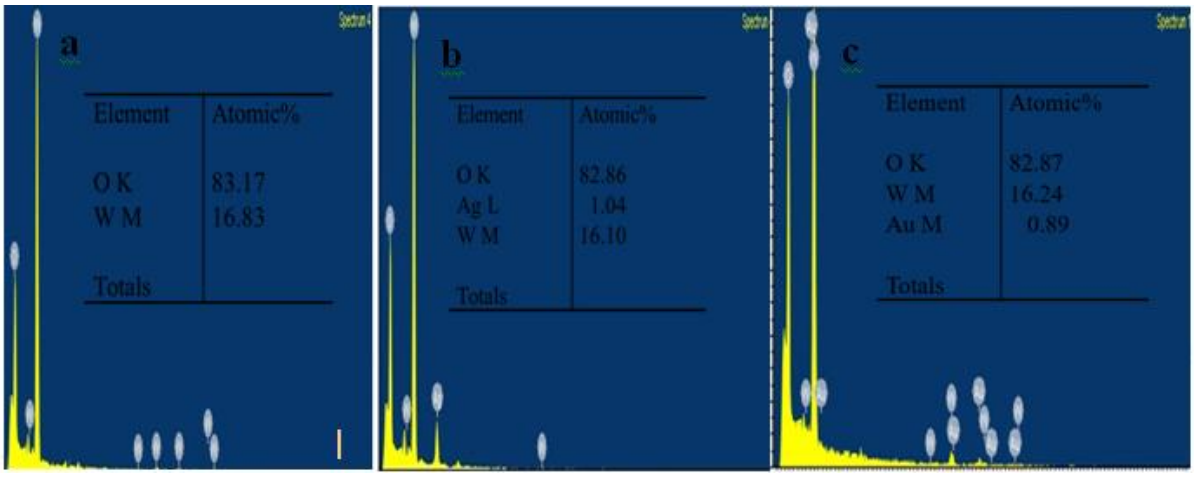

Fig.2. EDS spectra of WO_3 nanostructures: (a) pure, (b) 5%Ag doped and (c)5% Au doped

The microstructure of pure and doped nanostructure WO_3 films are shown in Fig.3. Fig3 (a) shows SEM image of pure WO_3 film deposited on the glass substrate. It clearly shows that nanoflakes are distributed uniformly on the substrate. The size of nanoflakes are decreased and porous structure appeared after doping the 5%Ag to WO_3 (Fig 3(b)). The nanoflakes are agglomeratedand cotton type nanostructure are appeared after doping 5%Au to WO_3 (Fig 3(c)).The formation of agglomerated nanoflakes was explained by nucleation- agglomeration, growth mechanism by Nguyen et al.[11]. The nanoflakes are agglomerated may be due to the physical attraction of nanoflakes, nucleation of growth process and early saturation.

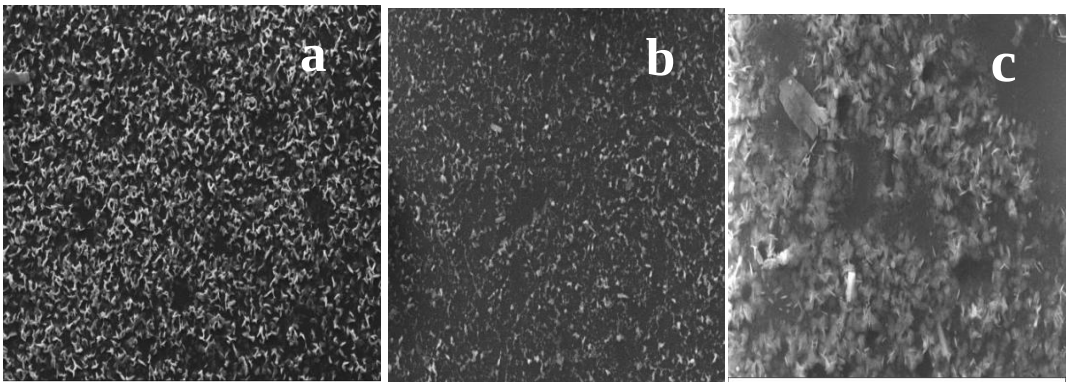

Fig.3. SEM images of WO_3 nanostructures: (a) pure, (b) 5%Ag doped and (c)5% Au doped

AFM is used to study changes in the surface morphology of the films. 2D images of pure, Ag and Au doped WO_3 films is shown inFig.4. TheWO_3films shows smooth surface compare to Ag and Au doped films and the RMS surface roughness was 26.3nm. When the 5%Ag added to WO_3, nano-icelands formed (Fig.4(b)) and the surface roughness increased from 26.33 to 28nm. The 5%Au doped WO_3films exhibited agglomerated spherical particle and the RMS surface roughness increases from 26.3to 30.5nm. From the AFM results, pure and doped films exhibited high surface roughness due to formation of nanostructure. However, Au doped WO_3 films exhibited slightly higher surface roughness than pure and Ag doped WO_3 films and these type of films are most suitable for gas sensor applications.

