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Use of optical emission spectroscopy to monitor the silane-argon plasma

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Abstract : Optical emission spectroscopy (OES) was used to characterize the radio frequency (*rf*) glow discharge plasma of flowing mixtures of silane and argon. The intensity variation of the peak at 414.2 nm arising due to SiH ($A^2\Delta - X^2\Pi$) transition has been studied with respect to power density in the range 20.4 mW/cm^2 to 787 mW/cm^2 for wide variation of silane to argon flow ratio from 5 : 95 to 40 : 60. The concentration of SiH* species was calculated by the proposed model based on the kinetics of the dominant reactions in the plasma. We see that the theoretically calculated curves can explain the general trend of variation of the experimental curves with increase of power density

Keywords : Optical emission spectroscopy (OES), *rf* glow discharge, silane, chemical kinetics

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1. Introduction

Plasma enhanced chemical vapour deposition (PECVD) of hydrogenated amorphous silicon (*a*-Si:H) thin film from the source gas silane is widely used in the industrial production of amorphous silicon based solar cells, thin-film-transistor (TFT) arrays in active matrix liquid crystal displays and other opto-electronic devices [1]. The plasma usually generated by 13.56 MHz radio frequency is of glow discharge type. The properties of a-Si deposited by this method have been found to be strongly dependent on the preparation conditions and also on the chamber design [2]. The influence of the complex reactions occurring within the plasma on the film properties is a subject of continuous studies aiming at better controllability of film properties. Amorphous silicon thin films deposited from silane diluted with noble gases under certain deposition condition have also given encouraging results [3,4]. Dilution of silane with argon has significant effect on the properties of the *a*-Si films and devices [5,6]. Bombardment of the growing film by the argon ions and the excited argon molecules and/or reaction of silane with ions and excited molecules of argon within the plasma are responsible for the structural changes in the film [7]. Among the primary dissociation products of SiH_4 in the discharge, the long-lived SiH_3 radical is widely accepted to be the main precursor for the formation of the film and the short-lived radicals like SiH_2 are believed to be important intermediate species which influence the film's quality. Experimental studies of different types of SiH_4 plasmas have been made by several plasma diagnostic techniques [8–10]. Among those techniques optical emission spectroscopy (OES) has received great attention for its non-invasive nature in adverse plasma conditions [11,12]. OES can measure the intensity of the emission lines from the excited atoms and molecules within the plasma. Metastable states of noble gases are supposed to play an important role in neutral-neutral reactions with chemically reactive molecules. In the argon (Ar) – silane (SiH_4) plasma, reactions between the metastable argon molecules and silane molecules significantly enhance the emission due to SiH* [13]. We have shown earlier that the intensity of the optical emission spectra due to SiH ($A^2\Delta - X^2\Pi$) transition observed by optical emission spectroscopy (OES) may be correlated with variations in the process parameters [14,15]. In this work we broadened the range of *rf* power density and the dilution

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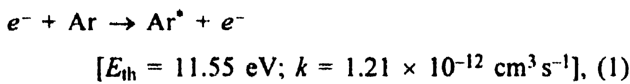
level to further check the efficiency of this technique. We have systematically studied the effect of the variations in *rf* power density from 20.4 mW/cm^2 to 787 mW/cm^2 and the silane to argon flow ratio from 5 : 95 to 40 : 60 on the emission intensity of the excited SiH (SiH^*). We have chosen the peak intensity of the line at 414.2 nm (I_{414}) due to SiH^* to monitor the plasma.

