Optical studies on ClAlPc (dye) decorated porous silicon for solar cell application

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Abstract— This Nanostructured porous silicon (PS) samples were prepared at a current density of 30 mA/cm^2 for etching periods 10, 20, 40 and 60 minutes. Then the surfaces of these PS samples were sensitized with derivative of Chloroaluminum Pc (ClAlPc) which is having higher solubility than Phthalocyanines. Then the effect of this dye ClAlPc on PS prepared at different etching periods are investigated using UV-vis absorption and Photoluminescence (PL) emission techniques. The minimum PL emission intensity shown by dye sensitized PS prepared at current density of 30mA/cm^2 and etching time period of 60 min reveals that it has good absorbance of radiation.

Index Terms—, Chloroaluminum Pc, Dye sensitized solar cells, Photoluminescence, Porous silicon.

1 INTRODUCTION

DYE Sensitized Solar Cells (DSSCs) are a new class of photovoltaic devices, formed by (like TiO_2) anode coated with an organic dye [1]. Silicon is the only material which can produce solar conversion efficiency to a level of 29% [2]. In the present scenario there is an immediate and urgent need for high efficiency solar cells which are cost effective per unit area to meet the scarcity of power and an alternate source of energy. But after the advent of nanomaterials, this has taken a new turn. The efficiency depends on the amount of solar radiation falls on the surface area of the material and if this surface is made larger, the open circuit voltage will be enhanced much. Devices based on interpenetrating networks of porous semiconductors have shown strikingly high conversion efficiencies, competing with those of conventional devices. The prototype of this family of devices is the dye-sensitized solar cell (DSSC) which realizes the optical absorption and charge-separation processes by the association of a sensitizer as light-absorbing material with a porous semiconductor of nanocrystalline morpohology.

Porous silicon is known to be a substance for sensors and photovoltaic cells. Its large specific surface area makes it convenient in practical applications [3]. Many works are available on metal coated porous silicon. But the solar cells prepared by these techniques have limited efficiency. Equal amount of works on solar cells have now appeared based on TiO_2 with and without dye sensitizers. Around 11% of efficiency is already reported for TiO_2 with ruthenium dyes [4]. Since these dyes are costly, people try to find the alternatives these days. The conversion efficiency of the TiO_2 coated with Pthalocyanine cells found to reach maximum at the intensity of 1.12 mW/cm^2 from the solar simulator [5]. Phthalocyanines are also used as sensitive materials to fabricate gas and humidity sensors [6 - 8], and the electrical measurements can be carried out either using planar or sandwich devices, but it has the limitation of low solubility in organic solvents (1M for 0.1g). Hence here, we used chloroaluminum phthalocyanine (ClAlPc) which is the halogenated derivative of Pc having more solubility (0.001M) on which much works is not reported to the best of our knowledge. ClAlPc has been expected as a promising photosensitizer, since it exhibits several favorable photo-physical properties like high absorption efficiency, high chemical stability [8-9]. In the present study, the properties of porous silicon coated with ClAlPc are investigated with the motive of fabricating solar cells.

2 EXPERIMENTAL

2.1 Materials and Methods

Samples used in this study are boron doped crystalline silicon (c-Si) wafers (thickness 517 μm and resistivity 0.2- 0.5 Ω cm) grown by Czochralski (CZ) method in (100). The porous samples were prepared by electrochemical anodic dissolution of doped silicon (p-Si) in 40% hydrofluoric acid, H_2O and ethanol with platinum electrode as cathode. The electrolyte was prepared by mixing HF (40%), H_2O and ethanol in 1:1:2 ratios. The porous layers on the surface of these samples (p-type c-Si) were prepared at a current density of 30 mA/cm^2 for etching periods of 10, 20, 40 and 60 minutes.

The ClAlPc material was prepared in laboratory from 20 g of phthalonitrile, 5 g of $AlCl_3$ which was refluxed in 100 ml of quinoline for 2 hr. The product was filtered and then the resulting precipitate was washed sequentially in toluene, carbon tetrachloride and acetone.The product was then dried at 70 ºC.

The prepared ClAlPc Dye (0.1g) was mixed in 5ml (0.001M)

ISSN 2229-5518

of ethanol. The resultant mixture is used as a sensitizer of porous silicon substrate for which Doctor Blade technique was used. The prepared samples were characterized by UV – vis and PL techniques.

3 Results and Discussion

The optical absorption spectra of Porous silicon (PS) and ClAlPc/PS were recorded. The PS samples show absorbance in the visible region. In the near UV region, pthalocyanine exhibits a single peak, representing the $\pi \rightarrow \pi^*$ transition that appears with peak position in the range about 300 – 350 nm depending on the nature of the substrate.

The absorbance peak for ClAlPc/PS is in the range of 300 – 500 nm. The intensity of absorbance peak of PS and dye sensitized PS samples increases with increasing etching time. The bandgaps were calculated by plotting Tauc's plot for both PS and ClAlPc/PS samples and are shown in figures 1 and 2 respectively and listed in the Table 1. The bandgap of the sample increases with increasing etching time.

