ISSN: 2321-8169
2240 – 2245

An Extensive Study of Main Issues and Techniques to Tenderize the Structural, Electricals, Optical and Magnetic Properties of Thin Films

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Abstract: Nano has made a significant role for the development of the semi conductor materials. It has offered tremendous innovation in semiconductor industry also. present paper discuss about the various processing and process for determining the issues and techniques to tenderize the structural, Electricals, optical and magnetic properties of thin films The most interesting properties of ZnO are its wide band gap and its high exitonic binding energy (60 meV) at room temperature which is much higher than that of ZnSe (20 meV), GaN (21meV). Because of this, it is expected that ZnO based devices will be more efficient. It also has peizo electric properties. It is unique having semi conducting, piezoelectric, and pyro-electric properties. Historically it is used as white pigment in watercolour and paints, and also an activator in the rubber industry. Further, Today it is expected that it can be used in fabrication of Solar cells ,Laser Diode ,UV-lasers,Thin film transistors, Transparent conductive contacts ,Surface acoustic wave devices ,Thin film gas sensors

Key Words: *Tenderize, quartz optical fiber , nanotubes , nanowires , nanorods , nanobelts , nanocables , and nanoribbons , Sintering, . Binding ,Surface diffusion (larger than bulk diffusion). Nucleation , Island growth , Coalescence ,Continued growth Physisorption , chemisorptions, weak Van der Waal forces*

Organisation of the paper: *[present paper main issues and techniques to tenderize the Structural,Electricals and magnetic properties has been classified into 7 topics, starting from the Introduction, followed by Topic 2 about literature review and study of thin films,Topic 3 is all about synthesis and analytical mechanism of thin films, Topic 4 various type of films. Topic 5 is all about of introduction of Zno. Followed by Topic 6 is about present work and motivation,Topic 7 is References and at last is about the author]*

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1.0 Introduction

Now a days, the Revolution has been made semi conductor industry . the `products of semiconductor industry are spread all over the world and deeply penetrate into the daily life of human being. The starting point of semiconductor industry was the invention of the first semiconductor transistor at Bell Lab in 1947. Since then, the semiconductor industry has kept growing enormously. In the 1970's, the information age of human being was started on the basis of the stepwise appearance of quartz optical fiber, III-V compound semiconductors and gallium arsenide (GaAs) lasers. During the development of the information age,silicon (Si) keeps the dominant place on the commercial market, which is used to fabricate the discrete devices and integrated circuits for computing, data storage and communication. Since Si has an indirect band gap which is not suitable for optoelectronic devices such as light emitting diodes (LED) and laser diodes, GaAs with direct band gap stands out and fills the blank for this application. As the development of information technologies, the requirement of ultraviolet (UV)/blue light emitter applications became stronger and stronger which is beyond the limits of GaAs. Therefore, the wide bandgap semiconductors such as SiC, GaN and ZnO, i.e. the third generation semiconductors, come forth and turn into the research focus in the field of semiconductor.

On one hand, the popularity to a large extent is due to the improvements in growth of high quality, single crystalline ZnO in both epitaxial layers and bulk form. On the other hand, especially since the emergence of the nanotechnology, novel electrical, mechanical, chemical and optical properties are introduced with the reduction in size,which are largely believed to be the result of surface and quantum confinement effects. Study of one dimensional (1D) materials has become a leading edge in nanoscience and nanotechnology. ZnO is a versatile functional material. 1D ZnO nanostructures such as nanotubes [17], nanowires [18], nanorods [19], nanobelts [20], nanocables [21], and nanoribbons [22] stimulate considerable interests for scientific research due to their importance in fundamental physics studies and their potential applications in nanoelectronics, nanomechanics, and flat panel displays. Particularly, the optoelectronic device application of 1D ZnO nanostructure becomes one of the major focuses in recent nanoscience researches [23-25]. During the last decade, ZnO epilayer, ZnO nanorods and various ZnO nanostructures have been grown by various techniques. A major advantage for ZnO nanostructures, e.g. nanowires and nanorods, is that they can be easily grown on various substrates and non-lattice materials including flexible polymers. In addition, ZnO nanorods can be advantageous with a low density of defects. The growth of defect-free structures is more likely for nanorods in comparison with epilayers, since the strain in the nanorods can be efficiently relieved by elastic relaxation at the free lateral surfaces rather than by plastic relaxation.

