THE PLASMA ENVIRONMENT IN AN $Ar/SiH_4/PH_3$ GAS MIXTURE GLOW DISCHARGE AND ITS RELATIONSHIP TO a-Si THIN FILM FORMATION

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ABSTRACT

A theoretical model of the positive column in plasmas produced in the gas mixture, $Ar-SiH_4-PH_3$(or B_2H_6), is developed. The plasma parameters which are important to those conditions applied to the deposition techniques for amorphous silicon(a-Si) solar cell production are emphasised. Particular attention is paid to these conditions which are significant in the deposition method of production.

1. INTRODUCTION

A plasma enhanced chemical vapour deposition(PCVD) technique has recently become important in the production of amorphous silicon(a-Si) semiconductor.(1) A number of authors have applied this method to produce low cost a-Si cell,(2) since Spear and Le Comber(3) 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 existence of the discharge and consequently diffuses into the lattice. Therefore, it is expected that the electrical properties of the a-Si is strongly related to the chemical composition of the plasma. However, most studies presented before were restricted to investigating the properties of a-Si itself.

In this work, a numerical model of the positive column of the glow discharge during the production of the a-Si semiconductor has been developed. Calculated results of SiH_4-Ar (for intrinsic a-Si) and SiH_4-PH_3(or B_2H_6)-Ar gas mixture (for p(or n)-type a-Si) positive column plasmas are presented and discussed in detail.

2. THEORETICAL MODEL OF GLOW DISCHARGE FOR a-Si PRODUCTION

The schematic diagram of the apparatus commonly used for the PCVD application is shown in figure 1. In the present model, silane(SiH_4) gas diluted in argon at a medium pressure, ($[SiH_4]/[Ar]\approx$few%) is used to produce intrinsic a-Si, and a small amount of PH_3 or B_2H_6 ($[PH_3]/[SiH_4]\approx$few%, $[B_2H_6]/[SiH_4]\approx$few%) is mixed as a doping agent to produce p-type or n-type a-Si. These conditions have been selected by Kuwano et al.(2) for their solar cell production.

Hereafter, we discuss the $Ar-SiH_4-PH_3$ gas mixture plasma since the $Ar-SiH_4-B_2H_6$ plasma leads to essentially similar chemical processes. We assumed that those shown in table 1 are considered to be the dominant reactions in the Ar-SiH_4-PH_3 plasma under those gas mixture ratios employed here. Production of ions from SiH_4 and PH_3 only occurs due to dissociative charge transfer with argon ions (Ar^+ and Ar_2^+) since direct ionization by electron impact can be neglected due to the small partial pressure of SiH_4 and PH_3 employed. The ion produced from the above charge transfer reactions are SiH_α^+ (α=0,1,2,3,4) and PH_β^+ (β=0,1,2,3). From the difference in energy of ionization between Ar and SiH_4 or PH_3, we anticipate that the amount of SiH_4^+ and PH_3^+ are very small.

Free radicals, SiH_γ (γ=0,1,2,3) and PH_δ (δ=0,1,2) are produced from the dissociative volume recombination of SiH_α^+ and PH_β^+, respectively. These molecular ions, SiH_α^+ and PH_β^+, and free radicals, SiH_γ and PH_δ, are those of main importance in the PCVD technique. In order to investigate the optimum deposition of thin film formation, the estimation of the number densities of these particles and their variation with electron temperature, T_e, should be conducted.

A method to estimate plasma parameters and ion composition for the medium pressure positive column plasma in which various chemical reactions occur has been developed by Ichikawa and Teii.[4] This method was used to calculate the plasma parameters and the densities of ions and free radicals of the Ar-SiH_4-PH_3 discharge. In the present model, the following assumptions are also used; (1) A quasi-neutral condition in the plasma; (2) A Maxwellian energy distribution for charged particles; (3) The same radial distribution for ions. Under these assumptions, the coupled governing equations of Ar^+, Ar_2^+, SiH_α^+, PH_β^+, Ar^*, and electron density can be expressed, respectively, as follows:

$$D_1\nabla^2N_1 + \alpha_{di}N_{g1}N_e - k_1N_1N_{g2} - k_3N_1N_{g3} - kN_1N_{g1}^2 + \alpha_{ci}N_mN_e + \frac{1}{2}f\alpha_{mi}N_m^2 = 0, \quad (2.1)$$

