

المستخلص

أكاسيد المعادن الشفافة الموصلة، هي نوع من المواد التي لديها موصلية كهربائية عالية وكذلك شفافية عالية في المنطقة المرئية من الطيف الكهرومغناطيسي. وتعتبر من المواد المهمة نظرا لاستخداماتها في العديد من الأجهزة الكهروضوئية التي نستخدمها بشكل يومي، كأجهزة الاستشعار الكيميائية، الخلايا الضوئية و أجهزة تحويل وتخزين الطاقة. يعتبر أكسيد الزنك من أهم المواد التي تحوي هذه الخاصية، وذلك بسبب صفاته المميزة، كقيمة طاقة الفجوة له التي تساوي 3.37 فولت، التي تجعل منه أحد أفضل الالكترونيات المرشحة للأجهزة الكهروضوئية. في هذا العمل تم التحسين من الصفات الضوئية والكهربائية من خلال مجموعة من تقنيات توليف المواد حيث تم استخدام كل من النحاس و الألومنيوم بتركيز مختلفة كمادة مطعمه لأكسيد الزنك، مع مراعاة الاحتفاظ على التركيب البنائي الخاص بأكسيد الزنك وذلك للاحتفاظ بالخصائص التي يتميز بها.

• الفصل الأول: يتضمن مقدمة مختصرة حول أهمية المواد فائقة الصغر (النانوية) وتكنولوجيا المواد ذات الأبعاد الفائقة الصغر. تليها مقدمة موجزة عن الأكاسيد المعدنية المنفذة للضوء والخصائص العامة للبنية التركيبية للمواد الفائقة الصغر و لأكسيد الزنك باعتباره أحد أكاسيد المعادن الواعدة.

• الفصل الثاني: يقدم استعراضا للخصائص الضوئية والكهربائية لأكاسيد المعادن المنفذة للضوء والأساليب التي تستخدم لتحضير أكاسيد المعادن المختلفة ومزايا هذه الطرق وعيوبها.

• الفصل الثالث: يتناول التقنيات المختلفة المستخدمة لتوليف أكاسيد الأغشية الرقيقة مع التركيز على تقنية المحلول الجيلاتيني (بالغمس) والتي تم استخدامها في هذه الأطروحة. كما تم في هذا الفصل ذكر الأدوات المستخدمة في هذه الدراسة والظروف التي تم فيها تحضير العينات.

• الفصل الرابع: يتناول نتائج ومناقشة دراسة الأغشية الرقيقة لأكسيد الزنك المطعمة بكل من النحاس والألومنيوم تمت دراستها بواسطة جهاز حيود الأشعة السينية والمجهر الإلكتروني الماسح. وأظهرت النتائج أن الأفلام المعدة متجانسة وموزعة بشكل جيد على طول الركيزة. كما أظهرت هذه الأفلام بنية بلورية سداسية والتي هي البنية المميزة لأكسيد الزنك. وقد لوحظ نقصان في ثوابت المصفوفة البلورية مع زيادة التركيز والذي تم رفعه إلى ٢٪ من الوزن في حالة الأغشية الرقيقة لأكسيد الزنك المطعم بالزنك والى ١٪ من الوزن في حالة الأغشية الرقيقة لأكسيد الزنك المطعم بالألومنيوم. وكذلك تم قياس الخصائص الضوئية للأفلام المعدة باستخدام جهاز مقياس الاستقطاب البيضاوي التي تم من خلالها تحديد سمك الأفلام، وحساب اتساع المنطقة الممنوعة بين منطقة التوصيل ومنطقة التكافؤ، ومعامل الانكسار ومعامل الفناء وكذلك النفاذية الضوئية. أظهرت الأفلام شفافية عالية على امتداد المنطقة المرئية من الطيف الضوئي. وأظهرت خصائص التيار مع الجهد الكهربائي سلوكا خطياً حتى ٣ فولط. حققت الأفلام مقاوميه منخفضة جدا في التركيزات المثلى من النحاس والألومنيوم لأفلام أكسيد الزنك.