2. Theory

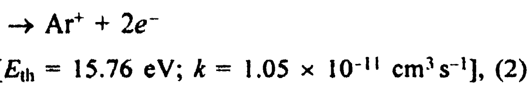
In PECVD process the deposited *a*-Si films are the products of numerous plasma chemical reactions. Dissociation of the source gas SiH_4 into the film forming radicals takes place by collisions with electrons, ions and excited species. Several models have been proposed to analyze the SiH_4 glow discharge plasma [16–18]. In SiH_4-Ar plasma the SiH_4 molecules dissociate into several neutral and charged radicals like SiH_3, SiH_2, SiH_3^+ *etc.* and a fraction of SiH_4 molecules excited to higher energy levels (threshold energy 8.4 eV) [19]. A fraction of Ar atoms is excited to metastable states (threshold energy 11.55 eV). The excited SiH_4 molecules dissociate into SiH^* which gives a characteristic emission band between 409 to 423 nm due to the radiative transition ($A^2\Delta$ - $X^2\Pi$). In silane plasma the electron temperature is around 1–2 eV. So the excitations of SiH_4 and Ar by electronic collisions require electrons in the high-energy tail of the electron energy distribution function (EEDF). Although, in principle, it is possible to calculate the evolutions of the different species within the plasma from the considerations of all the reactions going on there and their dependence on the multitude of external deposition parameters but the immensity in the number of those reactions makes this exercise impracticable. However, we may identify those reactions which directly lead to the formation of the film forming radicals like SiH_3, SiH_2 *etc.* and call them the dominant reactions. In Ar-SiH_4 plasma we consider the following reactions as the dominant reaction [16].

$e^- + Ar \rightarrow Ar^* + e^-$

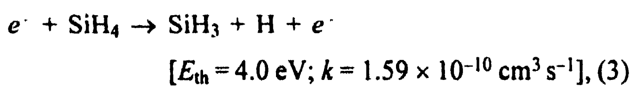


$[E_{th} = 11.55$ eV; $k = 1.21 \times 10^{-12}$ cm^{3}s$^{-1}]$, (1)

$\rightarrow Ar^+ + 2e^-$

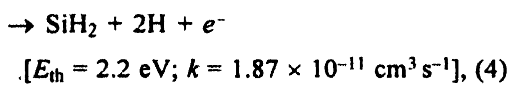


$[E_{th} = 15.76$ eV; $k = 1.05 \times 10^{-11}$ cm^{3}s$^{-1}]$, (2)



$e^- + SiH_4 \rightarrow SiH_3 + H + e^-$

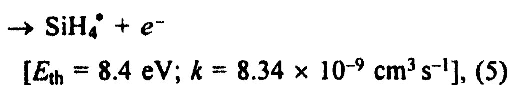
$[E_{th} = 4.0$ eV; $k = 1.59 \times 10^{-10}$ cm^3 s$^{-1}]$, (3)



$\rightarrow SiH_2 + 2H + e^-$

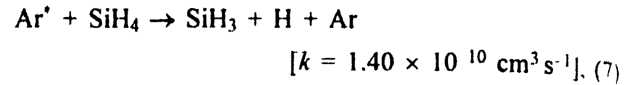
$[E_{th} = 2.2$ eV; $k = 1.87 \times 10^{-11}$ cm^3 s$^{-1}]$, (4)

$\rightarrow SiH_4^* + e^-$



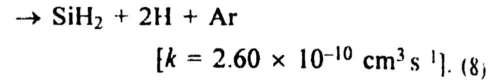
$[E_{th} = 8.4$ eV; $k = 8.34 \times 10^{-9}$ cm^3 s$^{-1}]$, (5)

$SiH_4^* \rightarrow SiH^* + H_2 + H,$ (6)



$Ar^* + SiH_4 \rightarrow SiH_3 + H + Ar$

$[k = 1.40 \times 10^{-10}$ cm^3 s$^{-1}]$, (7)



$\rightarrow SiH_2 + 2H + Ar$

$[k = 2.60 \times 10^{-10}$ cm^3 s$^{-1}]$. (8)

The above reactions may be analyzed in a self-consistent manner treating each one of them as a bimolecular reaction occurring in a streamline flow through the reaction zone. The reaction rate is expressed by,

$$k = \frac{(n_{0A} + n_{0B})^2}{n_{0A} - n_{0B}} \times \frac{(Nk_BT)^2}{VP^2} \times \ln \frac{n_{0B}(1-x)}{(n_{0B} - n_{0A}.x)}, \quad (9)$$

where n_{0A} and n_{0B} are the moles of reactants A and B entering the reaction zone, k_B is the Boltzmann constant, N is the Avogadro's number, P and T are the pressure and temperature in the reaction zone of volume V and x is the fraction of reactant A participated in the reaction.