$$D_2\nabla^2N_2 + kN_1N_{g1}^2 - k_2N_2N_{g2} - k_4N_2N_{g3} + \frac{1}{2}(1-f)\alpha_{mi}N_m^2 - \rho_1N_2N_e = 0, \quad (2.2)$$

$$D_3\ ^2N_3 + k_1N_1N_{g2} + k_2N_2N_{g2} - \ _2N_3N_e = 0, \quad (2.3)$$

$$D_4\nabla^2N_4 + k_3N_1N_{g3} + k_4N_2N_{g3} - \rho_3N_4N_e = 0, \quad (2.4)$$

$$D_m\nabla^2N_m + \alpha_mN_{g1}N_e - \alpha_{ci}N_mN_e - \rho_{mi}N_m^2 = 0, \quad (2.5)$$

$$N_e = N_1 + N_2 + N_3 + N_4, \quad (2.6)$$

where N is the number density; D_n (n=1,2,3,4) is in general the ambipolar diffusion coefficient; D_m is the diffusion coefficient of argon metastable atoms, and the subscripts, 1,2,3,4,m,g1,g2,g3,e, for N and D refer to Ar^+, Ar_2^+, SiH_α^+, PH_β^+, Ar^*, Ar, SiH_4, PH_3, electron, respectively. The appropriate reaction rate constants employed here, α, k and ρ, are shown in table 1. By solving equations (2.1) to (2.6), each ion density and the electron temperature are obtained as a function of N_e, P, R and the partial pressure of Ar, SiH_4 and PH_3. P is the total pressure and R is the radius of the discharge tube.

The densities of free radicals may be estimated if the radial profiles of the densities are assumed to be the zero-order Bessel function. The results are as follows:

$$[SiH_\gamma] = \rho_2N_3N_e/D_5(2.4/R)^2 \quad (2.7)$$

$$[PH_\delta] = \rho_3N_4N_e/D_6(2.4/R)^2 \quad (2.8)$$

$$[H\ \text{or}\ H_2] = [N_{g2}(k_1N_1+k_2N_2) + N_{g3}(k_3N_1+k_4N_2) + \rho_2N_3N_e + \rho_3N_4N_e]/D_7(2.4/R)^2 \quad (2.9)$$

where D_5, D_6 and D_7 are the diffusion coefficients of SiH_γ, PH_δ and H or H_2, respectively, and are calculated from the appropriate theory, averaging for various molecules.

The reaction rate constants for Ar^+, Ar_2^+ and Ar^* are relatively well-known.[5,6] However, reaction rate constants related to SiH_α^+, PH_β^+, SiH_γ and PH_δ, i.e. $k_1 \sim k_4$ and ρ_2, ρ_3, have notbeen reported.In the present calculation it is assumed that $k_1=k_2=k_3=k_4= 10^{-9}$ cm^3sec^{-1} and $\rho_2=\rho_3= 3x10^{-7}(T_e[K]/300)^{-0.4}$ cm^3sec^{-1}. These values were estimated from those for other SiH_4 ion-molecular reactions[7,8] and similarly structured ions such as CH_n^+ or NH_n^+.[9]

3. NUMERICAL RESULTS AND DISCUSSIONS

Number densities of various free radicals and ions in the discharge condition appropriate to solar cell production[2] are shown in figures 2, 3 and 4 as a function of P, R and N_{eo}, respectively, where each density and N_{eo} represent the axial number density at the center of the tube. Figures 5 and 6 show the electron temperature as a function of P and R for various N_{eo}. Density changes of SiH_α^+, PH_β^+, SiH_γ and PH_δ when the partial pressure of PH_3 to SiH_4 is changed are shown in figure 7.

