### Manufacturing Br:CO<sub>3</sub>O<sub>4</sub>/Si Heterojunction For Photodetector Applications

H. K. Hassun, B. K. H. Al-Maiyaly, B. H. Hussein<sup>\*</sup> Department of Physics, College of Education for Pure Science / Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq

This research including,  $CO_3O_4$  was prepared by the chemical spry pyrolysis, deposited film acceptable to assess film properties and applications as photodetector devise, studying the optical and optoelectronics properties of Cobalt Oxide and effect of different doping ratios with Br (2, 5, 8)%. the optical energy gap for direct transition were evaluated and it decreases as the percentage Br increase, Hall measurements showed that all the films are p-type, the current–voltage characteristic of Br:CO3O4 /Si Heterojunction show change forward current at dark varies with applied voltage, high spectral response, specific detectivity and quantum efficiency of CO3O4 /Si detector with 8% of Br ,was deliberate, extreme value with 673nm.

(Received September 18, 2022; Accepted January 4, 2023)

Keywords: Cobalt oxides, Br, Optoelectronic, Photodetector

#### **1. Introduction**

Cobalt oxides was individual of greatest significant evolution metal oxides which had enormous attention in numerous fields [1]. Cobalt(II,III) oxide is an mineral composite through the prescription Co<sub>3</sub>O<sub>4</sub>, where it was unique of two fit considered cobalt oxides, a black antiferromagnetic solid. By way of a diverse valence multifactorial, its formulation was occasionally inscribed such as CoIICoIII2O4 and sometimes by means of CoO•Co2O3, highly stable, nontoxic environment, relative abundance on earth, efficient abs option on the visible photons, thru double optical band gaps of 1.5 eV in addition to 2.2 eV [3]. Cobalt oxide is p-type semiconductor per a regular spinel structural [4], besides this one had several profitable or latent submissions in heterogeneous catalysts [5], terminal materials in Li-ion rechargeable batteries [6], solid state sensors [7], electro chromic devices [8], solar energy absorbers' [9], also pigments [10]. Cobaltoxide films have been equipped thru countless procedures for instance spray pyrolysis, sputtering, chemical vapor deposition, pulse laser deposition, sol-gel process, electrodeposition, etc. on diversity of substrates where separately statement technique propositions dissimilar compensations [11-16]. Midst the countless deposited procedures, the spray pyrolysis were the record appropriate process aimed at the provision of dopant thin films for the reason that that one easiness, low-cost investigational procedure, plus comfort of addition numerous doping material [17], a dopant was unique of the admirable behaviors towards advance the electrical conductivity. optical properties, and efficient photodetectors is individual of the outstanding methods to progress the above declared possessions. This research goals fabricate (p- Br:CO<sub>3</sub>O<sub>4</sub>/n-Si) heterojunctions photo detector and studies optoelectronic properties, responsivity and specific detectivity of visible light photodetector for  $Br:CO_3O_4$  junction, and the consequence of doping with diverse ratio of Bromine, similarly studies the application as a photodetector device.

## 2. Experimental

 $Co_3O_4$  thin films of (300)nm thickness, had been prepared by chemical spry pyrolysis deposition on substrates at temperature (673±20)K. using Preparing the solution used for the deposition (Co3O4), the water cobalt nitrate Co(NO3)2.6H2O was used with purity (98%) mixed

<sup>\*</sup> Corresponding author: bushrahhz@yahoo.com https://doi.org/10.15251/JOR.2023.191.15

with different percentage (2,5,8)% of NH<sub>4</sub>Br.6H2O, the assorted remained liquefied in distilled water using a magnetic agitator for (15min) towards get a perfect solution then this one is spray on the way to glass and silicon substrate through a detachment of around (~  $29\pm1$ )cm, the movement amount of the solution throughout spraying was attuned near (9 ml/min) and kept constant throughout the deposition process , annealing process done confidential furnace at (773K) for 1h . The results of the optical properties of all samples prepared (pure and doped) were found using UV–VIS spectrophotometer "OPTIMA SP-3000" within the wavelength range of (190-1100) nm. the value of the direct band gap can be relative with Tauc relative [18,19]. Moreover to determined Hall Effect measurements the Vander Pauw(EcopiaHMS-3000) was utilized. Suitable preparation was fortified for regulate the photodetector strictures, the structure comprises of HUIERDC P S(1502DD), DJ. Multimeter, Spectral responsivity could determine via utilize a mono chromatic light source through spectral variety (200–900) nm.

