

A Study of Electro-Optic Materials Properties towards Multifunctional Materials

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ABSTRACT

The push towards miniaturization and higher speeds in electronic devices has spurred a search for the identification and development of new multifunctional materials. Materials exhibiting more than single electrical, optical, magnetic, elastic, or other characteristic response, are known as multifunctional materials. These materials provide the possibility of integrating multiple functional properties, along with entirely new properties arising from cross-coupling, into a single system. Such multifunctional materials can be classified into a large number of systems including compound semiconductors, dilute magnetic semiconductors, colossal magneto resistive materials multiferroic materials. As a specific example of how multifunctional materials can be used to develop new devices, we consider new compound semiconductors for optoelectronic applications. Si, elemental semiconductor, was crucial for building the modern electronic industry. However Si is an indirect band gap semiconductor and thus is not an efficient light emitter or absorber. Photovoltaic and optoelectronic devices require a strong interplay between photons and electrons. Direct bandgap semiconductors are more suitable for such applications which show strong absorption or emission for the desired electromagnetic spectral range. III-V and II-VI compound semiconductors are widely used in optoelectronic devices e.g. infrared and visible light emitting diodes (LEDs), optical fiber communications and high efficiency solar cells, precisely because of the stronger coupling between the semiconducting and optical properties in these materials.

1. Introduction

Multi-functional spintronic materials having, for example, a strong coupling between the electron spin and the optical response, may offer other potential applications including quantum bits for quantum teleportation, quantum computation and communication, modulators, high frequency operating optical switches etc [6, 7]. Multifunctional materials having both semiconducting and ferromagnetic properties simultaneously, can potentially bridge the gap between data communication and data storage devices. These different materials properties can co-exist in undoped and transition metal doped compound semiconductors, called dilute magnetic semiconductors (DMS)[4, 5]. These materials open up the possibility of integrating the electron spin degree of freedom into the conventional charge-based electronic devices. As a further example, transistors based on semiconducting Si are used for data processing, while data storage is accomplished using ferromagnetic hard drives with the magnetic information being extracted using magnetic multilayers GMR (Giant Magneto resistance) structures as read heads, allowing their large storage capacity [3]. This proposal to utilize both the electron spin and charge in electronic devices falls under the general title of "spin electronics" or "spintronics". Spin dependent effects in these spintronic devices can arise from the interaction of the spin of the charge carriers with the magnetic properties of the materials. This is expected to lead to the development of next generation devices utilizing spin degree of freedom together with conventional microelectronics with a possibility of increased data processing speed, lower power

consumption, non-volatility and increased integration densities [6]. One specific requirement for realizing spintronic devices is the efficient injection of spin polarized carriers into the semiconductors. Dilute magnetic semiconductors may provide much better spin injection than ferromagnetic metallic electrodes, since the impedance mismatch due to different electronic structure of magnetic and semiconductor materials significantly hinder the spin injection process.

2. Semiconductors and their classifications

Semiconductors are defined as materials with an electrical resistivity (or conductivity) lying in the range of 10^{-2} (10^2) – 10^8 (10^{-8}) Ohm.cm (mho.cm⁻¹). Alternatively, materials with an energy gap (E_g) between a few meV (below which thermal excitations would produce large occupation of conducting states) and ~4 eV can also be considered semiconductors. Materials with a partially filled conduction band having a finite electronic density of states at the Fermi level or a very small overlap between conduction band and valence band with a negligible density of states at the Fermi level are metals or semimetals respectively, while those with an energy gap greater than 4 eV are insulators. These boundaries differentiating metals, semiconductors and insulators are not sharply defined and there are exceptions to these general rules. For example, aluminum nitride (AlN) and diamond are considered to be wide band gap semiconductors with $E_g \sim 6.2$ eV and 6eV respectively, while GaAs is classified as semi-insulating with $E_g \sim 1.5$ eV. The schematic energy band pictures of insulators, metals, and semiconductors are shown in Fig 1.

