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THE ROLE OF PLASMA PARAMETERS ON THE OPTICAL CHARACTERISTICS OF PCVD PRODUCED a-Si THIN FILMS

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1. INTRODUCTION

The plasma enhanced chemical vapour deposition (PCVD) technique has recently become an important method for the production of semiconducting amorphous silicon (a-Si) [1]. A number of authors have applied this method to produce a low cost a-Si solar cell, following Spear and LeComber [3] who showed that the control of valence electrons by doping an impurity is possible by employing the PCVD technique. In this method, various types of glow discharges in gas mixtures of SiH_4, PH_3, B_2H_6, Ar etc. are used, and Si is deposited on the substrate materials during the discharge. Therefore, it is expected that the electrical properties of the a-Si will be strongly related to the chemical composition of the plasma. However, most studies already presented were restricted to investigating only the properties of a-Si.

More recently, several attempts have been made to explain the production of Silane free radicals, $SiH_{\alpha=1,2,3}$. Turban et al. [4] and others [5,6] suggested the following reactions:

$$SiH_4 + e \rightarrow SiH_4^* + e \text{ (slow)} \tag{1}$$

$$SiH_4^* + e \rightarrow SiH_m + H_{4-m} + e \tag{2}$$

However, none of the authors have apparently been able to present actual reaction rates for these reactions. Ichikawa et al. [7] suggested that Silane free radicals can also be produced from the following reactions involving ions.

$$SiH_4 + Ar^+ \text{ or } Ar_2^+ \rightarrow SiH_\alpha^+ + H_{4-\alpha} + Ar \text{ or } 2Ar \tag{3}$$

$$SiH_\alpha^+ + e \rightarrow SiH_\beta^* + H_{\alpha-\beta} \tag{4}$$

The charge transfer reaction rates and volume recombination coefficients in these reactions are not currently well known. However, the general magnitude of the rates can be assumed from those involving similar ion species, such as CH_4. Ichikawa et al. [7] showed that sufficient Silane free radicals for film formation can be produced from the above reactions as well as similar amounts of Silane ions. Since both reaction rates depend on plasma parameters such as electron energy and plasma density, these parameters play an important role in the production of a-Si thin films. The parameters affecting the electron temperature and plasma density inside positive columns are summarized in Table I.

On the other hand, several attempts have been made to determine the dominant ion and neutral species, and the most important reactions that might occur in an Ar-Silane gas discharge are summarized in Table II.

In this work, the role of plasma parameters on the optical characteristics of PCVD produced a-Si thin films are studied experimentally, and some correlations between the preparation characteristics and optical properties are established.

2. EXPERIMENTAL APPARATUS

An argon-silane mixture gas plasma was produced in a 60 cm long 4 cm ID Pyrex Glass cylindrical discharge tube as shown in Figure 1. D.C. discharge with 2.64% diluted SiH_4-Ar gas mixture was used in present study. The cathode and anode are located at opposite ends of the discharge tube T-section to avoid disturbing gas flow and depositions. In this way, only the positive column part of the plasma is in a cylindrical section. The plasma parameters and profiles inside the positive column section of the discharge tube were measured by five 6 mm long 0.2 mm ID single electrostatic probes in axial positions spaced 5 cm apart, and determined by recent single and double electrostatic probe theories of Chang and Laframboise [8]. Volume averaged plasma density and ion compositions were determined from D.C. discharge current voltage characteristics and computer numerical models of Ichikawa et al. [7], respectively. 7 cm long 1.5 cm wide glass substrate and KBr single crystals are located 3 cm downstream of the cathode inside discharge tube, and faces to the axis at tube walls. Substrate was heated by cathode region plasma, therefore no extra heater is required for the present apparatus. The physical characteristics tested were IR and optical absorption spectra in order to detect the presence of hydrogen and determine the density of trapping centers in a-Si films and width of quasi-gap.

3. PLASMA PROPERTIES

DC discharge current-voltage characteristics with and without Silane gas is shown in Figure 2. Figure 2 shows that the self sustaining discharge voltage becomes larger when silane gas is present, since the electron temperature inside gas discharge must be large enough to maintain electron loss due to the volume recombination of silane ions, and the collisional loss due to the various elastic and inelastic collisions with heavier molecules.