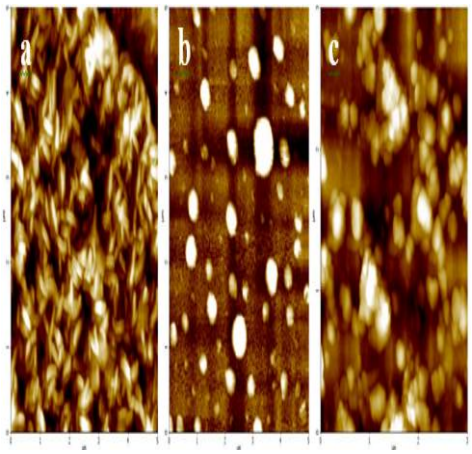

Fig.4. Two dimensional AFM images of WO_3 nanostructures: (a) pure, (b) 5%Ag doped and (c)5% Au doped

Optical transmittance spectra of pure,5%Ag and5%AudopedWO$_3$ films is shown in Fig.5. It is apparent from the transmittance spectra thepure films exhibited maximum transmittance than the Ag and Au doped WO_3 films in the visible region. Transmittance of pure WO_3 is maximum due to crystallinity and smooth surfaces. In the case of Ag, Au doped films the optical transmittance decreased may be due to the Ag, Au clusters reflecting the incident light or light scattered by near the grain boundaries. The transmittance of pure, 5%Ag doped and 5%Au doped WO_3 were 90%, 78% and 76% respectively. The change in transmittance spectra may be due to change of films surface morphology, carrier absorption with doping of metal particles [12].

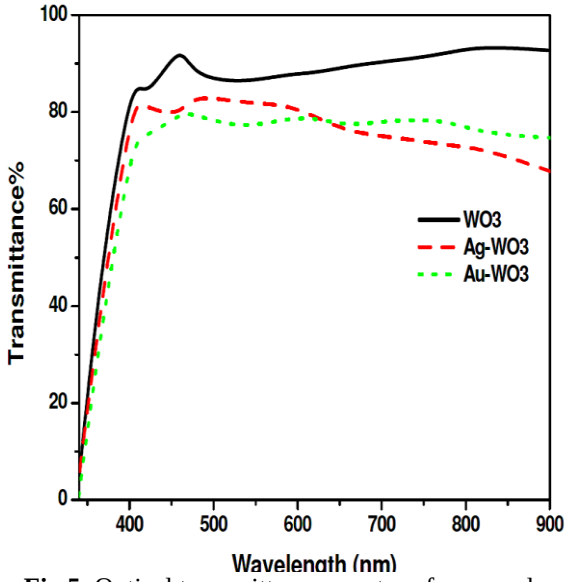

Fig.5. Optical transmittance spectra of pure and doped WO_3films

The intercept of the plot between $(\alpha h\nu)^2$versus hν gives the optical band gap (Fig.6). By extrapolating the linear portions of these plots to the photon energy axis, values of the optical band gap for pure, Ag and Au doped WO_3films are obtained. The obtained band gap values are 3.4, 3.24 and 3.09eV for pure, Ag and Au doped WO_3,respectively. It is clearlyappearedthat Ag, Au doped films have lower band gap than pure WO_3 films. This decreasing may be ascribed to the accumulation of donor energy levels of transition

Ag,Au ions in the actual band gap of WO_3[13]. The similar tendency was observed previously in Ni and Fe doped SnO_2 thin films [13,14]. The change in the crystallite size leads to change in optical properties of the metal oxide nanostructures [15].

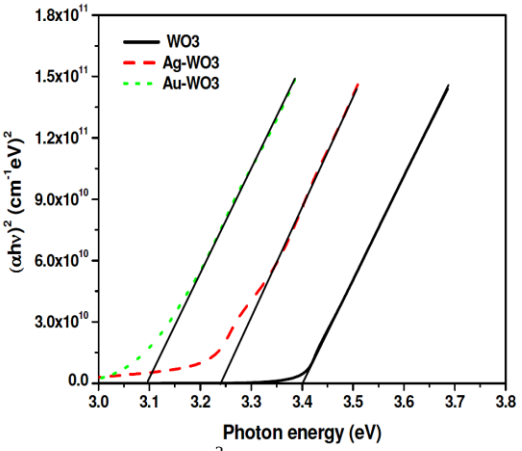

Fig.6. Plot of $(\alpha h\nu)^2$ vs $(h\nu)$ of pure and doped WO_3films

IV. CONCLUSIONS:

Pure, Ag and Au doped WO_3 nanostructure films were prepared by electron beam evaporation. The pure WO_3 films exhibited monoclinic phase. The Ag and Au doping changed the microstructure and surface morphologies of WO_3 and have rough surfaces compare to pure WO_3. The optical transmittance decreased from 90% to 76% after doping to WO_3. The Ag and Au doped WO_3 films having lower band gap than the pure films.

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