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Electrical Characterization of Nano-TiO_2/Nb_2O_5 Composite Thin Films Deposited Using Electrophoretic Deposition Technique

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Abstract— This paper reports the results of electrical characterization of TiO_2/Nb_2O_5 composite thin films. Uniform TiO_2 and Nb_2O_5 composites thin films were deposited on FTO coated glass substrate using electrophoretic deposition (EPD) technique. The EPD voltage of 35V (DC) and deposition time of 90s, were used for various volume fractions of Nb_2O_5 in composites. Uniform and crack free composite films were successfully deposited using the EPD technique as shown by the SEM micrographs. The Hall Effect equipment was used to characterize the films through measurement of current and the Hall voltage. Current against Hall voltage plot for films of various volume fractions of Nb_2O_5 were used to determine Hall coefficients and majority charge carrier density. The sign of Hall coefficient values revealed that TiO_2/Nb_2O_5 composite thin films had a net n-type polarity indicating electrons were the majority charge carrier in the composite films. The results showed that dye-sensitized solar cells should be fabricated with TiO_2/Nb_2O_5 composites thin films in ratio of 1:1 because such ratio 1:1 for TiO_2 and Nb_2O_5 in composite yielded the highest electron mobility in the films.

Keywords— Electrical characterization, TiO_2/Nb_2O_5 composites, Electrophoretic deposition, thin films, Hall Effect,

I. INTRODUCTION

Metal oxide semiconductors have become increasingly important in fabrication of photoanodes used in dye-sensitized solar cell (DSSCs). The efficiency of a DSSC in converting light into electric energy depends on factors such as effectiveness with which light is transmitted through the photoanode, the number of electrons injected into the photoanode and the ease with which electrons are transported through the photoanode. Metal oxide semiconductors used in fabrication of dye-sensitized solar cells are chemically stable and environmentally friendly materials that provide porous films for the cells. High surface area of porous photoanode enhances light harvesting from the increased dye adsorption.

Titanium dioxide (TiO_2) has been the most preferred metal oxide semiconductor to fabricate photoanodes in dye-sensitized solar cells because it is a material that is non-toxic, easily available, of relatively low cost material, environmentally stable, and used to fabricate solar cells with high conversion efficiency [1]. Several studies have been initiated to modify the electrical transport properties of TiO_2 using binary-system electrodes [2]. The TiO_2/Nb_2O_5 systems have been prepared by several methods like the DC magnetron technique [3], sol gel technique [4], power screen printing [5], and pulsed laser deposition [6]. The electrophoretic deposition (EPD) technique has not been fully elucidated to deposit porous, thin films in binary-system electrodes. Electrophoretic deposition technique is a colloidal processing technique that uses electrophoresis mechanism for the movement of charged particles suspended in a solution under an electric field, to deposit them in an ordered manner on an oppositely charged electrode to develop thin and thick films, coatings and free-standing bodies [7]. It is a simple and cost-effective technique usually requiring simple processing equipment and infrastructure. In this work, the EPD technique is used to coat a TiO_2/Nb_2O_5 composite porous thin film from nano sized powders of titanium dioxide (TiO_2) and niobium pentoxide (Nb_2O_5) onto a Fluorine doped tin oxide (FTO) glass substrate.

The deposited films were electrically characterized using the Hall Effect equipment. Since Edwin Hall discovered the Hall Effect in 1879, the Hall Effect using Hall meters has continued to provide the basis of many different practical applications. The Hall meters are used in anti-shoplifting systems, motion detection in car ABS systems, home alarm systems, iPhone digital compasses, and car electronic ignition systems [8]. Applications of the Hall Effect measurements are also critical in electrical characterization of semiconductor materials and films because the type of charge carrier, carrier density, and Hall mobility can be derived from the Hall voltage [9],[10]. For semiconductors, the band structure can give rise to both negative (electron-like) or positive (holes). In this work, electrical conductivity is therefore determined by the density and mobility of charges through TiO_2/Nb_2O_5 composite thin films in which volume fraction of Nb_2O_5 is varied in the composite.

II. METHODS

2.1 Film deposition by EPD technique

Masses in the range 0.01g to 0.3g of commercial TiO_2 nanopowder (Cas No. 13463-67-7 Aldrich), and Nb_2O_5 nanopowder (Cas No. 1313-96-8 Acros Organics BVBA, Belgium), and Magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$ 99.9%, Aldrich) pellets were added into 40 mL of propan-2-ol in a glass beaker to form EPD suspension. Magnesium nitrate hexahydrate pellets were added to suspension to provide magnesium ions to attach to semiconductors and thereby control the zeta potential of suspension [11].