In order to utilize the applications of nanostructure materials, it usually requires that the crystalline morphology, orientation and surface architecture of nanostructures can be well controlled during the preparation processes. However, it can also be a problem in other applications, for example, optoelectronic devices such as light emitting diodes and solar-cell devices, since the surface recombination rate may become dominating, resulting in a short carrier life time. So far, the knowledge about surface recombination in ZnO nanostructures is limited.

2.0. Literature Review and study on Thin film.

"Thin" is relative term but in general the layer of a material on a substrate with thickness less than 1000nm is known as thin film [1]. Thin films technology plays an important role in semiconductor technology as semiconductor industry demands for development of smaller and smaller devices especially in new generation of integrated circuit. Besides that, the thin films also have applications outside semiconductor technology which are summarized in the Table 1.1. Therefore, knowledge and determination of the nature, functions and new properties of thin films can be used for the development of new technologies for future applications. [2]

Table.1.1: Application areas of thin films other than semiconductor technology.

Application area	Examples
Optics	Antireflection coating; on lenses or solar cells, reflection coatings for mirrors. Coatings to produce decorations (colour, lustre), Interference filters. Photosensitive coating of "analog" film for old camera.
Chemistry	Diffusion barrier protection against corrosion / oxidation. Sensors for liquid / gaseous chemicals.
Mechanics	"Hard" layers (e.g. on drill bits).
	Adhesion providers. Friction reduction.
Magnetics	Hard "discs", Video / Audio tape."*SQUIDS*"
Electricity (without semiconductors)	Insulating / conducting films; e.g. for resistors, capacitors. Piezoelectric devices.
Thermal	Barrier layers, Heat sinks

2.1 Properties: Properties of thin films are different then that of bulk material. Some of them are often far better than those of bulk. This may be due to the fact that thin films;

1. are not fully dense.2. are under stress.3. have different defect structures than bulk .4. have *quasi* two dimensional .5. are strongly influenced by surface and interface

The important properties of thin films are the optical, mechanical, chemical, electrical and thermal behaviour. Optical properties include indices of refractions, absorption coefficient, non-liner optical properties. Mechanical properties include elastic module, plastic deformation, and internal stress / strain. Chemical properties include corrosion resistance in various ambient and reactivity situations. Electrical properties include conductivity, carrier mobility, hall coefficient, carrier type and concentration, work function, dielectric breakdown field, critical current density, dielectric function. Thermal properties include thermal expansion coefficient, thermal conductivity, specific heat, thermoelectric coefficient.

3.0 Synthesis and Analytical mechanism of thin films.

There are three possible events when an incoming species hit the substrate.

