COUPLING ORGANIC AND INORGANIC LUMINESCENT CONCENTRATOR FOR SOLAR CELLS: A NEW METHOD TO OPTIMIZE ENRGY FROM SUN

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Abstract

The purpose of this work is to study the influence of increasing the efficiency of a silicon solar cell by introducing a new method. This method includes coupling both inorganic and organic luminescent solar concentrator to a silicon solar cell. First, a chemical etching to the emitter of solar cells is obtained by using HF solution in order to form porous silicon (inorganic solar concentrator), usually known as stain-etched PS. This process may increase the surface area directed to the incoming solar radiation. In addition, it provides an antireflection coating (AR) to the cell surface, where the high refractive index of Silicon (used in manufacturing the silicon solar cells) at solar wavelengths creates large reflection losses that must be compensated for by applying antireflective coatings. Then we applied a thin layer of organic dye as an organic Luminescent Solar Concentrator (LSC) on the top of the cell to increase the absorption window from incident light, in order to get the advantage of potential band gap tuning, via light trapping. The control bare cell has efficiency of (11%), but obtained efficiency enhancement of the cell with dye (13.6%), the etched cell (18.7), and etched and dyed cell (23.8%).

Keywords: Photo voltaic cell, Porous silicon, Luminescent Solar Concentrators, Stock's shift

1. Introduction

Reducing the front surface reflectance of crystalline silicon (Si) solar cells is one of the most important issues for improving the cells efficiency. Several research groups have used porous silicon (PS) layers as an antireflection coating to reduce the surface reflectance (Prasad *et al.,* 1982; Smestad & Kunst, 1992; Tsu *et al.,* 1993; Bilyalov *et al.,* 1999). The refractive index for (PS) layers depends on its porosity and its morphology, the optimization of these factors may lead to an ideal antireflection coating for silicon solar cells (Peckering *et al.,* 1984). Porous silicon possesses other advantages and can also (i) enlarges the spectral sensitivity region (Bilyalov *et al.,* 2000), (ii) improves photo-generation of carriers (Bilyalov *et al.,* 2000; Vitanov *et al.,* 2000; Vitanov *et al.,* 1997), (iii) create simultaneously a selective emitter and an antireflection coating in the same step (Bilyalov *et al.,* 2000; Vitanov *et al.,* 2000; Vitanov *et al.,* 1997; Strehlke *et al.,* 2000).However, strong surface recombination related to the roughness of the surface after porous silicon layers formation on n+ doped emitter of conventional solar cells (Theiss *et al.,* in: G. Amato, C. Delerue, H.J. Von-Bardeleben, 1997; Boeringer & Tsu, 1994; Wang *et al.*, 1997), and the degradation of its parameters with time if special treatments to preserve the PS properties are not used (Gupta *et al.*,1995; Aroutiounian *et al.*,2004; Venkateswara *et al.*,1991). Porous silicon has attracted great attention due to its room temperature photoluminescence in the visible light range (Canham, 1990). Porous silicon shows different features in comparison to the bulk silicon such as shifting of fundamental absorption edge into the short wavelength and photoluminescence in the visible region of the spectrum. However, different hypothesis is reported on photoluminescence porous silicon surface. The first includes the quantum confinement effect which is due to the charge carriers in narrow crystalline silicon wall separating the pore walls, the second is due to the presence of luminescent surface species trapped in the inner walls as the source light emission and the third one is due to the presence of surface confined molecular emitters *i.e.* siloxene (Pavesi & Guardini, 1996). Porous silicon consists of a network of nano scale sized silicon wires and voids which, are formed when crystalline silicon wafers are etched electrochemically in hydrofluoric acid based electrolyte solution under constant anodization conditions. The precise control of porosity and thickness allows the tailoring of optical properties of porous silicon and has opened the door to a multitude of applications in optoelectronics technology. Such structures consist of silicon particles in several nanometer size separated by voids. Hence, porous silicon layers are regarded as nano materials which, can be obtained by the electrochemical etching of silicon wafer. Porous silicon structures has good mechanical robustness, chemical stability and compatibility with existing silicon technology therefore has a wide area of potential applications such as waveguides, 1D photonic crystals, chemical sensors, biological sensors, photovoltaic devices *etc.,* (Vasquez-A *et al.*, 2007). Photovoltaic's is a renewable energy which is helpful to reduce the pollution and climate change effects. Today, photovoltaic industry is dominated by silicon solar cells technology because of the reduced cost. Due to wide use of solar energy, there is the need of creation of new technologies and materials hence; porous silicon is expected to be promising one. The crystalline silicon is an important and dominant material over several years due to its well known properties and established infrastructure for photovoltaic manufacturing (Voos *et al.*, 1992). It is the basic material for the production of solar. Porous silicon is an easily fabricated material that has extremely high surface area to volume ratio, making it an ideal platform for surface based sensors, such as solar cells. In order to improve the performance of solar cells, two methods to the surface of the solar cell, namely, inorganic luminescent solar concentrator (Porous silicon layer) and the organic luminescent solar concentrator (dye) were applied.

