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Influence of physical properties on the growth of ZnO for device application

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ABSTRACT

Zinc oxide is an inorganic compound also known as zincite and occurs rarely in nature, generally in a crystalline form. It is usually orange or red in color due to presence of manganese impurity. It usually appears as a white crystalline powder, which is nearly insoluble in water. Most of ZnO which is used commercially is produced synthetically. ZnO is actually a wide bandgap semiconductor of the II-VI semiconductor group. The doping of the semiconductor is n-type which is due to oxygen vacancies. This has several favorable properties like high electron mobility, good transparency, wide bandgap for semi-conductivity, high room-temperature luminescence, etc. These properties are used in applications for electrodes in liquid crystal displays as well as in energy saving and heat protecting windows, electronic applications of ZnO as thin-film transistors and light emitting diodes. Because of its unique properties and versatile applications, it is used in transparent electronics, ultraviolet light emitters, piezoelectric devices and chemical sensors. © 2014 Trade Science Inc. - INDIA

KEYWORDS

ZnO;
Physical;
Electrical;
Optical;
Chemical properties.

INTRODUCTION

Nanotechnology is defined as the study of manipulating matter on the atomic and molecular scale. It covers various areas ranging from conventional device physics to completely new approaches based on molecular self-assembly, from developing materials having dimensions of the nanoscale to finding out whether we can control matter on the atomic scale. It is able to create many new materials with a vast range of applications, such as in medicine, biomaterials, electronics and production of energy. However, nanotechnology raises many concerns about toxicity and impact of nanomaterials on environment and their effects on glo-

bal economics^[1]. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nanoscale size dependent properties are often observed. Thus, the properties of materials generally change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material starts to become significant. For bulk materials larger than one micrometer, the percentage of atoms at the surface is insignificant in comparison to the number of atoms in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large sur-

face area of the material, which dominates the contributions made by the small bulk of the material. Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. Other size dependent property changes in the nanoparticle include quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super paramagnetism in magnetic materials^[2].

The important properties of nanostructured materials have started motivation among scientists to explore the possibilities of using them in technological applications. In particular, the electronic and optical properties of nanostructured materials have been of interest because of their potential applications in the fabrication of microelectronic and optoelectronic devices. As nanotechnology progresses and complex nanosystems fabricated, a rising impetus is being given to the development of multi-functional and size-dependent materials. Recent developments in nanoscience and nanotechnology have brought potential building blocks for a noscale electronic, optoelectronics, medicines and solar cells^[3]. The surface-to-volume ratio increases as the material dimension decreases to nano-order. The high surface-to-volume ratio of nanomaterials has significant implications with respect to energy storage density. Additionally, nanomaterials are found to be superior catalyst for hydrogen storage materials^[4]. Among the nanostructured metal oxides, zinc oxide (ZnO) is considered to be one of the best metal oxides that can be used at a nanoscale level. ZnO itself has normally a hexagonal or wurtzite structure and it is well-known as an n-type II–VI semiconductor with a wide direct band-gap of about 3.37 eV and a large exciton binding energy of 60 meV^[5]. From this point of view, nanostructured ZnO powders display a great power in many applications such as gas sensors, solar cells, varistors and photocatalyst with high chemical activity. Recently, extensive progress has been made on the research front of ZnO-based nanomaterials motivated by both basic sciences and potential advanced technologies^[6-11].

ZnO nanomaterials have been studied for the benefits associated with quantum confinement including reduced dark noise, increased absorption efficiency and the potential for large area and lower cost devices. The

nanostructures, however; often exhibit a strong, parasitic green photoluminescence caused by excess Zn²⁺ ions and oxygen deficiency^[12]. Solutions to these problems include developing effective surface modification, annealing treatment and producing stable ZnO quantum dots (QDs) that are unagglomerated, highly crystalline and monodisperse^[13]. The ability to create reproducible Ohmic or Schottky contacts is also associated with oxygen vacancies. These vacancies often dominate which tend to pin the ZnO Fermi level to the defect level, hindering the expected barrier producing relationship between the contact metal and semiconductor^[14].

PHYSICAL PROPERTIES

Molecular Weight of ZnO is 81.37 g/mol. Pure microcrystalline ZnO is white in colour and single crystal ZnO is colourless. ZnO turns lemon yellow on heating and reverts to white on cooling. The relative density of ZnO is 5.607. ZnO sublimates at atmospheric pressure at temperatures over 1200°C and under high pressure a melting point of 1975°C has been estimated.