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The suspension was then stirred using power sonic 405 vibrator for 10 minutes. The colour of the suspension whose pH was 4.9 turned milky white after vibration. Glass substrates (16mmx25mmx1mm) covered with a conducting layer of Fluorine doped tin oxide (FTO) (Pilkington, Hartford Glass Co. Inc., USA) having sheet resistances of 8Ω/square were used as electrodes in EPD setup (fig 1). The FTO coated glass substrates were then partially immersed in the suspension and a 35V DC-voltage applied in a parallel-plate configuration across electrodes. Each film was deposited on to cathode electrode for 90 seconds. The fabricated films were annealed at 400^0 C for 30 minutes and then allowed to cool gradually to room temperature (25^0C).

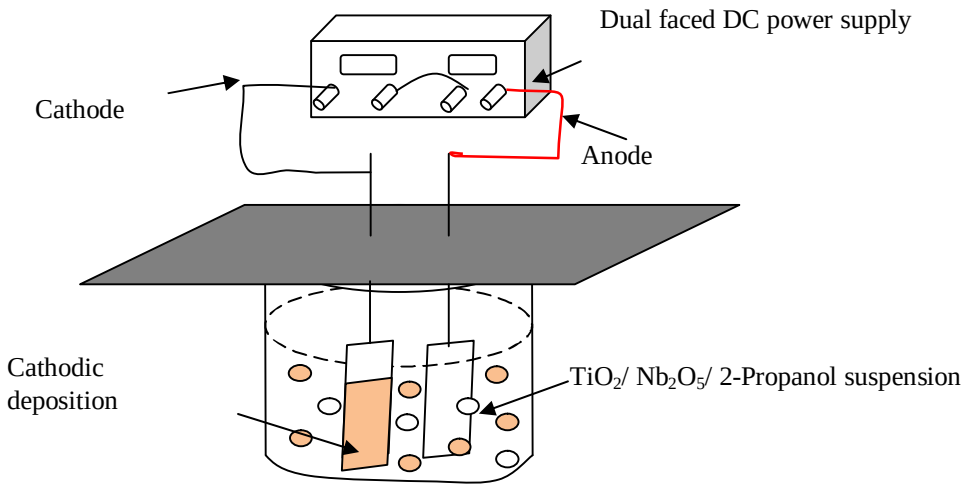


Fig 1 A schematic drawing of the EPD setup showing the two FTO covered glass slides partially immersed into TiO_2/Nb_2O_5/propan-2-ol suspension after [12], [7].

2.2. The Hall Effect measurement

The Hall voltage and current were measured using the configuration shown in figure 2, upon the application of magnetic field. The digital flux/gauss meter was used to measure the uniform magnetic field intensity (B), while constant direct current power supply was used to measure the Hall Voltage (V_H) and supplied electric current (I). The ten samples were mounted individually onto a printed circuit, clamped and attached to a stand placed between electromagnetic poles. The Hall voltage and current values were recorded at for magnetic field of 3 G (=0.0003T) (table 1). Measurements were carried out at room temperature (25^0C)