In order to enhance the optical response of the solar cell we use organic Luminescent Solar Concentrators (LSC). The LSC device is planer geometry of transparent material (matrix) impregnated with randomly dispersed guest dye molecules that lumince efficiently. Incident Photons whose wavelengths lie within the absorption band of the gust are absorbed and subsequently re-emitted at longer wavelengths (the difference in wavelength between the absorption and emission bands is termed Stock's shift).

Dye molecules absorb incident radiation and re-emit isotropically to host medium and re-absorption by luminescent molecules. Ideally, a large fraction of the light is trapped due to total internal reflection inside the plate and transferred to the solar cell surface to convert the radiant into electricity. LSCs are used due to recent advances in the stability of organic dyes and the efficiency of quantum dots, there has been an interest in (LSCs) as a key of photovoltaic devices.

The present work will report the fabrication and characterization of the new composed LSC which consists of inorganic etched silicon solar cell surface covered with organic luminescent dye species imbedded in a transparent substrate.

2. Theory

The most important advantages of using porous silicon in sun sensors and solar cells are: the highly textured nature enhances light trapping and reduces reflectance losses; its band gap may be adjusted for optimum light absorption also it behaves as a direct band gap semiconductor (similar to gallium arsenide and gallium phosphate) with a large quantum efficiency; the photo luminescent properties of porous silicon may be used to convert ultraviolet and blue light into light of a longer wavelength, improving the efficiency of solar cells. From the optics viewpoint, structures with sizes larger than the wavelength of incoming light enhances light trapping by reflecting incoming radiation in random directions (Stalmans *et al.*, 1998). Structures much smaller than the incoming wavelength alter the effective refractive index of the film and allow it to be tuned between that of silicon (Si) and ambient (Theiss, 1997). Meanwhile, the operation of organic luminescent solar collectors (LSC) is based on the idea of light pipe trapping of molecular or ionic luminance. This trapped light can be coupled out of the LSC into the underneath (the direction of attached solar cell) in such a way that the LSC provides concentrated, red shifted wavelength flux that is spectrally matched to the Photo voltaic cell so as to reduce the radiation heating and increase the electrical output of the photo voltaic cell. The LSC does not need to track the sun and in fact can produce highly concentrate light output under either diffuse or direct insulation.

If the dye molecule absorbs the incident photon, it will vibrationally relax to an excited single state on the time scale of Pico seconds to the excited triplet state via intersystem crossing. Four channels are then available by which the molecule can relax to its ground state:

1. Fluorescence from the excited singlet state,
2. Phosphorescence from the exited triplet state,
3. Nonradioactive transfer of the excitation to the nearby molecule,
4. Internal conversion of the excitation to molecular vibrations or phonons, which are dispersed in the lattice.

In the single dye LSC, the only transfer that can occur is to a similar dye molecule or to the matrix material, both of which effects are relatively negligible due to the dominance of intra-molecular effects. So the important types of energy transfer are fluorescence and phosphorescence (luminescence) and internal conversion. The conceptual operation of an LSC is illustrated by the diagram shown in Figure 1.

