

Study and Characterization of Non-linear Optical Properties of ZnS nanobelts

Nada Abdul Hadi Kareem
University of Al-Qadissiya, College of Education/Physics Department

Abstract

In this work, first we synthesized the nanobelts semiconductor ((ZnS manufactured through a chemical evaporation deposition (CVD). the films obtained diagnosed through x-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscope (SEM), was a study of non-linear optical properties. in comparison with the optical microscope, confocal microscope optical measurements, measurements of second harmonic generation using Ti : Sapphire laser femto second (800nm), showed that nanobelts ZnS prepared, had a Blue emission at a wavelength 400 nm, which can be attributed to the deep-level emissions resulting from defects or impurities.

1. Introduction

Semiconductor materials have been extensively researched due to their potential applications in optical photo catalytic, and optoelectronic fields [1-7]. Zinc sulfide ZnS is a II-VI compound semiconductor with a wide direct band gap ($E_g=3.6\sim 3.8$ eV) [8]. Moreover, ZnS has a high refractive index [9].

Many techniques including sputtering [10], molecular beam epitaxy [11]. Pulsed laser deposition [12], chemical path deposition (CBD), successive ionic layer adsorption and reaction [14], spray pyrolysis [15], and chemical vapor deposition (CVD) [16,17], have been proposed to fabricate the ZnS thin films. Non-linear optical properties of semiconductor nanostructures have attracted to its of attentions due to the potential optical microscopy [18], and optical communication [19], Second harmonic generation (SHG) is a nonlinear optical process that directly doubles the incident light frequency. It provides a convenient and efficient way to obtain ultraviolet emission with a near infrared laser, which shows a great promise for applications such as microscopic/probe [20], nonlinear optical converters [21,22], and all-optical signal processor [23,24]. In particular, SHG in nanobelts shows special advantages for nano scale coherent sources and integrated optical circuits, which have been widely studied in ZnO [25], Ga N[26], and KNbO₃ nanowires [20,27]. In this paper, we reported preparation and characterization of ZnS nanobelts, and Au catalysts effect on the as obtained ZnS nanobelts morphologies was discussed. Second- Harmonic generation measurements of the as- product are also investigated.

2- Experimental Details:

ZnS nanobelts were synthesized by chemical vapor deposition (CVD) using a simple conventional tube furnace with a 50 mm inner diameter quartz tube at 1050 C°, High purity powder (Alfa Aesar ,purity 99.99%) was used as a precursor and was put into a quartz boat that was placed in the center of a tube furnace .Patterned Au thin film coated silicon substrates were placed downstream of the source materials, serving as the deposition substrates. After the tube was sealed, a carrier gas of pure nitrogen was fled at a flow rate of 50 sccm (standard cubic centimeter per minute) . The source has been heated to 1050 C° at a rate of 30 C°/min and remain at this temperature for 1 hour .After cooling the tube furnace to the room temperature, a white products was deposited on Si substrate(. The collected products were characterized by a scanning electron microscopy (SEM, JSM-6701 F), high- resolution transmission electron microscopy (HRTEM, Tecnai G220) and X-ray diffraction (XRD, X 'Pert PRO, PANalytical B.V., Netherlands).