• الفصل الخامس: يمثل خاتمة النتائج الهامة والتوصية للعمل في المستقبل.

Chapter 1

Introduction

1.1 Nanomaterials and nanotechnology

The emergence of materials with nanoscale dimensions reveal a new surprising properties and behavior that does not exist at the bulk form of the material with the same composition. The uniqueness of Nanomaterials is due to their relatively large ratio of surface area to volume (**Qazi *et al.*, 2009**). As the quantity of molecules on the surface increases the amount of molecules located in the inner volume decreases, the process that enhances the surface reactivity. Furthermore, new quantum effects, that lead to enhancement of chemical reactivity and become much more important in determining the materials' properties and characteristics leading to novel optical, electrical and magnetic behaviors (**Gelin *et al.*, 2005**). As the particle size gets smaller this enabled high speed, high functional density and high sensitivity of small and lightweight devices and sensors. Also as quantization of carrier energy states increases this allows a variation in the band gap levels for each nanoparticle (**Gruner, 2006**).

Nanotechnology builds materials at nanoscale to create a novel applications of structures for devices and systems by monitoring the shape and size. At nanoscale, there are dramatic changes in the physical, chemical and biological properties such as electrical conductivity, magnetic susceptibility and color (**Aegerter *et al.*, 2004**).

The applications of nanotechnology are globally growing rapidly for the past decade. Such applications included field of medicine, electronics technology, energy and environmental concerns and toxicity (**Srinivasan *et al.*, 2008**).

Nanotechnology has two different methods of building nanostructures; Top-down technique, such as shrinking and reduction of larger material down to nanoscale and Bottom-up which involves accumulating smaller units to produce the nanoscale materials, including polymers, quantum dots and carbon nanotubes (**Choy, 2003**).

1.2 Transparent Conducting Materials

Transparent conducting materials are considered one of the promising materials owing to their fascinating characteristics because of their unique applications in multidisciplinary industrial potentials in science and technology such as transparent electrode materials in photovoltaic cells, touch-screen technology, light emitting displays liquid crystal displays and heat-mirror window-coatings (**Tu *et al.*, 1995**).

Transparent conducting materials are a combination of two properties one is the high transparency over the visible light range, second is the high electrical conductivity,

The first transparent conducting material was reported by K. Badeker (**Badeker, 1907**) , cadmium thin film was deposited by thermal oxidation leaving oxygen vacancies in its structure, producing a transparent conducting film. This was the first fabricating of an n-type transparent conducting material. Since then, awareness of the importance of this type of materials increased and caught a lot of attention to develop and study. Potential transparent conducting oxides have been extended to include, $\text{In}_2\text{O}_3:\text{Sn}$ (ITO),

ZnO: Al (AZO), GdInO_x, SnO₂ oxide SnO₂:F (FTO), Ga₂O₃ (Lee *et al.*, 2008 & Hamid *et al.*, 2008 & Hou *et al.*, 2006).

1.3 Metal Oxide Electronic Structure

The technique of producing conducting and transparent metal oxide thin film is dependent on the suitable dopant selection. The dopant selection process requires well knowledge of the band structure for the metal oxide. It is mandatory to consider the energy levels of the valence electrons, the energy levels the dopants created and the energy levels of the conduction band (Fay *et al.*, 2007).

The stability and conductivity of modern TCO materials, including doped zinc oxide and doped tin oxide, relies on the doping of the transparent metal oxides to yield a highly conductive thin film. The basis for selection of an appropriate dopant species relies on knowledge of the band structure for the metal oxide host. The relative energy levels associated with the valence electrons, the unoccupied conductance energy levels, and the energy levels created by dopant atoms in the host matrix, must be considered (Hartnagel, 1995).

Since inner most electrons are confined to the localized atoms, band theory deals with the valence electrons. According to Fynman model, neighboring atoms share their valence electrons with their levels to overlap (Solymar, 2010). The allowed electronic states, described by their respective wave functions are governed by the wave number k . This describes the arrangement of the allowed orbitals as periodic described by periodic wave functions (Cox, 1995).