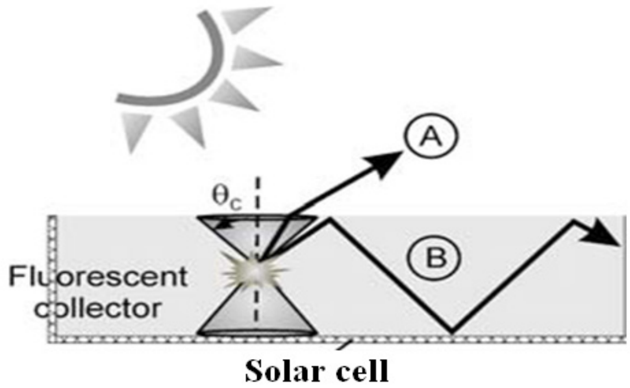

Fig.1. *Schematic diagram of fluorescent collector, showing the double escape cone with apex angle θ_C. In the simplified theory used in this paper, ray (A) illustrates the photon flux N loss which escapes from the front face of the collector, and ray (B) illustrates the flux Nwork which illuminates the solar cell.*

A transparent material called the matrix (poly vinyl alcohol) is impregnated with guest luminescent absorbers (for example, organic dye molecules) having strong absorption bands in the visible and UV regions of the spectrum, and also having an efficient quantum yield of emission. Solar photons entering the upper face of the plate are absorbed, and luminescent photons are then emitted. Snell's law dictates that a large fraction of these luminescent photons are trapped by total internal reflection; about 74% of an isotropic emission will be trapped in a matrix plate with an index of refraction of 1.49. Successive reflections transport the luminescent photons to the edge of the plate. The photon flux of an idealized LSC is the product of the absorbed solar flux, the fraction of the resulting luminescence that is trapped, and the geometric ratio of the area of the face directly exposed to sunlight divided by the area of the face that is covered by solar cells. Using the cell of Fig. 1 as an example, a unit length of the plate which is L units wide and D units thick will have a geometric gain Ggeom, which is given by:

$$\text{Ggeom} = LID = Af/Asc$$

Where, *Af* is the area of a face and Asc is the area of the solar cell.

A host material plate of 2 mm thick were used, so that a square meter photovoltaic solar cell (PSC) section will have a geometric gain of,

$$\text{Ggeom} = 222$$

Such a gain exceeds the concentration of other known nontracking collectors using lenses or mirrors. Thus a high-cost high-efficiency solar cell can be coupled to this high-gain low-cost concentrator for a potentially low-cost system.

However, as nature usually dictates, a practical LSC will have a number of parasitic losses that limit the actual concentration to values lower than Ggeom. Among these losses are inadequate absorption bandwidth, imperfect quantum efficiency, self-absorption of luminescence, absorption by the matrix material, reflective mismatches, geometrical trapping effects, and of course, the lifetime of the materials used. Clearly, system optimization means close attention to minimizing these various losses.

3. Experimental procedure

Figure 2 summarizes the experimental steps taken in this research: The bare cells were first studied, to be considered as a reference. The first sample is coated with a dye film. The other cell has been etched then coated with the dye.