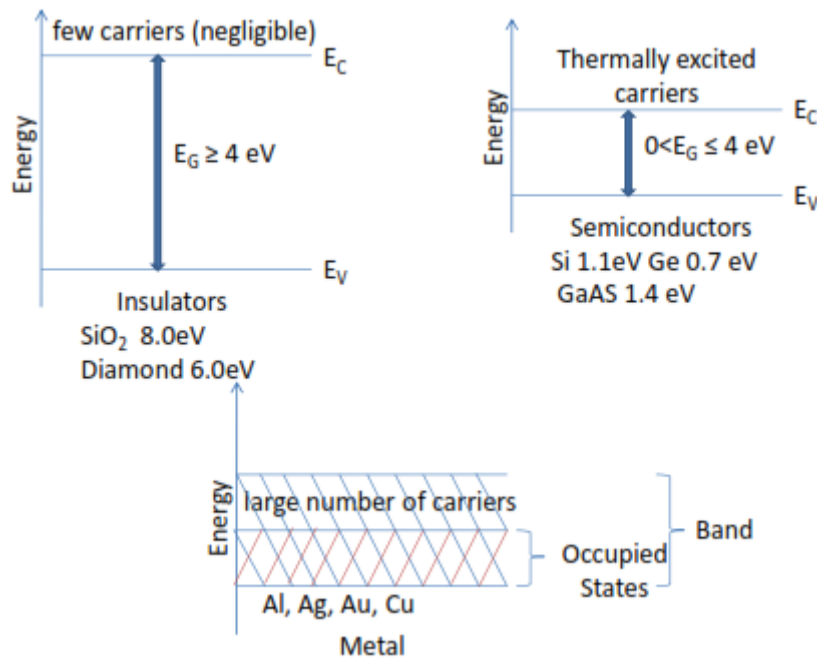


Figure 1: Schematic energy band diagram for insulators, semiconductors and metals

This energy band model classifies semiconductors into two types-direct band gap semiconductors and indirect band gap semiconductors. Semiconductors having the same value k_{min} of the wave vector k (in general $k = 0$) for the lowest energy state in the conduction band and the highest energy state in the valence band k_{max} i.e. the minima of conduction band and maxima of valence band lie at the same k , are called direct bandgap semiconductors. These include GaN, InN, and GaAs among others. A schematic $E-k$ energy band diagram for direct bandgap semiconductors is shown in Fig.2.2(a). Semiconductors for which wave vector minimum k_{min} of the conduction band is different from the wave vector maximum k_{max} of the valence band, that is the minima of the conduction band and maxima of the valence band do not have the same k ,

are indirect semiconductors, and include Si and Ge. The schematic $E - k$ energy band diagram for indirect semiconductor is shown in Fig.2.2(b). Electrical conduction in a pure semiconductor, whether direct or indirect, is due to thermally generated intrinsic charge carriers. These are in generally very small in numbers, for example only $\sim 10^9$ electrons/cm³ in silicon, and are only available in the conduction band at or above room temperature [13]. At very low temperatures, there will be no electrons in the conduction band of intrinsic semiconductors. This explains why an intrinsic semiconductor behaves as a perfect insulator close to absolute zero. The property that makes semiconductors relevant for many device applications is that their electrical conductivity can be tuned by adding small concentrations of impurities.

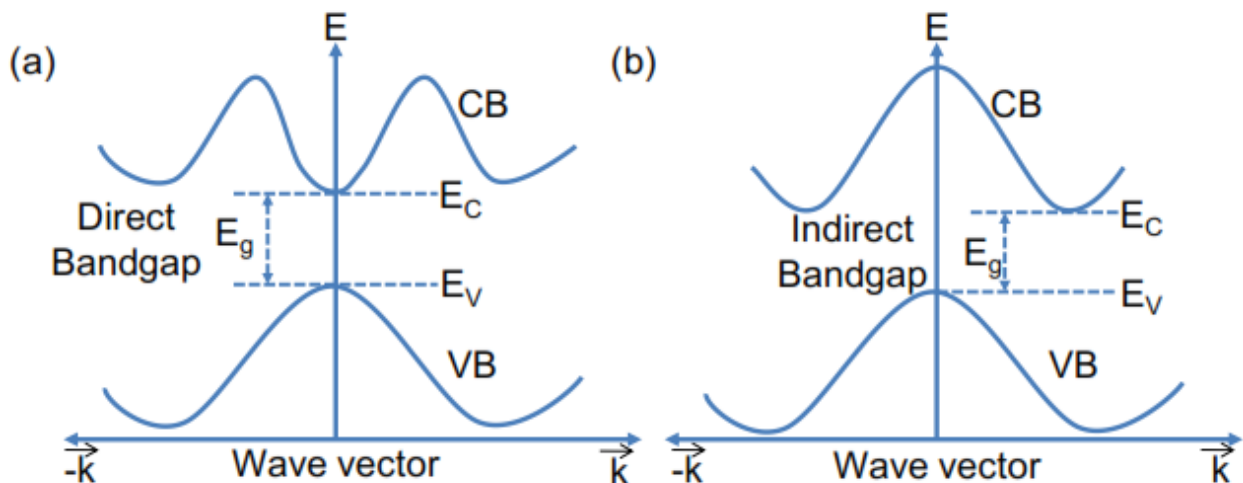


Figure 2: Schematic E-k diagram for (a) direct band gap semiconductor and (b) indirect band gap semiconductors

