

2017

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Recommended Citation

Abo Arais, Ahmed (2017) "Preparation and Characterization of a-Si:H and a-SiC:H Separate p-i-n Thin Films," *International Journal of Thin Film Science and Technology*. Vol. 6 : Iss. 3 , Article 4.
Available at: <https://digitalcommons.aaru.edu.eg/ijtfst/vol6/iss3/4>

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Preparation and Characterization of a-Si:H and a-SiC:H Separate p-i-n Thin Films

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Received: 2 Jul. 2017, Revised: 17 Aug. 2017, Accepted: 21 Aug. 2017.

Published online: 1 Sep. 2017.

Abstract: a-Si:H and a-SiC:H in undoped, buffer, p-type and n-type thin films were deposited by radio frequency (RF) glow discharge decomposition method on Croning 7059 glass substrates from silane gas (SiH₄) mixed with methane (CH₄) for undoped, buffer and B₂H₆, PH₃ were added for p-type and n-type thin films respectively. Gap state defects of a-Si:H and a-SiC:H thin films for both undoped and doped types have been investigated by constant photocurrent method (CPM). The minimum defect density of a-Si:H, i-film was found to be $2.5 \times 10^{16} \text{cm}^{-3}$ and for undoped a-SiC:H, buffer-layer was evaluated to be $8.8 \times 10^{16} \text{cm}^{-3}$. There was a gradual increase in defect density by alloying with carbon and also by doping p-type and n-type. The adding of carbon was widen the energy gap (E_g) and increased the Urbach energy tail (E_o). The low defect density layers were identified to be applied in p-i-n solar cells with expected high quality. The results were discussed according to weak bond-dangling bond conversion model and defect pool model.

Keywords: Amorphous materials, Thin films, Solar energy materials.

1 Introduction

a-Si:H solar cells have been applied as a renewable energy source and is becoming increasingly important because the main sources of energy as coal, oil, gas and uranium are limited and has some degree of dangerous [1]. Hanakawa reported the first successful application of boron-doped a-SiC:H films as window layers in a-Si:H solar cells [2]. a-SiC:H alloy films are of interest as materials for electronics and photovoltaic applications, such as a solar cell due to a wider band gap than that of a-Si:H and is used also in light emitting devices LED, charge coupled devices and linear image sensors [3]. Multi-junction solar cells are created from multiple p-i-n layers of a-S:H and a-SiC:H with different band gaps, so that they can absorb most of energy of the solar radiation [4]

Constant photocurrent method (CPM) is a well established technique for determining the defect density of a-Si:H [5]. CPM absorption of photon energy 1.2eV is simply correlated with the total defect density [6]. In this work undoped and doped a-Si:H, a-SiC:H layers have been

prepared and investigated by CPM. CPM is used to evaluate many factors such as the defect density (N_D), Urbach energy tail (E_o), energy gap (E_g) and Fermi energy level (E_F). These essential factors must be employed to have high efficiency solar cells by improving the quality of p-i-n separate layers from a-Si:H and a-SiC:H materials.

2 Experimental Details

2.1 Preparation a-Si:H And a-SiC:H Thin Flms

a-Si:H and a-SiC:H thin films were deposited by radio frequency (RF) glow discharge decomposition method on Croning 7059 glass substrates from silane gas (SiH₄) mixed with methane gas (CH₄) for i-layer and buffer-layer. In p-type layers, B₂H₆ is added and in n-type layer, PH₃ is introduced in the gas phase. Table 1 summarizes the preparation conditions of the samples. The radio frequency (RF) is kept constant for all different prepared thin layers, RF = 13.6MHz.

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2.2 Constant Photocurrent Method (CPM)

CPM is a method to measure the subgap absorption for $\alpha < 10^3 \text{ cm}^{-3}$ of film thickness $\leq 1 \mu\text{m}$, Vanecek (1983) [7]. By holding the photocurrent at a fixed value during the measurements one ensures a constant occupancy of gap state defects. This holds only if the localized-to-localized state transition probability is neglected. If this condition holds then α is inversely proportional to the number of photons required to keep I_{ph} constant. The value of the photocurrent is kept small enough so that the equilibrium occupation of the midgap defect level is not disturbed significantly. Typically two parallel coplanar ohmic Ag evaporated electrodes on the layers of width 5mm, length 10mm and separation 1mm are used to apply an electric field of typically 100V to measure the resultant photocurrent generated by the light beam. The absorption coefficient α can be measured by using CPM in the range 0.6-2.6eV. The absorption coefficient α deduced from CPM spectrum is a relative one which must be calibrated with optical absorption from transmission measurements.