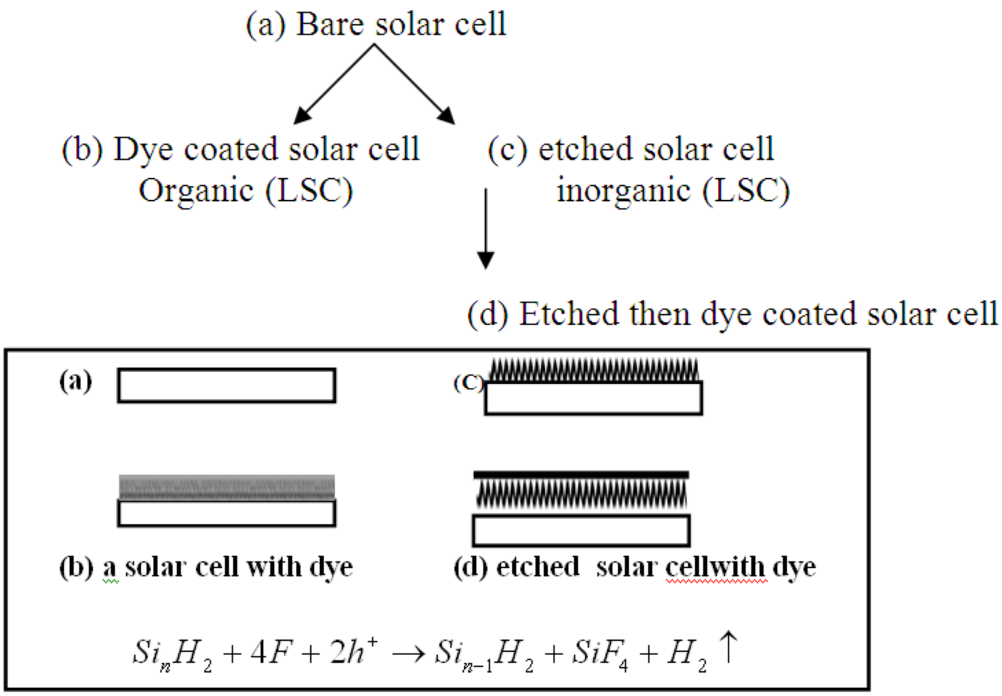

Fig.2. *Sample preparing steps and the etching equation*

One of the methods of producing the PSi is the photo-chemical dissolution of a silicon substrate in the presence of a hydrofluoric acid (HF). The porosity (percentage of empty space) of the PSi formed at the pore tips is affected by the HF concentration, the duration of the etch, temperature, and ambient lighting conditions. Therefore, the engineering of porous layers with desirable optical properties can be achieved.

In this work, the silicon solar cells samples were prepared by photo-chemical etching in 40% Hydrofluoric acid with ethanol with etching time of 3 min. The halogen lamp power density was kept constant during etching process at (0.154 W/cm^2). Randomly pits were formed in the surface as illustrated in figure (2). These pits were filled and covered with LSC aqueous layer and left to be dried under gravitational force sedimentation method.

Organic LSC were prepared from Poly Vinyl Alcohol (PVA) as a matrix doped concentration of 1x10^{-4} mole/liter. The dry sheet thickness was chosen to be (1mm).

Rhodamine 101 dye was selected for the study because, comparing with some other dyes used for the same purpose, the absorption curve of the cell nearly overlaps with the fluorescence spectrum of the dye; also it has good fluorescence intensity.

The cell is illuminated with a sun simulator lamp; all experiments were carried out in the laboratory conditions. The structure of etched silicon solar cell was investigated by optical microscope and optical reflectance analyzer. The I_{sc}, V_{oc}, I_{max}, V_{max} and cell efficiency of the solar cell were carried out and analyzed.

4. Results and discussion

Amorphous silicon solar cell has good response to incident radiation at about 1000 nm while this is not the peak radiation of solar spectrum. This means that the the solar energy is not utilized in a sufficient way. This affects the efficiency of solar cell. Two luminescent solar collectors were used to enhance the efficiency: Inorganic LSC (porous silicon) and organic LSC (dye).

4.1 Effect of inorganic LSC (porous silicon) on the performance of the solar cell

4.1.1 Optical properties

The keys obtained from the etching technique is increasing the area facing the incident radiation, this improves the compact ratio (surface to volume ratio). Also, studying the optical properties of the etched solar cell showed that the etched surface has an excellent reduction in the reflected radiation from the surface, as it is obvious in figure 3. The measurement showed that the reflectivity is reduced from 9.5% for unetched cell to the 1% for etched cell (porous), *i.e.* the porous silicon enhances the absorption via radiation trapping through the etched surface of the cell.

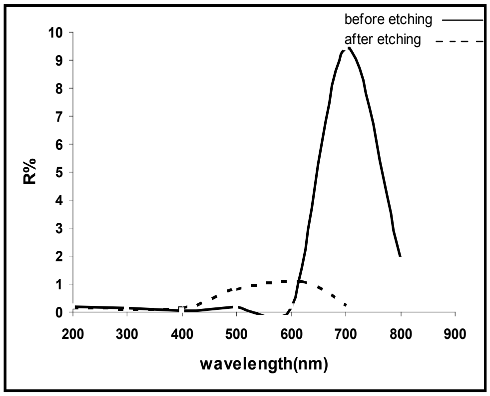

Fig.3. *The reflectance versus wavelength for the solar before etching and after etching (5min).*

