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Optoelectronic Devices Based on Chemical Vapour Transport Grown $NbSe_2$ Crystals

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Abstract. Transition metal chalcogenides have shown great potential in the field of solar cell fabrication owing to their strong light matter interactions and favourable band gap. Here in, chemical vapour transport grown $NbSe_2$ crystals are exploited for their optoelectronic applications. The $NbSe_2$ crystals are used for fabrication of working electrode of PEC solar cell. The PEC cell is tested by current-voltage characteristics in dark and illumination of power intensity 30 to 100 mW/cm^2. Typical performance parameters such as efficiency, fill factor, short circuit current and open circuit voltage are calculated. Besides, photodetector based on $NbSe_2$ crystal is fabricated and is tested under white light of 100 mW/cm^2 intensity. The devices show good photoresponse, suggesting the intended application in field of optoelectronics.

Keywords: Crystal growth, Photo electrochemical (PEC) Solar Cell, transient photo response, EDAX, efficiency.

INTRODUCTION

Recently, Transition metal dichalcogenides (TMDCs) have attracted intense research attention in electronics and optoelectronics due to their unique electrical and optical properties. TMDCs are most suitable materials for technical applications due to high chemical and environmental stability. Besides, tunable band gap and high carrier mobility make them most appropriate for applications optoelectronics [1-7]. The intensively studied members of TMDC family such as MoS_2, WS_2, WSe_2, WS_2 etc. have shown potential for flexible electronic devices including photovoltaic applications [8]. In this regards $NbSe_2$ crystals are relatively less studied layered compounds consisting of staked sandwiches of Se-Nb-Se tri-layers with strong covalentintra layer bonds and weak Van der Waals interlayer interactions. In present research, the $NbSe_2$ crystals are grown by chemical vapour transport technique with Iodine (I_2) as transporting agent [9]. The optoelectronic devices are based on $NbSe_2$ crystals are fabricated and studied under white light.

EXPERIMENTAL

The chemical vapour transport grown $NbSe_2$ crystals [9] were employed for fabrication of working electrode of photo-electrochemical solar cell. The $NbSe_2$ crystal is stacked on glass substrate, as shown in FIGURE 1. The copper wire was bounded on back surface of crystals using conducting silver paste for electrical measurements. The PEC solar cell was tested using Keithley- 2400 SMU in dark and under white light illumination of power intensity 30 to 100 mW/cm^2.For fabrication of photodetector, the $NbSe_2$ crystal is stacked on mica sheet and two copper wires are bounded on crystal periphery using silver paste, as shown in FIGURE 1. The switching action of photodetector is measured under white light of 100 mW/cm^2 intensity.

RESULTS AND DISCUSSION

The $NbSe_2$ crystals were mechanically cleaved using scotch tape to get fresh surface. The surface of cleaved crystal is observed under optical microscope. The crystals with clean surface were selected for fabrication of optoelectronic devices namely, photoelectrochemical solar cell and photodetector. For PEC solar cell, copper wire was used as counter electrode which completes the electrochemical reactions in a cell for better performance of solar cell. A mixture of 0.025M I_2 + 0.1M $[K_4Fe(CN)_6]$ + 0.1M $[K_3Fe(CN)_6]$ consisting of oxidized and reduced species having ionic nature was

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Flat band potential determination of $NbSe_2$ photoelectrode using Mott-Schottky plot

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Flat Band potential determination of $NbSe_2$ photoelectrode using Mott-Schottky plot