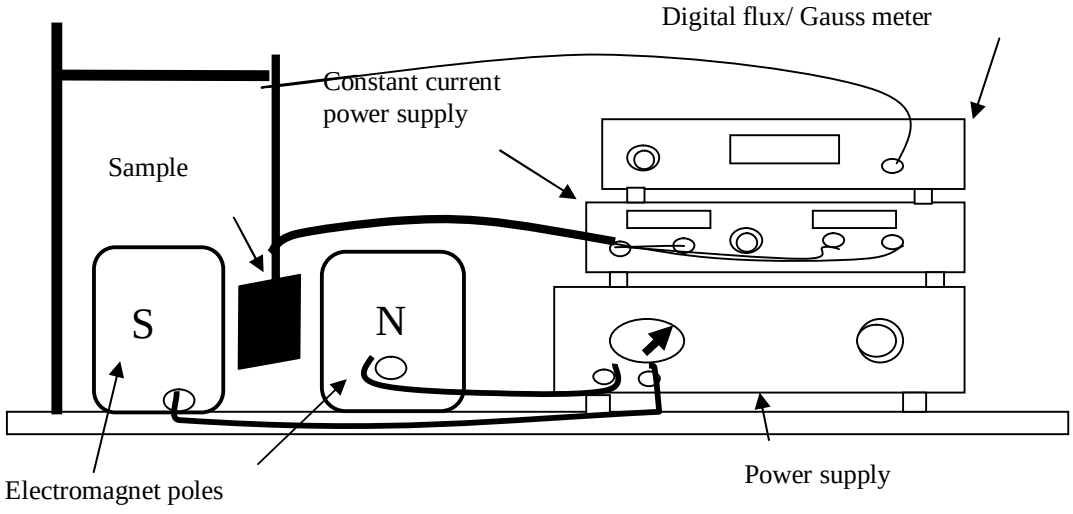


Fig 2 Schematic drawing of Hall Effect measurement showing meters that provide current and magnetic fields, and clamp for which support probes and samples. Available Chuka University laboratory.

The Four point probe

The four point probe, model SRM-232, used to measure resistivity of the composite thin films is shown in figure 3. The four probes are arranged in a linear fashion in which voltage is measured across the inner probes while current is measured across the outer probes. Four point probe operates by passing a calibrated constant current source of 4.53mA through the two outer tips (fig 3). The probe was manually operated by pressing the 4-point probe to the film. A current

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source was activated and the sheet resistance (R_S) values measured and displayed on the 16 digit LCD front panel display. The sheet resistance was used in equation 4 to determine the film resistivity (ρ).

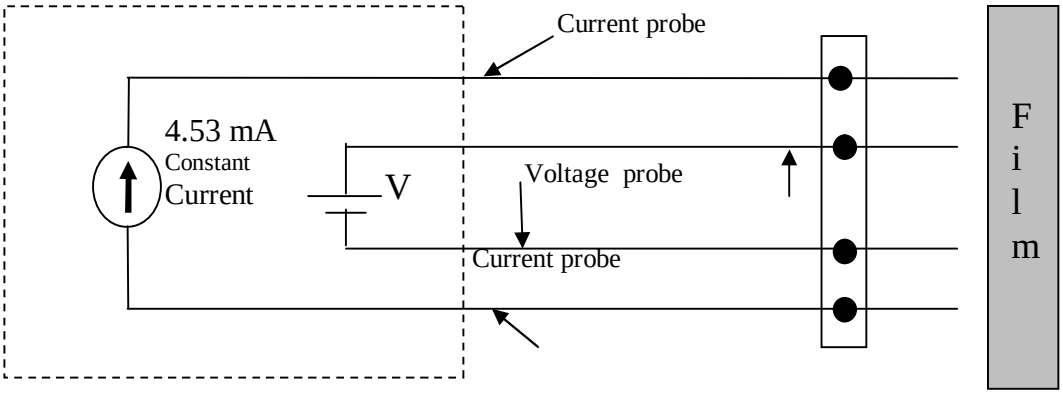


Fig 3 Functional block diagram of SRM-232 Four point probe. A constant current, 4.53 mA flows in ammeter. (after Bridge Technology).[13]

2.3 Characterization method

The Hall coefficient (R_H), is defined by equation (1) [14]

$$R_H = \frac{t\,V_H}{B\,I_x}(cm^3C^{-1}) \quad (1)$$

Where V_H is the Hall voltage measured along z-axis, I_x is current, B_y magnetic field and t is the sample thickness

The film thickness (nm) was derived from values of transmittance using Pointwise Unconstrained Minimization Approach (PUMA) software [15].

The number density of charge carrier is evaluated from fundamental charge and Hall coefficient according to eqn 2;

$$n_H = \frac{1}{qR_H}(cm^{-3}) \quad (2)$$

Using the four point probe, resistivity (ρ) is defined in terms of voltage (V), current (I) and thickness (t) by eqn 3

$$\rho = 4.532\,\frac{t\,V}{I} \quad (3)$$

Film resistivity is given by product of thickness and sheet resistance (R_S) (qn 4)

$$\rho = t\,R_S\ (\Omega\text{-}cm) \quad (4)$$

Thus, the Hall mobility is defined from conductivity (σ) according to eqn 5;

$$\mu_H = R_H\sigma \quad (5)$$

III. RESULTS & DISCUSSION

3.1 Morphological properties

Figs. 3a and 3b show the SEM image of the surface morphology of TiO_2/Nb_2O_5 composite thin films electrophoretically deposited using combination 0.01 g/40 mL, 90 s, and 35 DCV and at magnification of 5 K and 20 K, respectively. SEM used had extra high tension (EHT = 5.0 KV. The SEM images of deposited TiO_2/Nb_2O_5 composite thin films, reveal that TiO_2 and Nb_2O_5 nanoparticles in the composite films were of near uniform distribution with a small fraction of uncoated glass surface. The more connected the composite particles are to each other, the more the electron transport to the conductive substrate. The surface coating appears to adhere well to the glass surface. This adherence is attributed to magnesium ions attached to the surface of the metal oxide particles. In addition, these films have the desired porosity for dye absorption and are therefore suitable for application in the dye-sensitized solar cells.