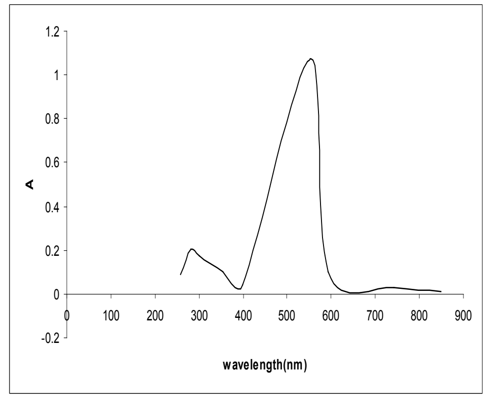

Fig.4. *The absorbance of bare solar cell*

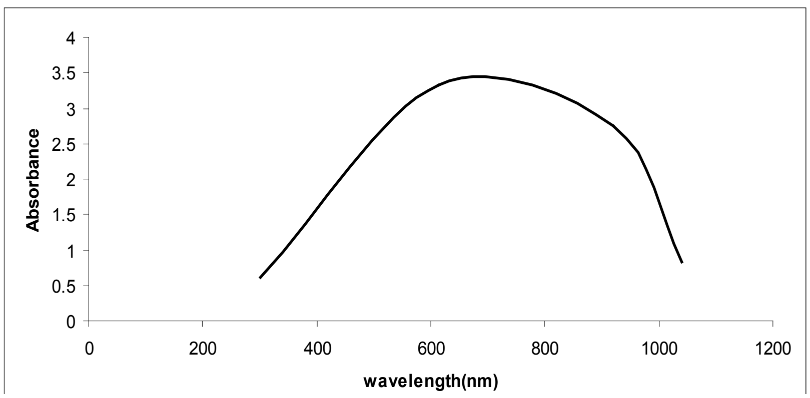

Fig.5. *Absorption of the inorganic luminescent solar collector (etched solar cell). Comparing the two figures above we can notice that the etching process has an obvious enhancement to the absorption peak and an excellent wide*

Comparing figures 4 and 5, the absorption of the etched solar cell was found to be improved. The absorption peaks are shifted upward and the absorption range is expanded from (450nm to 550 nm) in figure 4 to (400nm to 900 nm) in figure 5.

This provides very good window to the underneath layer (the organic luminescent solar collector). This property contributes in increasing the efficiency of the solar cell via permitting absorption and emission of sun radiation in broader range of energies. This wide range of the energy gap also gives an indication about this layer that it is a submicron silicon layer. The value of the efficiency (13.5%) is obtained at etching time of (5 min), noting that the reference efficiency (without etching) is 12%. This is found in table 1 Neglecting the transmission (very low values as shown in figure 6) and reducing the reflection give chance to better absorption of radiation and enhancing the efficiency of the system, this is shown in table 1.

Table.1 *Efficiency values for different solar cell systems.*

Tested system	Efficiency %
Bare solar cell	11.6
Inorganic LSC +cell	18.7
Organic LSC + cell	13.6
Coupled inorganic and organic LSCs	23.8

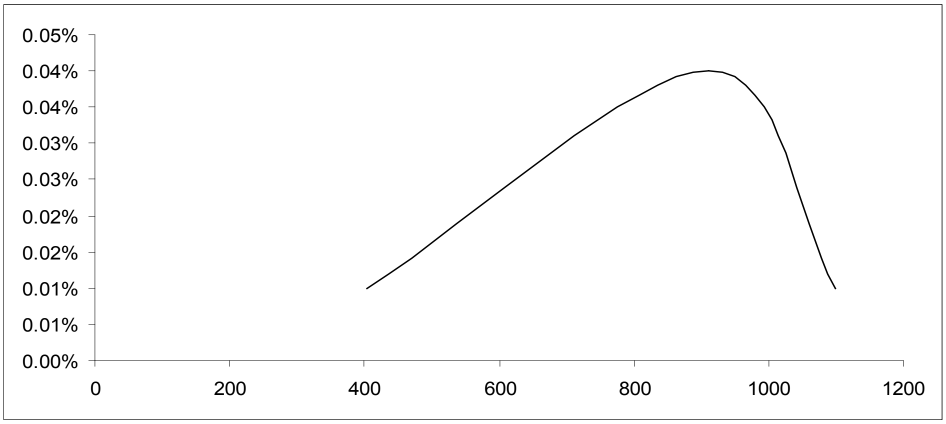

Fig.6. *Transmission versus wavelength of etched solar cell*

4.2 Effect of Organic Luminescent Solar Concentrator (LSC) on the performance of the solar cell

Any energy above the band gap energy is not utilized by the solar cell and instead goes to heating the solar cell and hence the ratio of photons to power is reduced. The inability to fully utilize the incident energy at high energies and the inability to absorb low energies of light represents a significant power loss in solar cells consisting of a single *p-n* junction, and hence to utilize the un-absorbed photons organic LSC is used. Figure 7 shows the peak absorption of the organic dye which excellently matches peak emission of the solar radiation.

