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Optical Properties of Pure and Doped (Kno3 & Mgcl2) Polyvinyl Alcohol Polymer Thin Films

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Abstract:- Polymer thin films find wide range of technological applications such as coatings, adhesives, lithography, sensors and as solid state electrochemical cells they can be directly deposited on to chips in any shape or size. In the present work pure and doped (KNO3 & MgCl2) polyvinyl alcohol thin films were synthesized using solution-casting method. The optical absorption spectra of synthesized thin films were recorded at room temperature over a wavelength range of 200-800 nm using JASCO spectrophotometer Model V-570. From the spectral data the optical constants such as band edge, optical band gap (both direct and indirect) were determined. The variation of optical band gap on doping is explained on the basis of incorporation of charge transfer complexes (CTCs) by the dopants. The absorption studies have led to a variety of interesting thin film optical phenomenon, which have thrown considerable light on the band structure of solids and phonic states.

Keywords:- Polymer thin films (PVA), solution casting method, optical absorption studies, charge transfer complexes(CTCs)

I. INTRODUCTION

Polymer thin film technology has made tremendous advancement in the last decade because of the range of technological applications that include coatings, lithography, organic light emitting diodes, sensors and electrochemical cells. In polymer thin films effects due to confinement and interfacial interactions are responsible for different physical phenomena that change with film thickness. They have high conductivity, light in weight, inexpensive, flexible etc. Polyvinyl Alcohol (PVA) is a good protective colloid for aqueous emulsions. Potassium and Magnesium are soft alkali metals with low melting point. The optical absorption studies of Silver Nitrate doped PVA films are studied in wavelength range 190-600nm [1]. The optical absorption properties of poly(3,4-dialkylthiophene) prepared by both electrochemical and chemical methods are studied [2]. The electrical and optical properties of poly(p-phenylene) films and the effect of AsF6 doping are studied [3]. The formation of charge transfer complexes between the polymer host matrix and the dopant are observed. In the form of thin films they have many potential applications in batteries [4] and sensors [5]. A fundamental understanding of the properties of polymer thin films is critical for the successful use of soft materials in current and future technologies particularly at the nano scale. Using the copolymers, composites, polymer blends and by doping them, the thermal, electrical, dielectric, mechanical and optical properties can be better achieved. The attention of researchers has drawn to study effect of doping because the optical properties of polymers can be tailored to a specific requirement by the addition of suitable dopant materials. optical properties of poly(ethylene oxide) based thin films containing 0,10,20,40 &50% of dead sea salts are studied [6]. Optical absorption spectra of Polyvinyl chloride doped with Cd and Pb were noted and absorption coefficient and optical energy gap were found [7]. Davis and Shalliday [8] reported that near the fundamental band edge, both direct and indirect transitions occur and can be observed by plotting $\alpha^{1/2}$ Vs α^2 as a function of energy. The effect due to change in film thickness include changes in glass transition temperature of polymers with decreasing film thickness and changes in the critical phase separation temperatures of A/B polymer blends. Destabilizing long range intermolecular interactions can also affect the lateral uniformity and stability of thin films below certain thickness.

In this paper pure and doped (KNO3 & MgCl2) polyvinyl alcohol thin films are synthesized using Solution-Casting technique. The optical properties of the thin films are observed using JASCO spectrophotometer model V-570 and optical constants are calculated.

II. MATERIALS AND METHODS

Polyvinyl Alcohol (PVA) , potassium Nitrate(KNO3) and Magnesium Chloride (MgCl2) are used with weight percentage of 90:10. Triple distilled water is used for preparation of various solutions.

2.1 Apparatus and instruments

A UV-Visible JASCO Spectrophotometer Model V-570 has been used for recording absorbance at wavelength range of 200 nm – 800 nm.

2.2 Synthesis of Polymer thin films

Films of pure polyvinyl alcohol (PVA) and pure PVA doped with potassium (KNO3) and pure PVA doped with Magnesium Chloride (MgCl2) with weight percentage of 90:10 were prepared using solution casting technique. PVA and dopants were dissolved in triple distilled water and the mixtures were stirred at room temperature for 10-12 hours. The stirred solution was cast on to polypropylene dishes and allowed to evaporate slowly at room temperature. After some time solid polymer layers are formed as thin films with a thickness of 150µm at the bottom of dishes. These films were dried rigorously in a high vacuum (10-3 torr) to eliminate the residual traces of water. Finally films were carefully separated from the dishes.