Typical electric field, E, and corresponding electron temperature, T_e, profiles inside positive column measured by probes are shown in Figures 3 and 4, respectively, where the dashed line represents flowing positive column theory of Miller et al. [9]. Figures 3 and 4 show that the electric field and the electron temperature profiles inside the positive column are relatively uniform and, the electron temperature values agree well with theoretical predictions. Figure 3 also shows that the electric field inside the positive column with silane gas is one order of magnitude smaller than that obtained with pure Ar gas. Typical plasma density profiles, N_e, inside positive column measured by electrostatic probes with and without silane gas are shown in Figure 5, where theoretical results [9] for corresponding conditions are also shown by a dotted line. In spite of the larger discharge voltage in the Ar-SiH_4 gas mixture the plasma density becomes much smaller when the Silane gas is present in the system. However, relatively uniform plasma density profiles are obtained even with and without the presence of Silane gas, where we must note that the Ar-SiH_4 mixture gas plasma density is one order of magnitude smaller compared with pure gas due to the volume-recombination effect. Figures 2 to 5 show that the plasma properties for a-Si thin film production environment in the present experimental apparatus are uniform, and therefore very suitable for larger sample productions.

4. OPTICAL CHARACTERIZATION OF a-Si FILMS

The typical IR response for our a-Si films shows an absorption peak in the region of 2100 cm^{-1} which is related to silicon-hydrogen groups [10] although the detailed identification is still controversial.

In Figures 6 and 7 we give the photon energy dependences of $(\alpha h\nu)^{1/2}$ and $\ln\alpha$ (α is the absorption coefficient) in the optical region for various plasma densities which allow one to determine the quasibandgap (E_o) and the slope of Urbach tail (W). The latter refers to the dependence $\alpha \backsim \exp(h\nu/W)$, characteristic for the presence of localized electronic states in the vicinity of mobility edges.

For samples 1 and 2 (deposited for 2 hrs. at 40 mA and 60 mA with estimated thicknesses of 2000 Å and 3700 Å; and $N_e = 3 \times 10^9$ $cm^{-3}$and $N_e = 5 \times 10^9$ cm^{-3}, respectively) the values are E_o = 1.26, and 1.87 eV and W = 0.44, and 0.72 eV respectively, which show the very strong dependence of a-Si on preparation conditions.

Relating W with the density of trapping levels, N, [11]

$$W \simeq 2\,\frac{e^2\gamma}{\varepsilon_o}(N \cdot \gamma^{-3})^{2/5} \qquad (5)$$

we obtained $N = 3.7 \cdot 10^{21}$; and $1.3 \cdot 10^{22}$ cm^{-3} respectively. Here $\varepsilon_o = 12$ is the dielectric constant of an a-Si [12] and γ is the constant of the exponential decay of the wave function of an electron (hole) localized on the trapping center (for a-Si we took $1/\gamma = 15$ Å; [13]).

These results confirmed the importance of preparation on the properties of hydrogenized amorphous silicon. In the frameworks of our particular apparatus the optimal value of deposition current should probably be in the region of 40-60 mA, since higher currents produce undesirable optical characteristics.

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TABLE I: Parameters Affecting the Positive Column Plasma

Electron Temperature (T_e)	Discharge tube radius and geometry Gas pressure and velocity Gas mixture ratio - volume recombination - ionization by metastables and electrons - diffusion coefficient - collision frequency Magnetic Field
Plasma Density (N_e)	Discharge current Gas Pressure Gas mixture ratio - ionization by metastables and electrons - volume recombination
Electric Field (E)	Discharge voltage Plasma density profiles Gas mixture ratio

TABLE II: Plasma Chemistry in an Ar-SiH_4 Mixture Discharge

(a)	Reactions for Argon	
	$Ar + e \rightarrow Ar^+ + e + e$	: Electron impact ionization
	$\rightarrow Ar^* + e$	: Excitation
	$Ar^* + e \rightarrow Ar^+ + e + e$	: Cumulative ionization
	$Ar^* + Ar^* \rightarrow Ar^+ + e + Ar$	: Meta-meta collision
	$\rightarrow Ar_2^+ + e$	
	$Ar_2^+ + e \rightarrow Ar^* + Ar$	: Recombination
(b)	Reactions for Silane	
	$SiH_4 + e \rightarrow SiH_n^+ + H_{4-n} + 2e$:	: Electron impact ionization
	$\rightarrow SiH_m + H_{4-m} + e$	: Dissociation
	$SiH_m^+ + e \rightarrow SiH_\beta + H_{m-\beta}$	: Recombination
(c)	Reactions between Argon and Silane	
	Ar^+ or $Ar_2^+ + SiH_4 \rightarrow SiH_\alpha^+ + H_{4-\alpha} +$ Ar or 2Ar	: Charge Transfer