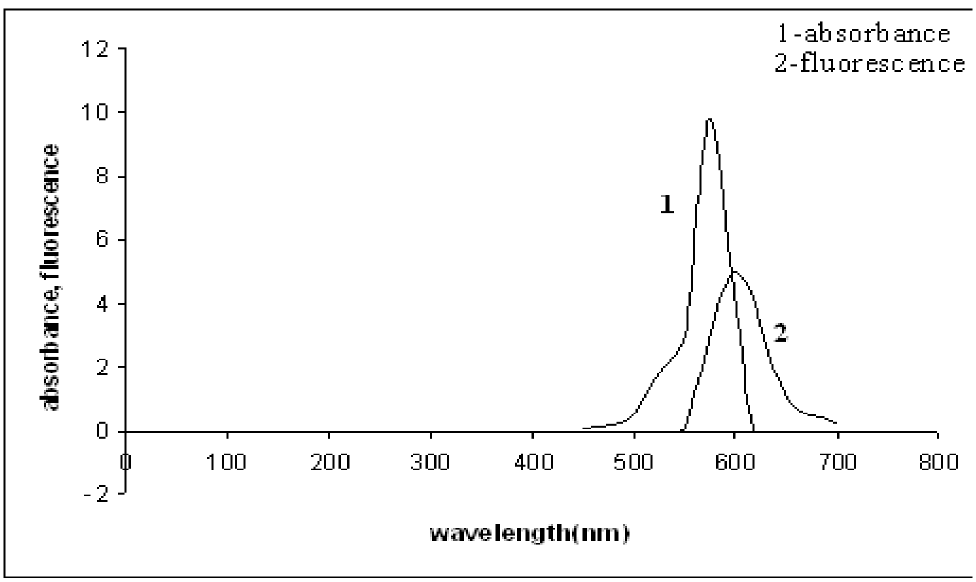

Fig.7. *Absorption and fluorescence spectra of organic dye. Notice the large overlap (stock shift) between the two spectra. Absorption can be enhanced for a high concentration LSC.*

LSCs absorb solar photons and re-emit them via fluorescence over a narrow band at longer wavelengths (red shift). This downshifted radiation is transported towards downward direction by total internal reflection to illuminate the solar cell. The tested absorbance and edge fluorescence spectra of the fluorescent collectors prepared in this work from polymeric solutions of organic dye are shown in figure 7. The plot indicates that the photons that are guided to the solar cell via the organic LSC are available within the range 500-670 nm. The peak intensity tends to shift to the longer wavelength region (red-shift), and this is very suitable for the absorption response of the solar cell. Applying the organic LSC, the module efficiency increased. This is due to the light being shifted from $\lambda < 500$ nm to $\lambda > 650$ nm

4.3 Effect of coupling inorganic and organic Luminescent Solar Concentrator on the performance of the solar cell

For the first time, coupling morphology gain in Nano-Porous Silicon and radiation shift gain in organic dye for solar cell surface is applied. The results are excellent. This is due to optimum absorption ability of solar cell to receive radiation (figure 8)

