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Formation and Characterization of Freestanding Membranes Based-Porous Silicon Doped Lithium-Ion

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Abstract: ***Silicon-based fuel cells membrane is under active development to supply chip-scale electrical power supply. In this paper, we demonstrate the use of lithium bromide loaded mesoporous silicon double layer as a membrane material for micro-fuel cell applications. Electrochemical etching is used to fabricate mesoporous silicon double layer surfaces. The effect of lithium bromide impregnation solution on mesoporous silicon freestanding is investigated. The FTIR and scanning electron microscopy are studied to demonstrate the presence of the Li ion in the MFr silicon film. The optical response of the MFr mesoporous silicon film has been performed by the reflectance measurements. The refractive index, absorption coefficient and bang gap change of mesoporous free-standing silicon film are discusses in this work.***

Keywords: Mesoporous silicon Freestanding; Membrane; Lithium Bromide (LiBr); Refractive index; Absorption coefficient; Band gap change

1. Introduction

Because of the remarkable material properties, porous silicon has attracted a great deal of interest in various applications areas. The high specific surface area of the porous layer enables its applications in electronic devices [1], [2], electric vehicles [3]. Silicon has become an attractive material as anode for lithium batteries application because it can react with lithium to form binary alloys with a maximum uptake of 4.4 lithium atoms per silicon atom $Li_{22}Si^{3}_{5}$ [4]. MFr is new type of silicon nanomaterial with potential uses in lab-on-chip devices, cell culture [5, 6], and tissue engineering [7]. MFr membranes are approximately 1000 times thinner than any polymeric membrane [8]. The MFr material is a 50μm thick, membrane made with scalable silicon manufacturing.

In this paper we report a facile method to realize thin film of freestanding mesoporous silicon membrane to be used as a proton exchange membrane in hydrogen fuel cell.

In the present work, we studied the morphological characteristics of mesoporous freestanding membrane with and without soaking in the LiBr solution. A simple method is used to evaluate the refractive index. The absorption coefficient (α) was achieved to determinate the band gap of (MFr) before and after soaking in LiBr solution.

2. Experimental

Freestanding mesoporous silicon can be fabricated by etching crystalline silicon wafers with an HF/Ethanol at a constant current density. The porosity and depth of the porous silicon can be controlled by varying the current density or concentration of hydrofluoric acid (HF) [9]. The porous silicon layer can be removed from the bulk silicon using either a one step process [10].

Prime grade, boron doped p^{+}-type (100) silicon wafers with thickness of 275 ± 25 μm and resistivity of about 0.01Ωcm were used to fabricate MFr, electrochemical anodization process in an electrolyte solution composed of HF (40%): ethanol with a volume ratio of 1:1 was used.

First, pores were etched into the silicon wafers at a constant current density of 10 mA/ cm^2 during 15 min delivered by a Potensiostat (Pg-201-2X) at room temperature.

Secondly current density was increased at 80mA/cm^2during 15min. The etchtime determined the depth of the pores [11].The MFr layer can be fabricated with an average pore diameter between 2 and 50 nm and thicknesses between 10 and 40 μm by adjusting the current density or HF concentration [12], this double porosity layer is estimated in order to assure the gases separation [13].

Then, the current density is suddenly increased causing the base of the pores to rapidly expand and overlap, thus lifting the porous silicon from the bulk substrate. This leads to separation of a 40 μm thick MFr membrane from the bulk silicon as illustrated and shown in a corresponding image in Figure 1.

After the fabrication process the MFr was removed from the etching cell and washed with DI water and dried inN_2 flow. MFr was treated with a LiBr solution, the solution was made by dissolving 5.53g of LiBr into 10 mL of desionised water and stirring at 60 °C for 15 min. After LiBr soaking, the (MFr/LiBr) film was heated to500°Cunder oxygen.

The infrared spectroscopy measurements of the sample were determined with a Nicolet MAGNA-IR560 spectrometer. The range of spectra was from 400 to 1200cm^{-1} and the UV−v is measurement of the film was done using

LAMBDA 950 UV–vis–NIR spectrometer equipped with an integrating sphere.

