ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
БІЛІМ ЖӘНЕ ҒЫЛЫМ МИНИСТРЛІГІ
МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ
РЕСПУБЛИКИ КАЗАХСТАН
MINISTRY OF EDUCATION AND SCIENCE
OF THE REPUBLIC OF KAZAKHSTAN

Л.Н. ГУМИЛЕВ АТЫНДАҒЫ
ЕУРАЗИЯ ҰЛТТЫҚ УНИВЕРСИТЕТІ
ЕВРАЗИЙСКИЙ НАЦИОНАЛЬНЫЙ
УНИВЕРСИТЕТ ИМ. Л.Н. ГУМИЛЕВА
GUMILYOV EURASIAN
NATIONAL UNIVERSITY

ЖАС ҒАЛЫМДАР КЕҢЕСІ

Студенттер мен жас ғалымдардың «Ғылым және білім - 2015» атты X Халықаралық ғылыми конференциясының БАЯНДАМАЛАР ЖИНАҒЫ

СБОРНИК МАТЕРИАЛОВ X Международной научной конференции студентов и молодых ученых «Наука и образование - 2015»

PROCEEDINGS of the X International Scientific Conference for students and young scholars «Science and education - 2015»

УДК 001:37.0
ББК72+74.04
Ғ 96

Ғ96
«Ғылым және білім – 2015» атты студенттер мен жас ғалымдардың X Халық. ғыл. конф. = X Межд. науч. конф. студентов и молодых ученых «Наука и образование - 2015» = The X International Scientific Conference for students and young scholars «Science and education - 2015». – Астана: http://www.enu.kz/ru/nauka/nauka-i-obrazovanie-2015/, 2015. – 7419 стр. қазақша, орысша, ағылшынша.

ISBN 978-9965-31-695-1

Жинаққа студенттердің, магистранттардың, докоранттардың және жас ғалымдардың жаратылыстану-техникалық және гуманитарлық ғылымдардың өзекті мәселелері бойынша баяндамалары енгізілген.

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УДК 001:37.0
ББК 72+74.04

ISBN 978-9965-31-695-1

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ПОДСЕКЦИЯ 1.5. ЯДЕРНОЙ ФИЗИКИ, НОВЫХ МАТЕРИАЛОВ И ТЕХНОЛОГИИ

УДК 004.94.

STUDY OF OPTICAL ABSORPTION SPECTROSCOPY DEPENDENCE OF ZnO NANOSTRUCTURES ON DOPED Cu CONCENTRATION

Iskakov Rustem Juldizovich
rustem.iskakov@nu.edu.kz
2nd year Master student majoring in “Nanomaterials and nanotechnology”
Supervisor: Myrzakhmet M. K. cand. ph.math. sc., associate professor
Department of Nuclear physics, L. N.Gumilyov Eurasian National University

Abstract

Cu doped ZnO nanostructures have been synthesized using sol gel method in gelatin media. UV-Vis spectroscopy in the range of 200-1000nm has been employed in order to study absorption behavior of synthesized nanomaterials. Data obtained from UV-Vis allowed to evaluate value of optical energy band gap E_g, as well as Urbach energy E_u. From the calculation it is found that the value of optical energy band gap varies upon dependence on the doped Cu concentration and have values ranging from 3.072-3.44eV. In the meantime the Urbach energy has been varied from 1.076 till 1.209 with respect to doped Cu concentration.

Introduction

Binary semiconducting oxide such as ZnO have attracted great attention, as it owns direct wide band gap of 3.4 eV and large exciton binding energy of 60 meV at temperature of 23˚C, thus these characteristics lead ZnO to exhibit special opto-electric property. Ternary alloy ZnO nanostructures are used in applications such as photocatalysis, sensors, excitons based lasing devices, thin film transistors, etc. Nevertheless, as ZnO has wide band gap, it can only respond to ultraviolet (UV) light, which is estimated as only 4% of the light in the light spectrum. In order to expand its optical absorbance band edge in the visible light range, large amount work has been accomplished – for instance, introducing dopants such as metal or non metal ions [1-3], or sensitizing with organic dyes, or introducing nanosized plasmonic nanoparticles – works such these have been carried out to make ZnO photoactive under visible light irradiation [4].