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Abstract: Semiconductors are an important category of materials involved in many applications in modern society. One such application revolves around the search for efficient and sustainable forms of energy, where in the use of semiconductors to assist conversion of light to electrical energy. Photoelectrochemical solar cell, though finding meagre application in energy harvesting through photovoltaic route, can be used as a tool to identify solid liquid interaction in presence of incident radiation to find out important material parameters. One such important parameter of PEC system is a flat band potential which relates bending of energy bands of semiconductor to develop a barrier separating photo-generated carriers. In this article, the authors have determined the flat-band potential of a crystalline semiconductor photoelectrode using the Mott–Schottky plot, which relates semiconductor–electrolyte interfacial capacitance to voltage. To demonstrate this approach we used a crystalline p-type $NbSe_2$ semiconductor electrode having a bandgap of 1.42 eV in an electrolyte of 0.025M I_2 + 0.1M $K_4[Fe(CN)_6]$+0.1M $K_3[Fe(CN)_6]$ with redox potential of 0.28 V. LCR meter with a suitable equivalent circuit, was used to extract interfacial capacitance data (C), which was then plotted with the electrode voltage via the Mott–Schottky equation (C^{-2}_{SC} versus V_{SCE}). From the x-axis intercept the flat-band potential was determined to be 0.66 V. The semiconductor parameter values come in the potential range of leading chalcogenides as a semiconductor crystals which can be suitable for photo electrochemical solar cell in the near future.

INTRODUCTION

Many naturally occurring substances, in particular the oxide films that form spontaneously on some metals, are semiconductors. Also, electrochemical reactions are used in the production of semiconductor chips, and recently semiconductors have been used in the construction of electrochemical photocells. So there are good technological reasons to study the interface between a semiconductor and an electrolyte. When a semiconducting electrode is brought into contact with an electrolyte solution, a potential difference is established at the interface. The conductivity even of doped semiconductors is usually well below that of an electrolyte solution; so practically all of the potential drop occurs in the boundary layer of the electrode, and very little on the solution side of the interface [1]. Semiconductors have energy gaps between the highest occupied electron band (valence band) and the lowest unoccupied energy band (conduction band). The size of the band gap E_g strongly influences the electrical and optical properties of the material. a material is a good conductor of electricity if E_g is small ($E_g < k_bT$) or when the valence and conduction band overlap: filled and vacant electronic energy levels then exist at virtually the same energy and electrons can move freely from one level to another with only small activation energies being required. Conversely, electrons in a completely filled band have no means for redistributing themselves in response to a field. In this article, authors have described an experiment to determine one of the fundamental properties of any semiconductor–electrolyte system; namely, its flat-band potential[4]. Semiconductors that are used in electrochemical systems often do not meet the ideal conditions on which the Mott-Schottky equation is based. This is particularly true if the semiconductor is an oxide film formed in situ by oxidizing a metal such as Fe or Ti. Such semiconducting films are often amorphous, and contain localized states in the band gap that are spread over a whole range of energies. This may give rise to a frequency dependence of the space-charge capacity, because localized states with low energies have longer time constants for charging and discharging. It is therefore important to check that the interfacial

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Tunable and anisotropic photoresponse of layered $Re_{0.2}Sn_{0.8}Se_2$ ternary alloy

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ABSTRACT

In order to produce high-performance optoelectronic devices, alloy engineering has been exploited in ternary transition metal dichalcogenides. In the present study, we demonstrated the effect of rhenium incorporation on the structural and electrical response in $SnSe_2$ layered crystals grown by direct vapour transport technique. Elemental conformation was characterized by EDAX. The powder X-ray diffraction shows the hexagonal phase and high crystallinity of grown compounds, which is also confirmed by the TEM SAED pattern. Perfectly hexagonal shaped microcrystals are shown in SEM surface micrograph. Raman spectra indicate the redshift in the vibrational mode peaks of $SnSe_2$ with the rhenium doping. Current-time characteristic was measured to study to the effect of alloy engineering on the photoresponse ability of the grown compound. Among all, $Re_{0.2}Sn_{0.8}Se_2$ ternary alloy shows the enhanced photoresponse under polychromatic illumination, showing the suppression of deep-level defect states after incorporation of Re in $SnSe_2$ lattice structure. These materials have a layered structure and exhibit the anisotropic conductivity. Hence the anisotropic photodetection characteristics of $Re_{0.2}Sn_{0.8}Se_2$ ternary alloy based photodetectors are further studied in detail. Photocurrent and photo responsivity are higher along the symmetric contacts, whereas along the asymmetric contacts both the quantities are lower in magnitude because the photogenerated carriers have to cross the perpendicular resistance of is layers stacked together by the weak Vander Waal's forces. Increasing the bias voltage enhances the photoresponsivity from 5.141 mAW^{-1} to 67.231 mAW^{-1} and photodetectivity 0.971 to 3.452×10^9 Jones. Anisotropic photoresponse was also studied under the monochromatic light. Results provide the significant understanding of tunable and layered structure dependent anisotropic photoresponse ability of TMDC materials.