These results show that (1) the dominant ion in the plasma is SiH_α^+ over a wide range of discharge condition in spite of its small partial pressure; (2) the number densities of free radicals, SiH_γ and PH_δ, increase with increasing P and R; (3) changing N_{eo} leads to the densities of SiH_α^+ and PH_β^+ being proportional to N_{eo} and those of SiH_γ and PH_δ being proportional to N_{eo}^2; (4) the electron temperature in the $Ar-SiH_4-PH_3$ plasma is always higher than that in the pure Ar discharge; (5) the density ratios, $[PH_\beta^+]/[SiH_\alpha^+]$ and $[PH_\delta]/[SiH_\gamma]$, are almost proportional to the ratio, $[PH_3]/[SiH_4]$. Here, we must note that the above results are also expected to be applicable to the $Ar-SiH_4-B_2H_6$ discharge.

These results enable us to deduce the conditions for optimum deposition of a-Si. In the typical discharge condition (P=1 Torr, R=1.5 cm and $N_{eo}=10^{10} \sim 10^{11}$ cm^{-3}), the densities of the free radicals, SiH_γ and PH_δ, are several times as large as those of the ions, SiH_α^+ and PH_δ^+, respectively. However, contribution of the ions to the a-Si film formation is expected to be very important because of the following reasons; (1) the ambipolar diffusion coefficient of the ion is larger than the diffusion coefficient of the free radical; (2) since the substrate material for the a-Si film is at floating potential, the electric field in the sheath of the material acts to accelerate the positive ion. On the one hand, as the absolute value of the floating potential increases with increasing electron temperatures, the rate of the ion deposition is enhanced.[10] On the other hand, when the electron temperature rises, the formation of free radicals decreases since the dissociative volume recombination coefficient is a decreasing function of T_e. Hence, it is expected that the optimum condition for film formation arises for P and R under a constant N_{eo} which is controlled by a RF power.

As shown in figure 4, densities of ions and free radicals increase with increasing N_{eo}. Consequently, the deposition rate is enhanced by an increase of N_{eo} (i.e. increase of the RF power). It is worth noting also that the electron temperature is little effected by the RF discharge power (figure 5 and 6).

ACKNOWLEDGEMENT

Support for this work provided by N.S.E.R.C. Grant 6414-41 (RMH + YI) is gratefully acknowledged.

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Table 1

Chemical reactions in the positive column in a plasma produced in a mixture gas of $Ar\text{-}SiH_4\text{-}PH_3$, where Ar* is the argon metastable atom and α , k , ρ represent the reaction rate constant for each reaction : The subscripts refer to the rate constant under consideration in the various reactions (Note that α is also employed as a subscript refering to the number of atoms in a molecule.)

(a) $Ar + e \xrightarrow{\alpha_{di}} Ar^+ + e + e$

(b) $Ar + e \xrightarrow{\alpha_m} Ar^* + e$

(c) $Ar^* + e \xrightarrow{\alpha_{mi}} Ar^+ + e + e$

(d) $Ar^* + Ar^* \xrightarrow{f\alpha_{ci}} Ar^+ + e + Ar$

$\xrightarrow{(1-f)\alpha_{ci}} Ar_2^+ + e$

(e) $Ar^+ + 2Ar \xrightarrow{k} Ar_2^+ + Ar$

(f) $Ar^+ + SiH_4 \xrightarrow{k_1} Ar + SiH_\alpha^+ + (H \text{ or } H_2)$ (α = 0,1,2,3,4)

(g) $Ar_2^+ + SiH_4 \xrightarrow{k_2} 2Ar + SiH_\alpha^+ + (H \text{ or } H_2)$

(h) $Ar^+ + PH_3 \xrightarrow{k_3} Ar + PH_\beta^+ + (H \text{ or } H_2)$ (β = 0,1,2,3)

(i) $Ar_2^+ + PH_3 \xrightarrow{k_4} 2Ar + PH_\beta^+ + (H \text{ or } H_2)$

(j) $Ar_2^+ + e \xrightarrow{\rho_1} Ar^* + Ar$

(k) $SiH_\alpha^+ + e \xrightarrow{\rho_2} SiH_\gamma + (H \text{ or } H_2)$ (γ = 0,1,2,3)

(l) $PH_\beta^+ + e \xrightarrow{\rho_3} PH_\delta + (H \text{ or } H_2)$ (δ = 0,1,2)

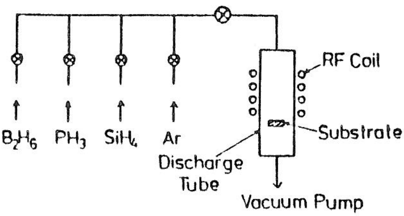

Figure 1. Schematic diagram of apparatus for a-Si production by PCVD method.