3. Discussion and results

3.1 Fourier Transform infrared Analysis (FTIR)

FTIR measurements were carried out in order to investigate the chemical composition of the obtained MFr. Infrared spectroscopy measurement was performed before and after soaking in the LiBr solution as shown in Figure 2a and 2b.In this spectrum, there are four bands around 628, 910,1062 and 2113 cm^{-1}, associated to the Si–Si bond,Si–H_2 scissors mode, respectively [14]. Abroad band centered at 789cm^{-1} corresponding to the Si–Li bond formation occurred in all the treated samples for the two studied porosity, indicating the interaction between lithium and silicon through the soaking process. LiBr, although has been dried, seems to be sufficiently hygroscopic that the infrared spectra show moisture traces when it is used.

3.2 Scanning electron microscopy (SEM)

Figure 3a and 3b shows the surface morphology of the mesoporous freestanding silicon layer before and after soaking in the LiBr solution. We can remarks that the pore is cover by lithium and a low layer of lithium is deposited at the surface of MFr.

3.3 Ultraviolet and Visible analysis

To analyze the MFr and understand its role in improving the performance of the MFr as a membrane material for the fuel cells application, UV-VIS specta in the wavelength range of 300 – 1800 nm of mesoporous freestanding silicon of each porosity before and after soaking in the LiBr solution are shown in Figure 4a and 4b.

Figure 4 shows a decrease of transmission with LiBr soaking for the two side of porosity. It is generally accepted that the loss in the transmission spectra is not due to the absorption but also due to scattering of LiBr into the mesoporous freestanding silicon.

For extracting refractive index from the transmission measurements, we have used this relationship in Eq 1.

$$nd = \lambda_1\lambda_2 / 2(\lambda_2-\lambda_1) \quad (1)$$

where n, e, and m denote the refractive index, thickness, and the order of m^{th} maximum, respectively. λ_1 and λ_2 are the two adjacent maxima in mth order.

The obtained refractive index for a gradient-porosity mesoporous freestanding film is illustrated in table 1.It appears obvious that for meso-PS layers, n_{PS} decreases as the porosity increases due to the fact that the volume fraction of voids rises as the porosity increases.

From this table, it is clear that, the values of this refractive index are increased with immersion in LiBr solution. This indicates that the pores are filled by Li-ions, the medium become opaque.

One can conclude that the films turn out to be opaque after soaking process. This is due firstly, to the absorption increase resulting and secondly, to the light scattering increase with crystallite size and particle clustering.

3.4 Determination of energy band gap

The study of optical absorption gives information about the band structure of mesoporous free-standing silicon membrane by plotting $(\alpha h\nu)^{1/2}$ as a function of photon energy (hν). The analysis of Thutupalli and Tomlin [15] is based on the following relations:

$$\alpha (h\nu)\, h\nu = B (h\nu - Eg)^2 \quad \text{and}$$

$$(\alpha h\nu)^{1/2} = f(h\nu).$$

The absorption coefficient (α) can be determined as a function of frequency using the formula:

$$\alpha = 1/d * [Ln (1-R)^2 / T]$$

Where R is the reflectivity, T is the coefficient de transmission and d is the thickness of the sample under investigation. The thickness d of mesoporous silicon film is constant before and after soaking in the LiBr solution.

Figure 5 shows the reflectivity spectra of the two side of mesoporous silicon film (a) the low porosity side $P_1$and (b) the high porosity side P_2.

Collect reflectivity and transmission data we can achieve the value of absorption coefficient and then the band gap energy variation after lithium soaking.

Figure 6a and 6b shows that for the two porosity sides the absorption coefficient increases after LiBr soaking.

By plotting $(\alpha h\nu)^{1/2}$versus photon energy (hν), each linear portion indicates a band energy gap (Eg). The band gap energies (Eg) obtained in the present work are given in Table 2. From this table, it is clear that, the values of these energies are decreased with the process of lithiation. This indicates that there is a charge transfer complexes arise between the porous silicon and the Li-ions.

By comparing the results obtained for Li doped with the ones for undoped MFr samples (Table 2), we can see that the LiBr doping decreases the band gap. The UV–Vis analysis shows that the optical band gap of the Li doped MFr silicon thin film decreases from 1.25 eV to 1.16 eV for the low porosity side and decreases from 1.37to 1.19 for high porosity.

