



## **On the preparation and growth of $\alpha$ -Si:H thin films by Hg-sensitised photochemical vapor deposition at low temperature**

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### **Résumé**

**A propos de la préparation et la croissance de couches minces de  $\alpha$ -Si:H à basse température par la technique Hg-Photo-CVD**

La technique Photo-CVD sensibilisée au mercure (Hg-photo-CVD) est largement utilisée pour déposer des couches minces de silicium amorphe hydrogéné ( $\alpha$ -Si:H). Cette technique présente plusieurs avantages notamment la possibilité d'effectuer des dépôts de films sans défauts sur des substrats à basses températures. Dans cet article, nous présentons un petit rapport sur le principe et les potentialités de cette technique. Nous rappelons un certain nombre de points fondamentaux relatifs au dispositif expérimental avec les particularités et fonctionnalités des différents éléments de l'appareillage. Nous examinons aussi quelques aspects fondamentaux de cette technique de dépôt tels que l'analyse des réactions en phase vapeur dans le réacteur, le modèle cinétique du processus de photo-décomposition du silane ainsi que le modèle de l'activité des réactifs en surface pendant la croissance des films.

**Mots-clés :** *Silicium Amorphe Hydrogéné ( $\alpha$ -Si :H), Couches Minces, Mercure, Dépôt photo-Chimique en Phase Vapeur (photo-CVD)*

### **Abstract**

Mercury-sensitized photo-CVD technique (Hg-photo-CVD) is widely used for growing amorphous silicon thin films ( $\alpha$ -Si:H). This attractive method allows damage-free thin film depositions at very low substrate temperatures without the deleterious effects of the other processes. This review reports on the principle and potential of this technique. It also recall and summarizes some fundamental issues such experimental systems or

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apparatus particularities, the analysis of gas-phase reactions in the reactor, the surface-reaction model of  $\text{SiH}_3$  and H during the film growth and all the kinetic model for lamp-induced Photo-CVD.

**Keywords:** *Hydrogenated Amorphous Silicon, Thin Films, Mercury, Photo-Chemical Vapor Deposition (photo-CVD)*

## 1- Introduction

Thin film technologies hold considerable promise for a substantial reduction of the manufacturing costs of solar cells due to the reduction of material costs and the deposition on large area substrates [1-5]. The thin film technologies for photovoltaic applications include a-Si:H alloys, CdTe, Cu(In,Ga)Se<sub>2</sub>, poly-Si,  $\mu\text{c-Si}$ /Poly-Si and dye/TiO<sub>2</sub>. The most advanced technologies are a-Si-alloys, CdTe and CIGS [1,2]. Solar cells and a range of other electronic devices technologies based on hydrogenated amorphous silicon (a-Si:H) have matured considerably over the last two decades. Since the first a-Si:H solar cell was made by Carlson et al. [6] the technology has improved tremendously, leading to reported initial conversion efficiencies exceeding 15% [7].

Solar cells based on a-Si:H offer many specific advantages. They are fabricated from extremely abundant raw materials and involve almost no ecological risk during manufacturing, operation, and disposal. With comparison to crystalline silicon, the a-Si:H material used in the fabrication is distinguished by a large optical gap in the required range for optimal performance [8]. It presents also a high optical absorption within the maximum of solar spectrum. So, a large part of solar energy is absorbed in a small thickness of the material allowing making structures in the form of very thin layers. Indeed, a thickness of 1  $\mu\text{m}$  material suffices to absorb the solar radiation efficiently.

Also, a-Si:H does not considerably suffer light induced degradation (Staebler-Wronski effect) [9]. Moreover, deposition of a-Si:H is much faster than crystalline silicon growth and can be carried out over much larger areas. Low process temperatures facilitate the use of a variety of low cost substrate materials such as float glass, metal or plastic foils [10-12]. All these characteristics are of great importance making a-Si:H a more attractive material for the elaboration of cheap photocells with good photovoltaic parameters.

