

Effect of substrate temperature on deposition rate of rf plasma-deposited hydrogenated amorphous silicon thin films

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We present a study about the influence of substrate temperature on deposition rate of hydrogenated amorphous silicon thin films prepared by rf glow discharge decomposition of pure silane gas in a capacitively coupled plasma reactor. Two different behaviors are observed depending on deposition pressure conditions. At high pressure (30 Pa) the influence of substrate temperature on deposition rate is mainly through a modification of gas density, in such a way that the substrate temperature of deposition rate is similar to pressure dependence at constant temperature. On the contrary, at low pressure (3 Pa), a gas density effect cannot account for the observed increase of deposition rate as substrate temperature rises above 450 K with an activation energy of 1.1 kcal/mole. In accordance with laser-induced fluorescence measurements reported in the literature, this rise has been ascribed to an increase of secondary electron emission from the growing film surface as a result of molecular hydrogen desorption.

Among the various deposition parameters involved in the preparation of hydrogenated amorphous silicon (*a*-Si:H) by rf glow discharge decomposition of silane (SiH₄) gas, the substrate temperature T_s has been the most studied because of its determining influence on the structure and optoelectronic properties of deposited *a*-Si:H films. Nevertheless, the effect of T_s on deposition rate r_D is to a great extent controversial. Some studies have shown that T_s has not any significant influence on r_D ,^{1,2} whereas some others have shown that r_D either increases³⁻⁵ or decreases^{6,7} as T_s rises.

In a study by Perrin *et al.*⁸ it was reported that the pressure dependence of r_D at constant T_s and rf power, is characterized by a sudden increase of r_D above a threshold pressure value due to a transition between two regimes (α and γ) of the SiH₄ rf discharge. In the same work, from the obtained pressure dependences of r_D at two T_s values, the above discrepancies about the T_s influence on r_D were ascribed to a shift of the threshold pressure of the α - γ transition as a result of a modification of gas density by effects of gas temperature. In fact, the relevant parameter in gas-phase processes is not the pressure P but the gas density N , and if the relation between P , N and the gas temperature T is taken into account,

$$P = NkT, \quad (1)$$

k being the Boltzmann constant, an increase of T at constant P is equivalent to a decrease of P at constant T to get a decrease of N , and vice versa. However, Perrin *et al.*⁸ reported that the effect of T_s on r_D in low P conditions cannot be only ascribed to a variation of N .

In order to get more insight into the T_s influence on r_D , we have prepared four series of *a*-Si:H thin films in an rf

plasma reactor described elsewhere.^{9,10} The films were deposited on *c*-Si wafers and Corning 7059 glasses at different conditions of P and T listed in Table I. Other deposition conditions were 30 sccm of SiH₄ flow rate and 20 mW/cm² of rf power density on the rf electrode. The deposition rate of the films was determined by real time ellipsometry^{11,12} and optical transmittance measurements.¹³

Figure 1 shows the deposition rate of *a*-Si:H films deposited in the high P region (series *B* and *D*) as a function of the ratio P/T . The temperature T is the local gas temperature in the vicinity of substrate surface which has been estimated equal to T_s as a first approximation. Thus, according to (1), the ratio P/T is proportional to the local gas density near substrate. For both series, r_D increases with the ratio P/T until reaching a maximum. This behavior is similar to the reported P dependence of r_D at constant T_s in the γ regime of the rf discharge.^{8,14,15} The rise of r_D in Fig. 1 shows the same dependence for both series, but the r_D data of films deposited at constant P of 30 Pa (solid line) have a stronger fall with P/T than those corresponding to films deposited at 300 °C of T_s (dashed line). This would suggest that the limitation of r_D owing to gas-phase polymerization reactions in the γ regime is more important at low temperatures, as evidenced by the observed appearance of a yellow silicon powder close to the exhaust aperture of the plasma chamber. Despite this, the overall P/T dependence follows similar trends for both series, supporting the hypothesis of Perrin *et al.*⁸ based on a variation of N by effects of T_s .