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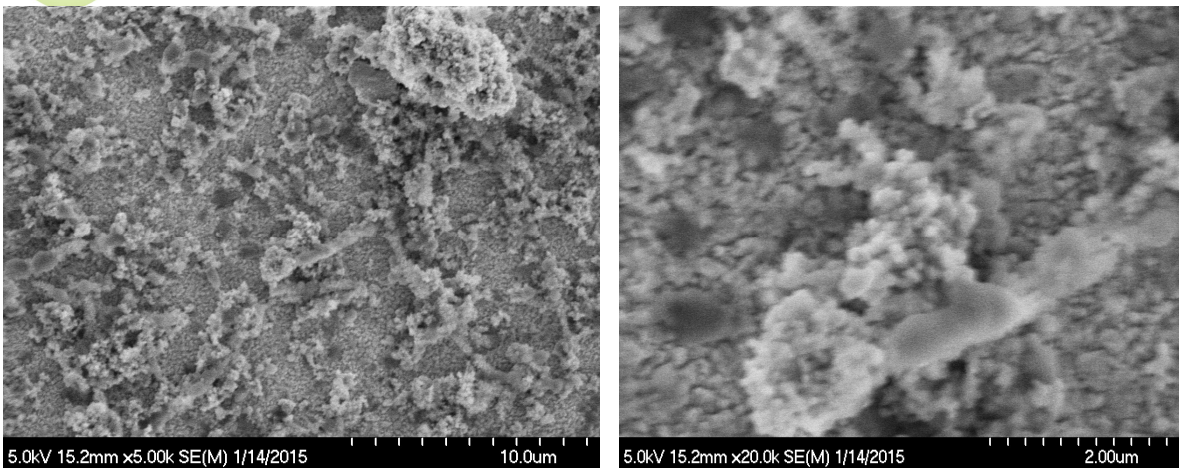


Figure 4 SEM image of TiO_2/Nb_2O_5 composite thin film deposited on $F:SnO_2$ (a) magnification = 5 K, and (b) magnification = 20K

3.2 Electrical properties

3.2.1 The polarity of charge carriers

The sign of the Hall voltage (V_H) and Hall coefficient (R_H)indicate a net positive carrier concentration for $F:SnO_2$ coated glass, TiO_2, and 0.1 volume fraction of Nb_2O_5 in composite films (figure 5). The majority charge carriers are positive charges or holes. Bulk TiO_2 is an n-type semiconductor. However, as pointed out by [2], the band structure of nanomaterials is greatly deviated from their bulk counterpart. The net positive carrier concentration is attributed to donor-type defects such as oxygen vacancies and titanium (cation) interstitials. The presence of titanium vacancies in TiO_2 cause p-type properties [16]

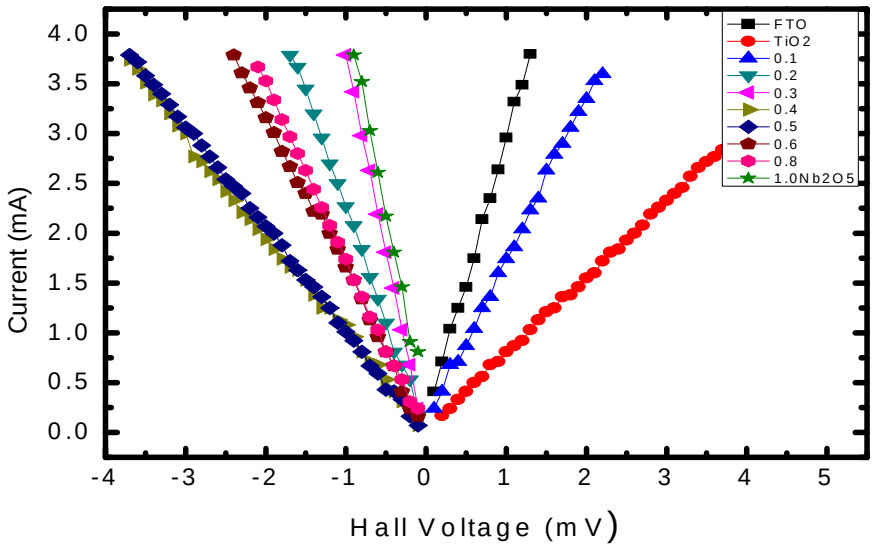


Fig 5 Current versus Hall voltage for varied concentrations of Nb_2O_5:TiO_2 composite films. Films corresponding to positive voltage are p-type while those with negative voltage are n-type