Several methods have been used to deposit amorphous silicon from silane or other silicon carrier gases [13,14]. These include: chemical vapor deposition (CVD), direct current (DC) and radio frequency (RF) glow discharge (plasma enhanced chemical vapor deposition), microwave glow discharge, electron-cyclotron resonance glow discharge, remote plasma-assisted CVD, controlled plasma magnetron (CPM) glow discharge, photolytic decomposition (photo-CVD), sputtering, cluster beam evaporation and hot-wire

decomposition. Of these, RF and DC glow discharge depositions are the most common and are those used by industry. The optimum a-Si:H material has traditionally been produced at a substrate temperature of around 250 °C and contains about 10% at. H. Some gas mixtures used to deposit a-Si:H contain SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub>, SiF<sub>4</sub> and H<sub>2</sub>, while others may use only SiH<sub>4</sub>. The most recent route to obtain higher quality films is to use H-dilution of the feedstock gases. This improves the initial film quality in some systems and leads to less light induced degradation in solar cells.

In our previous work [15-19], we have prepared a-Si:H thin films by radio frequency cathodic sputtering technique and we have studied how optical characteristics of these films change with increasing hydrogen pressure during the deposition stage as well as with classical post-deposition annealing [15-17]. Using the grazing x-rays reflectometry technique, we have also characterized some of the structural properties of a-Si:H very thin layers immediately after deposition as well as after surface oxidation or annealing [18,19].

Currently, a conception and realization of a new a-Si:H thin films deposition set up based on the Mercury-sensitized photo-CVD technique [20-22] is progressively developed in home laboratory. This new system should be quite similar to that developed by our collaborator Dr AKA Boko some years ago in France [23-26]. The specific research program that we are planning to carry out on this new system registers within the framework of a research project financed by the ministry of high education and scientific research of Morocco. It mainly consists in depositing a good quality a-Si:H thin films allowing to develop powerful terrestrial solar cells.

To conduct well this new research program, we initially performed an important bibliographical work aiming to seek and join together the maximum of scientific information and technical data published by the specialists of the subject [20-47]. After examining and analyzing these literature data, we noted some fundamental aspects, which characterize particularly the Mercury-sensitized photo-CVD technique. What we are trying to recall and review through the present bibliographical synthesis, which we are proposing in this paper.

## **2. Technique of photochemical vapor deposition**

Photo Chemical Vapor Deposition (Photo-CVD) technique, also named Photo-Enhanced CVD [48-54] is widely and regularly used for growing thin Silicon films. This attractive method allows damage-free thin film depositions at very low substrate temperatures (<300°C) without the deleterious effects of the others various techniques [42,55].

Because of the efficient generation of both SiH<sub>3</sub> radical, having a long lifetime in the gas-phase, and atomic hydrogen, having an important role of the surface termination, high quality amorphous, polycrystalline and epitaxial Si films were obtained by this

method [56].

As it is known, there are two major variants of the Photo-CVD technique depending on the source of excitation used in the decomposition process:

- Laser-induced Photo-CVD using high-energy coherent radiations as light source to cause a direct photolysis mechanism [57-59].
- Lamp-induced Photo-CVD using incoherent radiations as light source. Lamps, usually mercury (Hg), are used as photosensitizer for the deposition process (Hg-sensitization) because of mercury's high catalytic activity [20-22]. This is why such technique is widely named Hg-sensitized photo-CVD (Hg-photo-CVD).

In the first variant, various gas lasers such as excimers [48,57], Ar<sup>+</sup> ions [58], and CO<sub>2</sub> lasers [59] are often used because of their high power density. However, they are expensive and are inadequate as vacuum-ultra-violet (VUV) light sources. Moreover, a strict optimization of the technology is necessary. Namely, some effects, such as damage due to the high-energy photons may have disadvantageous results. This is why the second variant Hg-sensitized photo-CVD, which operates in a direct photo-CVD mode without the use of lasers, has been widely utilized for practical applications in spite of its principal disadvantages such as small Hg incorporation in the growth films [60] and the production of bad exhaust fumes.

