Investigation of defect structures in metal oxides via spectroscopic techniques

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Indroduction

Lately, zinc oxide (ZnO) has attracted much attention within the scientific community as a 'future material' instead of silicon; however ZnO is not newly discovered material. Research of ZnO has been extensively studied for many decades with our current industry. Growth technologies for the fabrication of high quality allowing for the realization of ZnO-based electronic and optoelectronic devices such as solar cells. ZnO is a direct and wide bandgap semiconductor. It is also an n-type semiconductor.

As fervent research into ZnO continues, difficulties such as the fabrication of p-type ZnO that have so far stalled the development of devices are being overcome.

Although it is asserted that ZnO is not useful in few ways, it should be main semiconductor material because it has a lot of advantages: large exciton binding energy, ability to grow single crystal substrates, wet chemical etching, low power threshold for optical pumping, radiation hardness and biocompatibility.All in all, it can safely be said that ZnO is a very suitable substance in the investigation of metal oxides.

Crystal structure

Crystal structures are one of the most important properties of ZnO. The crystal structures shared by ZnO are wurtzite(B4), zinc blende (B3), and rocksalt (B1), as schematically shown in Figure 1. Özgür et al. stated that at ambient conditions, the thermodynamically stable phase is wurtzite. The rocksalt (NaCl) structure may be obtained at relatively high pressures. Zinc-blende is stable only by growth on cubic structures (2005, p.4).

Wurtzite structure is a hexagonal lattice characterized by two interconnecting sublattices of Zn and O, such that each Zn ion is surrounded by a tetrahedra of O ions, and vice-versa. As Coleman and Jagadish stated that aside from causing the inherent polarity in the ZnO crystal, the tetrahedral coordination of this compound is also a common indicator covalent bonding with an ionicity of fi 0.616 on the Phillips ionicity scale. However, the Zn–O bond also possesses very strong ionic character, and thus ZnO lies on the border line between covalent and ionic compound (2006, p.6).Therefore, atoms in densely areas have high interaction with ionic conditions due to polarity. These interactions increase the emergence of defect generations in wurtzite structure

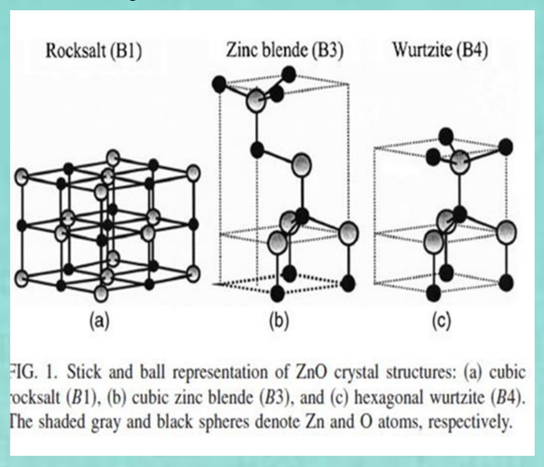


FIG. 1. Stick and ball representation of ZnO crystal structures: (a) cubic rocksalt (*B1*), (b) cubic zinc blende (*B3*), and (c) hexagonal wurtzite (*B4*). The shaded gray and black spheres denote Zn and O atoms, respectively.

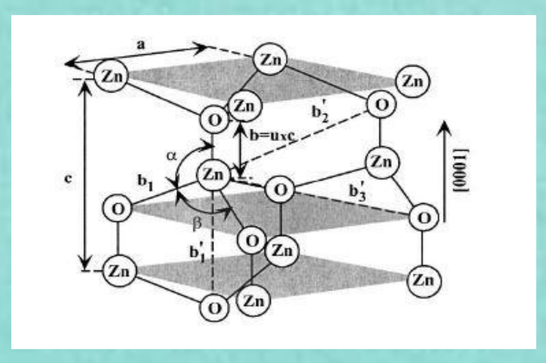


Figure 3:Schematic representation of a wurtzite ZnO structure having latticeconstants a in the basal plane and c in the basal direction; u parameter isexpressed as the bond length or the nearest-neighbor distance b divided by c(0.375 in ideal crystal), and α and β (109.47° in ideal crystal) are the bondangles