2.3 Optical Absorption Spectroscopy

The optical absorption spectra of undoped and KNO3 doped and MgCl2 doped films were recorded at room temperature over a wavelength region of 200-800nm using JASCO Spectrophotometer model V-570. From the spectral data the optical constants such as band edge, optical band gap (both direct and indirect) were determined. The study of optical absorption gives information about the band structure of solids.

III. RESULTS AND DISCUSSION

The study of optical absorption gives information about the band structure of solids. Insulators/semiconductors are generally classified into two types; (a) direct band gap and (b) indirect band gap. In direct band gap semiconductors, the top of the valance band and the bottom of conduction band both lie at same zero crystal momentum (wave vector). If the bottom of the conduction band does not correspond to zero crystal momentum, then it is called indirect band gap semiconductor. In indirect band gap materials transition from valence to conduction band should always be associated with a phonon of the right magnitude of crystal momentum. Davis and Shalliday [9] reported that near the fundamental band edge, both direct and indirect transition occurs and can be observed by plotting α½ and α2 as a function of energy (hν). The analysis of Thutpalli and Tomlin [10] is based on the following relations. (hνnα)2 = C1(hν-Egd) (hνnα)½ = C2(hν-Egi)

Where hν is the photon energy, Egd is the direct band gap, Egi is the indirect band gap, n, the refractive index, α is the absorption coefficient and C1, C2 are constants.

These expressions can be applied to both direct and indirect transitions and are helpful in the determination of the band structure of materials.

Optical absorption spectra of pure and KNO3 doped and MgCl2 doped PVA thin films were recorded in the wavelength range of 200 – 800 nm regions. The UV- Visible spectrophotometer gives the absorbance 'A' of the films in different spectral regions. The variation of absorption coefficient 'α' is directly observed with doping. Absorption coefficient 'α' is determined from the spectra as,

α = A/d

Where 'A' is Absorbance and 'd' is thickness of the film.

3.1 Absorption Edge

The value of absorption edge were calculated by extrapolating the linear portions of the curves obtained in α Vs hν plots to zero absorption values as shown in Figure 1.

For pure PVA film the absoption edge lies at 5eV and for doped films their positions are found to be displaced towards lower energy values.

3.2 Direct Band gap

When the direct band gap exists the Absorption coefficient has the following dependence on the energy of the incident photon.

αhν = C (hν -Eg)½

Where Eg is Band Gap

C is Constant controlled by specimen structure.

h is Plank's Constant

The direct band gap was evaluated from (αhν)2 Vs hν plots as in Figure 2. The allowed direct transition energies were determined by extrapolating the linear portions of the curves to zero absorption.

For pure PVA film the direct band gap lies at 5.3 eV while for doped films the values decrease with type of dopant.

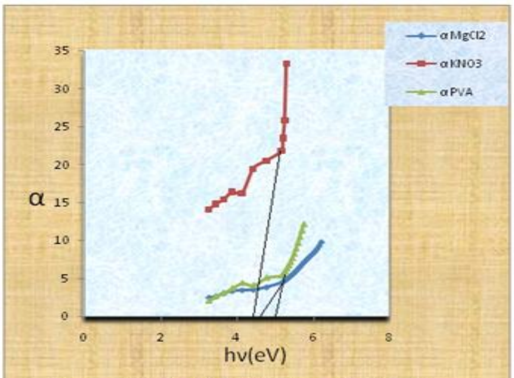

Fig 1: α Vs hν for PVA, PVA+KNO3, PVA +MgCl2 to determine Absorption Edge

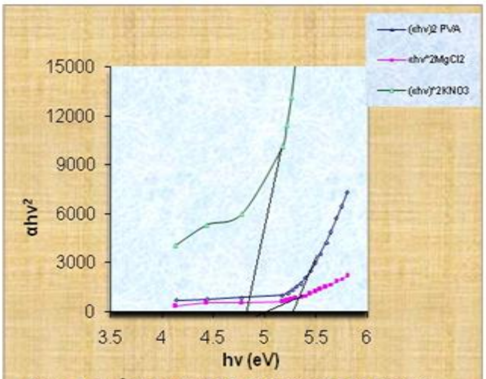

Figure 2. αhν² Vs hν for PVA, PVA+KNO3, PVA+MgCl2 to determine the Direct Band Gap