1. Introduction

Recently, transition metal dichalcogenides (TMDCs) have been widely investigated in the fields of optoelectronics and electronics due to their enrolled properties imposing great promise for future applications in high-performance devices. Due to their chemical and thermal stability, TMDC materials have a tremendous contribution in the field of sensing applications including a gas sensor, photodetector, field effect transistors, solar cell [1–4]. In the TMDC family, Tin Diselenide ($SnSe_2$) exhibits great potential for the optoelectronic application due to its unique band structure and high carrier mobility [5]. Xing Zhou et al. fabricated the single-layered $SnSe_2/MoS_2$ heterojunction based photodetector with high photoresponsivity [5]. Prathiban Ramasamy at. el. show applications of SnSe and $SnSe_2$ nanosheets as a counter back electrode in the dye-sensitized solar cell for the better energy conversion [6]. Extreme variation in the electronic properties of TMDC materials can be carried out to fit application criteria by bandgap engineering and thickness variation up to a single layer [7,8]. Besides these, properties of the TMDC material like semiconductor type, band gap etc, can be manipulated through doping by appropriate dopant elements [9].

Rhenium (Re) is Group 7 metal and prominent dopant in TMDC binary alloys. Doping of Re in WS_2 and MoS_2 leads to higher strain, improved photocatalytic activity, enhanced electric conductivity for sodium ion-batteries [9–11]. Re substitution in MoS_2 also induced the change in structure from 2H to 3R and strongly influence the separation of excitons [12]. The effect in photoresponse ability of TMDC layered material with the incorporation of Re is still not well explored as far as

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AC/DC conductivity and dielectric relaxation behavior of aqueous solutions of 1-butyl-3-methylimidazolium chloride

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The complex relative dielectric function $\varepsilon^*(f) = \varepsilon' - j\varepsilon''$ of aqueous solutions of 1-butyl-3-methylimidazolium chloride [BMiM][Cl] of varying concentrations, has been measured using precision LCR meter in the frequency range 20 Hz to 2 MHz at four different temperatures 293.15, 303.15, 313.15 and 323.15 K. Complex ac conductivity $\sigma^*(f)$ of the liquid samples have been determined from the measured $\varepsilon^*(f)$. DC conductivity σ_{dc} of the samples have also been determined. Values of σ_{dc} at different concentrations have been fitted to the empirical Casteel-Amis (CA) equation. The influence of concentration and temperature variation on the complex permittivity and electrical conductivity of the solutions of [BMiM][Cl] in distilled water has been discussed. The molar conductivities and the infinite dilution conductance of these ionic liquids have also been determined. Orientational relaxation behavior of the aqueous solutions of [BMiM][Cl] has also been studied by measuring complex permittivity in the frequency range 1 GHz to 20 GHz using vector network analyzer. Various processes contributed to the electrical/dielectric properties of the solutions of [BMiM][Cl] in distilled water have been explored.

Keywords: Ionic liquids, Dielectric properties, Electrical conductivity, Precision LCR meter, Casteel-amis model, Vector network analyzer