Films of Nb_2O_5 only, and films of Nb_2O_5 in TiO_2 with volume fraction between 0.2 and 0.8 yielded a net negative carrier sign indicated by both the Hall voltage and Hall coefficient. In these films, the electrons form the majority charge carriers.

Nb_2O_5 is reported to become an n-type semiconductor at lower oxygen content. The net electron concentration could also be due to donor impurities with hydrogen being a likely candidate. Unintentional impurities are likely sources of observed unintentional conductivities in metal oxide semiconductors. Hydrogen is a widely available impurity which diffuses as an interstitial impurity and is capable of assuming substitutional positions [17]. The

n-type behaviour of composites of TiO_2/Nb_2O_5 whose Nb_2O_5 concentration is in range 0.2 to 0.8 is attributed to incorporation of Nb^{+5}, and O^{-2} donor ions. Reference [18] similarly reported that TiO_2 can be made n-type by incorporation of shallow donor impurities (e.g. Nb, F, and H) and annealing in reducing environment.

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3.2.2 Hall coefficient

Figure 6 shows that the Hall coefficient values decreased as concentration of Nb_2O_5 in composite films increased with the lowest values at volume fraction of 0.4. According to equation (2), the Hall coefficient (R_H) decreases with increased charge carrier density (n) which is likely from increase in Nb_2O_5 volume fraction. Decrease in R_H also resulted from the increase in number of charge carrier mobility as shown in figure 7.

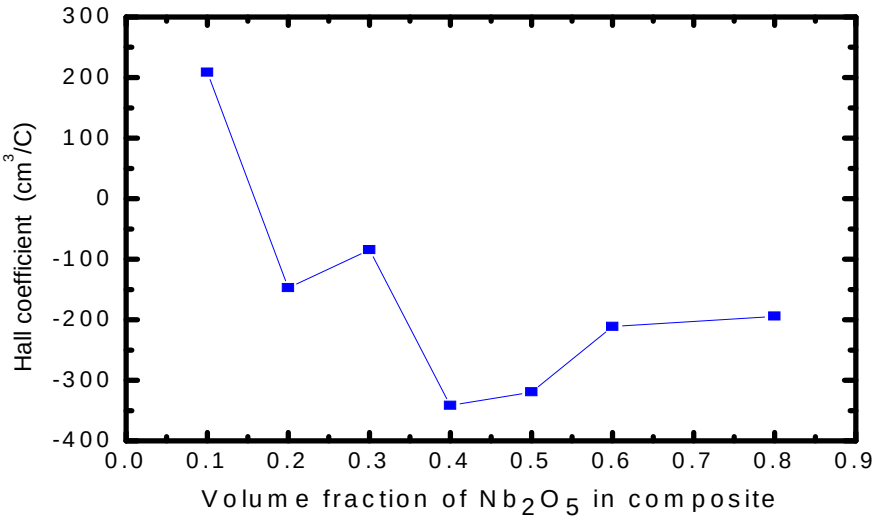


Fig 6 Hall coefficient versus volume fractions of Nb_2O_5 in TiO_2:Nb_2O_5 composite thin films

Table 1. Values of Hall coefficient, carrier density and carrier mobility for TiO_2/Nb_2O_5 composite thin films

Volume fraction Nb_2O_5	Hall coefficient (R_H) (cm^2/C)	Charge carrier concentration (cm^{-3})	Carrier mobility ($cm^2V^{-1}s^{-1}$)
0.1	208.33	3.00E+16	1.812
0.2	-147.33	4.24E+16	-1.218
0.3	-845.07	7.40E+16	-0.735
0.4	-341.71	1.83E+16	-2.971
0.5	-319.64	1.96E+16	-2.653
0.6	-211.20	2.96E+16	-2.607
0.8	-194.36	3.22E+16	-2.492

The values of Hall coefficient, carrier density and carrier mobility in table 1, compare closely with those obtained by other authors (table 2). The charge carrier density values of TiO_2/Nb_2O_5 composite thin films were lower than values reported (table 2) by a factor of two due to high values of Hall coefficient values. The two quantities are inversely related (eqn 2).