#### 3. Results and discussions

The optical absorption data were analyzed for pure  $Co_3O_4$  and doped with Bromine, as we can see in figure (1 a), absorbance spectra in the range (400-1100) nm has been examined, the result show increase approximately from (25% to 70%) at  $\lambda = 670$  nm with effect of doping, there is shift in absorption edges toward (700nm) wavelengths with Br adding which it may be associated to inhabiting of adding atoms into the interstate situations in the lattice and attributed to quantum confinement of nanoparticles, transmittance form of deposited films alteration with cumulative wavelength, and diminutions with growing Br ratio were show in Figure (1b), the transmittance value sharp fall from (56.13% to 26.13%) by way of 8% concentration Br, this lessening accredited to the introduction of impurity level, and as a result of the increased scattering of photons by crystal defects by doping [20,21].



Fig. 1. (a) Absorption spectra of Co<sub>3</sub>O<sub>4</sub> with effect doping [0,2,5,8]% Br,
(b) Transmittance, Reflection spectra for Co<sub>3</sub>O<sub>4</sub> with 8% Br.

The shifting of absorption edge to longer wavelength or lower energy indicating decreasing of  $Eg_{opt}$  with increasing ratio adding, Figure (2 a) expression schemes of  $(\alpha hv)^2$  as a function of photon energy (hv) for  $Co_3O_4$  thin films per diverse concentration for Br (0, 2,5,8) wt.%, and modification absorption coefficients with photon energy (hv)for 8% Br in Figure (2 b), the  $Eg_{opt}$  of Cobaltoxides films were originate near reduced [ 2.21 to 1.85] eV, aimed at films effected by doping ratio. This can be attributed to the fact that the impurity produces levels in the gap due to the merging of impurities with energy levels close to the edge of the band, which may contribute to making the bandgap narrow, and the reason may be due to changes in the composition caused by the presence of impurities. Moreover, the absorption coefficient  $\alpha$  indicates

a long band tail in the absorption curves besides we bargain lower value per lowers photon energy below (1.45eV), formerly activates with a regular escalation as a result of inhabiting of dopant particles into the interstitials locations in the lattice film.



Fig. 2. (a) Plot of  $(\alpha hv)^2$  versus (hv) of  $Co_3O_4$  thin films for different Br ratio, (b) The absorption coefficient of 8% Br doped  $Co_3O_4$  thin film.

From Figure (3a,b) entirely models deposited have a positive Hall coefficient (p-type charge, both the carriers concentration and Hall mobility intensifications and the Hall coefficient decrease with the swelling Br percentage, increasing the concentration of charge carriers and mobility respectively, with increased distortion ratios for  $Co_3O_4$ , explained on aggregate the levels of impurities in the interior the energy gap via cumulative the distortion ratios, which in turn leads to a decrease in the activation energy of electrical conductivity, which makes the charge carriers need less energy to move under the influence of the magnetic field and this leads to an increase in the concentration and movement of charge carriers, and this increase is consistent with the increase in electrical conductivity when increasing the distortion ratios [22].



Fig. 3. (a) Charge concentration and (b) Hall mobility for  $Co_3O_4$  thin film under effect of Br(0,2,5,8)% doping percentage.

I–V characteristics of pure in addition Br doping Cobalt oxides thin films were revealed on Figure(4), curvatures demonstration the connection amid current flowed over an electronics device then the apply voltage crossways that one stations. Br:Co<sub>3</sub>O<sub>4</sub>/ Si heterojunction per dissimilar proportion in forward as well as reverse bias, this one noticeable the current upsurge

exponentially per voltage on forward bias, whereas in reverse bias the current was increased slightly with voltage then didn't display slightly saturation or strident breakdown, the forward current have binary districts on behalf of totally photo detectors, on initial region the current is identical slight, this current is identified by means of recombination current befell at low voltage solitary [23].



-2 -1.75 -1.5 -1.25 -1 -0.75 -0.5 -0.25 0 0.25 0.5 0.75 1 1.25 1.5 1.75 2

*Fig. 4. I-V characteristics of Br: Co*<sub>3</sub>*O*<sub>4</sub>*/Si heterojunction for diverse Br ratio.* 

By the subsequent district on highest voltages, exponential rises of forward current since the partiality voltage potential surpasses the potential barriers. The voltage provides the electron adequate energy to incredulous the barrier height and drift that is named diffusion current. The uppermost current was with 8% Br ratio. The defects were confidential the energygap levels besides in the interior the depletion region performance by means of recombined centers then, motivation diminution current movement, diagonally the junction.