1 Introduction

Ionic liquids (ILs) have unique and fascinating properties like high thermal stability, high electrical conductivity, non flammability and high heat capacity, that make them a suitable candidate for their applications to modern science and technology[1,2]. Modern time application areas of ILs are as electrolytes (for fuel cells, sensors, super capacitors and batteries), solvents (in bio-catalysis, organic reactions, nanoparticles, polymerization), heat storage, as lubricants and additive, etc.[3,4]. One of the most important property of ILs is large value of ionic conductivity due to the presence of free cations, anions or both[5,6]. ILs are regarded as designer solvents because of the vast number of possible anions and cations to form an IL. ILs of desired conductivity can be designed via mixing[7,8]. Vila *et al.* [9] studied electrical conductivity behaviors of mixtures of some ILs with distilled water over the entire range of concentration and found that the electrical conductivity of the mixtures is higher than the ionic conductivity of the components of the mixtures. Electrical conductivity of the distilled water[10] (0.0092 S/m) at 303 K is comparatively much less than that of the [BMiM][Cl] (0.046 S/m) [11]. So, it will be interesting to study electrical conductivity behavior of diluted aqueous solution of [BMiM][Cl] over a range of concentration. In the present investigation we have taken 1-butyl -3-methylimidazolium chloride as solute and distilled water as solvent and solutions of [BMiM][Cl] of different concentrations were prepared. DC ionic conductivity of the aqueous solutions of [BMiM][Cl] were determined at four different temperatures from measurements of complex permittivity $\varepsilon^*(f)$ of the samples in the frequency range of 20 Hz to 2 MHz. The quantities, molar conductivity ($\wedge_m$) and molar conductivity at infinite dilution ($\wedge^0$) of ionic liquids has received cumulative attention of many researchers in recent past[12–17], because using these properties information on the effect of solvent structure on ionic association and solvation of ionic liquids can be obtained. We have determined molar conductivity ($\wedge_m$) and molar conductivity at infinite dilution ($\wedge^0$) from dc conductivity of the [BMiM][Cl] solutions. Orientational relaxation process of water is studied by many researchers[18–20] and it is observed that dipolar relaxation peak in ε"(f) spectra falls in the microwave

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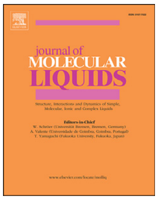

AC/DC conductivity and dielectric relaxation behavior of ionic solutions of 1-butyl-3-methylimidazolium chloride in methanol

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A B S T R A C T

The complex relative dielectric function, ε*(f) of solutions of 1-butyl-3-methylimidazolium chloride ([BMiM][Cl]) in methanol (MeOH) of varying concentration and temperature have been measured in lower (20 Hz–2 MHz) and microwave (200 MHz–20 GHz) frequency regimes using precision LCR meter and Vector Network Analyzer (VNA) respectively. Complex ac conductivity, σ*(f) of the liquid samples were determined from the measured low frequency ε*(f). DC conductivity, σ_{dc} of the samples were also determined. The influence of concentration and temperature variation on the complex permittivity and electrical conductivity of the solutions is discussed. σ_{dc} of pure [BMiM][Cl] and pure MeOH is significantly enhanced in diluted to moderately concentrated solution of [BMiM][Cl] in MeOH. Experimental values of σ_{dc} at different concentrations were fitted to the empirical Casteel-Amis (CA) equation. Static dielectric constant of ionic solutions was determined from complex permittivity measurements in the microwave frequency range, using which, information about the molecular interaction between [BMiM][Cl] and MeOH was revealed. Viscosity (η), molar conductivities (Λ_m), infinite dilution conductance (Λ^0) and Walden product (W) of the solutions were also determined. Orientational relaxation behavior of the mixture solutions in microwave frequency region is not influenced by variation in concentration of [BMiM][Cl] in MeOH. Different contribution arising in the dielectric spectra are discriminated.