Table 2 Comparison of Hall characteristics to those by several authors

Type of thin film	Hall coefficient (cm^2/C)	charge carrier density (cm^{-3})	carrier mobility ($cm^2V^{-1}s^{-1}$)	Ref
TiO_2	4.33	1.44×10^{18}	0.022265	[19]
TiO_2 Anatase	0.5	5.00×10^{18}	1	[20]
TiO_2 Rutile	-	1.00×10^{19}	0.2	[21]
TiO_2 Anatase	-	1.00×10^{19}	4	[22]
TiO_2 Rutile	-	2.50×10^{19}	0.1	[22]
SnS:Ag	0.8	7.24×10^{14}	14.3	[23]
GaAs (thick film)	2.7	2.3×10^{18}	0.0125	[8]

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3.2.3 Carrier mobility and density (n)

Mobility of electrons in films with concentrations (volume fractions) below 0.4 increased to maximum of 3 $cm^2V^{-1}s^{-1}$ at 0.4 and then decreased for higher concentration (figure 7). The low values of mobility resulted from electron-hole scattering since holes and electrons have opposite average drift velocities. The carrier mobility was highest at concentration of 0.4 which is close to ratio of 0.5 or half concentration because both TiO_2 and Nb_2O_5 nanoparticles are of almost equal sizes with close band gap energies. Increase in concentration leads to increase in packing density and decrease in defects density therefore the resistivity decreases. However, higher concentration leads to increased particle to particle boundary resistance which serve as dispersion centers causing increase in resistivity of the composite films.

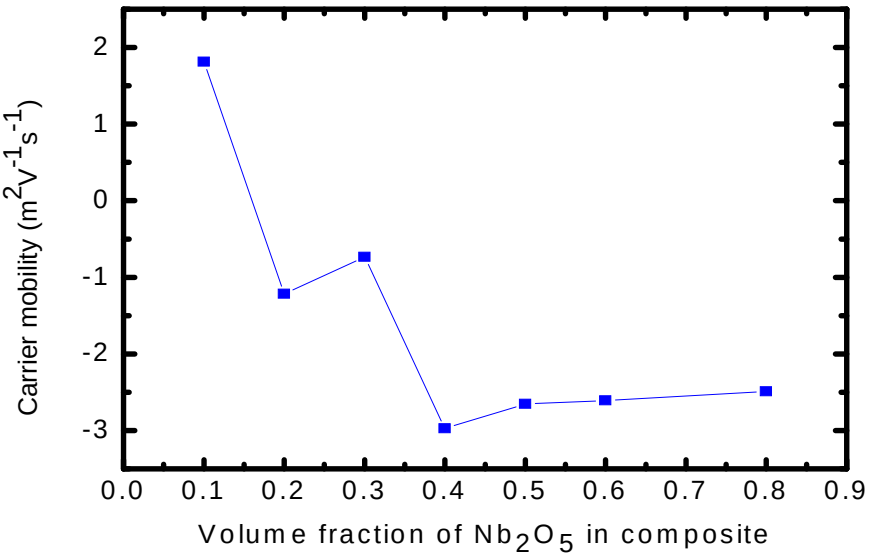


Fig 7 Mobility of charges in TiO_2/Nb_2O_5 composite for various volume fraction of Nb_2O_5

IV. CONCLUSIONS

Uniform TiO_2/Nb_2O_5 composites thin films were deposited on FTO coated glass substrate using electrophoretic deposition (EPD) technique at room temperature. The Hall voltage and current were used to calculate Hall coefficient, and determine the polarity of charge carrier and carrier density. The TiO_2/Nb_2O_5 composites films with volume fraction of Nb_2O_5 above 0.2 were n-type because the calculated values of Hall coefficient were negative. The TiO_2/Nb_2O_5 composites thin films prepared from ratio of 1:1 yielded the highest electron mobility. The results indicate that TiO_2/Nb_2O_5 composites thin films prepared by electrophoretic deposition technique should be in ratio 1:1 for TiO_2 and Nb_2O_5 for optimum electron mobility. Further work is needed to evaluate the potential of TiO_2/Nb_2O_5 composite thin films deposited by EPD in dye-sensitized solar cells application.

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