Study the Structure and Optical Properties of GNPs Doped WO₃ /PS by Spray Pyrolysis Deposition (SPD)

Saadallah F. Hasan ¹, Abdul-Majeed E Al-Samarai², A. S. Obaid³, Asmiet Ramizy ⁴
¹Ministry of Education, Direction of Education in AL-Anbar, Anbar, Iraq.
²Department of Physics, College of Education for Pure Sciences, University of Tikrit, Tikrit, Iraq.
³⁴Department of Physics, College of Science, University of Anbar, Anbar, Iraq.

Corresponding author: Saady69@yahoo.com, majeedsa2004@gmail.com, ahmed.s.obaid.alqayssei@gmail.com, asmat_hadithi@uoanbar.edu.iq

Abstract. In this studied gold (Au) nanoparticles doped tungsten oxide (WO₃) thin film was deposited on porous silicon (PS) substrate at the substrate temperature of 250°C by spray pyrolysis deposition method, with different Au doping concentration of (0, 1, 3, and 5%). The gold nanoparticles GNPs were prepared by using normal atmospheric air cold plasma. All films were annealed at 500°C for 1h. The X-ray diffraction peaks indicated that all films are polycrystalline with a hexagonal structure. The surface morphology was studied by AFM. The average grain size for pure thin film WO₃ was about 61 nm, and it decreased to be about 43.2 nm with increases the doping ratios for the film deposited at 5% of Au. FESEM image all doped and undoped films showed homogenous pattern structure on the porous silicon. The thickness of films was obtained from the cross-section of the FESEM, which was 323±5 nm. A blue-shifted showed based on the photolumineses (PL) peak position calculated of WO₃ as doping ratio increased, the bandgap for Au: WO₃ films lies between (2.85 to 3.02) eV.

Keywords: Thin films, Tungsten Oxide, Gold, Chemical spray pyrolysis, Porous silicon.

1. Introduction

In the past few years, the interest in tungsten trioxide (WO₃) increased quickly and remarkably potential materials and applications in Photovoltaic, solar cell and gas detection, etc. [1]. Among the electrochromic materials, WO₃ is more interesting because of its good lifetime, high-quality look, low constant time, affordable price, and nontoxic property [2,3]. The physical properties of a substance are greatly influenced by its structural arrangement and morphology. [4]. WO₃ is regarded as an n-type semiconductor with stable physicochemical properties [5]. It had a transparency of more than 80% in the visible region, and a wide bandgap (Eg) ranged from (2.5–3.2) eV. [6]. Among noble metals, Au nanoparticles possess many characteristics, because of, it has modern magnetic, chemical, and physical properties, WO₃ films can be elaboration via adding tiny amounts of GNPs into the pure WO₃ [7]. Gold nanostructures are frequently applied because of their size-dependent effects such as high optical absorbance due to surface plasmon resonance [8, 9]. Moreover, GNPs as metal nanostructures are conductive materials that have a significant effect on charge transferring. Therefore, GNPs with excellent stabilities can modify the electrochromic and electrochemical properties of WO₃ thin films. Porous silicon (PS) is a material with a nanostructure that is prepared through electrochemical methods by crystalline silicon. in the mid-1950s, Uhlir discovered porous silicon accidentally at Bell Laboratories [10]. PS possess many characterizations such as the ratio of large surface area to volume, simple fabrication, active surface chemistry, Also it is easily used as the microelectronic, Micro-
Electro-Mechanical Systems (MEMS), and applications like batteries, sensors electronics, optics, biomedicine, and solar cells. [11-13]. WO₃ can be prepared in several ways. The most important ways are the thermal evaporation [14], electrodeposition method [15], a sputtering technique [16], sol-gel [17], CVD [18], and spray pyrolysis deposition [19]. Attention has been focused on the SPD method, as it can simply prepare the films in the air. Therefore, it is considered one of the most attractive methods for preparing thin films due to a large surface area coating that can be obtained by used low-cost equipment with minimum energy consumption, and it allows the utilization of inexpensive precursor materials [22-20]. Essentially, SPD depends on a pyrolysis reaction on a heated substrate of the precursor, which spread as small droplets. Because of adding the surfactant of the precursor, the surface tension will be minimize, which let the figuration of small droplets above the substrate. Else, is the temperature of droplet increase more when approaching of the substrate that continuously adjusts the reaction rate [23]. The aim of the study is to study the effect of Au GNPs doping on the structural and optical properties of WO₃ thin film prepared by SPD.