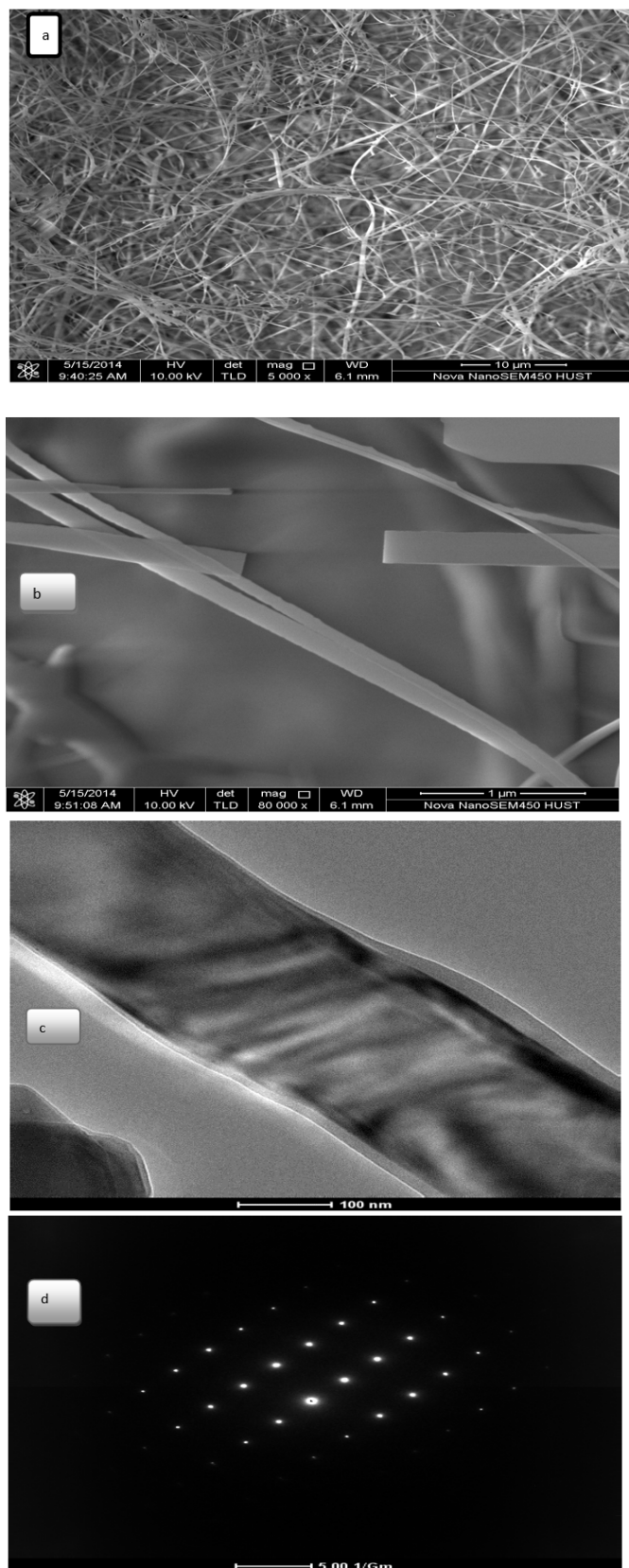


Figure 1(a) Low magnification SEM image, (b) high magnification SEM image, (c) Low magnification TEM image, (d) is the corresponding SAED pattern of the ZnS nanobelts. Second-harmonic generation measurements have been recorded at room temperature, using a mode-locked Ti/Sapphire laser with a wavelength of 800 nm with pulse duration of \sim fs, as the excitation light source.

