Optical and dielectric properties of polycrystalline gallium ferrite thin films on Pt/Si substrates

Monali Mishra, Smrutirekha Swain, Sukalyan Dash, Somdutta Mukherjee

**Abstract:** In this work, GaFeO$_3$ thin films are deposited on Pt/Si substrates using sol-gel spin coating technique. The effect of these films on different properties such as: structural, optical and electrical properties are investigated. X-ray diffraction (XRD) confirms that GaFeO$_3$ has orthorhombic $Pc2_1/n$ symmetry. Scanning electron microscopy reveals the uniform distribution of sol and crack free nature of the films. The optical absorption spectrum was recorded using DRS UV-Vis which showed the thin films are absorbed in the visible region. We have also performed experimentally which determines the flat band potential using Mott-Schottky equation. The width of the space charge region and charge carrier concentration of the thin films is also calculated. The dielectric properties of the thin films are also studied in this paper. This work opens up the possibility for the polycrystalline GaFeO$_3$ thin films to be used as photodelectodes.

**Keywords:** GaFeO$_3$ polycrystalline thin films, Dielectric properties, Mott-Schottky analysis.

1. Introduction

Transition metal oxides are effectively used as photoelectrode materials in photoelectrochemical cells for water splitting due to their very low chance of further oxidation during reaction [1]. Photoelectrodes are the semiconductors possessing band gap in the range of 1.5-2.5 eV [1]. The semiconductor materials possess band gap that determine their properties and the properties can be better understood by determining the electronic properties of this class of materials. The electrons jump from valence band to conduction band crossing the band gap leaving behind a hole in the conduction band. There is another concept of Fermi Level, an imaginary energy level at which the probability of occupation by an electron is $\frac{1}{2}$ at any finite temperature. In ideal condition, the semiconductor electrode and
electrolyte solution remains in a state of equilibrium with similar values of electrochemical potentials. The difference between the redox potential of the solution and the Fermi level of the semiconductor causes the movement of charge between the semiconductor and solution to equilibrate the two phases. The excess charge extends into the electrode to a certain distance which is called space charge region. Sometimes there is no charge transfer between the Fermi level of the semiconductor and the redox potential of the solution. The potential is known as flat band potential which can be calculated from the Mott-Schottky relationship. The flat band potential can determine the presence of gas evolution reaction at the counter electrode. For n-type semiconductor, if the flat band potential is more negative than the hydrogen half reaction potential, then hydrogen will be produced at counter electrode and oxygen will evolve in the photoelectrode surface (when the potential of the valence band edge at the surface is more positive than the oxygen half reaction) [2]. But for p-type semiconductor, if the flat band potential is more positive than the oxygen half reaction then oxygen will evolve at the counter electrode [2]. The flat band potential is an important parameter which can be used in the evaluation of photovoltaic performance. TiO$_2$, BaTiO$_3$, ZnO, SrTiO$_3$ etc. are examples of a few transition metal oxides used as photoelectrodes in the photoelectrochemical cell for water splitting [3]. The transition metal oxides (TMOs) such as, TiO$_2$, BaTiO$_3$, SrTiO$_3$ absorb photon in UV region while, the semiconductors such as: Si, CuO, CdSe etc. possess small band gap $\sim$1 – 1.7 eV and hence are effective in the visible region. Fe$_2$O$_3$ has intermediate band gap but due to its poor semiconducting behaviour it cannot be used as photoelectrode. In order to improve the duration (lifetime) of photoelectrochemical cell TMO semiconductors are doped with (adding impurities or creating intrinsic defect) [4], ion implanted using swift heavy ion (SHI) irradiation [5], dye sensitization [6] etc.. Complex metal oxides are more stable compared to their non oxide counterparts and they possess wide range of band gap $\sim$ 1.5-3 eV. Band gap is an important property of the semiconductor to be used as photoelectrode. GaFeO$_3$ is a mixed metal oxide and possess a band gap of $\sim$ 2.1 eV. Particularly, due to the small band gap of GaFeO$_3$ we explored the possibility of GaFeO$_3$ as visible light photocatalyst where we found THBP GFO nanocrystal exhibiting significant efficiency in photocatalytic dye degradation under visible light [7]. Recently, Dhanashekharan et. al. reported hydrogen production by water splitting using GaFeO$_3$ nanoparticles as a photocatalyst [8], suggesting GFO might be used as photoelectrode material for water photoelectrolysis.
GFO is a polar, piezoelectric material which exhibits near room temperature ferrimagnetism and room temperature piezoelectricity [9]. The magnetic transition temperature can be transformed to room temperature and above by changing its Ga to Fe ratio [10]. There are many reports which focus on the magnetic, magnetoelectric and magneto-optical coupling behaviour in polycrystalline or bulk single crystals of gallium ferrite. However, from the device application perspective thin films and nanostructures are more appealing since miniaturization. Thin films are of very low weight and more compatible in device making. There are very few reports in which GFO was grown epitaxially by pulsed laser deposition technique on YSZ (yttria stabilized zirconia) and STO (strontium titanate) substrates [10].