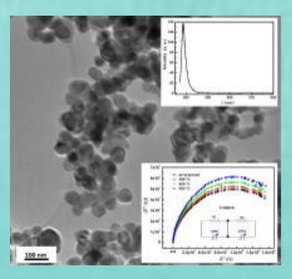
Lattice parameters

There are 4 lattice parameters,theye: a,c,u,c/a ratio As Özgür et al. stated that the lattice parameters of a semiconductor usually depend on the following factors: (i)free-electron concentration ii) concentration of foreign atoms; (iii) external strains (for example, those induced by substrate), and (iv) temperature. The lattice parameters of any crystalline material are commonly and most accurately measured by high resolution x-ray diffraction (HRXRD) for symmetrical and asymmetrical reflections(2005,p.6-7). According for the wurtzite ZnO, lattice constants at room temperature determined by various experimental measurements and theoretical calculations are in good agreement.These two slightly different bond lengths (a and b) will be equal if the following relation holds Figure 2.

$$u = \left(\frac{1}{3}\right)\left(\frac{a^2}{c^2}\right) + \frac{1}{4}.$$

Figure 2: u parameter is the bond length in wurtzite ZnO

Semiconductor Properties of ZnO



- ZnO is a semiconductor material with direct wide-bandgap Eg = 3.4 eV at 300K°
- The corresponding electron Hall mobility at 300K for low n-type conductivity is 200 cm^2/v.s
- It's hole mobility is 5–50cm^2/ V.s.
- Dielectric Constant of ZnO is 8.66 F/m
- Activation energy of ZnO is 60 meV
- It absorbs UV light below 375.75 A
- It has the large exciton binding energy of EB=60 meV at room temperature

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In light of this information we can clearly say that ZnO is suitable for optoelectronic applications such as Light Emitting Diode (LED's), solar cells, photo deters thanks to it's electrical and optical properties

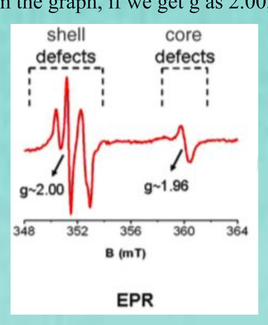
Defects

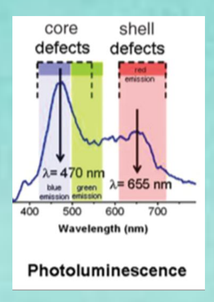
1. Zinc Vacancies (V_{Zn}) : are double acceptors.
2. Oxygen Vacancies (V_O) : O vacancy is a deep-negative U donor, where the +1 charge state is thermodynamically unstable. The g value of O vacancy is 1.995.
3. Zinc Interstitials(Zn_i): are shallow donor. Its the electron configuration configuration end with $4s^2$ which shows that it is diamagnetic. Its g factor is 1.96
4. Oxygen Interstitial : have been suggested to form several configurations, such as dumbbell or split interstitials. Its electron configuration ends with $2p^4$, $2p^5$, and $2p^6$, giving O_i,O_i^-,O_i^{-2} respectively.

Detection Techniques

One of them is ERP. ERP is a method for the determination of the geometric and electronic structure. ERP focuses to find the unpaired electron and nuclei. Therefore, if an atom is diamagnetic, ERP cannot find that defect. That's why, it is hard to detect zinc interstitial, Oİ-2 via ERP. However, we can detect other defects.

From the ERP graph, we can calculate the g factor. G factor helps us to determine what kind of defect we have. As we see from the graph, if we get g as 2.00, it means it is a shell defect. If we get g as 1.96, then it means that it is a core defect.





The other way to detect these defects is photoluminescence (PL).
The PL consists of 2 emission bands. One of them is located at the absorption edge, the other one is in the visible region. From the data we get from PL, we can find the type of defect we have. For example, if we get red emission in the range from 620 to 690 nm, it shows us that we have oxygen interstitials. If our range is between 690 to 750, then we have oxygen vacancies.