One of the most efficient method to narrow band gap by creating impurity levels in the forbidden gap for utilizing visible light is doping with metal ions. By introducing impurity levels below the conduction band or above the valence band they start act as a donor levels and acceptor levels, respectively. Existence of such levels forces semiconductor to be responsive to visible light [5].

Furthermore, materials doped with specific amount of dopants will enhance performance of materials. Recently, there were appeared a few papers describing significance of use Cu compounds due to it's not always been ferromagnetic. But there yet not many of papers describe the implementation and performance of applications based on $Zn_{1-x}Cu_xO$. Thus, hereby we present research paper on optical spectroscopy of $Zn_{1-x}Cu_xO$ semiconducting nanostructured material.

Cu transition metal is one of most interesting candidate as a dopant, because it owns similar to Zn electronic structure of shell, which at the end leads to own similar chemical and physical properties [6].

Many approaches such as co-precipitation, chemical vapor deposition, hydrothermal synthesis, and advanced ion implantation have been employed to dope metal ions into wide band gap materials.

Hereby, in this research work has been used a simple sol–gel in gelatin media method to synthesize Cu doped ZnO nanostructures. Gelatin served role of polymerization agent, and has terminated grows of Cu doped ZnO nanostructures during baking process, by preventing nanostructures to agglomerate as gelatin expands under continuous heating. Moreover, sol gel in gelatin media is a method that has obvious advantages over other known methods, as it could produce well aligned nanostructures of narrow size distribution and at the same time it is cheap and available for large scale production capacity [7].

Experimental

Materials

In this work, zinc nitrate (hexahydrate), cooper(II) nitrate hemi (pentahydrate), gelatin powder and other required chemicals of reagent grades have been used, obtained from Sigma Aldrich, and were used without further purification.

Synthesis of Cu doped ZnO nanostructures

In this work ZnO nanostructures has been synthesized with different amount of Cu concentrations been doped in Zn lattice. Overall 4 samples of different Cu concentrations has been synthesized, table 1.

Table 1. Samples with different Cu concentrations been doped in ZnO

Sample number	Molarity	ZnO (amount in %)	Cu (amount in %)
1	ZnO	100%	0%
2	$Zn_{0.99}Cu_{0.01}O$	99%	1%
3	$Zn_{0.97}Cu_{0.03}O$	97%	3%
4	$Zn_{0.95}Cu_{0.05}O$	95%	5%

To synthesize Cu doped ZnO nanostructures sol-gel method in gelatin media has been employed. After synthesis all samples have been sintered at 650°C temperature in order to burn out organical materials and obtain Cu doped ZnO nanoparticles.

Results and Discussions

Figure 1 shows us UV-Vis absorption spectra for ZnO nanostructures doped with different amount of Cu of totally 4 samples. The absorption spectra focused in the region of 350-550nm.

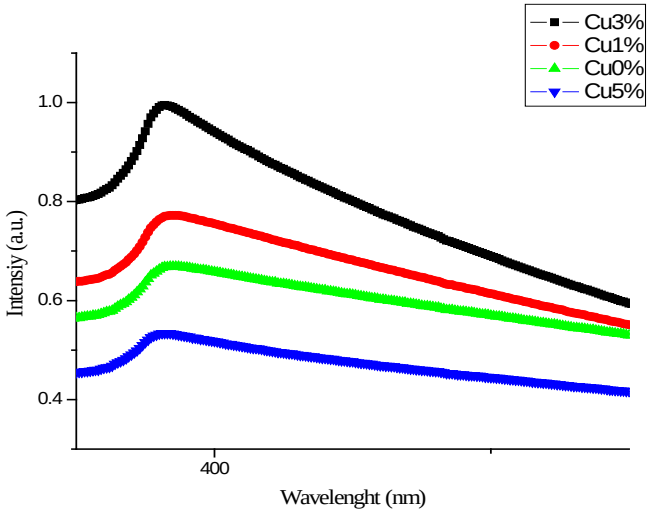

Figure 1: UV-Vis absorption spectra of varying concentrations of Cu doped in ZnO nanostructures