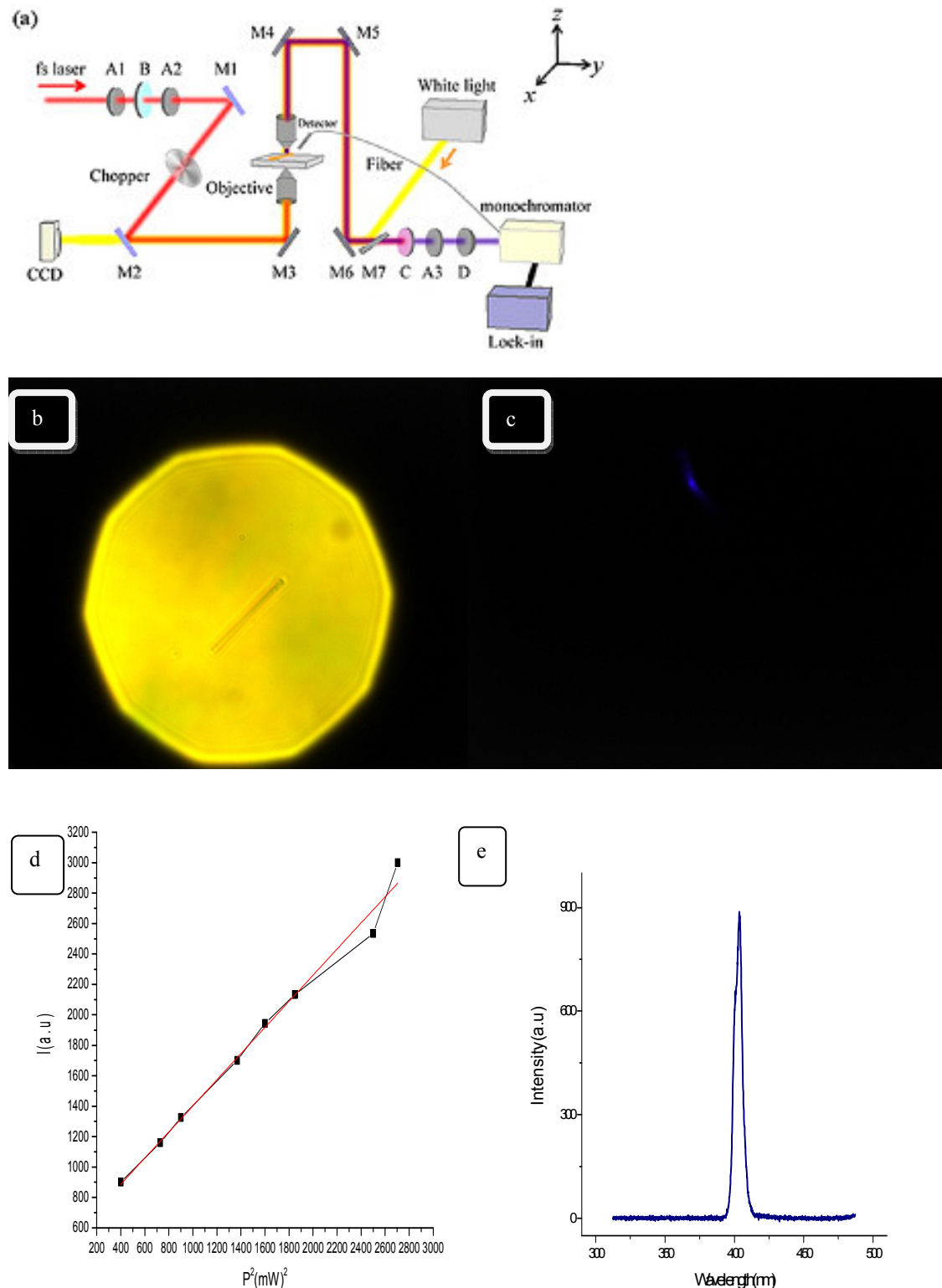


Figure 2(a) shows the experimental setup schemes of the SHG measurement, (b) shows the bright – field image of the ZnS nanobelt, (c) Shows the dark –Field image of the emitted SHG, (d) the spectra of the SHG under a pumping power of 20 mW ($\sim 31.8 \text{ kW/cm}^2$), (e) Shows the relation between power density of doubled frequency Ti:Sapphire irradiation and square value of power.

3. Results and Discussion:

Generally, the crystal structures of ZnS exist in two forms, that is, the cubic (Zinc blende) and hexagonal (wurtzite) phases. The cubic ZnS is stable at room temperature, while the hexagonal ZnS is formed as the

temperature is above 1020 C°[28]. The general morphologies of the as-made products were examined using SEM, which were showed in Figure1. Figure 1 (a) is low magnification SEM image of ZnS nanobelts, one can find large quantities of belt like structures covered on Si substrate. Figure1 (b) shows high magnified SEM image of ZnS nanobelts, this figure shows that the product consists of nanobelts with a diameter of Ca.45 nm (from the SEM, TEM measurements) and a length up to 4 μ m.

Figure 1 (c) shows a typical of low magnified TEM image of the as-grown single ZnS NBs and the corresponding SAED pattern, revealing that the as- synthesized ZnS nanobelts possesses single crystalline structure through the entire length. ZnS nanobelt grows a long [0001] direction as show in figure1(d).