2. Experimental

2.1 Preparation of WO₃ solution by Chemical Reaction

To obtain tungsten oxide, 5g of tungsten powder (W) with purity of (99.9%) was dissolved in 100 ml of hydrogen peroxide at a concentration of 30%. The reaction was carried out in a water bath at a temperature of 25°C until the reaction was complete for 10 min, and then the excess of hydrogen peroxide was eliminated at a temperature 150°C for 15 min in a magnetic mixer. Then 20ml of ethanol was added to reaction solution at a temperature of 70°C for a period of (1h) in a magnetic stirred with cover, but not tightly the beaker because the reaction is accompanied with strong heat.

2.2 Preparation of WO₃ thin film

Thin WO₃ can be deposited via spraying the solution on a hot substrate (PS) at a temperature of about 250°C. After the deposition process, the tungsten film left on a hot base for at least one hour to form the oxidation process and complete the crystal growth. The thermal spray method was used to prepare the films with a concentration of 0.21 M solution and a pressure of 1 bar, and the distance between the base and the nozzle was about 32 cm, the deposition rate was 10:15 sec.

2.3 Preparation of GNPs solution

The salts of aqueous tetrachloride HAuC₁₄.H₂O which is used as a range of purity (99%) are produced by SGMA (German company). The prepared quantity is 20 ml volume while the required weight is computing by the following equation:

Concentration (mole) = (mass (gram)) / (Molecular weight (g / mol) × volume (litter))

The gold salts solution was prepared in the required volume and a concentration of 1 mM, there after the argon gas tube is opened, the metal tube with a diameter of 1 mm is fixed vertically by the catcher, then the prepared solution was placed under the metal tube. The distance between the tube nozzle and the solution surface becomes 1mm when the beaker getting close to the metal tube. The inter gas quantity inside the metal tube was controlled by flow meter of speedometer and the gas tube. The voltage produced by the system gradually increases till the case of the plasma generated between the surface of the fluid and the tube.

3. Results and Discussion
3.1. X-ray diffraction

XRD pattern of pure WO$_3$ film and doped deposited WO$_3$ film with Au NPs on PS at substrate temperature of 250°C illustrated in fig.1. From the figure, it is observed the many diffraction peaks which indicated that the structure is polycrystalline for the pure and doped films, the planes (001), (110), (111), (300) and (002), at $\theta=22.79^\circ$, 24.388, 28.420, 33.680, 42.950, 46.590 respectively, were observed the preferred peak at (110) plane. The diffraction peaks and their relative intensity exactly match that of JCPDS 00-033-1387 for WO$_3$ hexagonal. This result corresponding with Ibrahim et al [24]. The peak at $\theta=28.42^\circ$ Indicate to silicon at (111) plane. When doped of Au at different concentrations, it was found that the intensity of the peaks of WO$_3$ began to gradually decrease towards fewer angles with increase doping ratio. This result may be due to the substituted of Au by lattice sites within WO$_3$. The doping with Au did not transform the orientation of WO$_3$ thin film crystalline outgrowth for the dominant planes, and outgrowth continues through the direction of (110), according to the drift competitive growth model, which is called “the model of the survival of the fastest-growing crystallites [25]. By Debye-Scherrer equation, the average crystallite size of the crystal is calculated based on the preferred peaks present in the XRD pattern [26],

$$D = \frac{k \lambda}{\beta \cos \theta}$$

Where $\lambda$ is the wavelength, $\beta$ is a full-width half of the maximum, $\theta$ is the Bragg angle, and ($k$) is form factor equal to 0.9. The result showed that the crystalline size decrease from (23.37 to 14.27) nm with increase doping ratios.