## 2-1. Hg-sensitized photo-CVD system

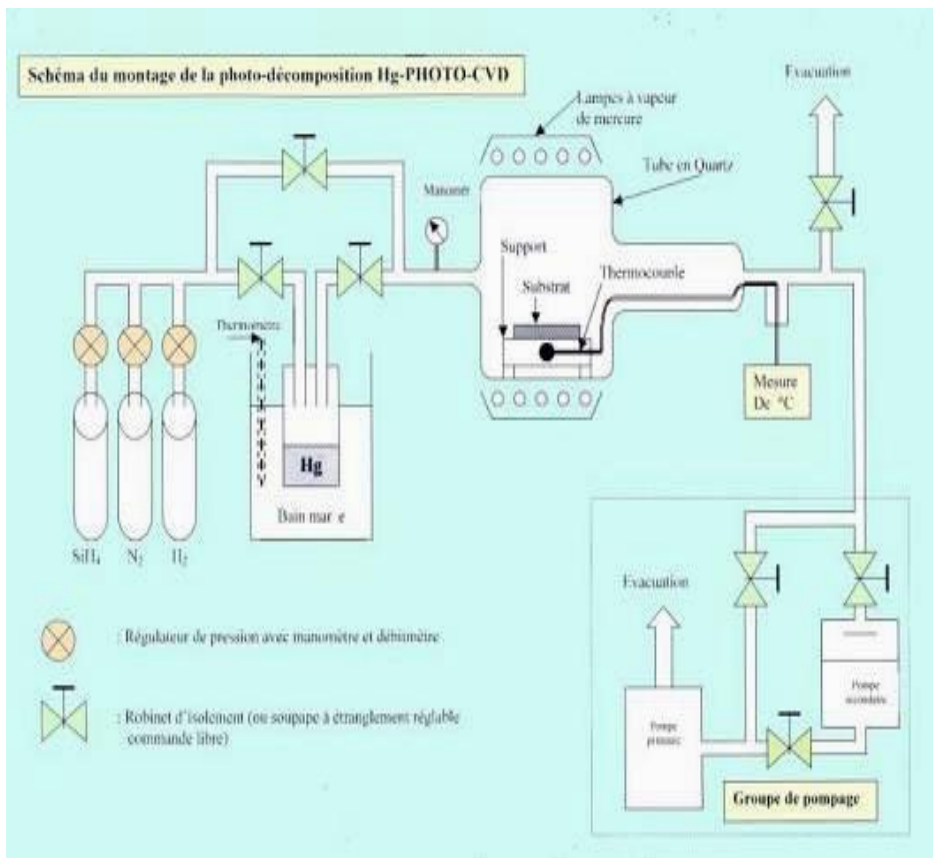
The schematic diagram of the photo-CVD apparatus we are developing in our laboratory was described elsewhere [61,62]. The set-up is very simple (*Figure 1*). It consists mainly of a cylindrical quartz reactor in the form of special tube whose size dimensions as specified elsewhere [61,62]. This tube, used as deposition chamber, is equipped with a small reservoir containing a small quantity of liquid mercury, which can be thermally controlled independently of the remainder of the system (Hg bath). The inner surface of the tube is coated with a low-vapor-pressure Fomblin vacuum oil to prevent any film deposition on.

The substrate-support can be of graphite or of stainless steel. It is heated through a thermo-coax wire and equipped with a thermocouple to measure its temperature. Well-cleaned high-resistivity crystalline Si (100) wafers or Corning 7059 glass can be used as substrates. The distance between the quartz tube external surface and substrates is about 2 cm.

The light source is a series of low-pressure Hg lamps radiating 253.7 nm (40 mW/cm<sup>2</sup> or ~30 mW/cm<sup>2</sup> at 3 cm distance) and 184.9 nm (less than 10 mW/cm<sup>2</sup> or ~ 5 mW/cm<sup>2</sup> at 3 cm distance) resonance lines. Since the transmittance of the quartz tube for the 253.7 nm and 184.9 nm wavelengths is 80 % and 20 % respectively, the 253.7 nm resonance line of UV light is dominantly irradiated into the reactor. The series of Hg lamps are set

up under an aluminum reflector placed at few cm with the top of the reactor. The vacuum system is composed of two pumps. The first one, with pallets, is used to obtain a primary vacuum and to purge gases of the reactor. The second is a diffusion pump allowing evacuation down to a pressure of  $10^{-6}$  Torr during the back out of the reactor prior to the growth.