When solving Schrodinger’s equation for an electron trapped in a periodic potential, a suitable solution with no scattering outside each trap is obtained, this came true since the crystal space is considered infinite, the solution which satisfies Bloch function. A continuous set of accumulated energy levels is formed as far as they have a minimal difference in energies. This set of concentric closely spaced energy levels is considered as a band. Having different quantum numbers, angular momentum and energy sizes, the valence shell orbitals control the and determine whether there is energetic overlap or not. So, the band structure has end up with periodic structure but with different sizes and different minima and maxima for each set of levels corresponding to each shell orbital (Atkins, 2001).

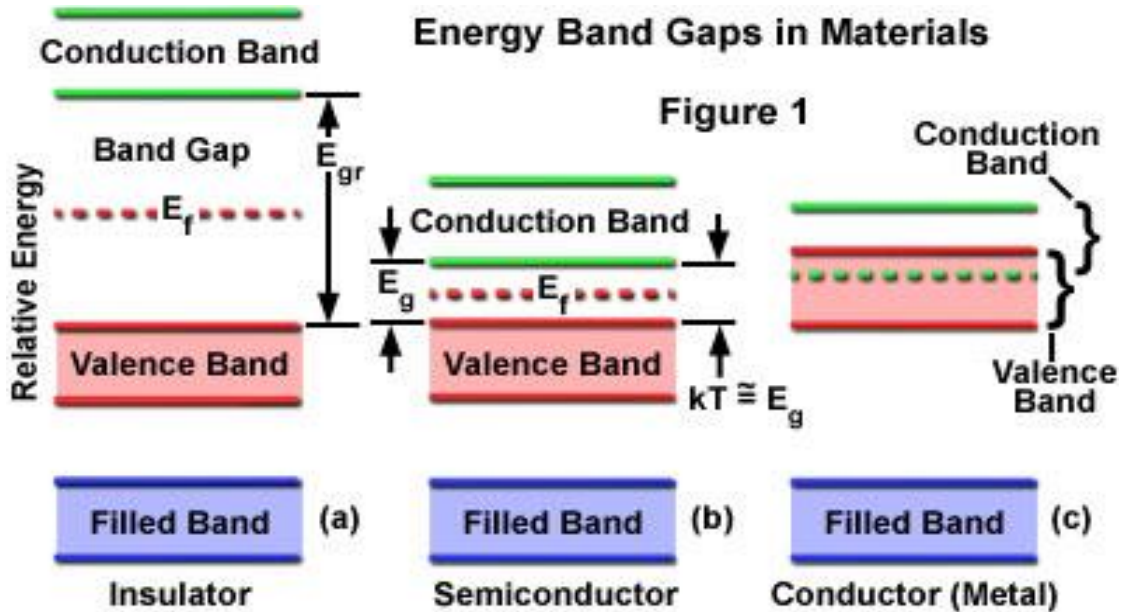


Figure 1.1: Schematic diagram for band theory of materials

If one of the bands is partially filled with electrons, delocalization of the electrons takes place and we end up with metallic conductivity. The fully occupied band is now called

valence band and the closest energy band, which is non-occupied, is named conduction band. This descriptive name is introduced because if any additional energy is given to the valence band electrons may result in delocalization and elevation of such electrons to transmit to the conduction band. According to its width, the energy gap between the conduction and the valence bands determines whether if the material is a conductor, insulator or semiconductor. Wide band gap, which doesn't allow the valence band electrons cross the *forbidden gap*, even in case of thermal conditions, indicates that the material is an insulator. Overlapped conduction band and valence band lead to a conducting material, while relatively narrow band gap, which under thermal conditions allows valence band electrons to cross it up to the conduction band, classifies the material as semiconductor (**Singleton, 2001**). To control the conductivity of the semiconductor of relatively wide band gap, it is required to introduce intermediate energy levels between the conduction and the valence bands. Doping process is one of the successful methods for narrowing the relatively wide band gap of semiconductors.