3 Results and Discussion

The optical absorption coefficient α of a-Si:H and a-SiC:H, p-i-n and buffer thin films were evaluated by using transmission (T) and reflection(R) measurements according to the equation:

$$\alpha = -(1/d) \ln [T / (1-R)] \quad (1)$$

Where d is the layer thickness.

The optical absorption coefficient $\alpha(\text{cm}^{-1})$ as a function of incident photon energy in the range (1.6-5eV) was shown in Fig (1). The optical energy gap was obtained from optical $\alpha(\text{cm}^{-1})$ by using Tauc plot as:

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g) \quad (2)$$

Where h is Planck's constant, ν is the frequency and B is a constant. The plot of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ was a linear line whose slope was B and the linear extrapolation intercept $(h\nu)$ axis was the optical energy gap E_g . E_g values by this method for different layers was listed in Table 1.

The increase in E_g by carbon alloying was due to the fact that C-H bond was greater than Si-H bond, this led some researchers to use E_g as a measure of carbon content in a-SiC:H materials [8]. Since Si-H bonds were weaker than C-H bonds, there will be the possibility of existing a number of bonds such as Si-C, Si-Si and C-C bonds, all these bonds will increase the optical energy gap E_g by more C content alloying [9].

The Fermi energy level E_F was determined from the dark DC conductivity by using the equation:

$$\sigma_D = \sigma_o \exp (E_a / kT) \quad (3)$$

Where σ_o is a constant, was taken to be $150(\Omega\text{cm})^{-1}$, T is the absolute temperature ($T=300\text{K}$), k is the Boltzmann constant and E_a is the activation energy in (eV). The typical CPM spectrum was calibrated with optical absorption to calculate the absolute defect absorption $\alpha_D(\text{cm}^{-1})$ and Urbach energy E_o as shown in Fig (2). The defect absorption α_D was estimated by the integrated excess absorption as the integration of the contribution of deep defects to the absorption up to Urbach energy.

The defect density N_D was calculated as follows:-

$$\alpha_{\text{excess}} = \alpha (E) - \alpha_{\text{Urbach}}(E) \quad (4)$$

$$\alpha_D = \int \alpha_{\text{excess}} (E) dE \quad (5)$$

$N_D = M \alpha_D$ where M is a constant

$$M = 10^{16} \text{cm}^{-2} \text{eV}^{-1}. \quad (6)$$

The Urbach energy (the valence band tail) whose characteristic energy E_o due to the exponential part of the absorption spectrum in the intermediate energies ($1.4 < E < 2.0\text{eV}$), was calculated by the equation:

$$\alpha (h\nu) = \alpha_o \exp (h\nu / E_o) \quad (7)$$

Where α_o is a constant CPM spectra of a-Si:H, a-SiC:H, for p-i-n and buffer thin films in annealed state at $T=300\text{K}$ were shown in Fig (3). The calculated E_o , and N_D from CPM measurements were listed in Table 1. It is clear that there was a gradual broadening increase of Urbach energy E_o by alloying a-Si:H with C and by doping with B or P, this was due to the increase of microstructure and the increase of weak bonds by alloying and doping processes.

The increase of N_D in doped layers (p-type and n-type) was due to the creation of charged dangling bonds, D^+ (positively charged) in p-type and D^- (negatively charged) in n-type layers in addition to D^o (neutral charged) in agreement with the defect pool model [10]. The a-Si:H, i-film has the lowest dangling bonds (defect density N_D) but p and n-films were highly defected with dangling bonds due to doping with boron in p-type and phosphorous in n-type. The increase of defect density (N_D) by alloying and doping a-Si:H films was attributed to the increase of weak bonds in the valence band i.e (E_o). According to weak bond-dangling bond conversion model [11], there was a direct correlation between E_o and N_D i.e the smaller E_o , the smaller N_D and the greater E_o , the greater N_D . This because the weak bonds in the valence band tail could be converted into dangling bonds within the energy gap (E_g) which enhance the defect density (N_D) These experimental results supported defect pool model and weak bond-dangling bond conversion model in explaining the gap state defects in amorphous hydrogenated silicon.