Further for electrical characterization ITO (indium tin oxide) and Pt was deposited on the YSZ and STO substrates using PLD technique to attain metal-insulator-metal capacitor like geometry. The whole deposition process is of very high cost that makes device fabrication costly. The electrical properties of the films are already discussed in the previous reports. In our previous paper we have achieved room temperature ferroelectricity of polycrystalline oriented thin films of GFO on commercially available Pt/Si and n-Si substrates using a low cost chemical solution deposition method [11]. When GFO is deposited on Pt/Si substrate or any other substrate strain is generated. The generation of strain may be due to the variation of thermal expansion between GFO and substrate or may be due to the defects formed during the deposition of the film [12]. The existence of strain may affect the ferroelectric, magnetic, dielectric as well as the optical properties of the films.

In this paper, we report the optical properties and the dielectric studies along with the voltage capacitance measurement of the polycrystalline thin films of GFO grown on Pt/Si substrates by the chemical deposition technique. We have analysed the Mott-Schottky analysis ($C^2$ vs. $V$) of the above sample to determine the flat band potential ($V_{FB}$) and charge carrier or donor density ($N_D$). The flat band potential helps in determining the position of band and the charge carrier density illustrates the efficiency of the semiconductor. The conduction and the valence band edge positions can be corroborated from the band gap calculated from UV-Vis DRS analysis.

**Experimental details**

The GFO Pt/Si (111) thin films were prepared by using spin coating method [8]. The films were characterized by using Zeiss, Merlin Compact field emission scanning electron microscope (FESEM) for microstructural analysis, Rigaku diffractometer with Cu-Kα
radiation for structural analysis and were subsequently investigated using impedance analyzer for the dielectric measurements. For dielectric measurement, Au was sputter coated on Pt/Si film with diameter of 0.2 mm using a shadow mask technique. Here Au acted as top electrode and Pt acted as bottom electrode. For Mott-Schottky measurement, the GFO thin films on Pt/Si (111) substrates were converted into electrodes by making Ohmic contact with a Cu wire using silver paint and were covered by epoxy. The electrodes were immersed in an aqueous solution of 1M KOH. The UV-Vis spectra of the thin films were recorded using bare Pt/Si as reference.

2. Results and Discussion

Fig. 1 (a) shows the FESEM micrograph of spin-coated GFO films grown on Pt/Si substrate. From the micrograph, it is noticed that the average grain size is around 45 nm and the GFO particles are well dispersed on the Pt/Si substrate. The uniform deposition of GFO sol on Pt/Si substrate by spin coating method can also be seen from the figure. The cross- sectional FESEM image of GFO grown on Pt/Si substrate is shown in Fig. 1 (b). The thickness of the thin films of GFO is found to be 200 nm.

![Fig. 1 (a) SEM micrographs of GFO thin films deposited on Pt/Si (111) substrate and (b) thickness of the film.](image)

Fig. 2 shows the XRD pattern of the GFO grown on Pt/Si substrate. The film diffraction pattern is dominated by the peaks correspond to the reflections from (020), (040) and (060) planes of orthorhombic $Pc2_1n$ symmetry of GFO. The estimated lattice parameters are $a=8.7$ Å, $b=9.4$ Å, $c=5.1$ Å [11]. There is no impurity phase found in the XRD pattern except the peaks of GFO and Pt/Si substrate.
Fig. 2 XRD pattern of GFO deposited on Pt-Si (111) substrate.

Fig. 3 (a) shows the optical absorption spectrum of GFO grown on Pt/Si substrate in the wavelength range of 200-800 nm. We got the absorption spectrum of the thin film from the Kubelka-Munk equation [13] which is represented by:

\[ F(R) = \frac{(1 - R)^2}{2R} \]  

Where R is the reflectance and F(R) is the absorbance.