The type of dopant used controls the conduction mechanism in these materials. If the dopant provides additional electrons to the host semiconductor, the system is called a n-type semiconductor, whereas if the dopants provides additional holes, the system is called a p-type semiconductor.

In general, a very small amount, less than one defect atom per million host atoms is sufficient to change the semiconductor properties for device applications. These defects can be beneficial or detrimental to the properties of the semiconductor.

In an intrinsic semiconductor, the charge carriers are thermally activated and usually the electrons and holes are

present in equal numbers. The electron and hole carrier concentrations in an intrinsic semiconductor are given by:

$$n = \int_{E_c}^{E_{top}} g_c(E) \times f(E) dE \tag{1}$$

And,

$$p = \int_{E_{bottom}}^{E_v} g_v(E) \times (1 - f(E)) dE \tag{2}$$

where $g_v(E)dE$, $g_c(E)dE$ are the number of valence and conduction band states per cm³ in the energy range E and $E + dE$ and $f(E)$ and $(1 - f(E))$ are the probabilities that an available state at an energy E will be occupied by an electron or a hole. The integration in Eq (1) is taken from the bottom of the

conduction band E_c to the top of the band while in Eq (2) the integral is taken from the bottom of the valence band to the top E_v . After simplifying the limits in the integral for Eqs (1) and (2) and using the Fermi-Dirac function $f(E)$ for the electron (or hole) distribution, these equations reduces to:

$$n = N_c \frac{2}{\sqrt{\pi}} F_{\frac{1}{2}}(\eta_c) \tag{3}$$

And,

$$p = N_v \frac{2}{\sqrt{\pi}} F_{\frac{1}{2}}(\eta_v) \tag{4}$$

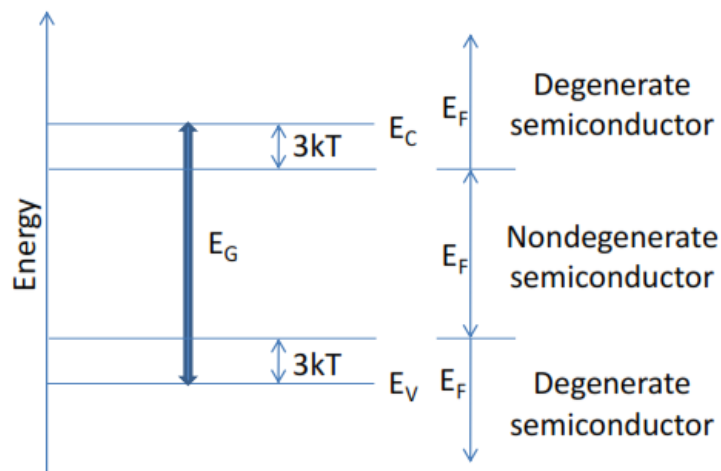


Figure 3: Schematic E-k representation of non-degenerate and degenerate semiconductors

where $N_c = 2(\frac{m_n^*kT}{2\pi\hbar^2})^{\frac{3}{2}}$ and $N_v = 2(\frac{m_p^*kT}{2\pi\hbar^2})^{\frac{3}{2}}$ are the effective density of conduction and valence band states and $F_{\frac{1}{2}}(\eta)$ is the Fermi-Dirac integral of order 1/2 and $\eta_c = \frac{(E_F - E_c)}{kT}$; $\eta_v = \frac{(E_v - E_F)}{kT}$ where E_F is the Fermi energy of the system. If the Fermi energy E_F lies in the range $E_v + 3kT \leq E_F \leq E_c - 3kT$, then the expression for n and p simplifies to:

$$n = N_c e^{\frac{(E_F - E_c)}{kT}} \text{ \& } p = N_v e^{\frac{(E_v - E_F)}{kT}} \tag{5}$$

These expressions for n and p are valid if E_F lies in the conduction or valence band and no closer than $3kT$ to either band edge. When E_F is confined in this range, the semiconductor is called non-degenerate and whenever E_F lies within $3kT$ of either band edge the semiconductor is called

degenerate. The schematic difference between non-degenerate and degenerate semiconductor is shown in Fig 3.

