

THE WO₃ NANOSTRUCTURE FOR FUNCTIONAL APPLICATIONS

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Abstract: Tungsten trioxide nanostructure (WO₃) were prepared on glass substrate by electron beam evaporation. The structural, composition, surface and optical properties were studied by X-ray diffraction (XRD), Raman spectroscopy, energy dispersive Spectroscopy (EDS), scanning electron microscopy (SEM), atomic microscopy (AFM) and photo luminescence (PL) respectively. From the results revealed that the WO₃ films have hexagonal nano structure with plate like morphology. The WO₃ nanostructures have high rough surface area and oxygen deficiency. These WO₃ nanostructure are more useful for different application.

Key words Tungsten trioxide, nanostructures, hexagonal shape, surface roughness

1. Introduction

Now a day's nanotechnology is exciting and rapid expanding growth in research area that crosses the borders of physical life and engineering sciences. Many functional nanoscale materials were prepared by two ways. One is top to bottom approach another one is bottom to top approach. In new development continue to push the resolution limits of the top - down approach, these increases in cost associated with each new level of manufacturing facility. This economic scenario and other scientific challenges with the top - down approach, researchers were entering to nanoscale structure material. That they were moved to the bottom - up approach material preparations, in which functional structures are assembled with well - defined chemically and physically fabricated nanoscale structures. There are several functional semiconductor nanostructures available such as light emitting diodes (LED), smart windows, gas sensors, nanogenerators, nanoplates, nano bows etc. [1-6].

Tungsten trioxide (WO₃) is one of the best materials for many functional applications. It exhibits a wide variety of novel properties like structural transformation, sub stoichiometric and tuneable band gap. These properties are useful for many applications such as electrochromic, optoelectronic devices, solar energy storages, LEDs and gas sensors. WO₃ thin films are deposited various physical and chemical methods like sputtering (RF and DC), thermal evaporation, electron beam evaporation, electrospinning, hydrothermal method etc. Among these methods electron beam evaporation is one of the best suitable method due to adherent, uniform and less impurity during thin film deposition [7-10].

In present work WO_3 nanostructures were prepared on glass substrate using electron beam evaporation at room temperature. The film structural, compositional, surface morphology and optical properties were investigated.

2. Experimental details

Pure tungsten oxide thin film was deposited using electron beam evaporation technique. The film has been deposited on a 12 mm x 12 mm glass substrate. The substrate was well cleaned with acetone before deposition. A 10 mm diameter WO₃ pellet (99.9% purity) was used as source targets for evaporation. The WO₃ was first baked in an oven at 373 K for 3 hours in vacuum before used for evaporation to remove any moisture in the material. The WO₃ was 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 8 cm from the source targets. The chamber was evacuated to a base pressure of



about 9.6 x 10^{-4} Pa and an accelerating voltage of about 45 kV was used during evaporation at room temperature. The deposition time was 8 minutes.

The crystallographic structure of the films was analysed by XRD (Seifert 3003TT X- ray diffractometer), using Cu K α radiation (k = 0.1546 nm) and Raman microscope system (JobinYvon T64000). The chemical composition of the films was analysed by Energy Dispersive Spectroscopy (EDS) attached with SEM (Oxford instruments Inca Penta FET X3). The microstructure and surface morphology of the films were studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. PL spectra were acquired by using an excitation source at 293nm (He-Cd laser) and a CCD camera (Acton, Winspec).

3. Result and discussions

The XRD pattern on WO₃ nanostructure were deposited on glass substrate was shown in Fig 1. The films showed amorphous nature. The broadness of peaks was indicated nanocrystalline were exist in the film. The broad peak exists around at 24° indicates hexagonal WO₃ structure, presence of very small nanoparticles [11]. The absence of fine diffraction peaks represents the grains are small. The two broad diffractions peaks were referred amorphous and nanocrystalline phase exist in the film. Compare to crystalline structure, amorphous structure to be loose that structure more suitable for diffuse molecules [12], which is suitable for light devices and gas sensing devices. No impurities were observed in XRD spectrum.



Fig1.XRD pattern of WO₃ nanostructures.

The chemical structure of WO₃ nanostructure films was observed by Raman spectroscopy. The Raman spectrum of WO₃ nanostructure shown in Fig 2. The peak centred at 344cm⁻¹ can be found in 200-100 cm⁻¹ region corresponding to W-O-W bending mode of the bridging oxygen. The two broad peaks appeared around at 570 and 780cm⁻¹ in the region 500- 800cm⁻¹ corresponding to symmetric and asymmetric vibrations of W⁶⁺ - O bonds (O-W-O stretching modes) [13]. The presence of broad peak around at 780cm⁻¹ is attributed to hexagonal phase of WO₃ [14]. The broad peak at 1098cm⁻¹ may be due to water molecule in the film. This Raman spectrum result was coinciding with XRD results. Both were proved film was contained WO₃ nanostructure with hexagonal phase.



The oxygen (O) and tungsten (W) atomic percentages were determined by energy dispersive spectroscopy (EDS)) and the results are reported in Table 1. The EDS spectrum of WO₃ was showed in Fig 3. The spectrum consists of W and O elements in the film. There is no other peak exist in the film.



Fig2.Raman spectrum of WO3 nanostructures.