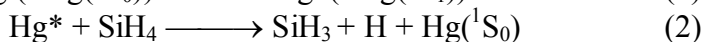
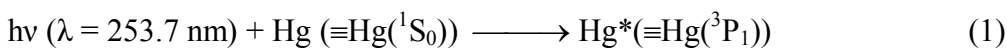
The reactant gases ( $\text{SiH}_4$ ,  $\text{H}_2$ , ...) are introduced into the reactor through the Hg bath usually kept at  $50^\circ\text{C}$ . Thus, a very small amount of Hg vapor is automatically mixed with the gases and introduced into the deposition chamber. The Hg vapor atoms then introduced are used to enhance dissociation of reactant gases [63] because of the weak optical absorption by the molecules in the 190-260 nm wavelengths region [64,65]. A conductance valve adjusts the total gas pressure in the reactor.



**Figure 1:** *Schematic diagram of the Hg-sensitized photo-chemical vapor deposition apparatus developed at home laboratory*

## 2-2. Principle of Hg-sensitized photo-CVD

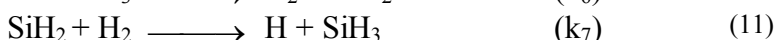
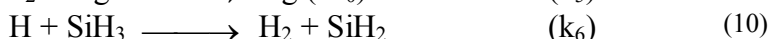
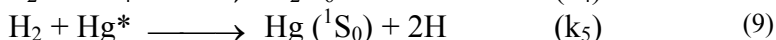
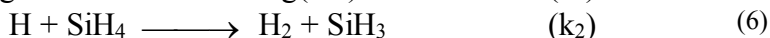
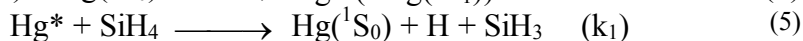
As well described in the literature [27,30], in the principle of Hg-sensitized photo-CVD technique, the 253.7 nm resonant radiation emitted by the low-pressure Hg-lamps is used as UV light source and the photons excite the Hg atoms from the ground state Hg ( $^1S_0$ ) to the excited state Hg ( $^3P_1$ ). Then the SiH<sub>4</sub> molecules are decomposed by colliding with the excited Hg atoms [66]. Thus, the photochemical reactions are much more selective than the reactions in the case of plasma-CVD. As a result of the Hg-sensitized reaction of SiH<sub>4</sub>, radicals such as SiH<sub>3</sub> and atomic H are generated as described in the reactions 1 and 2 below. H<sub>2</sub> molecules are also decomposed by the excited Hg and yield atomic H (reaction 3)[67].



To calculate the concentrations of SiH<sub>3</sub> and atomic H, an excited Hg (Hg\*) concentration inside the reaction chamber must be calculated. The method for the calculation of the Hg\* concentration in the Hg-sensitized photo-CVD technique has been described by Perrin and Broekhuizen [68].

## 2-3. Analysis of gas-phase reaction

Once the Hg\* concentration in the reaction chamber is calculated, the concentrations of the radicals generated by chemical reactions can also be estimated. The details of the calculation used to determine the radical concentrations are described elsewhere [30]. The elemental gas-phase reactions basically and usually adopted are as follows [69-72]:



The rate constants  $k_i$  at 300K, in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , are as follows:

$$k_1 = 6.4 \cdot 10^{-10}$$

$$k_2 = 4.3 \cdot 10^{-13}$$

$$k_3 = 1.5 \cdot 10^{-10}$$

$$k_4 = 1.0 \cdot 10^{-12}$$

$$k_5 = 5.0 \cdot 10^{-10}$$

$$k_6 = 1.0 \cdot 10^{-10}$$

$$k_7 = 2.6 \cdot 10^{-13}$$

The radical-radical reaction of hydrogen ( $H + H \rightarrow H_2$ ) is ignored in the calculation because of the very small rate constant of  $4.3 \cdot 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [73]. Consequently, the radical concentrations are calculated by solving the following gas-phase mass balance equations of  $\text{SiH}_3$ ,  $\text{SiH}_2$  and  $H$  with the boundary conditions on the Si substrate and the inner front surface of the quartz tube wall from which reactant gases in the reactor receive the UV light irradiation. In these calculations, we assume that the UV light is irradiated uniformly and that the macroscopic flow of the reactant gas is negligible:

$$D_{\text{SiH}_3} \frac{d^2[\text{SiH}_3]}{dx^2} = \frac{d[\text{SiH}_3]}{dt} \tag{12}$$

$$= k_1[\text{SiH}_4][\text{Hg}^*] + k_2[\text{SiH}_4][H] - 2k_3[\text{SiH}_3][\text{SiH}_3] - k_6[\text{SiH}_3][H] + k_7[\text{SiH}_2][H_2]$$

$$D_{\text{SiH}_2} \frac{d^2[\text{SiH}_2]}{dx^2} = \frac{d[\text{SiH}_2]}{dt} \tag{13}$$

$$= k_3[\text{SiH}_3][\text{SiH}_3] - k_4[\text{SiH}_2][\text{SiH}_4] + k_6[\text{SiH}_3][H] - k_7[\text{SiH}_2][H_2]$$

$$D_H \frac{d^2[H]}{dx^2} = \frac{d[H]}{dt} \tag{14}$$

$$= k_1[\text{SiH}_4][\text{Hg}^*] - k_2[\text{SiH}_4][H] + 2k_5[H_2][\text{Hg}^*] - k_6[\text{SiH}_3][H] + k_7[\text{SiH}_2][H_2]$$

The boundary conditions for these equations are shown in *equations (15) and (16)*, that is, the flux of each species impinging onto the surface is equal to the reaction rate at the surface:

$$\left[ D_j \frac{dn_j}{dx} \right]_{x=0} = \left[ D_j \frac{\beta_j \mathcal{G}_j n_j}{4} \right]_{x=0} \tag{15}$$

$$\left[ D_j \frac{dn_j}{dx} \right]_{x=L} = \left[ D_j \frac{\beta_j \mathcal{G}_j n_j}{4} \right]_{x=L} \tag{16}$$

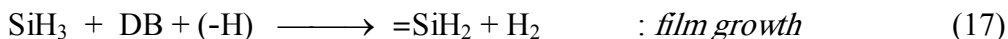
where  $x$  is the distance between the substrate and the inner front surface of the quartz tube wall from which reactant gases in the reaction chamber receive the UV light irradiation,  $D_j$  is a diffusion coefficient of the radical  $j$  ( $\text{SiH}_3$ ,  $\text{SiH}_2$  or  $H$ ) in the gas phase and  $n_j$  and  $\beta_j$  are the concentration and the surface reaction probability ( $0 \leq \beta_j \leq 1$ ) respectively. The mean velocity  $v_j$  is given by  $(8 R T_g / \pi M_j)^{1/2}$  where  $M_j$  is the molecular mass of the radical  $j$ .

The values of  $\beta_j$  on Fomblin oil ( $x = 0$ ) and on the surface of Si films ( $x = L$ ) are usually adopted with the following assumptions: On Fomblin oil,  $\beta_{\text{SiH}_3}$  and  $\beta_{\text{SiH}_2}$  are

smaller than  $10^{-3}$  since the growth rate of Si films on Fomblin oil is very small. The value of  $\beta_H$  on Fomblin oil has been reported to be about  $10^{-1}$  [74]. On the Si surface,  $\text{SiH}_2$  has a high sticking coefficient, since  $\text{SiH}_2$  can insert into a Si-H bond, therefore  $\beta_{\text{SiH}_2}$  of 0.7 has been selected in previous study [30].  $\beta_{\text{SiH}_3}$  on Si film was determined by Perrin [75] and has been reported to be  $10^{-1}$ . The reported values of  $\beta_H$  ranged from 0.6 to 0.8.