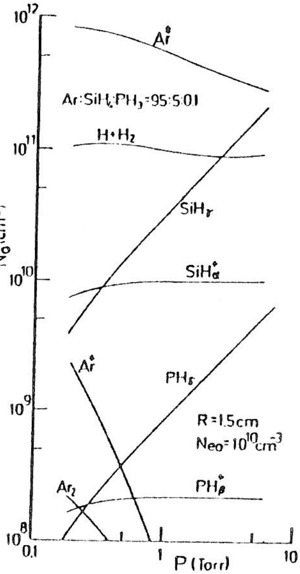

Figure 2. Particle densities at tube centre as a function of pressure.

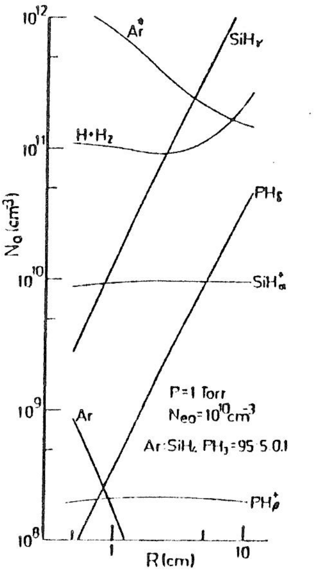

Figure 3. Particle densities at tube centre as a function of tube radius.

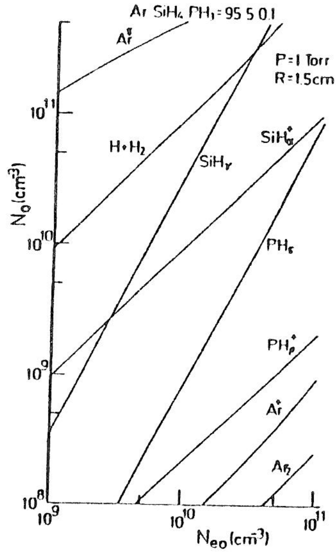

Figure 4. Particle densities at tube centre as a function of electron density.

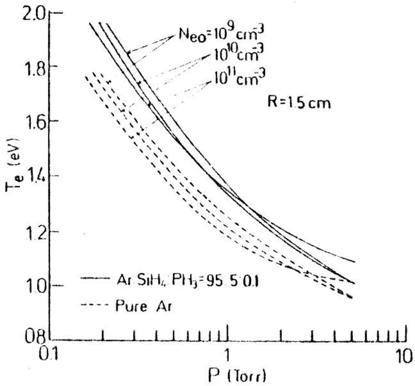

Figure 5. Comparison of electron temperature between pure Ar and $Ar-SiH_4-PH_3$ plasmas as a function of pressure.

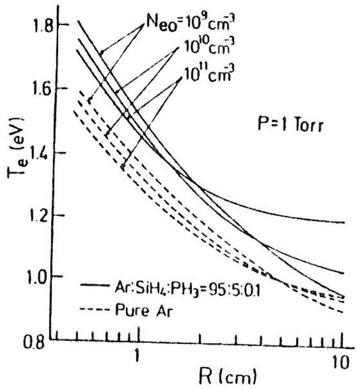

Figure 6. Comparison of electron temperature between pure Ar and $Ar-SiH_4-PH_3$ plasmas as a function of tube radius.

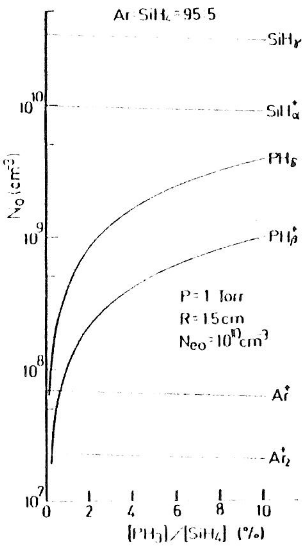

Figure 7. Variation of densities of SiH_α^+, PH_β^+, SiH_γ and PH_δ when density ratio of PH_3 to SiH_4 is changed.