3.3 Indirect Band gap

For indirect transitions which require phonon assistance the absorption coefficient has the following dependence on the photon energy.

αhν = A[hν -Eg+Ep]2 + B[hν -Eg - Ep]2

Ep is the energy of the phonon associated with the transition and A,B are the constants depending on the band structure.

The indirect band gaps were found from the plots of (αhν)½ Vs hν plots as in Fig 3.

For pure PVA the indirect band gap lies at 5.1 eV while for doped films the value decreases with raise of doping concentration as shown in following Table 1.

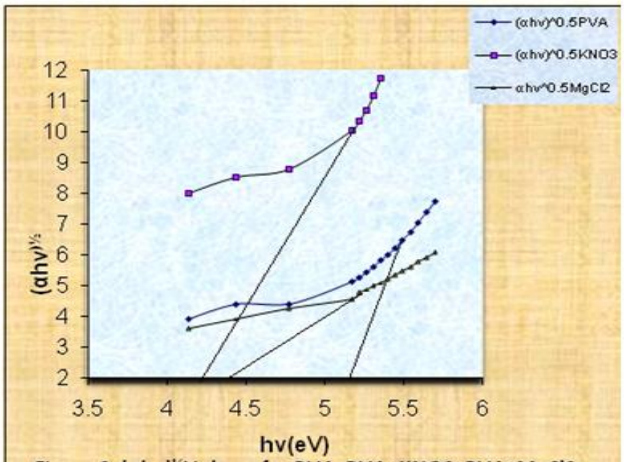

Figure 3. (αhν)½ Vs hν v for PVA, PVA+KNO3, PVA+MgCl2 to determine Indirect Band gap

SAMPLE	Absorption Edge(eV)	Direct Band gap(eV)	Indirect Bandgap(eV)
Pure PVA	5	5.3	5.1
PVA+$MgCl_2$ (Wg % 90:10)	4.6	4.95	4.45
PVA+KNO_3 (Wg % 90:10)	4.5	4.8	4.3

3.4 Discussion

The optical band gap corresponds to inter band transitions. The decrease in optical band gap and activation energy on doping may be explained on the basis of the fact the incorporation of small amounts of dopants forms Charge Transfer Complexes (CTCs) in the host lattice. These charge transfer complexes increase the electrical conductivity by providing additional charges in the lattice. This results in a decrease of activation energy. The formation of charge transfer complexes in the polymer due to halogens introduces additional absorption bands in the UV and Visible region of optical spectra. In the graphs the additional peaks in the wavelength range can be attributed to charge transfer complexes i.e the and gap values decrease with high ionic character.

IV. CONCLUSIONS

In this study the polymer thin films of PVA and doped (KNO3 and MgCl2) PVA are synthesized using Solution Casting Technique. However KNO3 has been found to be more ionic than MgCl2. From the studies it has been found that,

- The polymer thin films were synthesized economically, conveniently and quickly.
- The optical absorption studies conform the formation of Charge Transfer Complexes (CTCs) by showing the additional peak in doped films. Optical constants such as absorption edge, Optical band gap (direct, indirect) were calculated from absorption data. Their values are found to decrease from undoped film to doped films depending on the ionic character of dopant. It was observed that band gap values decrease with high ionic character.
- The direct and indirect band gap values explain that Potassium is more ionic than Magnesium.
- As a result of these studies complex multilayer optical device systems with remarkable reflection, antireflection, interference and polarization properties have emerged for both laboratory and industrial applications.
- The absorption studies have led to a variety of interesting thin film optical phenomena which have thrown considerable light on the band structure of solids and phonic states.

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