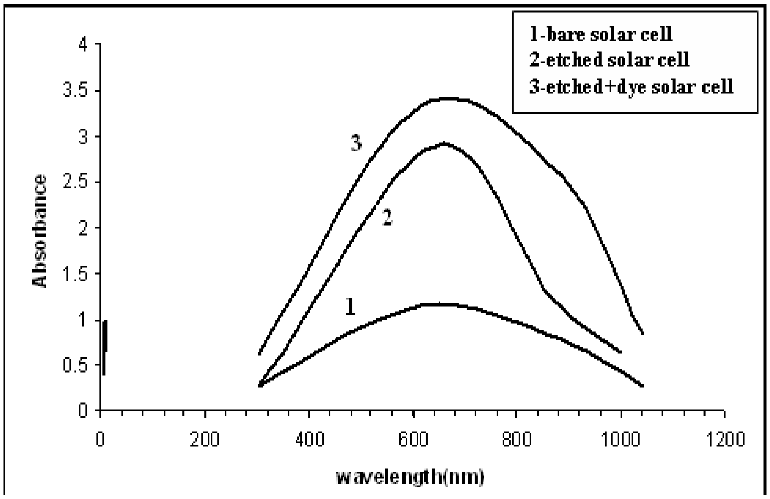

Fig.8. *Absorption spectra of 1- bare solar cell 2- etched solar cell 3- etched and dye coated solar cell*

A basic test is carried out to draw the I-V characteristic curve for all tested systems (figure 3-7). The bare cell gives the lowest curve while the etched and dye coated cell gives the widest curve. Etched cell absorption lies between both. Figure 9 shows I-V characteristic curve for all tested systems. Table 1 illustrates the results of calculated efficiency (efficiency values for different case of solar cell).

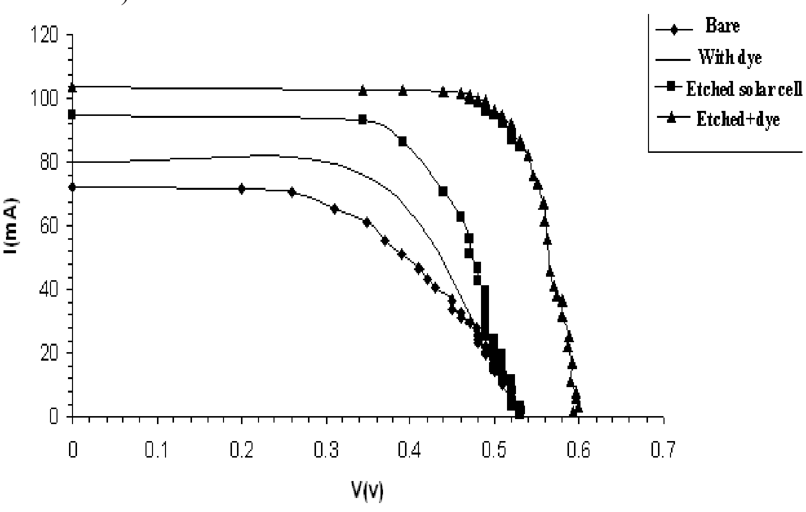

Fig.9. *I-V characteristic curve for all tested systems. Etched and dye coated cell gives best result among other curves.*

5. Conclusion

The light trapping and anti-reflection properties of inorganic solar concentrator, in addition to its simplicity of formation and broadly tunable morphology, makes it particularly well suited for photovoltaic applications. It has been used with the organic luminescent solar concentrator to enhance the efficiency of the solar cell used for all known purposes. The new method gives excellent results as it is illustrated in figure 10, where the bare cell has efficiency enhancement of (11%), the cell with dye (13.6%), the etched cell (18.7%), for etched and dyed cell (23.8%).

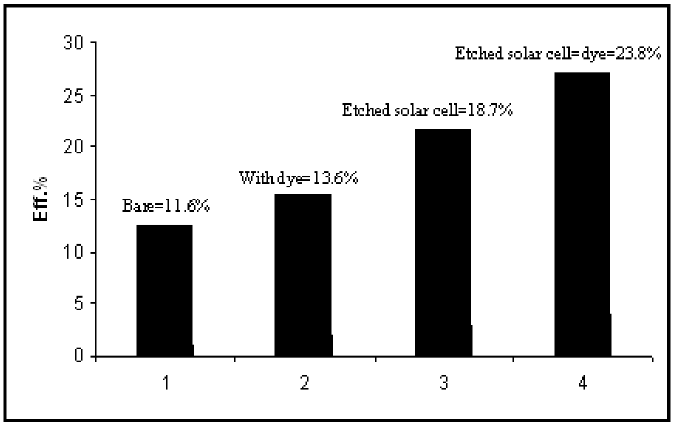

Fig.10. *Solar system efficiency enhancement, bare cell (11%), the cell with dye (13.6%), the etched cell (18.7), for etched and dyed cell (23.8%).*

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