Table 1: The preparation conditions of a-Si:H, a-SiC:H for buffer, p-i-n thin films and their optical energy gap E_g , Urbach energy E_o , Fermi energy E_F , and defect density N_D .

No.	Sample Comp.	Type	SiH ₄ Sccm	CH ₄ Sccm	B ₂ H ₆ Sccm	PH ₃ Sccm	Power W	Pressure torr	T _{sub} °C	Thickness nm	E _g eV	E _o meV	E _F eV	N _D (cm ⁻³)
1	a-Si:H	i	100	0.0	0.0	0.0	3.5	700	220	1020	1.70	50.5	0.68	2.5x10 ¹⁶
2	a-SiC:H	buffer	60	20	0.0	0.0	4.0	700	240	292	1.91	72	0.66	8.8x10 ¹⁶
3	a-SiC:H	buffer	60	40	0.0	0.0	4.0	700	210	310	1.94	102	0.66	4.4x10 ¹⁷
4	a-SiC:H	p	40	60	5	0.0	3.6	700	240	538	1.93	105	0.44	9.4x10 ¹⁸
5	a-SiC:H	p	40	70	5	0.0	3.6	700	210	418	2.04	103	0.48	8.6x10 ¹⁸
6	a-Si:H	n	80	0.0	0.0	5	3.5	700	240	700	1.64	88	0.27	9.0x10 ¹⁸

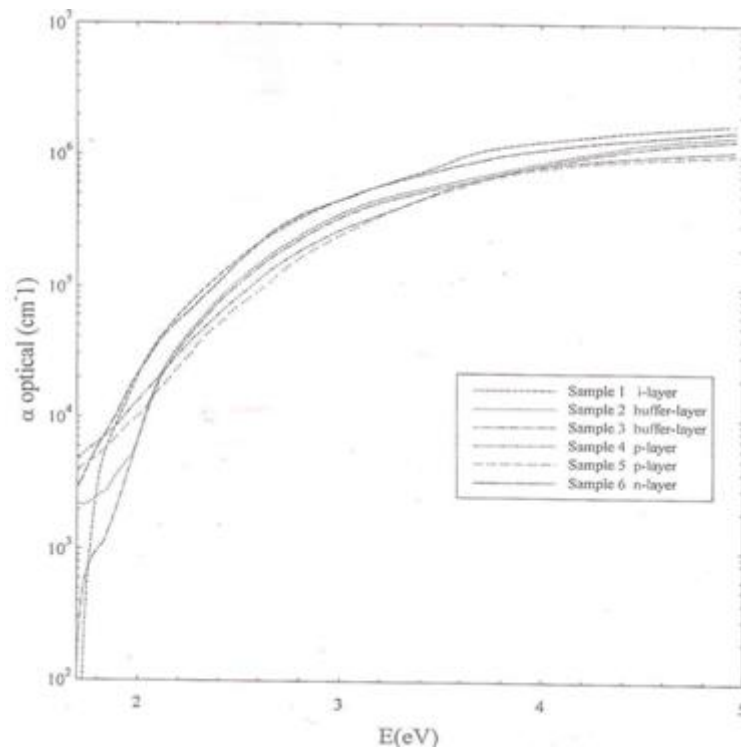


Figure 1: The optical absorption coefficient (α) as a function of photon energy (E) for different a-Si:H, a-SiC:H buffer, p- and n-type layers.