The deposition rate of films deposited in the low P region (series *A* and *C*) is shown in Fig. 2 as a function of the ratio P/T . Here, two different dependences are observed depending upon whether the films were deposited at

TABLE I. Deposition pressure P and substrate temperature T_s conditions of the four series (A-D) of α -Si:H films studied.

| Series | A | B | C | D |
|------------|---------|---------|------|-------|
| Symbol | (○) | (□) | (△) | (★) |
| P (Pa) | 3 | 30 | 3-13 | 24-43 |
| T_s (°C) | 100-350 | 200-400 | 300 | 300 |

constant P of 3 Pa (solid line) or at constant T_s of 300 °C (dashed line). These r_D values are lower than those shown in Fig. 1 and, at constant T_s show a minimum which points up the lowering of ion contribution to deposition against the increase of neutral radical contribution as P rises within the α regime of the discharge.⁸ In contrast, at constant P , r_D has a rapid decrease with the ratio P/T that cannot be explained by a modification of N .

As a matter of fact, the modification of N via relation (1) implicitly assumes the gas temperature T is affected by T_s . Although a detailed heat transfer calculation is out of the scope of this paper, in the high P regime it is reasonable that T will be close to T_s , because, for our plasma chamber geometry and SiH_4 flow rate used, the gas flow is in a viscous state with long residence times (≈ 1 s at 30 Pa). On the contrary, in the low P regime the gas is in a molecular state with shorter residence times (≈ 0.1 s at 3 Pa) and accordingly a less important influence of T_s on N could be expected. Anyway, a simply gas density effect cannot account for the observed increase of r_D as T_s rises at constant low P and then another explanation is required.

On the one hand, the rise of r_D with T_s might be due to an increase of sticking probability of deposition precursor

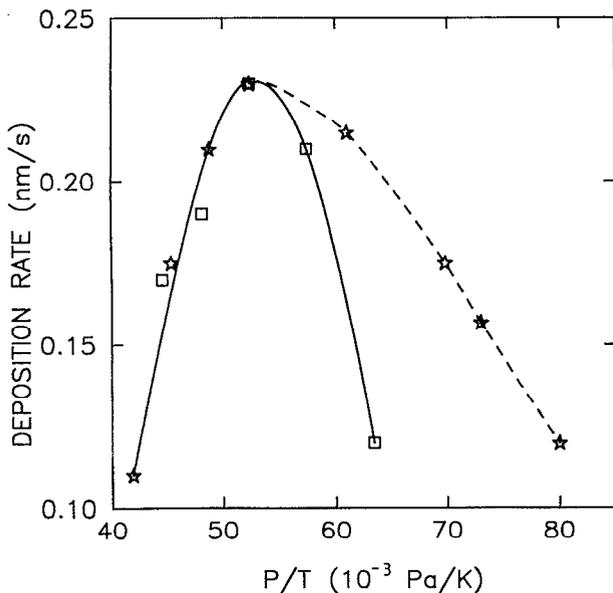


FIG. 1. Deposition rate of α -Si:H films as a function of the ratio between deposition pressure P and local gas temperature near substrate T considered equal to substrate temperature T_s , at a constant P of 30 Pa (squares) and at a constant T_s of 300 °C (stars).

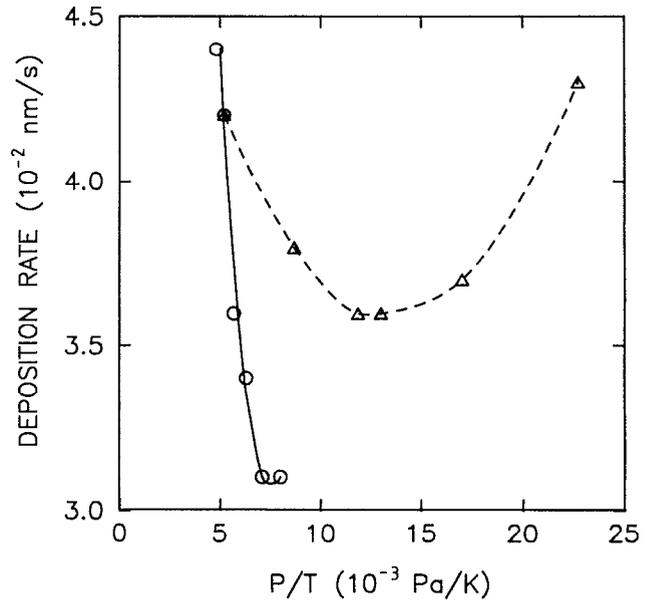


FIG. 2. Deposition rate of α -Si:H films vs the ratio pressure/temperature, P/T , at a fixed P of 3 Pa (circles) and at a fixed T_s of 300 °C (triangles).