As can be seen all 4 samples have different sites of prominent peaks that corresponds to specific wavelength and thus each sample should have different optical band gap energy.

Optical absorption coefficient αλ that has been used in order to calculate optical energy band gap is found by equation 1.

$$\alpha(\lambda) = 2.303\frac{A}{d} \quad (1)$$

where A is absorbance at specific wavelength and d is the thickness of sample.

Optical energy band gap has been evaluated from the Mott and Davis equation that describes the absorption due to the electronic transition within the band in relation with the optical band gap, equation 2.

$$\alpha(\lambda)h\lambda = const\left(h\lambda - E_g\right)^n \quad (2)$$

where E_g is the optical energy band gap, hλ is the photon energy, α(λ) is the absorption coefficient and n is the index that corresponds to the nature of materials and its interband electronic transition. The E_g has been evaluated by extrapolating photon energy versus the linear part of $(\alpha(\lambda)h\lambda)^{1/2}$, figure 2.

Moreover, at certain temperature the absorption coefficient α(λ) is always follows Urbach's rule near to the absorption edge, equation 3.

$$\alpha(\lambda) = const.\exp\left(\frac{h\lambda}{E_u}\right) \quad (3)$$

where E_u is Urbach energy, which can be described as localized state in the normally forbidden gap.

The Urbach energy could be evaluated from the graph of photon energy versus lnα(λ), figure 3. Optical energy band gap energies and Urbach energies for different samples with different doped Cu concentrations are listed in table 2.