3.2. Atomic force microscope (AFM)

3-D WO$_3$:Au/PS AFM images as shown in Fig. 2, display the topography of the WO$_3$ surface, which agreement with XRD result. Average diameter, roughness, and R.M.S of samples are illustrated in table 1. The pure WO$_3$ specimen has a granular structure, fully ordered, and closely packed on the surface. After doping it was found that the grain size, roughness and RMS decrease and this is agreement with [24] as showed in table 1.

3.3. Field Emission Scanning Electron Microscopy (FESEM) and EDX

Figure. 3 (a, b, c and d) showed the FESEM images of WO$_3$/PS doped with Au at 0,1,3,5%vol., respectively. It was clearly observed that all the samples showed approximately spherical-shaped particles, and having granulation and a tendency to agglomerate with uniform distributed size morphology with an average diameter of (22–97) nm. The images in agreement with another researcher group [27]. The crystalline size evaluated from XRD results so smaller than the FESEM, which decreases with increasing Au ratio. Fig (3-e) showed the thickness from the cross-section of PS and WO$_3$ thin film, which was about 21μm and 323±5 nm respectively, it displays the formation of nonparallel and partially cracked silicon walls, which result in asymmetrical and tight holes between them [28].

EDX analysis was showed in figure 4, which indicated the EDX analysis of the WO$_3$ nanoparticles that were produced by the spray pyrolysis method. The results exhibit the characteristic peaks of W and O present in the film. The peak intensity of W was reduced may be of the addition of Au ions at the site of W, and the O intensity peak stays constant for both pure and Au doped WO$_3$.

3.4. Photoluminescence

PL spectroscopy is one of the most important studies to mensuration the energy distribution of the photons emitted after optical excitation and to comprehend the electron-hole pair in semiconductor oxide. Using photoluminescence spectra, oxygen vacancy, and lattice deformation were analyzed for samples of pure tungsten oxide and Au NPs doped were illustrated in figure 5. Both pure WO$_3$ and doped thin film with Au exhibit blue emission as compared with the bulk WO$_3$. The energy gap increases as function of Au –doped this blue-shifted is due to a reduction to nano size, which the supports charge carrier quantum
confinement model [29]. The low intensity of PS and the thin film when doped, may be because the gold created traps to capture non-radioactive electrons, which reduced the intensity of emission and the loss of electron energy, which recombination into heat and not light. Conversely, there is a blue-shift peak towards higher energy, indicating a decrease in crystal size and thus an increase in the energy gap.

4. Conclusion

This paper demonstrates using spry method as easy and inexpensive method to synthesize pure WO$_3$ and doped with Au. XRD analyses that the crystal size decreases due to an increased doping ratio. AFM topography confirmed that the grain size in nanoscale, and it decreases with increase doping ratios. From FESEM, it was observed that all the samples showed approximately spherical-shaped particles with a porous structure having granulation and a tendency to agglomerate with a uniform distributed size. The energy dispersive spectrum (EDX) underlines the presence of W and O in the prepared materials. PL results showed a blue shift with an increased Au doping ratio in the prepared thin films.

References

[1] Mitsugi, F., Hiraia, E., Ikegami, T., Ebihara, K., & Thareja, R. K. (2002). WO3 thin films prepared by pulsed laser deposition. Japanese journal of applied physics, 41(8R), 5372. P. E. Hodgson, “Nuclear Reactions and Nuclear Structure”, Clarendon Press, Oxford, (1971);

[2] Pecquenard, B., Lecacheux, H., Castro-Garcia, S., & Livage, J. (1998). Electrochromic properties of peroxopolytungstic acid thin films. Journal of sol-gel science and technology, 13(1-3), 923-927. C. Kalbach, Phys. Rev. C47 (1993) 587;