1. The atom may be just reflected from the substrate and then runs to infinity.

 ISSN: 2321-8169
2240 – 2245

2. The atom may be just reflected from the substrate and then hits an incoming atom and is redirected to the substrate.

3. The atom may loosely bind to one or two of the substrate atoms. This is known as binding or absorption of atoms.

The steps in thin film formation are as follows

1. Binding (Physisorption and Chemisorption)

2. Surface diffusion (larger than bulk diffusion)

3. Nucleation

4. Island growth

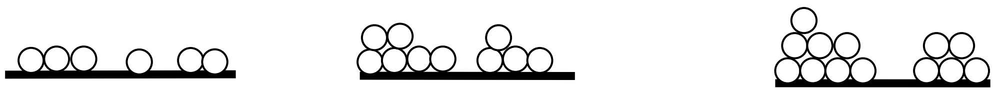
5. Coalescence

6. Continued growth

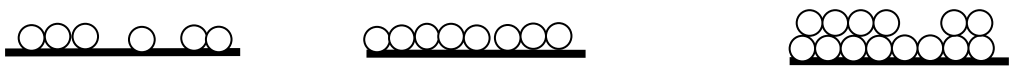
There are two kind of absorption processes (1) Physisorption (2) chemisorption. Physorption is the process in which, incoming atoms are attached to one or two of substrate atoms by weak Van der Waal forces. Physisorption is achieved under super saturation condition. Due to high density of atoms, under super saturation condition, the atomic distance is so small that Van der Waal forces come into the picture. Condensation occurs because of Van der Waals forces. Deposition rate is directly proportional to the pressure and inversely proportional to square root of absolute temperature. After absorption, atom is known as adatom. Physisorbed atom may jump to suitable position in its neighbourhood. This is known as diffusion of atom in two dimensional surfaces. Atoms diffused on the surface in order to find each other and epitaxial (or most active site). At suitable site, physisorbed atom is chemisorbed by strong bounding.

Chemisorptions will happen when incoming atoms bind by one of the strong bonding mechanisms. An adatom has positive absorption energy E_a relative to zero energy in the vapour. The adatom can diffuse on the surface with migration barrier energy E_d. Surface diffusion is more probable event than desorption as $E_d < E_a$. During the course of diffusion, adatoms can find each other and form clusters of atoms mostly at irregularities of surface such as steps or vacancy. This is initial phase of layer growth, known as nucleation. After nucleation the next step is growth. There are three different growth modes.

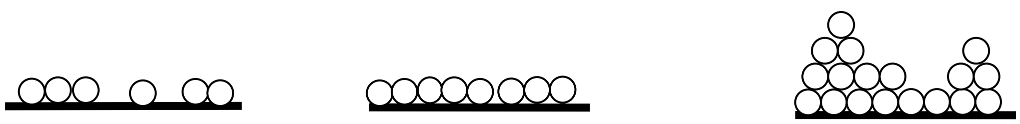
3.1Volmer- weber: - This is also known as island growth. Island can be formed when bond between atoms are stronger than that of between atom and substrate. Slow diffusion rate is also responsible for island formation.



3.2 Frank- Van der Merwe:- This is layer by layer growth of film. This situation arises when bond between atoms are weaker than that of between atom and substrate. Fast diffusion rate is also responsible for this.



3.3 Stranski-Krastanov: - This is known as mixed growth mode. In this mode initially there is layer by layer mode and then Island is formed.

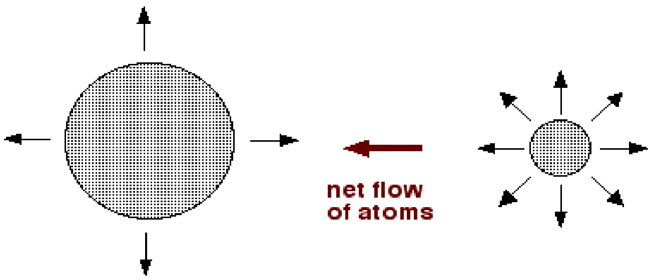


When density of island increases, the mean free path of diffusing adatom is equal to the island separation. In this case adatom will attach itself with much higher probability to existing islands than to create new ones. Approaching coverage of about half a monolayer, islands eventually coalesce which decreases their density.

There are three common mechanisms for island coalescence.

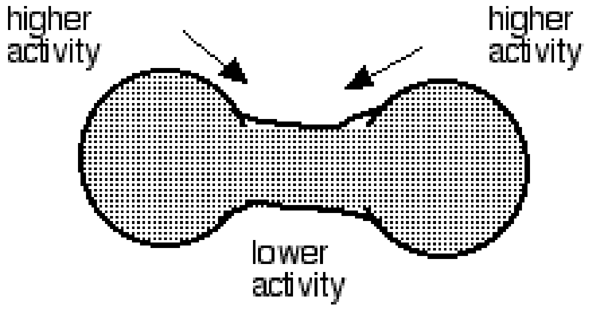
3.4 Oswald ripening

The basic principal of Oswald ripening is based on the curvature of island. More convex curvature implies higher activity of atoms and hence more escape of atoms. As atoms leave small islands more readily than large islands, the atoms forming small cluster will move towards large cluster.



