Review Article on ZnO thin films by Spray Pyrolysis

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Abstract

Zinc Oxide (ZnO) is a semiconductor with a wide band gap equal to 3.37 eV & large exciton binding energy. It has excellent chemical and thermal stability, low cost, richly abundant, environment-friendly, non-toxic nature, strong oxidizing power, high photosensitivity, and high resistance to radiation damage. ZnO is an attractive material for applications in electronics, photonics, acoustics, and sensing. Thin films of ZnO may be manufactured by spray pyrolysis technique. In this article doped and undoped thin films of ZnO synthesized by spray pyrolysis are discussed. Doping of ZnO thin films changes the properties of ZnO thin films.

Keywords- ZnO thin films, optoelectronics, spray pyrolysis technique.

1. INTRODUCTION

The II-VI compound semiconductors are of great importance due to their applications in various electro-optic devices. In materials science, Zinc oxide (ZnO) is called II-VI semiconductor because zinc and oxygen belong to the 2nd and 6th groups of the periodic table, respectively. It usually appears as a white powder, nearly insoluble in water. Zinc oxide (ZnO) is a wide bandgap (3.3 eV at room temperature) semiconductor that is desirable for many applications. It is attractive for forming various forms of nanostructures, such as nanorods, nanowires, and nanobelts [1]. Transparent transistors fabricated from ZnO have been reported. With its high exciton binding energy, ZnO is a good candidate for room temperature UV lasers. Its large piezoelectric constant is promising for ultrasonic transducers. ZnO is transparent and electrically conductive, making it an ideal material for solar cell windows. The mineral form of ZnO can be found in nature and is known as Zincite. Zinc oxide has the hexagonal wurtzite structure. ZnO nanomaterials are promising candidates for nanoelectronic, optoelectronic and solar cells devices [2]. Compared with other semiconductor materials, ZnO has higher exciton binding energy (60 meV), is more resistant to radiation, and is multifunctional with uses in the areas as a piezoelectric, ferroelectric and ferromagnetic. ZnO based semiconductor and nanowire devices are also promising for the integration on a single chip. So far, the various applications of ZnO nano-materials such as biosensors and UV detectors.

2.1 Addition of dopant

The process of adding controlled impurities to asemiconductor is known as doping. The amount of impurity, or dopant, added to an intrinsic (pure) semiconductor varies its level of conductivity. Doped semiconductors are often referred to as extrinsic. By adding impurity to pure semiconductors, the electrical conductivity may be varied not only by the number of impurity atoms but also, by the type of impurity atom.The materials chosen as suitable dopants depend on the atomic properties of both the dopant and the material to be doped. In general, dopants that produce the desired controlled changes are classified as either electron acceptors or donors. A donor atom that activates donates weakly bound valence electrons to the material, creating excess negative charge carriers. These weakly bound electrons can move about in the crystal lattice relatively freely and can facilitate conduction in the presence of an electric field. The donor atoms introduce some states under, but very close to the conduction band edge. Electrons at these states can be easily excited to the conduction band, becoming free electrons, at room temperature. Conversely, an activated acceptor produces a hole. Semiconductors doped with donor impurities are called n-type, while those doped with acceptor impurities are known as p-type[3]. The n and p type designations indicate which charge carrier acts as the material's majority carrier. The opposite carrier is called the minority carrier, which exists due to thermal excitation at a much lower concentration compared to the majority carrier.

2.2 Characteristics of Thin Films

The properties of thin film changes appreciably when it is cooled to a very low temperature or heated at a higher temperature (above room temperature). The study of the changes in the properties of thin film with temperature provides a great deal of information about the properties of thin films. In general the physical properties of thin film are determined by a number of factors, such as

2.3 The nature of substrates

It may be non-crystalline solids e.g., glass of vitreous silica or crystalline such as cleavage plates of rock salt or mica. To select a particular substrate one has to take into consideration of the lattice parameter of the substrate so that it matches to the lattice parameter of the grown film, otherwise structural mismatch may create mechanical fracture in the film. It is also necessary to consider the melting point of the substrate material. It should be comparable with that of the film materials.