1. Introduction

In recent past ionic liquids (ILs) have emerged as a very important class of materials due to their unique and fascinating properties like high thermal stability, high electrical and thermal conductivity, non-flammability, high heat capacity, low vapor pressure [1,2]. These properties have made them a suitable candidate for numerous applications in modern science and technology [3–7] and topic of extensive research in the scientific community. In resent past many attempts have been made to study properties of ILs through dielectric relaxation spectroscopy (DRS) [8–17], conductimetric measurement [18–22] and physico-chemical methods [23–27]. DRS is most powerful and widely used experimental technique for study of molecular response, underlying physics of molecular interactions in liquid mixture and various relaxation processes. Study of transport properties with the help of conductometric technique are of the key importance to understand the behavior of the ionic solution and also it aids to gain information about ionic mobility, solvent viscosity and the nature of the interactions between ion-ion and ion-solvent in ionic solution. Such studies conducted at different temperatures are expected to shed new light on the mechanism and extent of ion-ion and ion-solvent interactions and solvation of ILs in solutions. ILs are exclusively composed of ions, they are good candidate for any applications where high ionic conductivity is needed [9]. However, the miscellaneous applicability of pure ILs in certain fields has been restricted due to their high viscosity which hinders their performance within reaction media. For example, [BMiM][Cl] can be used as neoteric solvent in cellulose processing [28] and the high viscosity of the cellulose solution has brought some difficulty to the engineering [25]. The mixture of ILs with solvent is one of the effective tactics to overcome the problem and enhancing its electrical conductivity. Many researchers [23–25,29,30] have confirmed this finding and shown that viscosity exponentially decreased with the solvent concentration, and consequently increased ion mobility. Furthermore, mixture of ILs with their co-solvent demonstrate improved and more desirable thermodynamic and transport properties in many processes [31]. However, the resultant properties of binary mixtures depend on the type of

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Density, Viscosity, Molar Volume, Speed of Sound and Excess Properties for the Binary Mixtures of 3-Bromoanisole and Methanol at 293.15 K Temperature

Abstract: *Experimental values of density, viscosity and speed of sound at 293.15 K temperature for the binary mixtures of 3-bromoanisole (3-BA) with methanol (MeOH) were presented over the whole range of mixture composition. From these data, excess molar volume, excess viscosity and excess speed of sound have been calculated. The excess results were fitted to the Redlich-Kister (RK) type polynomial equation.*

Introduction

Physical properties of liquid mixtures are required in most engineering calculations where fluid flow or mixing is an important factor in many practical problems concerning mass transport applications [1,2]. From the measured physical properties, excess properties of the binary mixtures can be calculated. To understand the nature of molecular interactions the excess functions of physical parameters of binary liquid mixtures are considerably important [3]. Many attempts have been made by researchers to understand the nature and degree of interactions in liquid mixtures using excess properties [2,4-6]. 3-bromoanisole (3-BA) is a derivative of anisole and is an aromatic compound of the ether group. Anisole and its derivatives are used as solvents and are useful in chemical reactions as intermediates to obtain target materials like dyes, perfumery, agrochemicals and pigments [7,8]. On the other hand, methanol (MeOH) is an associative liquid and are wildly used in industrial fields like oil industry, refrigeration, air conditioning and others [2]. Physical properties of anisole with different solvents have been reported by many researchers [1,2,9,10]. But no such study of bromo-substituted anisole is reported in literature. The focus of the present study is to see the effects of concentration variation on the physical properties of the mixture constituents (MeOH and 3-BA) and also to understand the molecular interaction with the help of physical properties and its excess function.

Chemicals, Sample Preparation and Measurements

3-BA (extra pure, 99% purity) and MeOH (HPLC grade, 99.7 purity) were supplied by Spectrochem Pvt. Ltd. (India) and Ranbaxy Pvt. Ltd. (India) respectively. Total eleven different binary mixture samples were prepared by volume fraction of 3-BA in MeOH. Density of pure liquids and their mixtures were measured using double arm Pycnometer and a capillary bore with an internal diameter of 1 mm. The densities are accurate to ±0.1 kg m^{-3}. Viscosity of pure liquid and their binary mixtures were measured using the Ostwald viscometer. The error in the measurement of viscosity is within ±0.1%. Speed of sound were measured with an ultrasonic interferometer (Model F-81s). The temperature was maintained using a constant temperature water bath with an accuracy of ± 0.1 K.