1.4 Metal Oxide Doping

Balancing between the conductivity and transparency is important since the wide band gap have relatively high carriers concentration in the conduction band would cause absorption of electromagnetic radiation and as it is known the conductivity increasing as thickness of the film increase but that will affect the transparency of the film, introducing doping is the appropriate way to improve each properties (**Edwards *et al.*, 2004**).

The presence of dopant species into a metal oxide can result in n and p-type metal oxide materials, at the n-type one of the basic atoms of the source material will be

exchanged with dopant atom, causing a non-bonding electron that generates a donor energy level near the conduction band. At the p-type an absence of an electron generates an empty acceptor energy level above the valence band that accepts an electron leaving a positive ‘hole’ behind (Ginley, 2000).

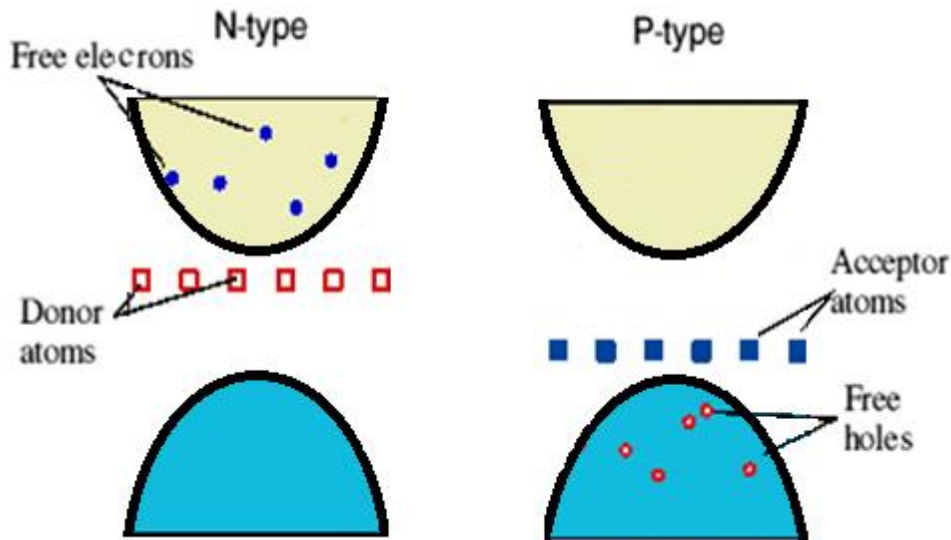


Figure 1.2: Schematic diagram for n-type and p-type semiconductors

1.4.1 n-Type Transparent Conductors

The introduction of small amount of foreign transition or pentavalent atoms into the regular crystal lattice of semiconductor metal oxides create a dramatic change in their electrical properties. These foreign atoms act as donor and creating a free electrons which are free to move through the crystal. Indium oxide, zinc oxide and tin oxide together with dopant materials such as group V in the periodic table and transition metal ions are examples of n-type transparent conducting oxides, as they have excellent electrical conductivity with high optical properties (Pulker, 1999).

Tin-doped Indium oxide is considered as the finest transparent conducting oxide that has been studied and used over the last years. Despite its environmental stability, high electrical conductivity $\sim 10^4 \Omega^{-1} \text{ cm}^{-1}$ and transparency (over 80%), this system has some significant drawbacks due to the high cost and lack of indium. Additional disadvantage of this composition is its diffusion of the films with time which negatively affects the device processing. Due to these drawbacks researchers found alternatives such as doped zinc oxide, which has considerably acceptable characteristics such as non-toxicity, low cost, high performance, and high mechanical stability. All these optimum opto-electrical properties of ZnO made it a promising material for transparent conducting electrodes (**Hosono, 2007**).

N-type transparent conducting oxides are classified under two forms of structure, first form has tetrahedral coordination of oxygen, ZnO is the exclusive well-known oxide that has this coordination. Second family has an octahedral coordination. This is the largest and the most complex family of transparent conducting oxides, such as CdO, In_2O_3 , SnO_2 , $\text{Cd}(\text{In}_2\text{O}_4)$, Cd_2SnO_4 (**Zhang *et al.*, 1999 & Gross *et al.*, 2007**).