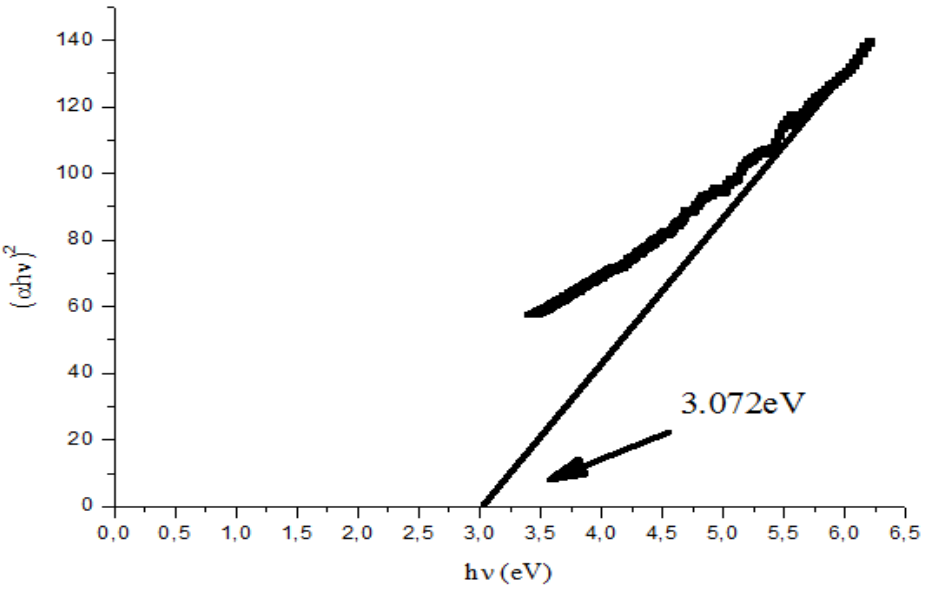

Figure 2: Evaluated Optical energy band gap for $Zn_{0.97}Cu_{0.03}O$

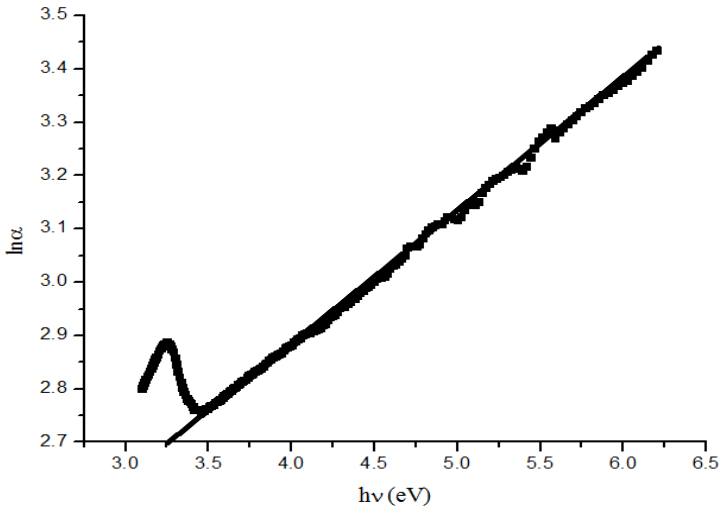

Figure 3: Evaluated Urbach's energy for $Zn_{0.97}Cu_{0.03}O$

Table 2: Cu concentration dependent optical energy band gap energy and Urbach energy

Sample	Optical energy band gap, E_g(eV)	Urbach energy, E_u(eV)
$Zn_{0.97}Cu_{0.03}O$	3.072	1.067
$Zn_{0.99}Cu_{0.01}O$	3.195	1.126
ZnO	3.219	1.170
$Zn_{0.95}Cu_{0.05}O$	3.44	1.209

In figure 4 is shown dependence of Optical band gap energy on Cu concentrations. As can be seen as we dope Cu amount from 1% till 3% optical band gap energy decreases.

However, at Cu amount been 5% instead of further decrease in optical band gap energy, conversely increase occurred.

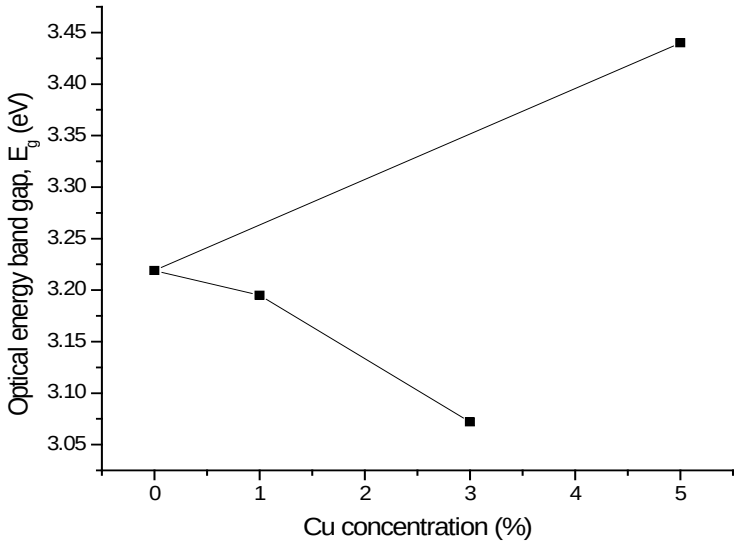

Figure 4: Optical energy band gap dependence on Cu concentration

The same trend of unexpected increase in Urbach energy is seen in figure 5 when sample has been doped with 5% of Cu.