#### 2-4. Surface-reaction model of $\text{SiH}_3$ and H

The surface-reaction model of  $\text{SiH}_3$  and H has been well described by Abe et al. [27]. At temperatures lower than  $250^\circ\text{C}$ , the Si(100) surface is assumed to be almost terminated by hydrogen atoms with forming dihydride structures [76]. The radicals impinging on the surface migrate and react on the H-terminated surface. As a surface-reaction model, one always considers only two species,  $\text{SiH}_3$  and H, and two types of sites on the surface, which are dangling bonds (DB) and Si-H bonds (-H). The effects of  $\text{SiH}_2$  radicals are neglected because the flux ratio  $\text{SiH}_2 / \text{SiH}_3$  on the surface is estimated to be about 0.01 under experimental conditions [27]. The following three reactions are taken into account for the reaction model of Si epitaxy on the dihydride surface:



The first reaction is the film growth:  $\text{SiH}_3$  radical migrates on the H-terminated Si (100) surface, then the radical is chemisorbed at dangling bond, resulting in the growth of Si. Here, " $=\text{SiH}_2$ " is a newly created dihydride structure. The second reaction is the abstraction of bonding hydrogen by  $\text{SiH}_3$  radical. The third reaction is the dangling bond termination by atomic hydrogen. Therefore, from this surface-reaction model, the equation for the change in the hydrogen surface-coverage ratio " $\theta$ " is given by:

$$N_S(d\theta/dt) = \beta_S J_S N_S (1-\theta) L_S \sigma_A - \beta_S J_S N_S \theta L_S \sigma_B + \beta_H J_H N_S (1-\theta) L_H \sigma_C \quad (20)$$

where  $L_S$  and  $L_H$  are the migration lengths of  $\text{SiH}_3$  and H respectively.  $\sigma$  is a two dimensional cross section of each reaction.  $\beta$  is the total surface-loss probability of each radical, and the values of  $\beta_S$  and  $\beta_H$  are reported to be 0.1 and 0.8 respectively [75].  $J_S$  and  $J_H$  are the flux of  $\text{SiH}_3$  and H, which can be obtained through calculation of the gas-phase reactions, respectively.  $N_S$  ( $6.8 \cdot 10^{14} \text{ cm}^{-2}$ ) is the surface atomic density of Si (100). In steady state,  $(d\theta/dt)$  goes to zero. Thus, equation (20) is deduced to be:



$$\theta = \frac{\beta_H J_H L_H \sigma_C + \beta_S J_S L_S \sigma_A}{\beta_H J_H L_H \sigma_C + \beta_S J_S L_S (\sigma_A + \sigma_B)} \tag{21}$$

From the growth reaction, the growth rate equation is also given by:

$$\text{Growth rate} = \beta_S J_S N_S (1-\theta) L_S \sigma_A m / \rho \tag{22}$$

where  $m$  ( $4.66 \cdot 10^{-23}$  g) is the mass of Si atom and  $\rho$  ( $2.329$  g/cm<sup>3</sup>) is its atomic density. Using *equation (21)*, *equation (22)* is transformed into the following:

$$\text{Growth rate} = \frac{(\beta_S J_S)^2 L_S \sigma_A L_S \sigma_B N_S m / \rho}{\beta_H J_H L_H \sigma_C + \beta_S J_S (L_S \sigma_A + L_S \sigma_B)} \tag{23}$$

### 3. Kinetic model for lamp-induced Photo-CVD

This kinetic model, based on collision theory of chemical reactions, has been proposed for laser and lamp-induced photo-CVD from GeH<sub>4</sub> and SiH<sub>4</sub> by Tao [33]. In a lamp-induced photo-CVD reactor, some reactant molecules absorb the UV photons and are photo-chemically excited. Their deposition is classified as photochemical deposition. Most reactant molecules do not have the chance to absorb the UV photons, so their deposition is still thermally driven. The overall deposition is composed of photochemical deposition and thermal deposition.

In an elementary gas-solid deposition reaction, there are two premises for a reactant molecule to deposit onto the substrate, according to the collision theory of chemical reactions [27]: (1) The reactant molecule must have enough energy to be activated and (2) the reactant molecule must collide with the substrate to deposit onto it. The growth rate depends on the number of activated reactants molecules, which strike the substrate.