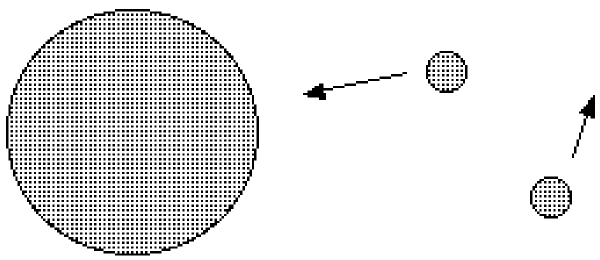
3.5. Sintering

The principal of this mechanism is based on the fact that group of small clusters have large surface energy than that of one large cluster of same volume. Therefore small clusters combine to form a large cluster in order to achieve more stable state of minimum surface energy.



3.2 Cluster migration

Small clusters move randomly and absorbed by larger clusters.



After coalescence there is continuous growth in the film.

4.0 Type of Films

There are three types of thin films

1. Amorphous: Films have disordered atomic structure.
2. Polycrystalline: Films are made of many tiny crystalline grains of materials
3. Single crystal: All parts of films have same crystallographic orientation.

4.1 Thin Film deposition methods

The act of applying a thin film on a surface is known as thin film deposition. We can divide deposition methods in two broad categories.

(a) Physical method

(b) Chemical methods.

5.0 Introduction of ZnO

Knowing the importance of thin films particularly in semiconductor industry, we have plan to work with semiconductors. We have opted to work with wide band gap semiconductor materials because the conventional semiconductors like Silicon (Si) and Germanium (Ge) can not operate at high power and temperature due to their small band gap. Wide band gap materials are capable to operate at high power and temperature condition. There are many wide band gap materials like GaN, ZnS, ZnSe etc. but we focused on Zinc oxide, a II-VI compound semiconductor material, because it has some advantages over other wide band gap semiconductor materials. Such as [3,4]

a. Wide and direct Band gap (3.34 eV)
b. Exitonic binding energy (60 meV)
c. Low toxicity
d. Thermal and chemical stability.
e. Bio degradable and bio compatible.

Table 1.2: Comparison of exciton binding energy of different semiconductors.

Wide band gap semiconductors	**Exciton binding energy (meV)**
ZnO	60
GaN	21
ZnSe	20
ZnS	36

Exciton binding energy of other wide band materials are tabulated in Table 1.2.[5,6] Normally all II-VI compound semiconductor crystallize in two phase cubic zinc blende and hexagonal wurtzite hence ZnO (fig.1.1). In cubic zinc blende zinc atoms reside at all the corners and face centres of the cube. Oxygen atoms arrange themselves at four of tetrahedral sites. In the hexagonal wurtzite structure, each is surrounded by four cations at the corners of a tetrahedron and vice versa. This tetrahedral coordination is a typically sp^3 covalent bonding. Besides having covalent bonding, ZnO has a substantial ionic character. In fact ZnO is a compound whose ionicity resides at borderline between covalent and ionic semiconductor. Besides having cubic zinc blende and hexagonal wurtzite structure ZnO is also found in cubic rocksalt structure. Thermodynamically most stable state at room temperature is wurtzite. The zinc-blende structure can be obtained by growing ZnO on cubic substrate and rock salt phase stabilized under high pressure conditions.