[3] Heckner, K. H., & Kraft, A. (2002). Similarities between electrochromic windows and thin film batteries. Solid State Ionics, 152, 899-905. C. Kalbach, “User’s Manual for PRECO-2006, Exciton Model Preequilibrium Nuclear Reaction Code with Direct Reactions", Triangle Universities Nuclear Laboratory, Duke University, (2007);

[4] Nishioka, D., Tsuichiya, T., Higuchi, T., & Terabe, K. (2020). Oxygen-tolerant operation of all-solid-state ionic-gating devices: advantage of all-solid-state structure for ionic-gating. Japanese Journal of Applied Physics, 59(SI), SIIG09. J. Csikai&S.Nagy, Acta Physica 21 (1966) 303;

[5] GUO, X. Z., KANG, Y. F., YANG, T. L., & WANG, S. R. (2012). Low-temperature NO2 sensors based on polythiophene/ WO3 organic-inorganic hybrids. Transactions of Nonferrous Metals Society of China, 22(2), 380-385. W. Scobel, M. Blann, T. T. Komoto, M. Trabandt, S. M. Grimes, L. F. Hansen, C. Wong, B. A. Pohl, Phys. Rev. C30 (1984) 1480;

[6] Simchi, H., McCandless, B. E., Meng, T., & Shaforman, W. N. (2014). Structural, optical, and surface properties of WO$_3$ thin films for solar cells. Journal of alloys and compounds, 617, 609-615.P. Guazzoni, L. Zetta, P. Demetriou, P. E. Hodgson, Z. Phys. A — Hadrons and Nuclei 354 (1996) 53;

[7] Ibrahim, I. M. (2018). The effect of gold nanoparticles on WO$_3$ thin film. Iraqi Journal of Physics (IJP), 16(36), 1-28.I. C. Sagrada Garcia, J. F. Lecolley, F. R. Lecolley, V. Bildeau, G. Ban, J. M. Fontbonne, G. Iis, J. L. Lecouey, T. Lefort, N. Marie, J. C. Steckmeyer, C. Le Brun, J. Blomgren, C. Johansson, J. Klug, A. Orhn, P. Mermod, N. Olsson, S. Pomp, M. Osterlund, U. Tippawan, A. V. Prokofiev, P. Nadel-Turonski, M. Fallot, Y. Foucher, A. Guertin, F. Haddad, M. Vatre, Phys. Rev. C 84 (2011) 044619.;

[8] He, T., Ma, Y., Cao, Y., Yang, W., & Yao, J. (2001). Enhanced electrochromism of WO$_3$ thin film by gold nanoparticles. Journal of Electroanalytical Chemistry, 514(1-2), 129-132.

[9] Nagai, J., McMeeking, G. D., & Saifoh, Y. (1999). Durability of electrochromic glazing. Solar energy materials and solar cells, 56(3-4), 309-319.

[10] Uhlir Jr, A. (1956). Electrolytic shaping of germanium and silicon. Bell System Technical Journal, 35(2), 333-347.

[11] Levitsky, I. A. (2015). Porous silicon structures as optical gas sensors. Sensors, 15(8), 19968-19991.
[12] Pérez, M., Dutt, A., de la Mora, B., Mon-Pérez, E., Villagrán-Muniz, M., García-Sánchez, M. F., & Santana, G. (2018). Effect of ammonia plasma treatment on the luminescence and stability of porous silicon. Materials Letters, 216, 277-280.

[13] Lukianov, A., & Ihara, M. (2018). Free-standing epitaxial silicon thin films for solar cells grown on double porous layers of electrochemically oxidized porous silicon dioxide. Thin Solid Films, 648,1-7.

[14] Lozzi, L., Ottaviano, L., Passacantando, M., Santucci, S., & Cantalini, C. (2001). The influence of air and vacuum thermal treatments on the NO2 gas sensitivity of WO3 thin films prepared by thermal evaporation. Thin Solid Films, 391(2), 224-228.