2.4 Substrate temperature

The temperature of substrate during deposition of film may affect the film properties. At low temperature polycrystalline films with high densities of structural imperfections are formed on both vitreous and crystalline substrate, but a high temperature oriented single crystal films are formed on crystalline substrates.

2.5 Deposition rate and film thickness

The temperature at which epitaxy occurs is dependent on the deposition rate. Substrate temperature decreases with increasing deposition rate. Film thickness mainly depends on deposition rate and deposition time. If the deposition rate increases, the film thickness also increases having the same deposition time.

2.6 Post-deposition annealing of the films

Heating the film to a higher temperature after deposition and cooling it back to room temperature is known as annealing. Properties of the deposited films are related to the annealing temperature. The post-annealing process removes some defects of the films. It plays an important role in the surface mobility of the atoms.

3. Application Areas of Thin Films

Thin films are widely used in today's technology, and their applications are expected to be even more widespread in future. Thin films are of current interest owing to their potential use in light emitting

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diodes and laser diodes. Besides this other photo-electronic device e.g., photovoltaic solar cells, photoconductive devices, light-emitting diodes, coatings, sensors, integrated components for telecommunication etc., are now under active consideration of the experimental physicists. In recent time popular utilization of this films as the absorber of the solar cells.

4. Crystal structure of Zinc oxide

Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zincblende, and the rarely observed cubic rocksalt. The wurtzite structure is most stable at ambient conditions and thus most common. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral. Hexagonal and zincblende polymorphs have no inversion symmetry . This and other lattice symmetry properties result in piezoelectricity of the hexagonal and zincblende ZnO[4].

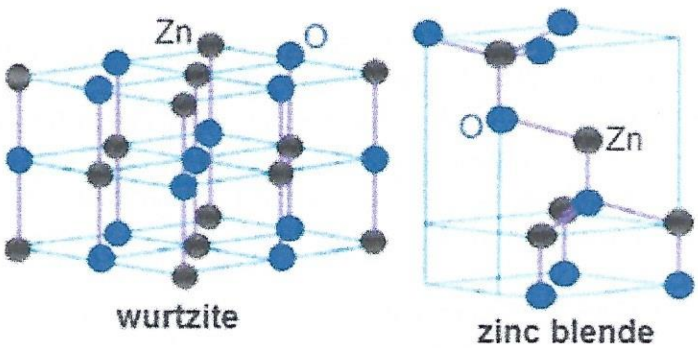

Figure1. structure of ZnO

5. Fe doped ZnO thin films

Among the transition metal dopants, iron (Fe) is chemically stable and exists in two possible oxidation states, Fe^{2+} and Fe^{3+} having ionic radii (0.78 Å and 0.64 Å) close to ionic radius of Zn2+ (0.74 Å). Thus, it can easily enter into Zn lattice sites either substitutionally or interstitially without disturbing the crystal structure of ZnO and can contribute more charge carriers in order to improve its conductivity. Hence, few research groups have studied the characteristics of Fe-doped ZnO films synthesized by various physical and chemical techniques like RF and DC magnetron sputtering sol-gel, spray pyrolysis [5], hydrothermal process, electrodeposition and dip coating technique . Although Fe-doped ZnO films can be grown using different methods . Hence, a simple, vacuum free and cost effective spray pyrolysis method is used to deposit the Fe-doped ZnO thin films.

6. Al doped ZnO thin films

Aluminium doped zinc oxide thin films can be deposited on glass substrate by using spray pyrolysis technique. The X-ray diffraction study of the films revealed that the both the undoped and Al doped ZnO thin films exhibits hexagonal wurtzite structure[6]. The preferred orientation is (002) for undoped and up to 3 at % Al doping, further increase in the doping concentration to 5 at % changes the preferred orientation to (101) direction. The surface morphology of the films studied by scanning electron microscope, reveal marked changes on doping[7]. Optical study indicates that both undoped and Al doped films are transparent in the visible region. The band gap of the films increased from 3.24 to 3.36 eV with increasing Al dopant concentration from 0 to 5 at % respectively. The Al doped films

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showed an increase in the conductivity by three orders of magnitude with increase in doping concentration[8]. The maximum value of conductivity 106.3 S/cm is achieved for 3 at % Al doped films.

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