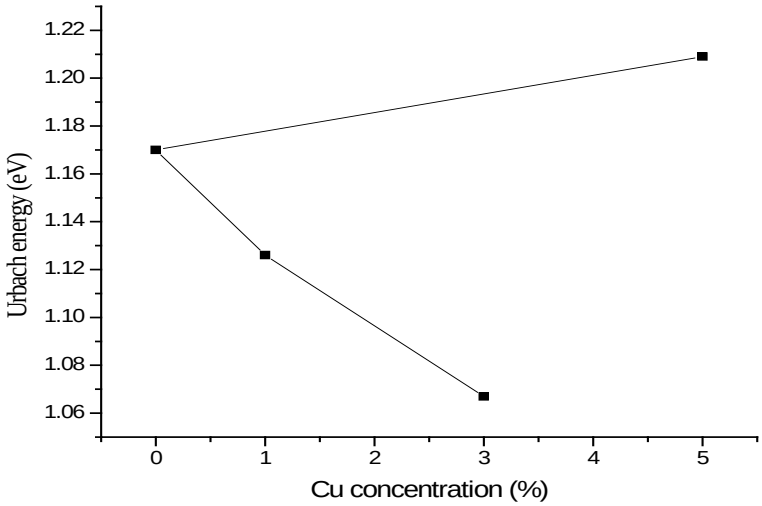

Figure 5: Urbach energy dependence on Cu concentration

Such unexpected behavior could be explained as chemical instability due to doping Cu more than specific value. Both figure 4 and 5 represents strong Cu concentration functional dependence of optical properties of ZnO nanostructures.

Conclusion

The optical properties of Cu doping concentrations on ZnO nanostructures are analyzed by using E_g and E_u. Strong dependence of E_g and E_u on Cu concentration is noticed and mechanism is understood. ZnO's nanostructures could be optimized for optical applications such as light emitting diode, photocatalyst, dye-sensitized solar cell, etc. by tuning optical properties such as E_g and E_u.

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УДК 53.043

ПОЛУЧЕНИЕ И СВОЙСТВА НАНОЭМИТТЕРОВ НА ОСНОВЕ ПЭТФ

Алешова Назгуль Ерлановна
aleshova.nazgul@mail.ru
Магистрант 1 курса Евразийского национального университета имени Л.Н.Гумилева, Астана, Казахстан
Козловский Артем Леонидович
artem88sddt@mail.ru
Докторант 2 курса Евразийского национального университета имени Л.Н.Гумилева, Астана, Казахстан
Научный руководитель – К.К. Кадыржанов

В настоящее время применение автоэмиссии в качестве технологии генерации свободных электронов ограничено по сравнению с термоэлектронной эмиссией, широко использующейся в современной сканирующей электронной микроскопии, из-за сверхвысоких градиентов электрического поля ($E \geq 10^7$ В/см) чтобы получить технологически применимые эмиссионные токи. Особое внимание уделяется тому, что высокая напряженность электрического поля должна быть достигнута при сравнительно низких напряжениях подаваемых на излучающую систему. Тем не менее, полевая эмиссия имеет ряд чрезвычайно полезных функций, которые могут быть применены для создания устройств с уникальными характеристиками, таких как излучатели, которые могут обеспечивать плотности тока 10^6 А/см^2, нанодиоды и нанотриоды со временем отклика порядка 10^{-13} секунд, приборы для микроволновой электроники и т.д. Современные требования к микро и наноструктурным активным элементам электроники в определённой степени определили развитие автоэмиссионных технологий. Вышеуказанные значения напряженности электрического поля могут быть получены при достаточно низких подаваемых напряжениях (около 100-200 В) при условии, что межэлектродное расстояние и диаметр излучающих кончиков достаточно малы [1-7].

В данной работе рассмотрен метод для изготовления автоэмиссионных конусообразных нанокатодов на основе Co, с использованием в качестве шаблонной матрицы полиэтилентерефталатной пленки (ПЭТФ). Данный метод подходит для массового