[15] Vijayalakshmi, R., Jayachandran, M., & Sanjeeviraja, C. (2003). Structural, electrochromic and FT-IR studies on electrodeposited tungsten trioxide films. Current Applied Physics, 3(2-3), 171-175.

[16] Purans, J., Kuzmin, A., Parent, P., & Laffon, C. (2001). X-ray absorption study of the electronic structure of tungsten and molybdenum oxides on the O K-edge. Electrochimica acta, 46(13-14), 1973-1976.

[17] Cantalini, C., Wlodarski, W., Li, Y., Passacantando, M., Santucci, S., Comini, E., & Sberveglieri, G. (2000). Investigation on the O3 sensitivity properties of WO3 thin films prepared by sol–gel, thermal evaporation and rf sputtering techniques. Sensors and Actuators B: Chemical, 64(1-3), 182-188.

[18] Sivakumar, R., Raj, A. M. E., Subramanian, B., Jayachandran, M., Trivedi, D. C., & Sanjeeviraja, C. (2004). Preparation and characterization of spray deposited n-type WO3 thin films for electrochromic devices. Materials Research Bulletin, 39(2), 1479-1489.

[19] Yang, T., Zhang, Y., & Li, C. (2014). Large scale production of spherical WO3 powder with ultrasonic spray pyrolysis assisted by sol–gel method for hydrogen detection. Ceramics International, 40(1), 1765-1769.

[20] Bertus, L. M., Enesca, A., & Duta, A. (2012). Influence of spray pyrolysis deposition parameters on the optoelectronic properties of WO3 thin films. Thin Solid Films, 520(13), 4282-4290.

[21] J. M. Rzaij, N. F. Habubi, "Room temperature gas sensor based on La2O3 doped CuO thin films", Applied Physics A (2020) 126:560

[22] Bertus, L. M., & Duta, A. (2012). Synthesis of WO3 thin films by surfactant mediated spray pyrolysis. Ceramics International, 38(4), 2873-2882.

[23] Bertus, L. M., Faure, C., Danine, A., Labrugère, C., Campet, G., Rougier, A., & Duta, A. (2013). Synthesis and characterization of WO3 thin films by surfactant assisted spray pyrolysis for electrochromic applications. Materials chemistry and physics, 140(1), 49-59.

[24] Isam M. Ibrahim1, Niran F. Abdul-Jabbar2, Abeer H. Fezaa, (2018)."The effect of gold nanoparticles on WO3 thin film", Iraqi Journal of Physics Vol.16, No.36, PP. 11-28.

[25] Ramizy, A., Ibrahim, A. S. M. I. M., & Eisa, M. H. (2014). Performance of Multi-Function Devices Fabricated from La2O3-Doped NiO Thin Films. Journal of Ovonic Research Vol, 15(1), 37-42.

[26] Mahyoub, A. R., & Rashidi, A. (2012). Preparation of different WO3 nanostructures and comparison of their ability for Congo red photo degradation. Digest journal of nanomaterials and biostuctures, 15(2), 587-591.
Figure 1: XRD of the WO₃:Au/PS at annealing of (500 °C).

Figure 2: AFM image of WO₃ doped (0, 1, 3, 5) % ratios of Au at annealing temperature (500 °C).
Table 1: AFM parameters of WO₃ doped (0, 1, 3, 5) % ratios of Au at annealing temperature (500 °C).

| Au (%) | Ave. diameter (nm) | Roughness (nm) | R.M.S (nm) |
|--------|-------------------|----------------|-------------|
| 0%     | 61.0              | 8.8            | 11.1        |
| 1%     | 60.1              | 7.9            | 10.7        |
| 3%     | 53.3              | 5.4            | 6.8         |
| 5%     | 43.2              | 3.6            | 4.7         |

Figure 3: FESEM images of WO₃/PS (a) 0%, (b) 1%, (c) 3%, (d) 5% of Au, (e) cross section of WO₃/PS.
Figure 4: Energy-dispersive X-ray (EDX) spectra of WO₃

Figure 5: Photoluminescence spectra for WO₃ with different doping concentration