Figure (5) illustration the I-V characteristics of the  $Br:Co_3O_4/Si$  samples in dissimilar occurrence power density (60,100, 183) mW/cm<sup>2</sup>, be situated measure below dark and illumination condition. Upon illumination of the junction, extra carriers are generated in addition to forward current increases. Likewise the illuminating junctions augmented the reverse bias current as predictable since the electron-hole pair generation in the depletion region if the occurrence photon energy is superior than the lowest direct band gap of the heterojunction, besides Br ratio make the optical energy gap decrease plus condensed electrical resistivity and this result in upsurge the concentration carriers in addition there mobility and that style the lighting current improved through collective Br dopant percentage.



19

Fig. 5. I-V characteristics for  $Br: Co_3O_4/Si$  heterojunction at pure and Br (2,5,8)%, with diverse incident power density.

Spectral Responsivity  $(R_{\lambda})$ , demarcated by photocurrent generated per unit of power of the incident light intensity on active areas, rendering to equation [24].



Fig 6. Photo response spectral aimed at  $Br:Co_3O_4$ / Si hetero junctions with pure and Br (2,5,8)%.

Figure (6) shows the responsivity extending (400-1000) nm wavelength of pure  $Co_3O_4$  in addition doped with Br heterojunctions measuring lower than (3V) reverse bias, the illustrations

have a respectable response in visible area, besides the highest photo respons(650-700)nm, conferring through the band gap (1.84eV) of Co<sub>3</sub>O<sub>4</sub>: Br (8%)/Si.

The consequence of Bromine proceeding the spectral response qualified to enhanced optoelectronic characteristics, wherever amplified carriers concentration may bring about to rise the illumination current formerly the spectral response intensification. Therefore the advantage requires a sturdy visible response emerges and the response intensity is enhanced with Br content in films[25].

The dissimilarity of quantum efficiency in addition specific detectivity per the wave length were show in figure (7), The quantum efficiency value increase from (37.79 to 76.77)% for Br:Co<sub>3</sub>O<sub>4</sub>/Si heterojunctions on outcome doping, this accredited to the growing in the absorption incident radiation in thin film which is generating electron-hole pairs. Furthermore, we obvious that the specific detectivity rises with increasing ratio, due to the increase spectral responsivity and decreases of noise equivalent power (NEP), as we can see in figure (8), where the minimum NEP occurs when responsivity has the maximum value, the NEP decreases when the films doping with Br upsurge due to decrease noise current.



*Fig. 8. The variation of noise equivalent power (NEP) thru wavelength on behalf of Br:Co<sub>3</sub>O<sub>4</sub>/Si heterojunctions at dissimilar Br doping ratio.* 

## 4. Conclusions

In height recital photodetectors occupied in visible region and successfully fabricated Br:Co<sub>3</sub>O<sub>4</sub>/ Si photodetector ,were prepared thinfilm Co<sub>3</sub>O<sub>4</sub> pure and doping by chemical spry pyrolysis technique, optical absorption studies show optical transitions was direct and value of optical energy gap decreases with increasing of doping, the mobility increases with increasing of Br proportion. Also, under illumination, the photocurrent increases with increases doping, the 8% Br: Co<sub>3</sub>O<sub>4</sub> photo detector displayed a main responsivity for visible region than pure nanostructures.

# References

[1] Manickam M, Ponnuswamy V, Sankar C, Sureh R., Inter J light and electron optics 2016; 127:5278-5284; <u>https://doi.org/10.1016/j.ijleo.2016.03.008</u>

[2] Greenwood, Norman N.; Earnshaw, Alan (1997). Chemistry of the Elements (2nd ed.). Butterworth-Heinemann. p. 1118. ISBN 978-0-08-037941-8.

[3] Malkeshkumar Patela,b, Mohit Kumara,b, Hong-Sik Kima,b, Wang-Hee Parka,b, Eun Ha Choic, Joondong Kima, Materials Science in Semiconductor Processing, 74 (2018)74-79; https://doi.org/10.1016/j.mssp.2017.09.018

[4] B. Varghese, T. C. Hoong, Z. Yanwu, M. V. Reddy, B. V. R. Chowdari, A. T. S. Wee, T. B. C.