The metastable argon (Ar^*) is formed by the electron impact excitation of the ground state argon atoms which is governed by the eq. (1). The formation of Ar^* depends upon the *rf* power density. The energy loss process of Ar^* is given by the eqs. (7) and (8). We assume that a fraction Ar^* is used in energising the slow electrons and the rest in dissociating the silane molecules. In the high argon dilution region, silane is mostly dissociated by the collision with Ar^*. Hence the concentration variation of SiH_4 may be obtained from the reactions (7) and (8). Further in absence of argon the high-energy tail of the electron energy distribution function (EEDF) contributes a small no. of high-energy (>8.4 eV) electrons in the plasma. Then the SiH^* is mainly obtained from de-excitation of SiH_4^* according to the eqs. (5) and (6). The net concentration of SiH^* may be calculated by applying the eq. (9) with the help of the reactions with which the SiH^* species is involved.

3. Experimental

A schematic diagram of capacitively coupled *rf* (13.56 MHz) PECVD chamber along with the optical spectrograph is shown in Figure 1. The plasma was generated in the space between two capacitor plates (diameter 12.7 cm, spacing 4.2 cm) in a cylindrical stainless steel reaction chamber. The *rf* power was applied *via* a matching network to the top electrode. The lower electrode was grounded. Before each run, the chamber was initially evacuated to a base pressure of 10^{-6} Torr. The silane and argon gas mixture was then flown across the plasma reaction zone by using mass flow controllers.

The plasma was studied by optical emission spectroscopy (OES). The optical arrangement consisted of a lens system that focussed the light emitted from the entire region of the plasma into the slit of a ¼ m spectrograph. The detector was

a 1024 element calibrated photo diode array with the maximum resolution of 0.1 nm. A computer was used to scan

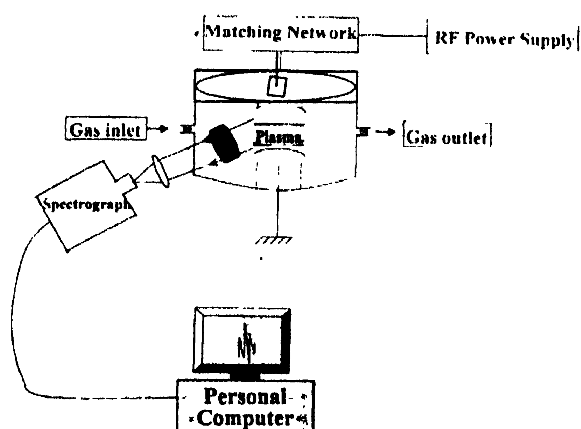


Figure 1. Schematic diagram of the PECVD chamber with optical emission spectroscopy set up.

the spectra and acquire data. Each spectrum was obtained by averaging 10 exposures of 10 s each. The intensity of the peak at 414.2 nm was monitored to study the radiative transitions due to SiH ($A^2\Delta$ – $X^2\Pi$). For power density variation the chamber pressure and temperature were kept constant and power density was varied from 20 mW/cm^2 to 787 mW/cm^2 at different flow ratio of silane and argon. For flow variation a set of spectra at a fixed *rf* power density, pressure and temperature was taken on the same run by varying the silane to argon flow ratio with the total flow rate held constant at 100 sccm.

4. Results and discussion

Variation of rf power :

We have observed the changes in optical emission spectra with the variation of *rf* power density from 20 mW/cm^2 to 787 mW/cm^2 at various percentages of silane in silane-argon mixture. The total flow was maintained constant at 100 sccm. The other constant process parameters were chamber pressure 0.2 Torr and substrate temperature 200°C. In Figure 2 we have shown the evolution of optical emission spectra due to SiH ($A^2\Delta$ – $X^2\Pi$) transition with the changes in *rf* power density at 20% of silane in silane-argon mixture. The peak at 414.2 nm due to SiH* ($A^2\Delta$ – $X^2\Pi$) and another peak at 415.8 nm due to a transition between the Ar molecular levels ($3p_6 \rightarrow 1s_5$) have been marked on the spectra. These peaks indicate how the densities of the SiH* and Ar* change with the *rf* power density. The Ar* emission line however, does not exactly correspond to the density of Ar* due to the cascade contribution from the higher energy levels [20].