Fig3. EDS spectrum of WO₃ nanostructures. Tab1. EDS elemental percentage of WO₃ nanostructures

Element	Atomic %
OK	83.17



The SEM image of WO₃ nanostructure was represented in Fig 4(a) that showed WO₃ nanoplate like structure irregular rectangular and hexagonal shapes have thickness nearly 140nm and average length were 190nm. Chin et al. [15] reported WO₃ nanostructure prepared by electrochemical anodization technique. The 2D AFM image of the WO₃ nanostructure was shown in Fig 4(b). This image was consistence of stacks nanoplates. That has average surface roughness of 93nm. The high porosity of the hexagonal and rectangular WO₃ nanostructure have seen through AFM. It should lead to efficient sensing property of the thin film and have light-harvesting capabilities. Abraham et al. [16] observed ultrathin WO₃ nano disks.



Fig4. (a) SEM micrograph of WO₃ nanostructures (b) 2D AFM image of WO₃ nanostructures.





PL emission spectrum has been used to study the surface defects, impurities in structure, bandgap and



oxygen deficiency in the metal oxide semiconductors materials. In Fig5 shows photoluminescence (PL) spectra of WO₃ nanoplates was showed peak at 577 nm. The emission wavelength indicates in the visible range of yellow emission due to oxygen deficiency in WO₃ nanoplates. Bo et al. [17] observed ZnO nanostructure prepared by chemical method, the films exhibited yellow emission at 590nm indicated interstitial oxygen vacancy. PL emissions associated with decay of an electron from conduction band to valence band from conduction. band to charged vacancy state (v¹⁺ v²⁺ or vacancy state (v⁰ or v¹⁺ to valance band that created oxygen deficiency in WO₃ [18].

Conclusions

In summery the prepared WO_3 film was nanostructure with hexagonal phase. That was confirmed by XRD and Raman studies. Further SEM observations was showed that nanoplates and had high surface roughness. PL spectrum observed that WO_3 nanoplates have oxygen vacancies. These oxygen vacancies were responsible for various dimensions of nanostructures. These characteristics of the films are suitable for many functional applications such as gas sensors, light harvesting etc.

References

- [1] M. Ani Melfa Roji, Ajith Bosco Raj, RSC Adv, 7 (2017) 33642.
- [2] Y.Badour, S. Danto, C. Labrugère, Cu-Doped and Un-Doped WO₃ Photochromic Thin Films. *J. Electron. Mater.* 51, 1555–1567 (2022). https://doi.org/10.1007/s11664-021-09389-3
 [3] D. Vasanth Raj, N. Ponpandian, D. Mangalaraj, A. Balamurugan, C. Viswanathan, Ionics 20 (2014) 335.
- [4] M. Charles Lieber, Zhong Lin Wang, MRS bulletin, 32 (2007) 99.
- [5] Y. Cui and C.M. Lieber, Science 291 (2001) 851.
- [6] W.L. Hughes, Z.L. Wang, J. Am. Chem. Soc. 126 (2004) 6703.
- [7] M. C. RAO, Journal of Non-Oxide Glasses, 5 (2013) 1.
- [8] Wei-qi Wang, Xiu-li Wang, Xin-hui Xi, Zhu-jun Yao, Yu Zhong, Jiang-ping Tu, Nanoscale, 10 (2018) 8162.
- [9] K.V. Madhuri, M. Bujji Babu, Materials Today: Proceedings 3 (2016) 84.
- [10] K. Anukul Thakur, V. Mukta, Limaye, Swastik Rakshit, Koustav N. Maity, Varun Gupta, Parul Kumar Sharma, B. Shashi Singh, Materials Research Express, 6 (2018) 1.
- [11] Davidn Nagy, Tamas Firkal Eszter Drotar, 'Agnes Szegedi, Krisztina Laszl Imre Miklos Szil ' agyi, RSC Adv, 6 (2016) 9536.
- [12] Zhi Li, Minghong Yanga, Jixiang Dai, Gaopeng Wang, Chujia Huang, Jianguan Tang, Wenbin Hu, Han Song, Pengcheng Huang, Sensors and Actuators B, 206 (2015) 564.
- [13] R. Huirache-Acuñ, F. Paraguay-Delgado, M.A. Albiter, J. Lara-Romero, R. Martínez-Sánchez Materials Characterization, 60 (2009) 932.
- [14] Luu Thi Lan Anh, Pham Tuan Phong, Han Viet Phuong, Duong Vu Truong, Le Xuan Vuong, Pham Trung Son, Do Duc Tho, Dang Duc Vuong, Nguyen Huu Lam, Nguyen Cong Tu, Vietnam Journal of Science and Technology, 56 (2018) 127.
- [15] ChinWeiLai, Journal of Nanomaterials, 2015 (2015)56358.
- [16] Abraham Wolcott, Tev R. Kuykendall, Wei Chen, Shaowei Chen, Jin Z. Zhang, J. Phys. Chem. B, 110 (2006) 25288.
- [17] Fan Hai Bo, Y. Shao, Chin Phy Lett, 24 (2007) 2108.
- [18] Matteo Gerosa, Cristiana Di Valentin, Giovanni, J. Phys. Chem. C, 120 (2016) 11716.