Activation means that there is threshold energy  $E_c$ . If the energy of a reactant molecule is higher than  $E_c$ , it will decompose and deposit when it strikes the substrate. Otherwise, it will return into the gas phase after a collision. In the collision theory, a molecule is treated as a hard sphere, so its energy consists of its kinetic energy  $E_k$ , its potential energy  $E_p$ , and its internal energy  $E_i$ . Activation requires that:

$$E_k + E_p + E_i \geq E_c \tag{24}$$

For an ideal gas, the potential energy  $E_p = 0$ . In the classical thermal deposition process, reactant molecules are not photo-excited. Their internal energies can be approximated by a constant, which is the ground-state energy  $E_i^0$ . Thus, *equation (24)* can be simplified as:

$$E_k \geq E_c - E_i^0 = E_a \quad (25)$$

Accordingly, activation means that the kinetic energy of a reactant molecule must be higher than a critical value  $E_c - E_i^0$ , denoted by  $E_a$ .

In lamp induced photochemical deposition, some reactant molecules absorb the UV non-monochromatic photons emitted by the lamps and are photo-chemically excited. The excitation is either dissociate or non-dissociate. In the non-dissociate case, the internal energies of photo-excited molecules are no longer at the ground state:

$$E_i = E_i^0 + \sum_j h \nu_j \quad (26)$$

where  $h\nu_j$  is the energy of a particular photon,  $h$  is the Planck constant, and  $\nu_j$  is the frequency of the photon. The summation is over all the photons absorbed by a reactant molecule. Thus, *equation (26)* can be written as:

$$E_k \geq E_c - E_i^0 - \sum_j h\nu_j = E_a - \sum_j h\nu_j = E_a^* \quad (27)$$

which represent the lamp-induced photo-chemical excitation process. From this equation, we can easily note that the apparent activation energy becomes smaller in non-dissociate photochemical deposition than in the classical thermal deposition [77].

In the dissociate case, photo-excited molecules turn into new species. *Equation (24)* can be applied to the new species:

$$E_k \geq E_a^* \quad (28)$$

where  $E_a^*$  is the activation energy for new species to decompose and deposit onto the substrate. As discussed above, the activation energy for new species deposition is smaller than that of the parent molecules.

At equilibrium, the Maxwell distribution [78] indicates that, in a unit time, the number of reactant molecules which collide with a unit area of the substrate with kinetic energies between  $E_k$  and  $E_k + dE_k$  is:

$$d\Gamma = 2 \pi \gamma N_r \left( \frac{1}{2 \pi m_r^* k T} \right)^{3/2} m_r^* E_k \exp\left(-\frac{E_k}{kT}\right) dE_k \quad (29)$$

where  $N_r$  is the number of reactant molecules in a unit volume of the gas phase,  $\gamma$  is the fraction of those photo-excited. So, the number of photo-excited reactant molecules in a unit volume of the gas phase is given by  $N^* = \gamma N_r$ .  $m_r^*$  is the mass of a photo-

produced species,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. Integrating equation 29 from  $E_a^*$  to  $+\infty$ , we can derive the number of the activated photo-excited reactant molecules which strike a unit area of the substrate in a unit time:

$$\Gamma = \gamma N_r \left( \frac{1}{2 \pi m_r^* k T} \right)^{1/2} (E_a^* + kT) \exp\left(-\frac{E_a^*}{kT}\right) \tag{30}$$

We have the ideal gas law  $P_r = N_r k T$ , so the growth rate from photo-excited molecules is:

$$R_p = \frac{\Gamma}{N_0} = \gamma \frac{P_r}{N_0} \left( \frac{1}{2 \pi m_r^* k T} \right)^{1/2} \left( \frac{E_a^*}{kT} + 1 \right) \exp\left(-\frac{E_a^*}{kT}\right) \tag{31}$$

where  $P_r$  is the partial pressure of the photo-excited reactant molecules,  $N_0$  is the number density of atoms in the growing film. In the non-dissociate case,  $m_r^* = m_r$ . Simultaneously, thermal deposition proceeds as:

$$R_t = (1 - \gamma) \frac{P_r}{N_0} \left( \frac{1}{2 \pi m_r k T} \right)^{1/2} \left( \frac{E_a}{kT} + 1 \right) \exp\left(-\frac{E_a}{kT}\right) \tag{32}$$

The total growth rate is then given by the following *equation (33)*:

$$R = R_p + R_t = \gamma \frac{P_r}{N_0} \left( \frac{1}{2 \pi m_r^* k T} \right)^{1/2} \left( \frac{E_a^*}{kT} + 1 \right) \exp\left(-\frac{E_a^*}{kT}\right) + (1 - \gamma) \frac{P_r}{N_0} \left( \frac{1}{2 \pi m_r k T} \right)^{1/2} \left( \frac{E_a}{kT} + 1 \right) \exp\left(-\frac{E_a}{kT}\right) \tag{33}$$

It should be noted that this last equation is valid for small  $\gamma$ , which is the fraction of photo-excited molecules. Only when  $\gamma$  is small can we expect a simple linear behavior. When  $\gamma$  is large, gas-phase reactions can be very complicated.