In Figure 3, we have plotted the variation of the normalized I_{414} with the change in *rf* power density for silane to argon

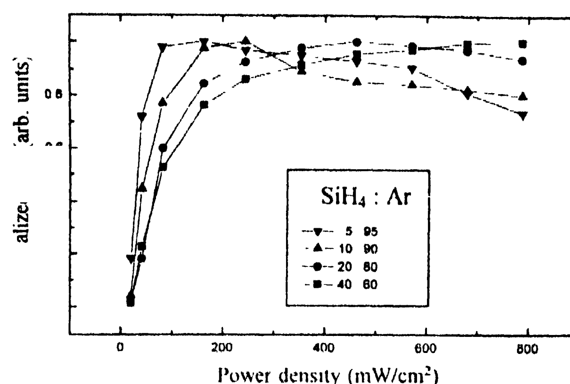


Figure 3. Variation of the normalized peak intensity at 414.2 nm (I_{414}) with power density at different flow ratio

flow ratios of 5 : 95, 10 : 90, 20 : 80 and 40 : 60. Initially there is a sharp increase in I_{414} with the increase of *rf* power density for every flow ratio. However, at a higher power density there is a tendency of decrease of the I_{414}. The intensity becomes maximum at some intermediate power density. We also observe a shift in the position of the maximum towards higher power density with increase in silane to argon flow ratio.

Theoretically calculated SiH* density (normalized) obtained with the help of eq. (9) have been plotted as a function of *rf* power density in Figure 4. We observe a

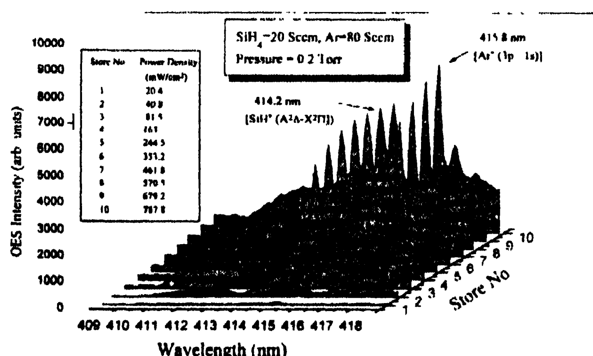


Figure 2. Evolution of the emission spectra due to SiH ($A^2\Delta$ – $X^2\Pi$) transition with *rf* power density at a definite pressure and flow ratio

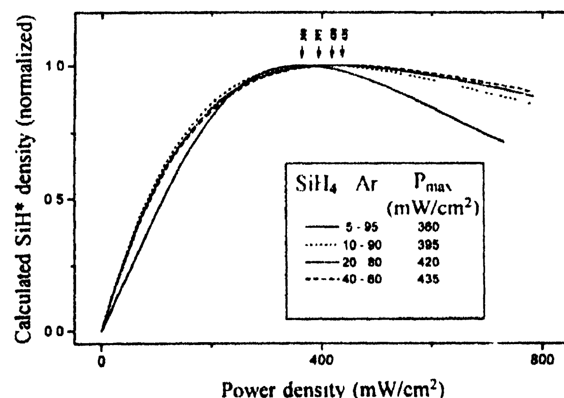


Figure 4. Variation of the calculated SiH* density (normalized) with respect to *rf* power density at different flow ratio.

similarity in the general trend of theoretically calculated curves with the experimental ones depicted in Figure 3. The initial sharp rise in I_{414} may be explained by the increase in electron density in the plasma with the increase of *rf* power density. The SiH* may be formed in the plasma either by direct electronic collision with the SiH_4 molecule with the formation of an intermediate SiH_4^* state [21] or by electronic excitation of SiH from the ground state [13]. At higher power the slight fall in the emission intensity may be due to the emission of secondary electrons from the electrodes by bombardment of ions. As the energy of the secondary electrons is low the average electron temperature will decrease [22]. This will decrease the SiH* formation and corresponding lowering of I_{414} may thus be explained. The maximum intensity of SiH* is reached at a power density when nearly all the silane molecules are dissociated. For higher silane concentrations more electrons are necessary for dissociation of all the silane molecules, which requires higher power The shift of the maximum in I_{414} towards higher power density can thus be explained.