The vapor pressure of ZnO at 1500°C is 12mm. The refractive index of ZnO is $w = 2.004$ and $e = 2.020$.

Crystal structure

ZnO has the wurtzite hexagonal crystal structure. Commercial ZnO show this crystal structure only under electron microscopic examination. The precise shape of the crystal depends on the method of formation. In regular zinc oxide these vary between acicular needles and plate shaped crystals. ZnO can be induced to form a very large variety of crystalline shapes using specialized deposition methods, which is currently a very active area of research. ZnO usually crystallizes in three different forms: hexagonal wurtzite, cubic zinc blende and cubic rock salt which are shown in Figure 1. The latter is the most rarely found. The wurtzite structure is most stable at ambient conditions and is hence most common^[15].

Mechanical properties

ZnO is a relatively very soft material with approximate hardness just 4.5. Its elastic constants are relatively smaller than those of other III-V semiconductors. The high heat capacity and high heat conductivity,

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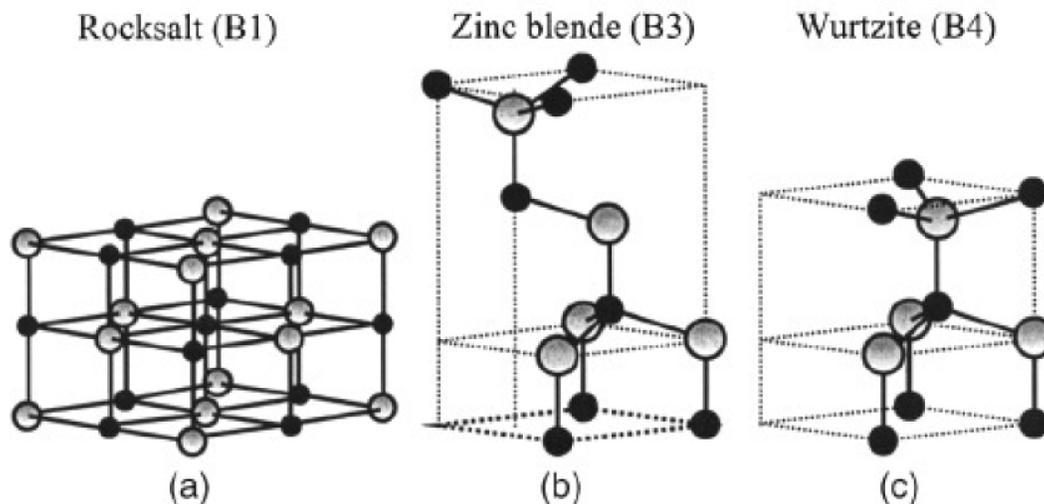


Figure 1 : Stick and ball representation of ZnO crystal structure; black and gray spheres denote Zn and O atoms

low values of thermal expansion and high melting points are some of the characteristics of ZnO. ZnO has been proposed to be a more promising UV emitting phosphor than GaN because of its larger exciton binding energy. Among the semiconductors bonded tetrahedrally, it's found that ZnO has the highest piezoelectric tensor. This makes it an important material for many piezoelectric applications, which require a high degree of electromechanical coupling among them^[16].

Piezoelectric effect and polar surfaces

Piezoelectricity of ZnO has been extensively studied for various applications in force sensing, acoustic wave resonator, acousto-optic modulator, etc. The origin of the piezoelectricity lies due to its crystal structure, in which the oxygen atoms and zinc atoms are tetrahedrally bonded. In such a structure which is non centrosymmetric, the center of positive charge and negative charge can be displaced due to external pressure induced lattice distortion. This displacement results in local dipole moments, thus a macroscopic dipole moment appears over the entire crystal. In fact, among the tetrahedrally bonded semiconductors, ZnO has the highest tensor which provides a large electro-mechanical coupling^[17]. Another result of the non-centrosymmetric ZnO crystal structure is its spontaneous polarization and polar face dominated nanostructures. The crystal structure of ZnO can be visualized in a way that oxygen atoms and zinc atoms are tetrahedrally bonded. These tetrahedrons stack along a particular direction. Due to the effect of spontaneous polarization, the position of

positive charge is displaced from that of negative charge in that fixed particular direction. The net result of this spontaneous polarization is a charged ZnO surface. In order to achieve minimized energy, the charged surface results in unique nano-ring and nano-coil structure.