From the figure, we can see that three strong absorption regions are present around \( \lambda = 301, 481 \) and 746 nm. A graph is plotted between \( h\nu \) (photon energy) and \( [F(R)h\nu]^2 \) to get the band gap energy which is shown in Fig. 3 (b). The optical band gap energy is calculated using Tauc’s relation by the following equation:

\[ (\alpha h\nu) = A(h\nu - E_g)^n \]

Where, \( \alpha \), \( h\nu \), and \( E_g \) are absorption coefficient, photon energy and band-gap energy, respectively. \( n = 2 \) for direct band gap semiconductor and \( n = \frac{1}{2} \) for indirect band-gap semiconductor. The band-gap energy of the thin film of GFO grown on Pt/Si substrate is found to be 2.9 eV. Another absorption peaks are observed at 481 nm (2.57 eV), 587 nm (2.1 eV) and 746 nm (1.66 eV) is shown in insert of fig 3(a). The peak at 2.57 eV is assigned to
$^6A_{1g} \rightarrow ^4A_{1g}, ^4E_g$, the peak at 2.1 eV is assigned to $^6A_{1g} \rightarrow ^4T_{2g}$ and the peak at 1.66 eV is identified as $^6A_{1g} \rightarrow ^4T_{1g}$ transition [14]. The later one arises due to the crystal field splitting of FeO$_6$ octahedron with $O_h$ symmetry at the first approximation [14]. The calculated optical band gap value of the thin film grown on Pt/Si substrate is slightly high compared to that reported by Sun et.al. [12]. The reason behind the band-gap modification could be the small microstrain (0.006) [11] in the film by the substrate that induces the lattice deformation leading to the displacement of Fe ions in the FeO$_6$ octahedron affecting the crystal field splitting [15]. GFO deposited on Aluminium Oxide substrate by PLD technique has a high band-gap as compared to our sample, GFO deposited on MgO substrate has similar type of band gap as GFO deposited on Pt/Si substrate [12].

![Fig. 3](image)

**Fig. 3** (a) Absorption spectra of GFO grown on Pt/Si (111) substrates, and (b) band gap of the thin film.

Dielectric constant ($\varepsilon'$) and dielectric loss ($\tan \delta$) of the thin film of GFO grown on Pt/Si substrate is plotted against frequency which is given in Fig. 4 (a and b). The characterization is done at room temperature over the frequency range of $10^2$ to $10^6$. From the impedance data we calculated the real and imaginary part of the dielectric constant by the following two equations:

$$\varepsilon' = \frac{Z''}{\omega C_0 Z^2} \text{ and } \varepsilon'' = \frac{Z'}{\omega C_0 Z^2} \quad (3)$$

Where, $C_0$= capacitance ($\varepsilon_0 A/d$) ($\varepsilon_0$ is the permittivity of free space, $A$ is the area of each sputtered gold dot, $d$ is the thickness of the film)

$\omega$= angular frequency ($2\pi f$)
and $Z^2 = (Z')^2 + (Z'')^2$.

The real part of the dielectric constant ($\varepsilon'$) is plotted against varying frequencies as shown in Fig. 4 (a). We know that dielectric constant has various polarization contributions: interfacial, dipolar, ionic and electronic polarization. At low frequency, all these polarizations except electronic polarization which occur at high frequency are responsible for dielectric constant. So we observe a strong dispersion in dielectric constant at low frequency region which gradually becomes stable towards high frequency region. This type of behaviour of the dielectric constant can be explained by using Maxwell-Wagner and Koop’s model [16] which states that dielectric materials consist of two inhomogeneous layers i.e. the conducting grains and the poor conducting grain boundaries. In the low frequency range, at grain boundaries, the charge carriers become more active and in the high frequency region, at grains, they become more energetic. Therefore more energy is needed to move the charge carriers in the low frequency region. In the high frequency region, less energy is required to move the charge carriers as the resistance offered by the grains is low which results, the low dielectric constant at high frequency region [17]. The intrinsic polarization i.e. true polarization of the material appear at high frequencies ~ MHz. The plot of dielectric constant shows the intrinsic nature and the value of dielectric constant at $10^6$ Hz is found to be 10 which is small as compared to the dielectric value reported by Sun et al. [18] Mohamed et al. [19] found the dielectric constant (at 1 kHz) of Cr doped GFO is 22.7 which is comparable with our result. The dielectric constant of GFO prepared by solgel method is found to be 19 (at 100 kHz) which is also comparable with our calculated value [20].