1.4.2 P- Type Transparent Conductors

The p-type transparent conducting oxides reported so far generally have less conductivity than that reported for n-type transparent conducting oxides. The large electronegativity of oxygen is the reason behind the strong localization of the valance band edge of oxides by generating a deep trap in the location of the positive hole which does not get affected even under an applied field. It is required for the strong localization of the valance band edge to be decreased or the energy band structure must be adjusted to

increase the mobility of the holes (West, 1999). The importance of developing this kind of transparent conducting oxides helps in transparent electronics, manufacturing of oxide diodes and transistors and contributes to the new electronic devices applications, however, the synthesis of p-type transparent conducting oxides still a challenge. The structure of the p-type transparent conducting oxides shows cationic linear coordination interaction with oxygen, such as CuAlO_2 and SrCu_2O_2 (Song *et al.*, 2008).

1.5 ZnO and its nanostructures

Zinc oxide (ZnO) is well-known II-VI semiconductor that has three crystalline structure; hexagonal wurtzite, cubic zinc-blend, and cubic rock salt. At ambient conditions the stable phase is wurtzite (Fig. 1.3), while the zinc-blend is obtained by appropriate growth on substrates with cubic structure and the rock salt is mainly formed at relatively high pressure (Birkholz, 2006).

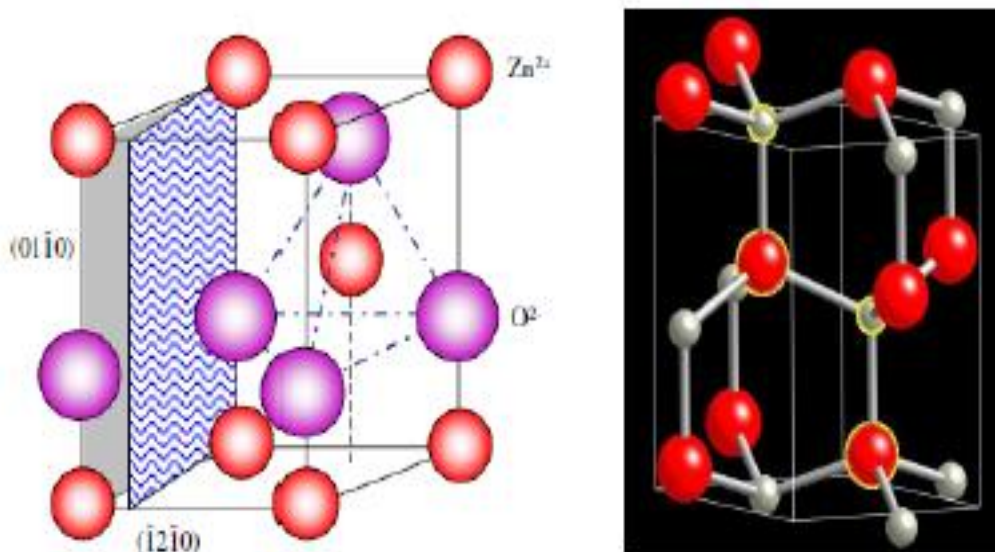


Figure 1.3: Two schematic representations of the ZnO wurtzite crystal structure.

The hexagonal wurtzite phase is the most common stable structure. It is found in nature as zincite, which has a crystal structure with 0.52 nm along c axis, and 0.32 nm along a axis, with ratio $c/a \sim 1.633$ for ideal hexagonal unit cell. In fact the wurtzite structure of ZnO crystal is slightly deviate from the ideal value. Both oxygen and zinc ions form hexagonal-close-packed type sublattice with polar symmetry, the displacement b between the two hexagonal close-packed (hcp) sublattices along the c -axis is 0.375 times the c parameter (Birkholz, 2006).