Simulation

Electron Paramagnetic Resonance (EPR) is a spectroscopic technique that detects unpaired electrons. It is a very useful and powerful sensitive technique used for the characterization of the nature of magnetic impurities/defects and spin dynamics in materials that have paramagnetic defects in nanocrystalline zinc oxide. (Zargar at al., 2015) Microwave energy was used in the experiment. As known, the resonance condition arises when the microwave energy equals the Zeeman energy.

$H = g\beta BSz$

E= h x V (Microwave Energy)

E=g x β x B (Zeeman Energy)

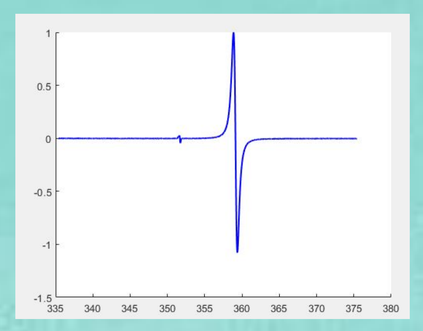
h x V =g x β x B (Resonance Condition)

h= Planck Constant, V= microwave energy frequency s-1 , g= g factor,β= Bohr magneton constant, B: external Magnetic Fiel

ZnO places in a magnetic field and the microwave beam send to the magnetic field. The resonance condition appears as an EPR signal. EPR spectra were simulated by using the toolbox called EasySpin in MATLAB program to understand this signal. The aims were how to plot the EPR data and simulate these spectra by using EasySpin. EPR data was given by supervisor Emre ERDEM in advance. This EPR data was plotted and then simulated.

Plotting EPR spectra by MATLAB

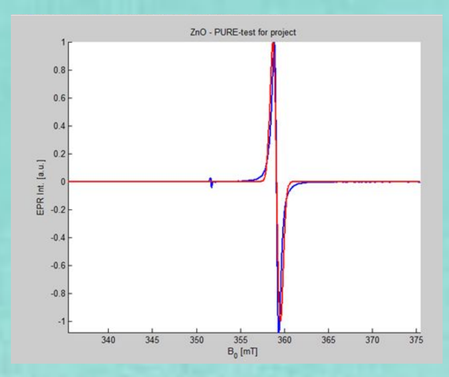
```
cd C:\e
clear all
load znopure.txt
I = znopure(:,3)'; % the sign ' symbolize the transpose of the coloumn I=intensity (y-axis)
I = I - I(1); %normalization
I = I / max(I); %normalization
B = znopure(:,2)'; % B=magnetic field (x-axis)
B = B / 10; %note that x-axis is magnetic field in mT unit, 10 Gauss=1 mT
figure(1)
clf %clear figure
hold on %keep all figures in one plot
plot(B,I,'b','LineWidth',1.5); %Linewidth:is the thickness of the line
plot(Bsim,Isim,'r','LineWidth',1.5);
axis([min(B) max(B) min(I) max(I)])
title('ZnO - PURE-test for project')
xlabel('B_0 [mT]'); %labeling of the x-axis
ylabel('EPR Int. [a.u.]'); %labeling of the y-axis
```



Following Matlab code was used for simulating the EPR spectra

```
%**********here is the parameters for SIMULATION******

g   = [1.962 1.962 1.962]; %play little bit...g-factor from the resonance (matrix so it
lw   = 1; %(in mT giving the peak to peak linewidth)

%useful commands for Easyspin to describe our ZnO crystal system
Sys = struct('S',1/2,'g',g,'lw',lw); %constructing my sample system in physical variable
Exp = struct('Range',[335.4 375.4],'mwFreq',9.86228,'Temperature',300); %defining exper
Opt  = struct('nKnots',40,'Verbosity',1,'Intensity','on'); %in new versions some of ther

%Calculation of the spectra
[Bsim,Isim] = pepper(Sys,Exp,Opt); %Bsim (simulated magnetic field), Isim: (simulated in
Isim    = Isim / max(Isim);


%************************************************
```

The Experimental and Simulated EPR Spectra of ZnO in MATLAB



Applications

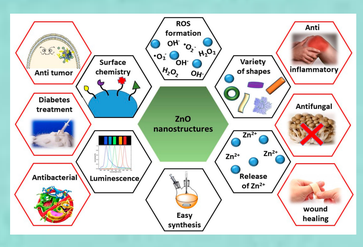


Figure 8. Diagram summarizing the main characteristics of ZnO nanostructures (black hexagons) and their principal applications in biomedicine (red hexagons). (Moezzi A. et al., 2012, p.3)

What attracts Manufacturing Industries about ZnO?