The decrease of the LiBr optical band gap after Lithiation process may be due to the change of the film density and the increase in grain size. The band gap decreases induct the increases of conductivity after the lithiation process. Therefore, the reduction in band gap is favorable for the enhanced performance of mesoporous silicon membrane for fuel cells application.

4. Conclusion

We have demonstrated the process for generating a gradient porosity layers in mesoporous free-standing silicon as a membrane material for fuel cells applications.

We have studied the effect of the lithiation process on structural and optical properties.

The surface morphology of MFr silicon film is columnar, before the lithiation process we can observe the structure of the pore but after the lithiation the pore is filled with lithium bromide solution and a fine layer of this solution are deposited at the surface of the porous film.

Our results show that MFr without LiBr has a low refractive index compared to MFr with LiBr for the two-porosity studied. One can conclude that the mesoporous silicon films turn out to be opaque after lithiation process. This is due to the absorption increases. The band gap decreases after soaking in LiBr solution these results confirm the choice of LiBr as filler for porous silicon membrane for fuel cells application.

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Figures Captions

Figure 1: Protocol of realization of double porous silicon layer from the underlying bulk silicon.
Figure 2: FTIR spectra of mesoporous freestanding silicon film before (a) and after(b) soaking in the LiBr solution.
Figure 3: SEM image of mesoporous freestanding silicon layer surface before (a) and after (b) soaking in the LiBr solution.
Figure 4: Transmission spectra of MFr before and after soaking in the LiBr solutionfor the (a) Low porosity side and(b) high porosity side.
Figure 5: Reflectivity spectra of MFr before and after soaking in the LiBr solutionfor (a) Low porosity side and(b) high porosity side.
Figure 6: Thevariation of absorption coefficient of mesoporous free standing silicon membrane before (a) and after (b) soaking inLiBr solution.

Tables Captions

Table 1: Variation of refractive index of mesoporous free-standing membrane before and after soaking in the LiBr solution.

Table 2: Impregnation effect of LiBr solution on the MFr film on optical band gapbefore and after soaking in the LiBr solution.