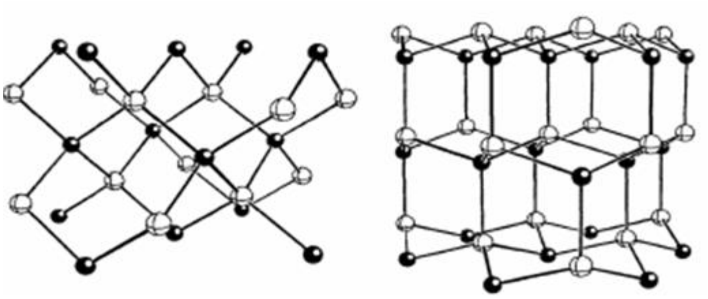


Figure 1.1. Crystal structures of ZnO : Cubic zinc blende and hexagonal wurtzite

5.1 Application of ZnO

The most interesting properties of ZnO are its wide band gap and its high exitonic binding energy (60 meV) at room temperature which is much higher than that of ZnSe (20 meV), GaN (21meV). Because of this it is expected that ZnO based devices will be more efficient. It also has peizo electric properties. It is unique having semi conducting, piezoelectric, and pyro-electric properties. Historically it is used as white pigment in watercolour and paints, and also an activator in the rubber industry. Today it is expected that it can be used in fabrication of [7-12]

- Solar cells
- Laser Diode
- UV-lasers
- Thin film transistors
- Transparent conductive contacts
- Surface acoustic wave devices
- Thin film gas sensors

6.0 Present work and motivation

Knowing the utility of thin films and properties of ZnO it was very fascinating to pay attention to the synthesis techniques and properties of ZnO thin films. Although there are several reports available on study of ZnO synthesis by different methods and its properties but still there remain some unanswered questions. For example origin of red and green luminescence is still controversial fact. Lacking of p-type ZnO is also a big issue. In the present thesis we have tried to study ZnO with the help of swift heave ions. The uniqueness of present work lies on the selection of synthesis process and ion species and energy of ions used for SHI irradiation.

Swift heavy ions widely utilized for modification of the properties of the material by depositing enormous amount of energy in to the material and make it attractive for device applications. More than half a century has passed already since the advancement of the field of ion-solid interaction to the state-of -art that we know today. Ion beam effect on the materials depends on the ion energy, fluence and ion species. Few reports are available on modification of properties of ZnO by SHI.

D.C. et al.[3] has deposited ZnO films with a thickness of 120 nm on Si and quartz by electron beam evaporation at the substrate temperature of 300 °C. The samples were irradiated with 100 MeV Ag ions at different ion beam fluences of 1×10^{10}, 7×10^{10}, 1×10^{11}, 3×10^{11}, 7×10^{11}, 1×10^{12}, 3×10^{12}, 7×10^{12}, and 1×10^{13} ions cm^{-2}. Self-affine nanostructures have been produced on the surface of ZnO thin film via the SHI irradiation at normal incidence and atomic force microscopy_AFM was used to investigate these structures.

D.C. et al [13] also done Optical and structural studies on ZnO films by SHI. Highly c-axis oriented ZnO films (120 nm thick) were deposited by e-gun evaporation and were irradiated by 100 MeV Au ions at different fluence from 5×10^{11} ions/cm^2 to 5×10^{13} ions/cm^2. XRD and AFM results reveal that at low fluence, the film quality is improved as line arrangement of grains is achieved and roughness is reduced due to the strain relaxation between the grains. But at higher fluence, the disordering induced agglomerations of grains was observed. Further, they observe that the roughness of the surface increased. they have concluded from absorption spectra and FTIR analysis that the basic lattice of ZnO and bonding were not modified due to the irradiation. The photoluminescence measurement showed that the luminescence property had been modified. There was blue shift in the PL of irradiated samples due to the creation of anti-site oxygen or oxygen vacancies. We, therefore, conclude that the films should be irradiated at low fluence to improve the films quality.

ZnO films, prepared using chemical spray pyrolysis (CSP) technique, were irradiated using 120 MeV Au ion beams with fluences 1×10^{12}, 3×10^{12}, 1×10^{13}, and 3×10^{13} ions/cm^2 by P. M. Ratheesh Kumar et al.[15]. Thickness of film is found to be .54 μm.Changes in the structural, optical, and electrical properties after irradiation were characterized using x-ray diffraction, x-ray photoelectron spectroscopy, optical absorption and transmission, photoluminescence, and electrical resistivity measurements. Optical absorption edge remains unaffected after irradiation. PL and XRD peak intensities decreased after irradiation with swift heavy ions. As ion fluence increases resistivity was found to be decreased and carrier concentration increased. These results indicate that more and more oxygen vacancies were created due to irradiation.

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