- Luminescent properties
- Low-cost
- Low-toxicity
- Biocompatibility
- High Catalytic Efficiency
- Strong Adsorption Capability
- High Isoelectric Point

Rubber Industry

•Global production of zinc oxide amounts to about 105 tons per year

•The thermal conductivity of typical pure silicone rubber is relatively low; however, it can be improved by adding certain thermal conductivity fillers, including metal powders, metal oxides and inorganic particles.

Textile industry

Offers a vast potential for the commercialization of nanotechnological products. In particular, water repellent and self-cleaning textiles.

The Pharmaceutical and Cosmetic Industries: Due to its antibacterial, disinfecting and drying properties ZnO is widely used in the production medicines for instance, for epilepsy, and later for diarrhea.

The Electronics and Electro-technology Industries: ZnO also exhibits the phenomenon of luminescence (chiefly photoluminescence—emission of light under exposure to electromagnetic radiation). Zno is more resistant to UV rays, and also has higher electrical conductivity

Discussion and Conclusion

(ZnO is a promising material with a range of different properties that emphasizes its uniqueness in the era of nanotechnology. Also, ZnO is an encouraging semiconductor material due to the activity that is commonly used for decades in a wide range of applications which has a high resistance to the severe processing condition. Crystal structures are one of the most important properties of ZnO. The crystal structures shared by ZnO are wurtzite - the thermodynamically stable phase, zinc blende - stable only by growth on cubic structures, and rocksalt rare structure, but might be obtained at relatively high pressures. Additionally, there are 4 lattice parameters, they are a,c,u,c/a ratio; As Özgür et al. stated that the lattice parameters of a semiconductor usually depend on the following factors: free-electron concentration of foreign atoms; external strains (for example, those induced by substrate), and temperature. (2005,p.6-7)

ZnO is a semiconductor material with direct wide-bandgap approximately 3,437 eV at 300 K. ZnO's Defects and impurities affect the electrical conductivity. Thus, Electrical conductivity is created by electron mobility. (Büyük G. İ. at al, 2019) The electrical properties are the large exciton binding energy of EB=60 meV at room temperature makes ZnO a prominent candidate for device application. (Erdem E.,2012)

However, there are 4 types of defects. ZnO has a crystal structure; therefore, there are 2 possible defects for such a structure - vacancy and interstitial. Due to the fact that ZnO has 2 types of atoms. It is possible to have 4 types of defects. Hence, 2 methods are in use to find those imperfect structures. First one, ERP is a method for the determination of the geometric and electronic structure and it focuses on finding the unpaired electron and nuclei. The second one is the photoluminescence method - PL. The PL consists of 2 emission bands. One of them is located at the absorption edge, the other one is in the visible region. From the data received from PL, it is efficient to find defects by this data.

Zinc Oxide has been noticed for its luminescent properties along with low - toxicity, high catalytic efficiency, strong adsorption capability and biocompatibility. Hence, those properties turned ZnO into one of the central nanomaterials for manufacturing. It is widely used in the rubber industry, in pharmaceutical and cosmetic purposes, textile factories for its air - permeability and UV lights resistance and takes essential part as a semiconductor the electronics and electrotechnology industries.

Also, simulations detecting EPR spectra were simulated by using the toolbox called EasySpin in MATLAB program to understand this signal. The aims were how to plot the EPR data and simulate these spectra by using EasySpin. EPR data was given by supervisor Emre ERDEM in advance. This EPR data was plotted and then simulated.

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