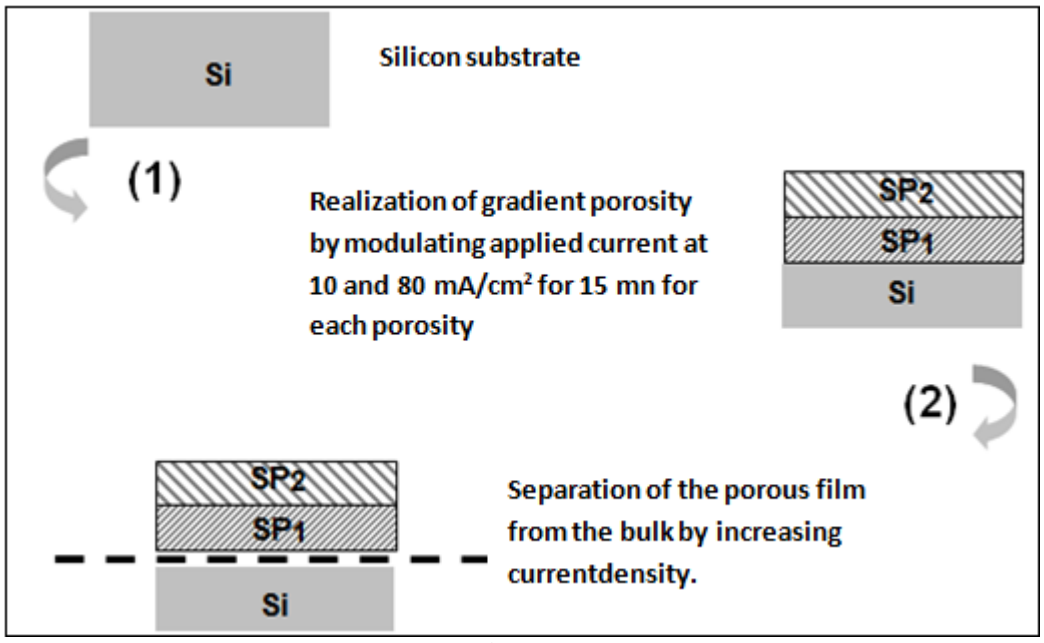


Figure 1

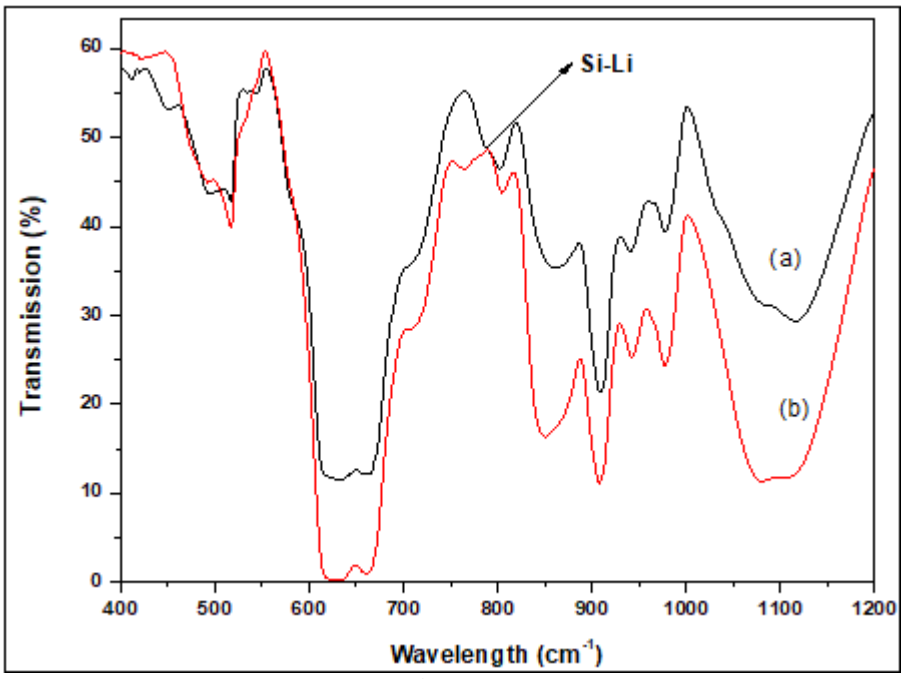


Figure 2

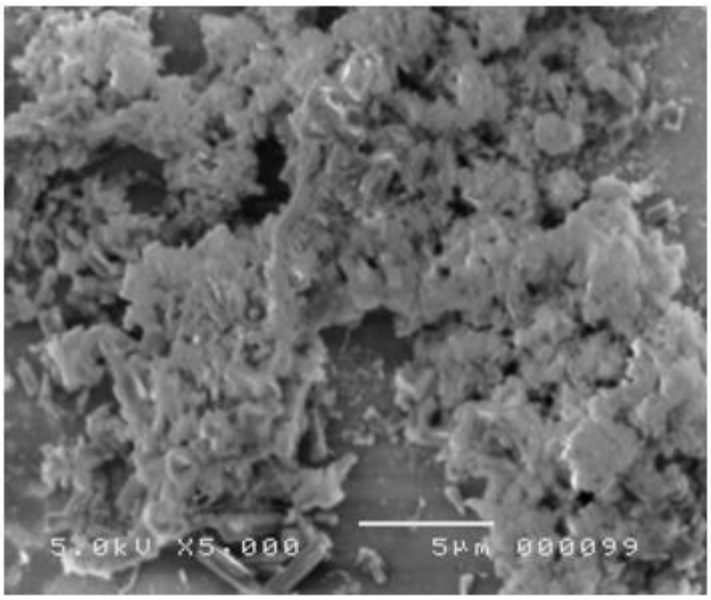
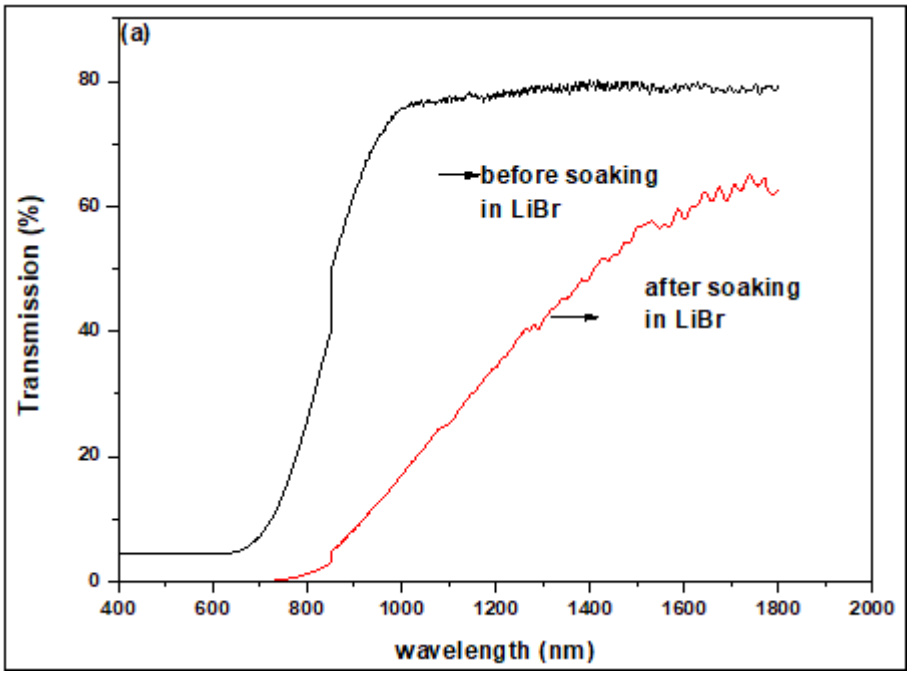