In the ZnO crystal structure every oxygen atom is surrounded by four zinc atoms arranged at the corners of a tetrahedron, therefore the ZnO structure can be labeled as a sequence of alternating planes consists of coordinated tetrahedral Zn^{2+} and O^{2-} ions, alternated along c -axis. In ideal cell of tetrahedron the angles α and β are 109.47° . In Table 1.1 the wurtzite ZnO lattice parameters are reported, together with some other useful properties.

Undoped ZnO normally shows an n-type conductivity owing to the intrinsic donor defects resulted either from zinc interstitials or oxygen vacancies. The n-type conductivity is simply developed by increasing the existence of oxygen vacancy introduced by doping with In, Ga and Al. Oppositely p-type ZnO is more difficult to be developed. Furthermore the strong piezoelectricity of ZnO is due to the tetrahedral coordination in ZnO crystal structure, the un-centro-symmetric wurtzite structure and the large electro-mechanical coupling. Now the interest is to provide ZnO in nanostructured forms, since it enhances the properties derived from the dimension reduction to nanostructures. It is known that nanostructures have a high surface-to-volume ratio,

therefore critically enhancing the properties related to surface states corresponding to the bulk material or non-nanostructured films (Stradling, 1990).

Table 1.1: Basic physical properties of ZnO at 300 K°.

Parameters	Values
Lattice constants at 300K	a=0.32495nm c=0.52069nm
Density	5.67526 g/cm³
Molecular mass	81.389 g/mol
Melting point	2250 K
Electron effective mass	0.28 m_o
Hole effective mass	0.59 m_o
Static dielectric constant	8.656
Refractive index	2.008-2.029
Band energy gap at 300K	3.37 eV
Exciton binding energy	60 meV
Thermal conductivity	0.6 – 1.16 W/K.m
Specific heat	0.125 cal/g °C
Electron mobility	~ 210 cm²/Vs

In addition, quantum confinement effects (such as quantization of the charge carrier energy levels and possible tuning of the energy gap, that increased probability of the energetic transitions, etc.) may appear when nanostructure dimensions are comparable to the exciton Bohr radius of the constituting material, thus further enhancing the possible efficiency in technological devices. Anyway it must be underlined that quantum confinement effects are hardly obtainable in zinc oxide nanostructures, because of the

very small excitonic Bohr radius of ZnO (~ 1.8 nm). Quantum confinement in ZnO nanostructures has been reported in literature (Solyman & Walsh, 1990).

1.6 Aim of the present status

- Investigation of the influence of the copper dopant on the optical and electric properties of ZnO thin film.
- Investigation of the influence of the aluminum dopant on the optical and electric properties of ZnO thin film.
- Determination of the optimum dopant concentration to attain proper optoelectronic and optical properties.

1.7 Thesis outline

- Chapter one: represents a short introduction about the importance of nanomaterials and nanotechnology followed by brief introduction about transparent metal oxides and general properties of zinc oxide nanostructure as a promising metal oxide.
- Chapter two: gave a review for the optical and electrical properties of the transparent metal oxides and the methods that were used to synthesis different metal oxides and their advantages and disadvantages.
- Chapter three: reported the methods mainly used for synthesis of TCO thin films with focusing on sol-gel dip-coating technique which has been used in

this dissertation. This chapter also showed the instruments used in this work and the conditions at which the samples were characterized.

- Chapter four: in this chapter the copper doped zinc oxide and aluminum doped zinc oxide thin films were characterized by the x-ray diffraction and the scanning electron microscopy. The results showed that the prepared films are homogenous and well distributed along the substrate. These films showed a hexagonal crystalline structure which is the characteristic structure of zinc oxide. A reduction of the lattice constants were observed up to 2 wt% in case of copper doped ZnO and at 1 wt% in case of aluminum doped ZnO thin films. The optical properties of the prepared films were measured via ellipsometry from which the thickness of the film, optical band energy, refractive index, extinction coefficient, and transmittance were determined. The films showed high transparency along the visible region. I-V characteristics for the prepared films showed a linear regression up to 3 Volt. The films achieved very low resistivity at the optimum concentrations of the Cu and Al doped zinc oxide films.
- Chapter five: represents the conclusion for the significant results and recommendation for future work.