Evaluation of Different Parameters

The measured density (In TABLE 1) was used to find the molar volume of the mixture and were calculated from following equation [11]

$$V_m = \frac{X_1 M_1 + X_2 M_2}{\rho_m} \qquad 1$$

Where X is mole fraction, M is molecular weight and suffix 1, 2 represent compound 3-BA and MeOH respectively. The excess of molar volume, viscosity and speed of sound of these binary mixtures were calculated using the general relation [11]

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Regular Article

Investigation of optical, electrical and optoelectronic properties of SnSe crystals

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Abstract. The optical, electrical and optoelectronic properties of tin selenide crystals are of immense significance for application in photodetectors and energy conversion and storage devices. The transition metal chalcogenides possess a layered structure that interacts with each other through van der Waal forces and can also offer sites for intercalation. The low molecular weight materials like GeSe and SnSe are found in an orthorhombic structure. In this article, the optical, electrical and optoelectronic properties of as-grown tin selenide crystals are investigated. The chemical composition of the crystals grown with the aid of direct vapour transport (DVT) technique is confirmed through energy Dispersive analysis of X-rays (EDAX), at the same time the morphological analysis is accomplished using optical microscopy and Scanning Electron Microscopy (SEM). The grown crystals are characterized by powder X-ray diffraction (XRD) method to assess the structural properties of the material. The XRD evaluation found out the orthorhombic structure of the crystals with the space group ${}^{16}_{2h}D$ ($P_{\rm cmn}$) having lattice parameters $a = 11.490$ Å, $b = 4.440$ Å and $c = 4.135$ Å. The crystallinity of grown samples was verified by transmission electron microscopy (TEM). The single crystalline nature of grown crystals was revealed by SAED pattern. The indirect optical band gap of 1.0065 eV, Urbach energy and steepness parameter are calculated utilising UV–VIS-NIR spectrophotometer. The optical absorption of as-grown SnSe crystals has been measured close to the fundamental absorption edge at room temperature. Both types of transitions, i.e. direct and indirect, are involved in the absorption process. Electrical transport properties like resistivity measurements (parallel and perpendicular path to the c-axis) had been carried out on these crystals within the temperature range 297–673 K. Anisotropy in resistivity measurements in both the directions, i.e. parallel and perpendicular direction to the c-axis was discovered. The p-type semiconducting nature was confirmed with the aid of Hall-effect measurements. For the photodetection properties of SnSe crystals, light source (670 nm) having an intensity of 3 mW/cm^2 at distinctive biasing voltages is used. The outstanding detection properties are revealed from the responsivity, specific detectivity and external quantum efficiency (EQE) of pure SnSe crystals.

1 Introduction

Photo functional materials are a large circle of relatives of photoactive compounds that may switch, absorb, store, transfer, or utilise light energy. Two-dimensional (2D) layered structures compounds have recently emerged as a brand new platform for growing novel photo-functional materials. They are explored, and their applications are found in the areas of light-harvesting, photoluminescence, photocatalysis, biological imaging, band structure engineering, photochromic sensors, and optoelectronic devices [1]. Layered materials can be detached into discrete sheets with improved electronic properties using a new short and upfront technique. Fragile sheets of material can showcase superior properties, which include augmented electrical conductivity, as compared with the three-dimensional (3D) bulk layered material [2,3]. SnSe crystals belong to IV–VI layered binary semiconducting compound class with a band gap of 1.0 eV wherein the layers are coupled via weak van der Waals interactions [4–6]. It exhibits typical anisotropy of a layered structure [7–14]. These layered compounds have produced a great deal of interest due to their exciting electronic properties and potential applications in optoelectronic, photovoltaic and thermoelectric devices [9,15,16]. SnSe has a layered orthorhombic structure. It has space group $P_{\rm nma}$ at room temperature [17]. It suffers a phase transition (PT) from the room-temperature $P_{\rm nma}$ phase to high-temperature $C_{\rm mcm}$ phase at ∼700 K [18,19]. SnSe prefers a Se-rich composition at low temperatures and a Se-poor composition at higher temperatures ($T > 600$ K), i.e., its real stoichiometry varies with temperature [20]. SnSe single crystals always exhibit p-type characteristics [21]. SnSe additionally showcase fantastic thermoelectric performances [22–25]. It has

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