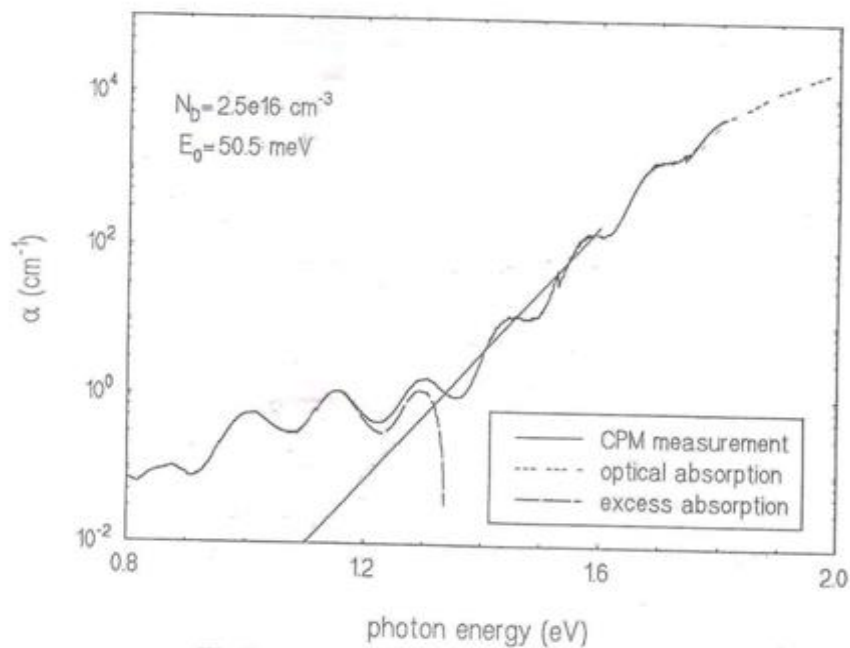


Figure 2 : Constant photocurrent method (CPM) calibrated with optical absorption at 1.8eV and the method to evaluate the Urbach energy (E_0) and excess absorption (α_D) of undoped a-Si:H.

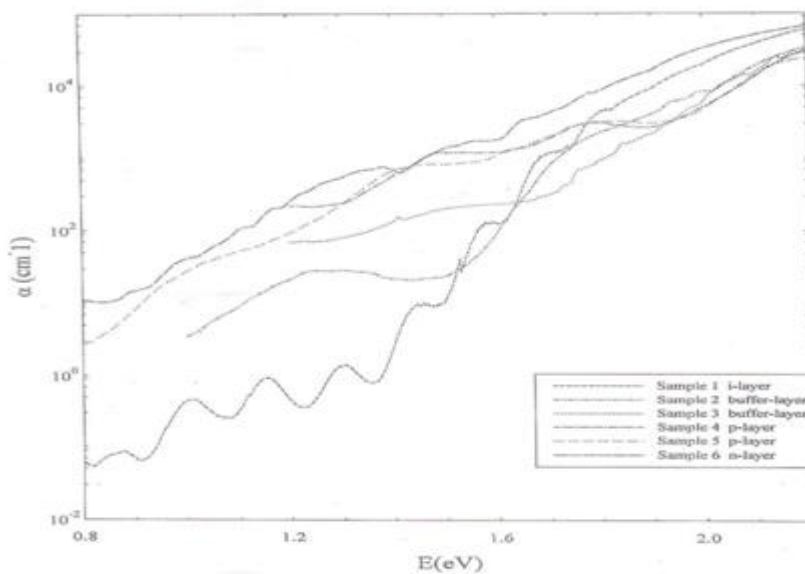


Figure 3: Constant photocurrent method (CPM) of a-Si:H and a-SiC:H for i-, buffer, p- and n-type.

4 Conclusions

There was a gradual enhancement of defect density N_D by alloying with C in a-Si:H and also by doping process (n-type and p-type). This was explained by weak bond-dangling bond conversion and the defect pool models.

The addition of C would widen the energy gap (E_g) and increased Urbach energy tail (E_o).

The a-Si:H, i-layer sample No.1 has a minimum defect density ($N_D=2.5 \times 10^{16} \text{cm}^{-3}$) and minimum Urbach energy ($E_o=50.5 \text{meV}$) and the buffer layer sample No.2 with ($N_D=8.8 \times 10^{16} \text{cm}^{-3}$) and ($E_o=72 \text{meV}$). These layers could be used in solar cells with expected high efficiency.

Acknowledgement

The author express deep thanks to Dr. C.Benking and Dr.Thomas Eickhof for their financial support in KFA institute of thin film (ISI)-Photovoltaic, Julich, Germany.

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