The frequency dependence of dielectric loss of thin films of GFO grown on Pt/Si substrate is shown in Fig. 4 (b). We can see that the dielectric loss increases as the frequency increases. This also shows the similar type of behaviour which is observed in dielectric constant. The loss or tan $\delta$ means the dissipation of energy in the dielectric material. As the frequency increases from $10^2$ Hz to $10^6$ Hz, the tan $\delta$ or loss also increases from 0.1 to 0.5. So we can say that our sample is weakly lossy in nature.
To understand the charge carrier concentration/potential distribution of GFO at the Semiconductor Electrolyte Interface (SEI), the capacitive measurements were undertaken. The flat band potential and the doping density were calculated by plotting $C^{-2}$ against the applied voltage, where $C$ is the observed capacitance. The total capacitance at electrode-electrolyte interface is the sum of the Helmholtz layer capacitance ($C_H$) and the space charge capacitance ($C_{SC}$). The Helmholtz capacitance on the electrolyte side of the interface is assumed to be so large that its inverse in the following equation is negligible.

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_{SC}} \approx \frac{1}{C_{SC}} \quad (4)$$

Using the Boltzmann distribution to describe the distribution of electrons in the space charge region and Gauss law relating the electric field through the interface to the charge contained within that region, Poisson’s equation can be solved to give the Mott–Schottky equation:

$$\frac{1}{c_{SC}^2} = \frac{2}{\varepsilon_r \varepsilon_0 A^2 N_{Dopant}} \left( E - E_{fb} - \frac{KT}{e} \right) \quad (5)$$

**Fig. 4** Frequency dependant (a) dielectric constant, and (b) dielectric loss.
Fig. 5 Mott-Schottky plot for GFO on Pt/Si substrate measured at 1 kHz.

Here $C$ and $A$ are the interfacial capacitance and area, respectively, $N_D$ is the number of donors, $V$ is the applied voltage, $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, and $e$ is the electronic charge; $\varepsilon$ is the dielectric constant of the material and $\varepsilon_0$ is the permittivity of free space ($8.8542 \times 10^{-12}$ Fm$^{-1}$). Therefore, a plot of $1/C^2$ against potential should yield a straight line from which $V_{fb}$ can be determined from the intercept on the $V$ axis. The value of $N_D$ can also be conveniently found from the slope using following equation:

$$Slope = \frac{2}{\varepsilon \varepsilon_0 A^2 N_{Dopant}} \quad (6)$$

If the slope of the M-S plot is positive, then the semiconductor electrode is of n-type. For n-type semiconductor there is sharp decrease in capacitance when the anodic bias is increased above the flat band potential.

$$W^2 = \frac{2\varepsilon_0 \varepsilon_r (V-V_{fb})}{e N_D} \quad (7)$$

Here, the Mott-Schottky measurement was carried out using potential scan technique using a three electrode Ivium electrochemical work station at 1 kHz. Ag/AgCl and Pt were used as a reference and counter electrode, respectively.

The slope of the linear part of the curve in the Mott-Schottky plot is positive, indicating the n-type semiconducting behaviour of GFO electrode. The n-type GFO thin films can be used in the photoelectrode for solar cells, computers, microchips, photocatalyst for water treatment...
The $V_{fb}$ determined from the extrapolation of GFO electrode is of the order of 0.05 V (V vs Ag/AgCl). The charge carrier concentration $N_D$ and width of the space charge region $W$ is calculated to be $1.77 \times 10^{17}$ cm$^{-3}$ and 303 nm respectively. Very recently Sun et al. [21] reported the n-type behaviour of GFO deposited on FTO substrate and also found similar values of $N_D$.

3. Conclusion

We studied the impedance of the GFO thin films grown on Pt/Si substrate derived by chemical solution deposition technique. The dielectric constant is intrinsic in nature. The as-grown thin films are weakly lossy in nature. We have also discussed the optical properties of the thin film of GFO. With the help of Mott-Schottky analysis we found that our films are n-type in nature which opens up the possibility to use as photoelectrodes in photoelectrochemical cell. The intrinsic dielectric nature and moderate band gap makes the sample as a promising candidate for multiferroic and optical device application.

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4. Reference

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