Figure 3



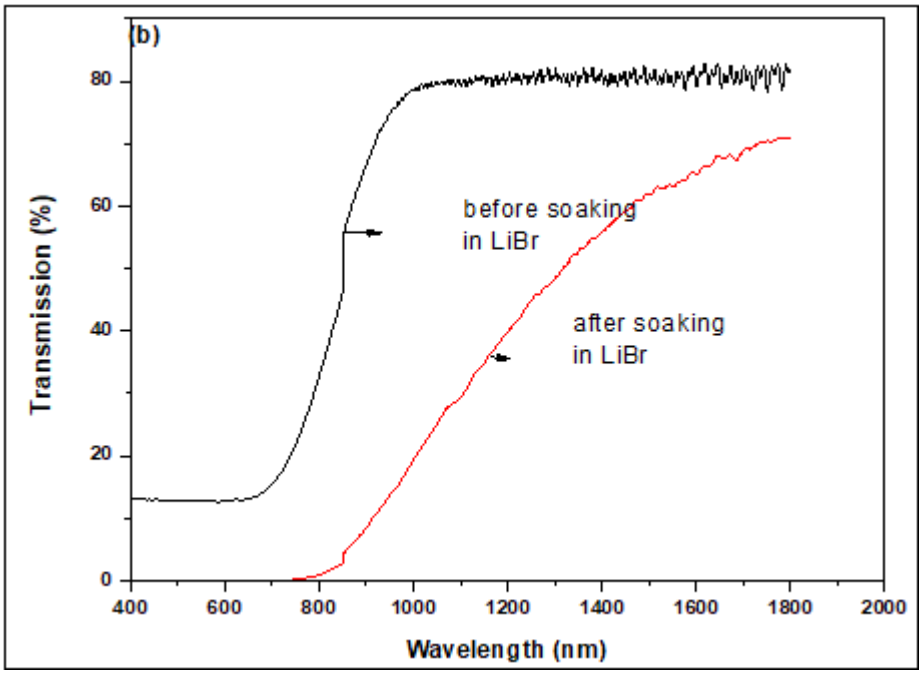
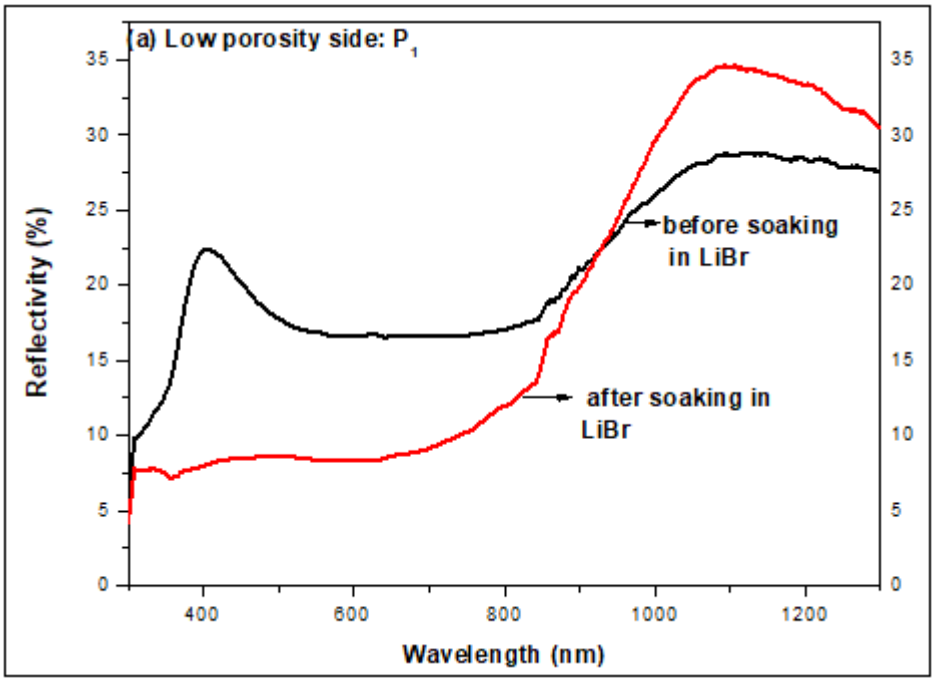