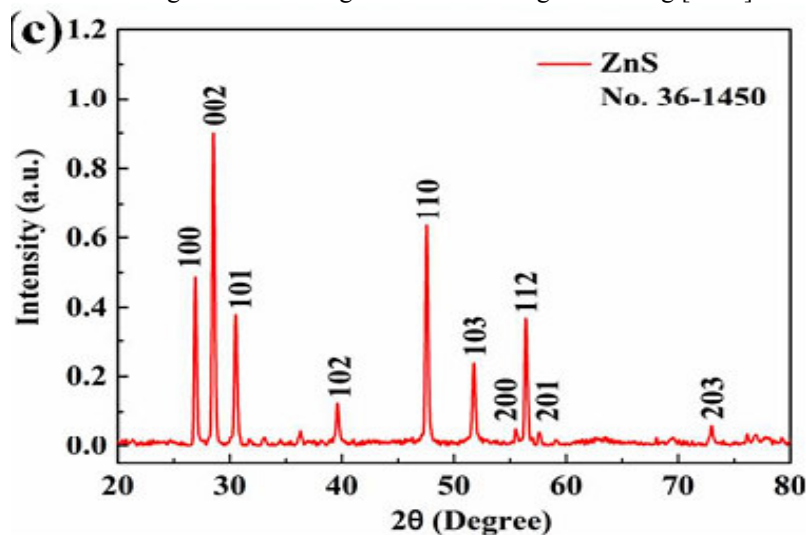


Figure (3) shows XRD pattern.

Figure (3) shows XRD pattern of the as-grown products. All diffraction peaks can be indexed as hexagonal wurtzite structured ZnS with lattice constant of $a=3.822 \text{ \AA}$ and $b= 6.269 \text{ \AA}$ J CPDS . card:79-2204 [28]. Suggesting that the synthesized product has a high purity.

In the SHG experiment, a conventional confocal microscope configuration shown in figure 2(a) was used for optical measurements at room temperature. A mode-locked Ti/sapphire oscillator (spitfire, spectrapysics, 800 nm, 50 fs,800 MHZ) acted as the pumping source and the beam was spot by 40 x objective to e at adiameter of 4 μ m.

A small pump spot contributes to a relatively large pumping power density since the laser power is limited in our experiment, leading to a high SHG signal for the precise process. The transmitted signal was collected with the same objective and focused by a lens to the monochromator equipped with a photomultiplier (Hamamatsh CR131) and a lock- in amplifier (SRS,SR830). A750 nm short-pass filter was placed in front of the monochromator to flitter out the pumping laser light. A half-wave plate (A_2) at 800 nm and a Glan prism (A_3) were combined to measure the polarization properties of the surface second-harmonic generation (SHG) .

Figure 2 (b) shows the optical image of a long ZnS nanobelt. The Highly directional blue-violet signal radiates to the nanobelt growth- axis at an average pumping power of 4mW ($\sim 31.8 \text{ KW /cm}^2$), as shown in Figure 2 (c).

The far-field spectra in Figure 2(d) show a strong peak at 400 nm, exactly the frequency doubling signal of the pumping laser at 800 nm. Figure 2(e) presents the measured second- harmonic generation (SHG) intensity as a function of the square of the pumping power P^2 .

4. Conclusions

ZnS nanobelts have been synthesized by chemical vapor deposition (CVD), we can clearly see that the intensity increases linearly with P^2 —indicating the SHG response in our experiment.

Femtosecond pulsed laser with a near- infrared wavelength. ZnS NBS, generates second- harmonic generation light with increasing intensity as the angle between the incident fundamental beam and the nanobelt symmetry axis is increased.

References

- [1] X.Wu, P.Jiang, Y.Ding, W.cai,S.SXie,andZ.L.Wang, "mismatch Strain induced of ZnO/ZnSheterostructureed rings, ol.19,pp.2319-2323,2007.
- [2] M.Y.Lu, Y.A.chung, M.J.chen,Z.L.Wang, and L.J.chen,"Intercrossed sheet.Like.Ga-doped ZnS nanostructures with superstructures with superbphotocatalytic activity and photo response", The Journal.