So far we have considered undoped intrinsic semiconductors, where number of electrons is the same as number of holes and their density can be written as:

$$n = p = n_i = (N_c N_v)^{\frac{1}{2}} e^{-E_g/2kT} \tag{6}$$

Where $E_g = E_c - E_v$ is the band gap. The concentration of charge carriers can be changed by introducing dopants leading to extrinsic semiconductors. The charges can be electrons, holes, positively charged ionized donors (which donate electrons to the conduction band), and negatively charged ionized acceptors (which donate holes to the valence

band). Under equilibrium conditions the total charge due to extrinsic impurities and charge carriers is zero, that is, the system contains no net effective charge. This is known as the "charge neutrality condition", even though charged entities are present everywhere in the semiconductor.

Mathematically charge neutrality condition is expressed as:

$$p - n + N_D^+ - N_A^- = 0 \tag{7}$$

where p, n, N_D^+ and N_A^- are the number of holes, electrons, positively charged donors and negatively charged acceptors per unit volume. Using the charge neutrality

condition and the relation $n.p = n_i^2$, the carrier concentrations n and p under non degenerate conditions for an extrinsic semiconductor are given by:

$$n = \frac{N_D - N_A}{2} + \left[\left(\frac{(N_D - N_A)}{2} \right)^2 + n_i^2 \right]^{\frac{1}{2}} \tag{8}$$

And,

$$p = \frac{n_i^2}{n} = \frac{N_A - N_D}{2} + \left[\left(\frac{(N_A - N_D)}{2} \right)^2 + n_i^2 \right]^{\frac{1}{2}} \tag{9}$$

These equations provide the electron and hole carrier densities in an extrinsic semiconductor. For intrinsic

semiconductors $N_D = 0 = N_A$; substituting these into the

equations above one find $n = n_i = p$ under equilibrium conditions. For n-type extrinsic semiconductors, where the excess electron charge carriers are provided by donor

impurities, $N_D - N_A \simeq N_D \gg n_i$. Thus for n-type extrinsic semiconductors the previous equations for electron and hole concentrations become:

$$n \simeq N_D \& p \simeq \frac{n_i^2}{N_D} \tag{10}$$

and similarly for p-type extrinsic semiconductors, where the excess charge carriers are holes and are provided by

acceptor impurities $N_A - N_D \simeq N_A \gg n_i$. In these materials the hole and electron carrier concentrations are given by:

$$p \simeq N_A \& n \simeq \frac{n_i^2}{N_A} \tag{11}$$

This flexibility in tuning the carrier concentrations and type of charge carriers in semiconductors make them useful for numerous microelectronic applications. In many cases, it is difficult to avoid introducing various defects during and subsequent to the fabrication process leading to highly degenerate systems. These accidental charge carriers cloak the intrinsic materials properties of the semiconductor and may

make them unsuitable for the desired application. We will discuss the effect/influence of numerous defects introduced during and after the growth process for highly degenerate n-type InN and In₂O₃ compound semiconductors and will explore some possible application for these highly degenerate semiconductors.

3. Nitride compound semiconductors

Alloying a group III element with nitrogen (group V) produces a nitride compound semiconductor, e.g. GaN, InN, AlN binary alloys, InGaN, InAlN ternary alloys, or InGaAlN quaternary alloys. Recent developments in nitride semiconductors over other group III-V semiconductors open up the possibility of full spectrum solid state light sources, from infrared (IR) to the ultra violet (UV). Among these nitride semiconductors GaN, having a wide bandgap $E_g \sim 3.4$ eV, is one of the most studied semiconductors. This material has led to the development of various lasing devices e.g. blue, green, and white light emitting diodes (LED) and laser diodes (LDs). A number of unanswered questions remain concerning the properties of the binary compound InN, in particular the value of the band gap E_g . The previously accepted band gap value of InN was ~ 1.8 eV, is now attributed to various donor defects in the system. The recent improvements in the quality of InN samples suggests that the correct band gap is $\sim 0.7-0.9$ eV [17, 18], which is in agreement with the density functional theoretical (DFT) calculated band gap values in the local density approximation (LDA) [19]. This new bandgap value of InN allows the In_{1-x}Ga_xN solid solution series to have band gap values ranging from the infrared 0.7 eV ($x=0$) to the ultraviolet 3.4 eV ($x=1$), which would cover the entire solar spectrum. This wide band gap range for In_{1-x}Ga_xN system provides the possibility