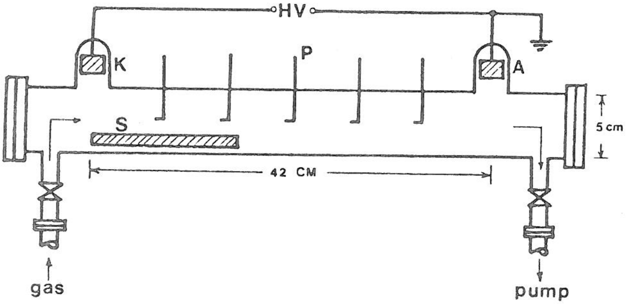


FIG. 1. SCHEMATIC OF EXPERIMENTAL SET-UP (K: CATHODE; A: ANODE; HV: POWER SUPPLY; S: SUBSTRATE; P: SINGLE PROBE)

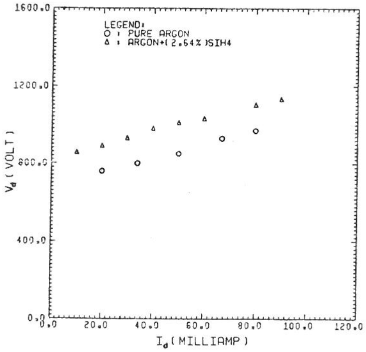


FIG. 2. DC DISCHARGE CURRENT-VOLTAGE CHARACTERISTICS WITH AND WITHOUT SILANE GAS (P_T=0.8 TORR)

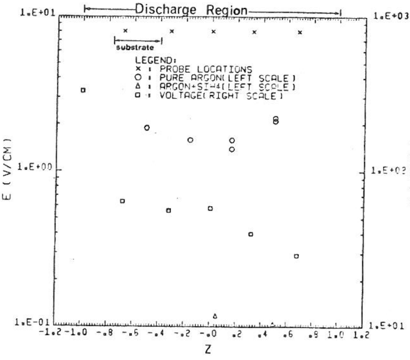


FIG. 3. ELECTRIC FIELD AND VOLTAGE PROFILES IN POSITIVE COLUMN

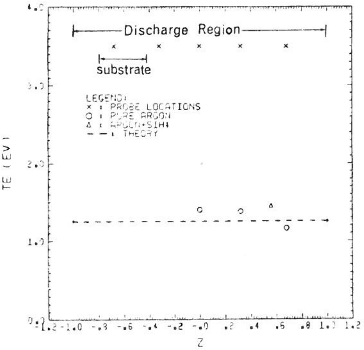


FIG. 4. ELECTRON TEMPERATURE PROFILE INSIDE POSITIVE COLUMN FROM THEORY AND EXPERIMENT

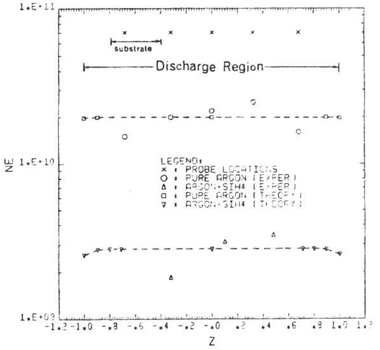
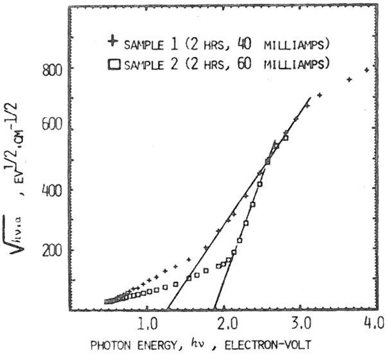
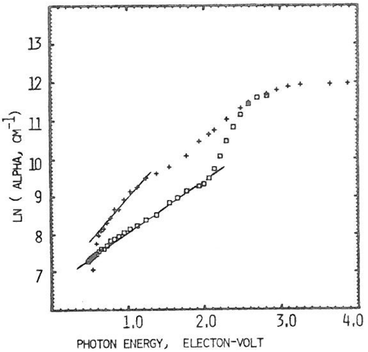


FIG. 5. PLASMA DENSITY PROFILES INSIDE POSITIVE COLUMN FROM THEORY AND EXPERIMENT



PHOTON ENERGY, $h\nu$, ELECTRON-VOLT

FIG.6. EXTRAPOLATION OF ENERGY GAP FROM THE OPTICAL ABSORPTION



PHOTON ENERGY, ELECTON-VOLT

FIG.7. OPTICAL ABSORPTION IN URBACH COORDINATES