Variation of flow ratio :

In the Figure 5 we have shown variation in I_{414} with the percentage of silane in the silane-argon mixture. The constant

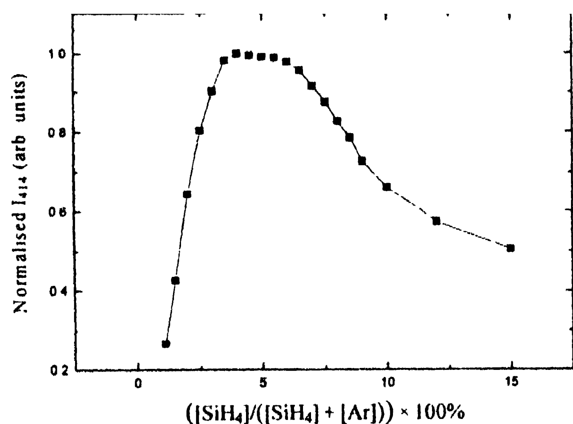


Figure 5. Variation of the normalized peak intensity at 414 2 nm (I_{414}) with SiH_4 concentration.

process parameters were total flow 100 sccm, pressure 0.2 Torr, *rf* power density 30 mW/cm^2 and substrate temperature 200°C. Theoretically calculated normalized SiH* concentration has been plotted in Figure 6. Here also we see that the general trend of experimental and theoretically calculated curves are similar in nature. First, there is a sharp increase in I_{414} with the increase of silane percentage and at higher percentage of silane, intensity sharply falls. This may be explained in the following manner. With increase of argon dilution the density of the excited argon (Ar*) molecules increases. As the threshold energy of metastable Ar* is high (> 11.55 eV) they will supply a large amount of energy to the slower electrons on collision. The mean energy of the

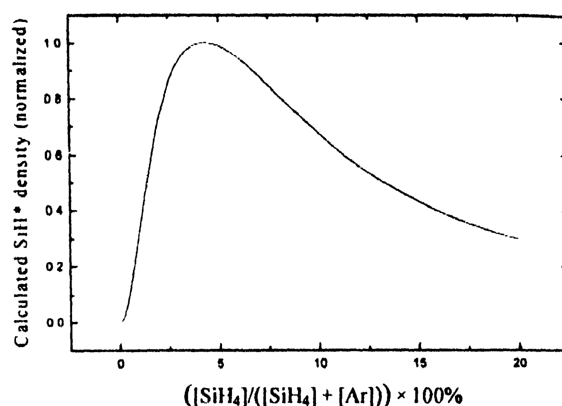


Figure 6. Variation of the calculated SiH* density (normalized) with respect to SiH_4 concentration.

electrons will therefore increase. So more silane molecules will dissociate or go to higher vibrational level. Direct dissociation of silane by collision with the metastable argon molecules (*via* reactions (7) and (8)) also takes place with the increase of argon concentration. The intensity of the 414.2 nm peak (I_{414}) will therefore increase with increase of argon dilutions. However, with further increase in argon dilution there will be depletion of silane molecules with a consequent sharp fall in the intensity of I_{414}. There is, therefore, a maximum obtained in the variation of the I_{414} With increase in silane percent Ar* density decreases and so also the SiH* intensity.

5. Conclusion

In this paper we have studied the variation of the peak intensity (I_{414}) at 414.2 nm (due to SiH*) with respect to wide range of power density and silane to argon flow ratio. The concentration of SiH* has been calculated by considering the dominant reactions in the glow discharge plasma of SiH_4-Ar mixture. We see that the behaviors of the experimental and theoretically calculated curves are very similar. So this model can be applied for different flow-type chemical reactions by the proper choice of dominant reactions. Physical explanation of the behavior of the intensity variation with different process parameters has been attempted. Effectiveness of the above method of characterizing the silane-argon discharge by OES method has recently been demonstrated in predicting correctly the growth rate of *a*-Si:H alloy films with respect to different process parameters [23].

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