to fabricate multi-junction solar cells covering the entire solar energy spectrum. Another advantage of nitride compound semiconductors over other semiconductors is that these are, in general, high band gap materials (except InN), which may be useful for high-power electronic devices. Additionally In_{1-x}Ga_xN exhibits superior high energy radiation resistance and chemical resistance, which make this system advantageous for space applications.

4. Dielectric Materials

One of the most extensively studied groups of ceramic materials belongs to the ferroelectrics. The ferroelectrics are the subgroups of dielectrics. Dielectric materials are electrical insulators (i.e., they do not possess free electrical charges under ordinary circumstances). Dielectrics are the materials in which electrostatic field can persist for a long time. These materials offer very high resistance to the passage of direct current and therefore, sharply differ from metal, semiconductor and superconductors. A good dielectric material should have high dielectric strength so that they should be able to resist high voltage without undergoing degradation and/or becoming electrically conducting. They should also have low dielectric loss in an alternating field. Some dielectrics can generate a potential difference when subjected to mechanical stress, or change physical shape if an external voltage is applied across the material. This property is called piezoelectricity. Piezoelectric materials are another class of very useful dielectrics. Some ionic crystals and polymer dielectrics exhibit a spontaneous dipole moment which can be reversed by an externally applied electric field. This behavior is called the ferroelectric effect. These materials are analogous to the way ferromagnetic materials behave within an externally applied magnetic field. Ferroelectric materials often have very high dielectric constants, making them quite useful for capacitors. It is well known fact that dielectric properties of ceramic materials depend on their composition, structure and experimental conditions. The dielectrics are electrical insulating materials, which can be polarized by the application of electric field. All the dielectrics are insulators but all the insulators are not dielectrics. The atoms and molecules of dielectrics are influenced by an external field and hence the positive charges are pushed in the direction of the field while negative charges in the opposite direction from their equilibrium position. This movement of opposite charges to opposite directions results in a dipole creating an electric field of its own. This process of production of electric dipoles out of neutral atoms and molecules is referred to as polarization. Dielectrics may be

broadly divided into (i) polar dielectrics and (ii) non polar dielectrics.

- Polar (dipole) dielectrics- in polar dielectrics, a finite and permanent polarization known as spontaneous polarization (P_s), exist even after the removal of the applied electric field. Polar dielectrics are those in which the possibility of center coinciding of the positive as well as negative charge is almost zero (i.e., they don't coincide with each other). They all are of asymmetric shape.
- Non-polar (neutral) dielectrics- In the case of non-polar dielectrics, there is no permanent or spontaneous polarization in the absence of an electric field. The centres of both positive as well as negative charges coincide with one another, so the dipole moment of each molecule in non-polar system is zero. Thus individual molecule after the application of electric field behaves as induced dipole. All those molecules which belong to this category are symmetric in nature.

5. Conclusion:

Materials that simultaneously exhibit different physical properties provide a rich area of research leading to the development of new devices. For example, materials having a strong coupling between charge and spin degrees of freedom are essential to realizing a new class of devices referred to generally as spintronics. However, these multifunctional systems pose new scientific challenges in understanding the origin and mechanisms for cross-control of different functionalities. Thin films of InN nitride compound semiconductors and closely related alloys have been investigated to understand the effects of intrinsic defects on the materials properties while considering possible applications of highly degenerate InN thin films. As grown rf sputtered InN films on c-axis (0001) sapphire exhibit highly degenerate n-type behaviour due to oxygen defects introduced during growth. The effect of oxygen in InN matrix has been further investigated by intentionally adding oxygen into the films. These studies confirm that oxygen is one of the main sources of donor electrons in degenerate InN. Above some critical concentration of oxygen, secondary phases of In₂O₃ and In-O-N complexes were formed. It was also possible to tune the carrier concentration to produce changes in the plasmon frequency, which varied from 0.45 eV to 0.8 eV. This characteristic energy scale suggests that these highly degenerate InN thin films could be used for thermo photovoltaic cells, optical filters, and other IR electro-optic applications.

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