Physical chemistry C, Vol 113, pp.12878-12882, 2009

- [3] H.Zeng, W.Cai, and P. liuetal., "ZnO-based hollow nanoparticles by selective etching, elimination and reconstruction of metal-Semiconductor interface, improvement of blue emission and photo catalysis," ACS nano, Vol.2, no.8, pp 1661-1670, 2008.
- [4] X.wu, w cai, and F, Qu, "Tailoring morphologies and wettability property of ZnO ID nanostructures" Acta physica Sinica, Vol. 58, pp.8044-8049, 2009.
- [5] H.B. Zeng, G.T. Duan, and W.P.Cai, "Blue luminescence of ZnO nanoparticles process", Advanced Functional materials, Vol.20, pp.561-572, 2010.
- [6] L.J Yu, F.Y. Qu, and X.Wu, "Facial hydrothermal synthesis of novel ZnO nanocubes" Journal of Alloys and compounds, Vol.504, pp. L1-20110.
- [7] J.Wang, Y.Jiao, Y.Liu, and X.Wu, "Gas phase growth of wurtzite ZnSn nanobelts on a large scale," Journal of nano Materials, Vol 2013.
- [8] K.Ahn, J.H. Jeon, and S. Jean et al, "chemical bonding states and atomic distribution within ZnO(s,o) Film prepared on CIGS /Mo/ glass substrates by chemical bath deposition," current Applied physics, Vol. 12, no.6, pp. 1465-1469, 2012.
- [9] X.C. Jiang, Y. Xie, and L. Y. Zhu, "simultaneous in situ formation of ZnSn nano wires in a liquid crystal template by γ - irradiation," chemistry of materials, Vol.13, pp.1213-1218, 2001.
- [10] D.H. Hwang, J.H. Ahn, K.N. Hui, K.S. Hui, and Y.G. Son, "structural and optical properties of ZnS thin films deposition by RF magnetron Sputtering" Nanoscale research Letters, Vol. 7 article 26, pp.13, 2012.
- [11] S. Yano, R. Schoder, H. Sakai, and B. Ullrich, "High- electric- field photo current in thin -film ZnS formed by pulsed- laser deposition," Applied physics Letters, Vol.82.no.13, pp. 2026- 2028, 2003.
- [12] M.W. Huang, Y.W. Cheng, K. Y. Pan, C.C. Chang, F.S. Shieu, and H.C. Shih, "The preparation and cathodoluminescence of ZnS nanowires grown by chemical Vapor deposition," Applied surface sciences, Vol.261, pp.665-670, 2012.
- [13] G.Xu, S.Ji, and C.Ye, "Effect of ZnS and CdS coating on the photo voltaic properties of CuInS₂ -Sensitized photoelectrodes," Journal of materials chemistry, Vol.22, no. 11, pp. 4890-4896, 2012.
- [14] K.Nagamani, N.Revathi, P.Prathap, Y. Lingappa, and K. T. Reddy, "AL-doped ZnS layers synthesized by solution growth method," current applied physics, Vol.12, no.2, pp.380-384, 2012.
- [15] G.L. Agawane, S. W. Shin, and M.S. Kim et al, "Green route fast synthesis and characterization of chemical bath deposited nano crystalline ZnS buffer layers," current Applied physics, Vol. 13, no. 5, 850-856, 2013.
- [16] F. Peng, S. Ou, P. Chuan, B. Wu, and D. Wu, "Structural, Surface Morphology and optical properties of ZnS film by chemical bath Deposition at Various Zn/S Molar Ratios," Journal of nanomaterials Article ID 594952, 2014.
- [17] H. Harutyunyan, S. Palomba, J. Renger, R. Quidant, and L. Novotny, "Non linear Lett, Vol .10, pp. 5076-5079, 2010.
- [18] C.J. Barrelet, H.S. Ee, S.H. Kwon, and H.G. Park, "non linear mixing in nanowire subwavelength wave guide," nano Lett. Vol. 11, pp. 3022-3025, 2011.
- [19] W. Liu, K. Wang, Z. Liu, G. Shen and P. Lu, "laterally Emitted surface Second harmonic Generation in a single ZnTe nanowire," Nano Letters, Vol. 13, pp. 4224-4229, 2013.
- [20] Y. Zhang, N.K. Grady, C.O. Ayla, and N.J. Halas, "Three- dimensional nanostructure of second- harmonic light," Nano Lett. Vol 11, pp.5519-5523, 2011.
- [21] N. Talebi, and M.J. Shahabadi, "photonics application and technology world market series" pp. 42-47. Business briefing.
- [22] M.L. Ren, and Z. Y. Li, "Giant enhancement of Second Harmonic generation in distributed Bragg reflector mirror," Opt Express, Vol. 17, pp.14502-14510, 2009.
- [23] P. Dong, J. Upham, A. Jugesure, and A. G. Kirk, "Second harmonic generation in Semiconductor wave guide directional couplers," Opt. Express, Vol 14, pp. 2256-2262, 2006.
- [24] P. B. Mehl, L.R. House, A. Uppal, J.A. Reams, and J.R. Kirschbrown, "room temperature excitonic whispering gallery mode lasing" advanced materials 2006, 441, 489.
- [25] J.P. Long, B.S. Simpkins, D. J. Rowenhorst, and P.E. Pehrsson, "Far-Field imaging of Optical second harmonic Generation in a single GaN nanowires," Nanolett, vol7, pp. 831-836, 2007.
- [26] M. M. Lee, J.T. Miyasaka, T.N. Murakami, H.J. Snaith, "optical properties of ZnS nanowire lasers and waveguides" science 2012, 338, 643
- [27] B.G. Ibert, B. H. Frazer, and H. Zhang et al, " X-ray absorption spectroscopy of the cubic and hexagonal poly types of Zinc sulfide," physical Review B- Condensed matter and materials physics, Vol. 66. No.24, Article ID 245205, 2002.
- [28] Z. Gang, L. Cheng, J. Zou, X. Yao, and, H. Cheng, "Zinc sulfide nanowire array on Silicon Wafers for field emitters" Nano technology, Vol.21, Article ID 065701, 2010.