radicals adsorbed on the growing α -Si:H surface, in competition with surface recombination reactions. Nevertheless, the sticking probability of SiH_3 radical, considered as the main precursor radical for our discharge conditions,¹⁶ has been reported to be independent of T_s up to temperatures near 300 °C.¹⁷ Moreover, as to the other radicals such as Si, SiH, and SiH_2 , T_s has not any influence on their sticking probability.¹⁸

On the other hand, in a paper concerning laser-induced

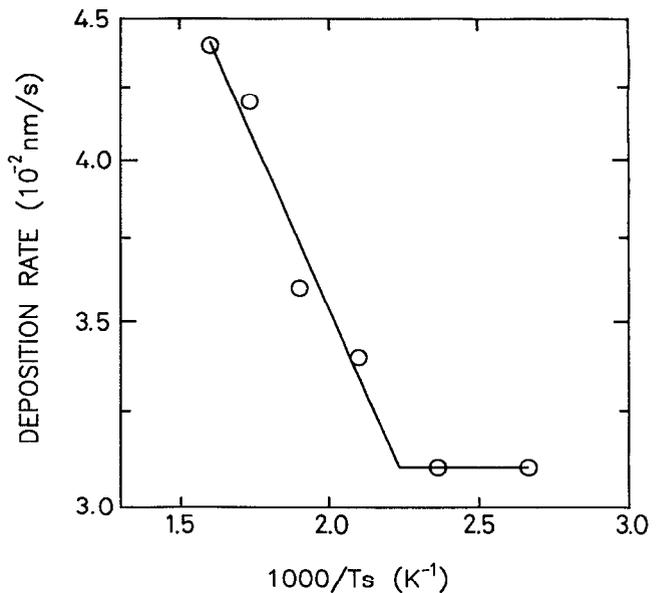


FIG. 3. Arrhenius plot of the deposition rate of α -Si:H films deposited at 3 Pa of pressure in the substrate temperature, T_s , range between 100 and 350 °C.

fluorescence (LIF) measurements,¹⁹ a sharp increase of SiH radical concentration near substrate with increasing T_s above 450 K was reported. This was ascribed to an increment of the efficiency of secondary electron emission from the film surface by desorption of molecular hydrogen. From the Arrhenius plot of the LIF signal intensity an activation energy of 1.3 kcal/mole was obtained.¹⁹ An increase of secondary electron emission will lead to an enhancement of current density of fast electrons, promoting silane ionization and dissociation near substrate, thus explaining the increase of r_D with T_s . In Fig. 3 we have represented the Arrhenius plot of the logarithm of r_D vs T_s^{-1} , where an activation energy of 1.1 kcal/mole has been calculated for T_s above 450 K. The clear agreement between the activation energy value derived from the LIF data and that calculated from Fig. 3 corroborates the hypothesis based on an increase of secondary electron emission efficiency. Furthermore, it establishes a proportionality between the α -Si:H deposition rate and the SiH concentration near substrate measured by LIF,

$$r_D = C[\text{SiH}], \quad (3)$$

C being a constant. In addition, this interpretation is in accordance with the decrease of α -Si:H work function reported by Roca *et al.* from *in situ* Kelvin probe measurements,⁵ who also found an increase of r_D as T_s rises, in similar discharge conditions to ours.

In conclusion, the T_s dependence of r_D in high P conditions (30 Pa) is consistent with a modification of gas density by gas heating, whereas an increase of secondary electron emission by hydrogen desorption accounts for the observed increase of r_D with T_s in low P conditions (3 Pa).

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