Figure 4



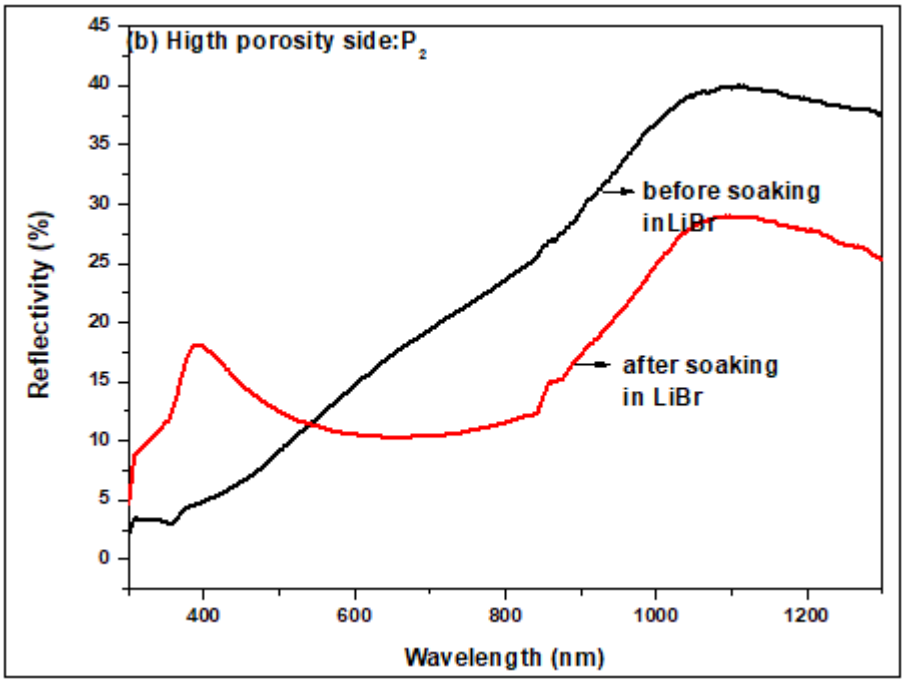
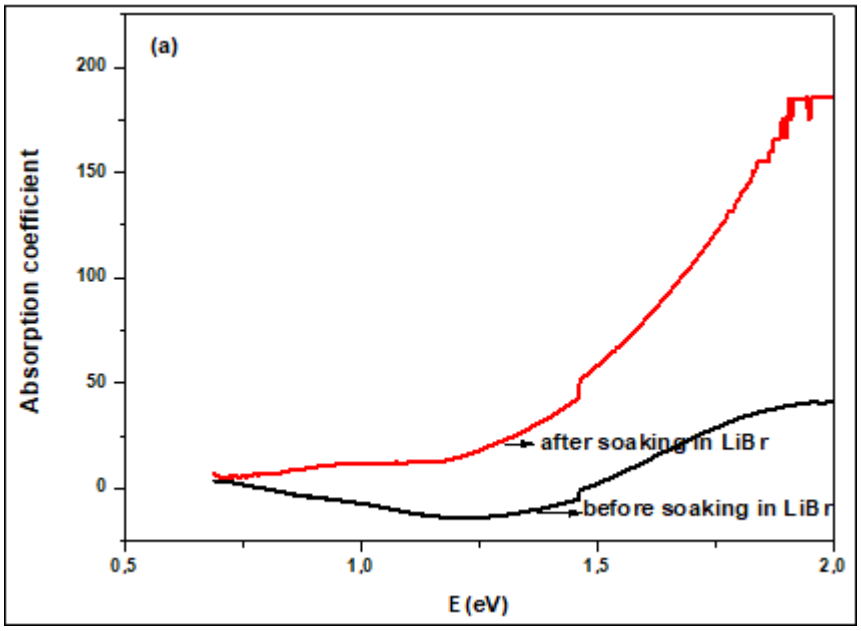