الى حضرة المقوم (2) :

تحية طيبة.....

اورد الى حضرتكم اجوبة اسئلتكم الكريمة على البحث المقدم الى حضرتكم.

- 1- تم انجاز البحث خارج العراق
- 2- العلاقة بين (P^2) , وكثافة الطاقة (I) هي علاقة طردية
- 3- استخدم الضوء ابيض كمصدر للانارة من اجل التصوير بالكاميرا
- 4- تم استعمال 40 x objective وذلك للحصول على 4μ Spot size of laser
- 5- (second harmonic generation) يعتبر ZnS nanowire بنفس موقع اللوح المنصف الموجي
- 6- المادة البيضاء حصلنا عليها بعد ترسيب مادة كبريتيد الخارصين تصبح بعدها مادة بيضاء مترسبة على لوح السليكون وللحصول على التولد التوافقي الاهتزازي يجب استخدام الليزر المضاعف التردد.

مع جزيل الشكر والتقدير.

دراسة وتشخيص الخواص البصرية غير الخطية للاحزمة النانوية لمادة (كبريتيد الخارصين)

ندى عبد الهادي كريم

جامعة القادسية

كلية التربية/ قسم الفيزياء

nadahadi2012@gmail.com

الخلاصة :

في هذا العمل ، اولا قمنا بتركيب nanobelts شبه الموصل (ZnS) التي تم تصنيعها من خلال طريقة ترسيب التبخير الكيميائية (CVD). الأفلام التي تم الحصول عليها تم تشخيصها عن طريق حيود الأشعة السينية (XRD) ، المجهر الإلكتروني النافذ (TEM) ، المجهر الإلكتروني الماسح (SEM) ، وتمت دراسة الخصائص البصرية غير الخطية . بالمقارنة مع المجهر الضوئي العادي ، وقياسات مجهر متحد البؤر الضوئي ، ثانيا قياسات التولد التوافقي الاهتزازي باستخدام Ti:sapphire ليزر فيمتو ثانية (800nm) ، أظهر أن nanobelts ZnS التي تم تحضيرها ، كان لها حزم انبعاث زرقاء عند طول موجي 400 نانومتر والتي يمكن أن تعزى إلى انبعاثات المستوى العميق الناجم عن عيوب أو شوائب .