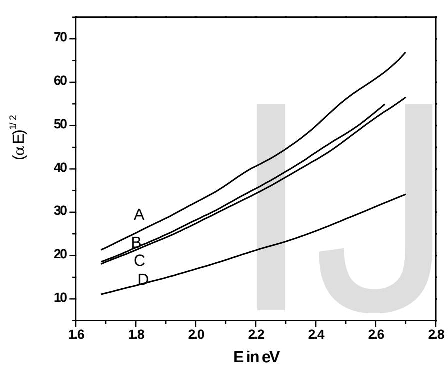

Fig. 1. Tauc's plot for Porous silicon prepared at 30 mA/cm^2 (A) 10 min. (B) 20 min. (C) 40 min. (D) 60 min.

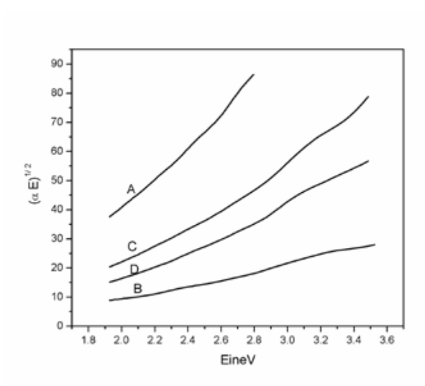

Fig.2. Tauc's plot for ClAlPc/ Porous silicon prepared at 30 mA/cm^2 (A) 10 min. (B) 20 min. (C) 40 min. (D) 60 min.

TABLE 1

Band gap of the samples from UV – Vis spectra

Sample	Porous silicon (eV)	Porous Silicon Coated With ClAlPc (eV)
A	1.76	1.80
B	1.78	1.89
C	1.82	1.92
D	1.87	1.95

The Photoluminescence (PL) spectra were recorded at room temperature with exciting wavelength (365 nm). The PL spectra of porous silicon and ClAlPc/Porous silicon are shown in figures 3 and 4 respectively.

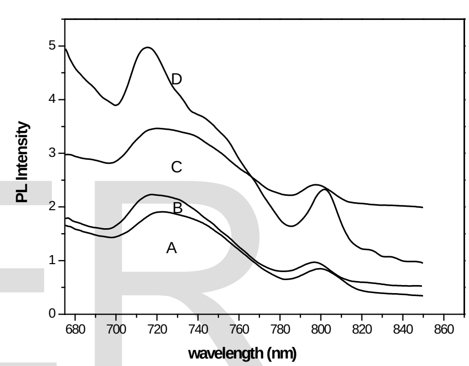

Fig. 3. PL emission spectra of Porous silicon at 30 mA/cm^2 (A) 10 min. (B) 20 min. (C) 40 min. (D) 60 min.

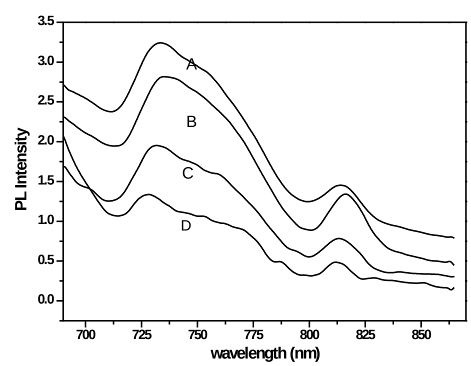

Fig.4. PL emission spectra of ClAlPc/PS at 30 mA/cm^2 (A) 10 min. (B) 20 min. (C) 40 min. (D) 60 min.

For PS samples, the PL emission is centered around 720 nm. The observed peaks are at S band (400 – 800 nm). This

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band has been tuned across the entire visible range from deep red to blue. The shift in the peak towards higher energy region shows the occurrence of blue shift with respect to bulk silicon. It is reported in literature [10 – 12] that a nanosturctured porous layer formed during etching process results in a blueshift in bandgap of PS due to the nanocrystallites formed. And this shift in optical bandgap from that of crystalline silicon (1.1 eV) is because of stronger quantum confinement of charge carriers in the PS layers due to the smaller mentions of the PS nanocrystallites [13]. Further the PL emissions of PS are slightly blue shifted with increase in etching time [11], which could be due to the decrease in nanocrystallites of silicon with increase in porosity of the samples. The porosities of the samples were calculated using gravimetric method, which are in the range of 55 % to 75 and the porosity increases with increase in etching time. For the dye sensitized PS, the PL emission is shifted to 735 nm which may due to the presence of chlorine in the dye. There is an increase in porosity and intensity of absorption with increasing etching time. This is due the confinement of particles into a lower dimension, leading to higher efficiency. The minimum emission intensity shown by ClAlPc/PS prepared at at current density of 30mA/cm^2 for etching time of 60 min (Fig.4) indicates that it is a good absorber of radiation and can be used for solar cell application.

4 Conclusion

Nanostructured porous silicon (PS) samples were prepared at a current density of 30 mA/cm^2 for etching periods 10, 20, 40 and 60 minutes. Then these samples were characterized using UV absorption and PL emission technique. The band gaps are calculated and compared. The band gap slightly increases with increase in etching time. To study the effect of dye sensitizer, on these samples, the surface of these PS samples was sensitized with derivative of Chloroaluminum Pc (ClAlPc). The dependence of absorption and emission intensities on these samples indicate that ClAlPc/PS prepared at current density of 30mA/cm^2 for etching time of 60 min indicate that it is good absorber of radiations and can be used for solar cell application.

Acknowledgment

The authors acknowledge the University Grant Commission (UGC), India, for financial support in the form of Major research project (F.No.**41-941/2012 (SR)**).

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