ELECTRICAL PROPERTIES

The fundamental study of the electrical properties of ZnO nanostructures is crucial for developing their future applications in nanoelectronics. ZnO has a quite large band gap of 3.37 eV at room temperature. The advantages of a large band gap include higher values of breakdown voltages, sustaining large electric fields, high-temperature and high-power operations. ZnO has n-type character, in the absence of doping. Non-stoichiometry is usually the origin of n-type character. Due to defects such as oxygen vacancies and zinc interstitials, ZnO nanowires are reportedly show n-type semiconductor behavior. The main impediment of ZnO for wide-ranging applications in electronics and photonics rests with the difficulty of p-type doping. Successful p-type doping for ZnO nanostructures will greatly enhance their future applications in nanoscale electronics and optoelectronics. P-type and n-type ZnO nanowires can serve as p-n junction diodes and light emitting diodes (LED)^[18].

OPTICAL PROPERTIES

ZnO is generally transparent to visible light but

strongly absorbs ultra violet light below 3655⁰A. The absorption is typically stronger than other white pigments. In the region of visible wavelengths, regular ZnO appears white, but rutile and anatase titanium dioxide have a higher reactive index and thus has a superior opacity. The band gap energy is 3.2 eV; this corresponds to the energy of 3655⁰A photons. Under ultra violet light zinc oxide is photoconductive. The combination of optical and semiconductor properties make doped zinc oxide a contender for new generations of devices. Solar cells require a transparent conductive coating, indium tin oxide and ZnO (doped) are the best materials. Intrinsic optical properties of ZnO nanostructures are being intensively studied for implementing photonic devices. Photoluminescence spectra of ZnO nanostructures have been extensively reported. Excitonic emissions have been observed from the photoluminescence spectra of ZnO nanorods. It is shown that quantum size confinement can significantly enhance the exciton binding energy. Strong emission peak at 380 nm due to band-to-band transition and green-yellow emission band related to oxygen vacancy are observed. PL spectra show that ZnO nanowire is a promising material for UV emission, while its UV lasing property is of more significance and interest. Due to its near-cylindrical geometry and large refractive index (~2.0), ZnO nanowire/nanorod is a natural candidate for optical waveguide. The additional advantages of ZnO nanowire lasers are that the excitonic recombination lowers the threshold of lasing and quantum confinement yields a substantial density of states at the band edges and enhances radiative efficiency. Optical waveguiding using dielectric nanowire also achieved considerable progress. Recently, ZnO nanowires were reported as sub-wavelength optical waveguide. Optically pumped light emission was guided by ZnO nanowire and coupled into SnO₂ nanoribbon. These findings show that ZnO nanostructures can be potential building blocks for integrated optoelectronic circuits^[19].

CHEMICAL PROPERTIES

ZnO occurs as the mineral zincite or as white powder known as zinc white. It is usually orange or red in colour due to manganese impurity. Crystalline ZnO is thermochromic, which changes from white to yellow

colour when heated and reverting to white colour on cooling. This change in colour is caused by a very small loss of oxygen at high temperatures. ZnO is amphoteric, that is it reacts with both acids and alkalis. With acid it reacts to form familiar compound such as zinc sulfate. With alkali it forms zincates. ZnO decomposes to form zinc vapor and oxygen at about 1975⁰A °C, indicating its considerable stability. Heating with carbon converts ZnO into Zn, which is more volatile. Commercial ZnO shows a measurable but low level of water solubility, 0.005 g/litre. ZnO exposed to air absorbs both water vapour and carbon dioxide^[20].

CONCLUSIONS

The, the properties of materials generally change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material starts to become significant. Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. Other size dependent property changes in the nanoparticle include quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super paramagnetism in magnetic materials. ZnO is considered to be one of the best metal oxides that can be used at a nanoscale level. ZnO itself has normally a hexagonal or wurtzite structure and it is well-known as an n-type II-VI semiconductor with a wide direct bandgap of about 3.37 eV and a large exciton binding energy of 60 meV. For this reason, nanostructured ZnO powders display a great power in many applications such as gas sensors, solar cells, varistors and photocatalyst with high chemical activity.

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