Figure 5



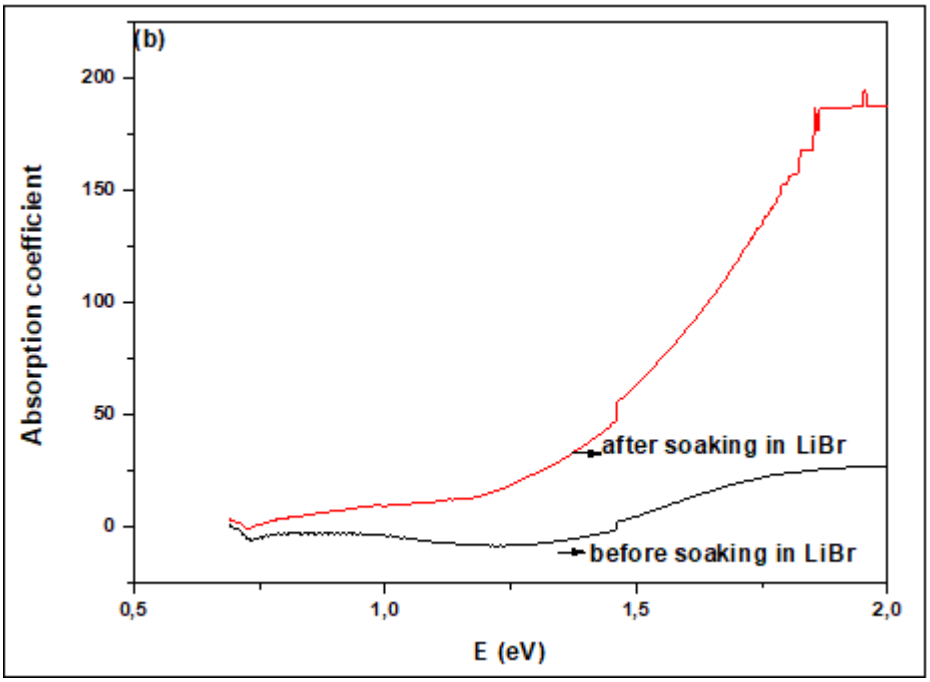


Figure 6

Table 1

Refractive index (n_{PS})	Low porosity side	High porosity side
MFr without LiBr	2.19	1.7
MFr with LiBr	2.44	1.9

Table 2

Sample no.	E_g (eV)(Low porosity side)	E_g (eV)(Higth porosity side)
Free standing	1.25	1.37
Free standing with LiBr S/3	1.16	1.19