A common case in lamp-induced photo-CVD is that a photo-sensitizer, usually mercury, is used to absorb photon energy and then transfer the energy to reactant molecules by collision interactions (Hg-sensitized photo-CVD). The chemistry and physics in this case are more complicated than in direct photochemical excitation. However, the result of the indirect photochemical excitation is similar to that of the direct one:  $SiH_4$  molecules are converted into more reactive species, such as  $SiH_2$ ,  $SiH_3$ ,  $Si_2H_6$ ,  $Si_2H_5$  and  $Si_2H_4$  [79]. Equation 28 can be applied to these new species, and the total growth rate has the same format as *equation (33)*.

In the literature, the experimental growth rate of Hg-sensitized photo-CVD from SiH<sub>4</sub> as a function of Hg vaporizer temperature [80] has been compared with this present model. The fraction of photo-excited molecules  $\gamma$  is, in the simplest case, proportional to the partial pressure of Hg, which can in turn be expressed as:

$$P_{\text{Hg}} = A \exp\left(-\frac{\Delta H_v}{kT_{\text{Hg}}}\right) \quad (34)$$

where  $P_{\text{Hg}}$  is the partial pressure of Hg,  $A$  is the pre-exponential factor,  $\Delta H_v$  is the heat of vaporization, and  $T_{\text{Hg}}$  is the temperature of the Hg vaporizer. Therefore,  $\gamma$  can be written in the same way with a new pre-exponential factor  $B$ :

$$\gamma = B \exp\left(-\frac{\Delta H_v}{kT_{\text{Hg}}}\right) \quad (35)$$

Combining *equation (31)* and *equation (35)*, we get the growth rate from photo-excited molecules as a function of Hg vaporizer temperature:

$$R_p = B \exp\left(-\frac{\Delta H_v}{kT_{\text{Hg}}}\right) \frac{P_r}{N_0} \left(\frac{1}{2 \pi m_r^* k T}\right)^{1/2} \left(\frac{E_a^*}{kT} + 1\right) \exp\left(-\frac{E_a^*}{kT}\right) \quad (36)$$

In summary, lamp radiation produces photo-excited molecules, which are more reactive than parent molecules. The photochemical excitation of reactant molecules is either dissociate or non-dissociate. Lamp-induced photo-CVD is composed of two processes: extrinsic photochemical deposition from photo-excited molecules and intrinsic thermal deposition from normal reactant molecules. The growth rates of both photochemical deposition and thermal deposition are derived by means of statistical physics.

Photochemical deposition dominates at low temperatures, and thermal deposition becomes prominent as the temperature rises. The transition temperature from photochemical deposition to thermal deposition is obtained as a function of fraction of photo-excited molecules and activation energies of photochemical deposition and thermal deposition.

#### 4. Conclusion

Photochemical Vapor Deposition (Photo-CVD) technique is widely and regularly used for growing thin Silicon films. This attractive method allows damage-free thin film depositions at very low substrate temperatures without the deleterious effects of the other various techniques. After examining and analyzing various works published in the literature on Photo-CVD process and experimental procedures, we noted some fundamental aspects, which characterize particularly the Mercury-sensitized photo-CVD technique.

This review reports on the principle and potential of this technique. It also recall and summarizes some fundamental issues such as particularities and details of Hg-sensitized photo-CVD systems or apparatus, the analysis of gas-phase reactions in the reactor, the surface-reaction model of  $\text{SiH}_3$  and H during the film growth and the whole kinetic model for lamp-induced Photo-CVD as well described and detailed elsewhere in other papers.

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