20

Vincent, C. T. Lim, C. H. Sow, Adv. Funct. Mater. 17, 2007, pp. 1932-1939; https://doi.org/10.1002/adfm.200700038

[5] F. Svegl, B. Orel, I. Grabec-Svegl, V. Kaucic, Electrochim. Acta, 45, 2000, pp. 4359-4371; https://doi.org/10.1016/S0013-4686(00)00543-0

[6] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Tarason, Nature, 407, 2000, pp 496-499; https://doi.org/10.1038/35035045

[7] H. Yamaura, J. Tamaki, K. Moriya, N. Miura, N. Yamazoe, J. Electrochem. Soc. 144, 1997, pp. L158-L160; <u>https://doi.org/10.1149/1.1837710</u>

[8] F. Svegl, B. Orel, M. G. Hutchins, K. Kalcher, J. Electrochem. Soc., 143, 1996, pp. 1532-1539; https://doi.org/10.1149/1.1836675

[9] M. G. Hutchins, P. J. Wright, P. D. Grebenik, Solar Energy Mater. 16, 1987, pp. 113-131; https://doi.org/10.1016/0165-1633(87)90013-X

[10] T. Sugimoto, E. Matijevic, J. Inorg. Nucl. Chem. 41, 1979, pp. 165-172; https://doi.org/10.1016/0022-1902(79)80506-0

[11] V. R. Shinde, S. B. Mahadik, T. P. Gujar, C. D. Lokhande, Appl. Surf. Sci. 252, 2006, pp. 8539-8543; <u>https://doi.org/10.1016/j.apsusc.2005.11.070</u>

[12] C. L. Liao, M. T. Wu, J. H. Yen, I. C. Leu, K. Z. Fung, J. Alloys Compd. 414, 2006, pp- 259-264; <u>https://doi.org/10.1016/j.jallcom.2005.07.021</u>

[13] N. Bahlawane, E. F. Rivera, K. Kohse-Ho inghaus, A. Brechling, U. Kleineberg, Appl. Catal.
B: Environ. 53, 2004,pp. 245-255; <u>https://doi.org/10.1016/j.apcatb.2004.06.001</u>

[14] Y. Makimura, A. Rougier, J. M. Tarascon, Appl. Surf. Sci. 252, 2006, pp. 4593-4598; https://doi.org/10.1016/j.apsusc.2005.07.086

[15] E. Barrera-Calva, J. C. Martı'nez-Flores, L. Huerta, A. Avila, M. Ortega-Lopez, Sol. Energy Mater. Sol. Cells, 90, 2006, pp. 2523-2531; <u>https://doi.org/10.1016/j.solmat.2006.03.024</u>
[16] I. G. Casella, M. Gatta, J. Electroanal. Chem. 534, 2002, pp. 31-381 <u>https://doi.org/10.1016/S0022-0728(02)01100-2</u>

[17] Tatar M, Duzgun B., Paramana J Phys 2012; 79, 1:137-150; https://doi.org/10.1007/s12043-012-0288-3

[18] Maki Samir A, Hassun Hanan K., Ibn AL-Haitham J Pure Appl Sci 2017;29(2):70-80.

[19] B. K. H. AL-Maiyal, B. H. Hussein and H. K. Hassun, Journal of Ovonic Research, 16 (5), (2020).

[20] V.R. Shinde, S.B. Mahadik, T.P. Gujar, C.D. Lokhande, Applied Surface Science 252, 20 (2006) 7487-7492; <u>https://doi.org/10.1016/j.apsusc.2005.09.004</u>

[21] Suhad A. Hamdan and Iftikhar M. Ali, Iraqi Journal of Physics, 2019, Vol.17, No.40, PP. 77-87; <u>https://doi.org/10.30723/ijp.v17i40.408</u>

[22] K. L. Hordee, A. J. Bard, "J. Electro. Chem. Soc." Vo1.124, No.2, Pp.215-223, (1979).
[23] Tuzun S, Oktik S, Altindal ,Mammadov T S., J Thin Solid Films 2006; 511-512: 258; <a href="https://doi.org/10.1016/j.tsf.2005.12.104">https://doi.org/10.1016/j.tsf.2005.12.104</a>

[24] Hanan K. Hassun, Bushra H. Hussein, Ebtisam M.T. Salman, Auday H. Shaban, Energy Reports 6 (2020) 46-54; <u>https://doi.org/10.1016/j.egyr.2019.10.017</u>

[25] Azhar I.H, Sahar I.M, Renewable Energy, Environment TMREES17, 21-24 April 2017, Beirut Lebanon