MODELING OF CLUSTER FORMATION AND PARTICULATE GROWTH DURING AMORPHOUS SILICON FILM DEPOSITION

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ABSTRACT

Low pressure silane processing plasmas are widely used to deposit thin films in the semiconductor industry such as in the fabrication of thin film solar cells. Recently it was found that the presence of extremely small particles in the amorphous hydrogenated silicon film enhance the performance of solar cells. Understanding of the pathways leading to the formation and growth of such particles in the plasma will allow optimization of the process parameters for the manufacture of efficient solar cells. The present contribution is an attempt to develop a comprehensive particle nucleation and growth model for silane plasma.

I. INTRODUCTION

Silane plasmas at low power and low density are widely used for the deposition of amorphous hydrogenated silicon films for solar cells. Particle formation during the deposition process was long considered detrimental to film quality. However, recently it was discovered that films which contain nanocrystalline inclusions—so-called "polymorphous films"—have superior electronic and transport properties compared to conventional amorphous films [1, 2]. The incorporation of silicon nanoparticles (1-2 nm) in the film is assumed to be a principal reason for the improvement which has led to increased stability against light-induced defect creation (Staedler Wenzel effect) which leads to a degradation of the solar cell efficiency. Thus, formation of extremely small particles in the deposition process can be considered beneficial for the production of efficient solar cells. An insight into the process of particle formation in such plasmas will substantially help in optimizing the deposition parameters. A model which predicts particle formation as a function of various process parameters such as plasma power, pressure, substrate temperature and precursor gas composition will be a valuable tool towards this end. In this paper we present results obtained using a plasma chemistry model coupled to a particle growth model, that uses the above process parameters as input parameters to the model.

II. DESCRIPTION OF THE MODEL

Bouchoule and Boufendi [3, 4] characterized the particle growth process in a silane plasma as a three-step process involving initial gas phase nucleation followed by growth due to coagulation of particles and growth due to surface deposition of radicals. Once formed, the particles affect the plasma parameters as well as the chemical clustering mechanism that leads to nucleation of particles. To include these effects we are developing a model which couples a plasma chemistry module to a particle growth module that
includes coagulation and surface growth.

The plasma chemistry module leading to the nucleation of particles has previously been described [5]. Briefly, it builds on the neutral clustering model of Swarthout and Grushack [6] and includes silicon hydride species such as saturated silanes, double bonded silanes, silylene [6-radicals, silyl mono-radicals, anions of silylenes and silyls as well as molecular and atomic hydrogen. Electrons are included as a separate species with a temperature different from the surrounding gas, whereas \( \text{SiH}_x \) is included as the only positive ion. The thermochemical properties of the neutrals were calculated using group additivity rules [6] and those for the anions were calculated by assuming that the enthalpy of the anions differed from that of the neutrals by an amount equal to the electron affinity of the neutral. Electron affinities were obtained either by absolute calculations or extrapolations [7]. Reactions between silicon hydrides were included by extrapolating from known reactions between smaller silicon hydride species. Reaction rate constants were incorporated based on those of known reactions or by estimation. All clustering reactions leading to the formation of clusters with more than 10 silicon atoms were considered as irreversible. Clusters with more than 10 silicon atoms were classified as "mucic". Such "mucic" were considered as a source term in the particle growth module.

In our present work, we include surface reactions in addition to gas phase reactions described in [5]. Gas phase species are assumed to react on the surface area of the particles once the particles are formed. A typical surface reaction leading to the formation of either \( \text{SiH}_x \) or \( \text{Si} \) being deposited on the particle surface with the release of hydrogen, e.g.,

\[
\text{SiH}_x + 2\text{Si}(S) \rightarrow 2\text{SiH}(S) + \text{Si}(B) + \text{H}_2,
\]

and

\[
\text{SiH}_x \rightarrow \text{Si}(B) + 1.5\text{H}_2,
\]

where \( \text{Si}(S) \) and \( \text{SiH}(S) \) represent surface species and \( \text{Si}(B) \) represents a silicon atom forming part of the "bulk" silicon within the particle. Radicals are assumed to stick with a probability of one. Surface reactions thus represent a sink term for the gas phase species. Thus, the conservation equation for the \( k \)th chemical species includes gain/loss terms due to gas phase reactions \( S_{\text{GB}} \), loss terms due to surface reactions \( S_{\text{PS}} \) and loss due to diffusion \( S_{\text{DP}} \). For simplicity we apply a binary diffusion coefficient to all species assuming that each species diffuses in a background gas consisting of pure \( \text{SiH}_x \) (which is the most abundant species at any given time). The diffusion term is not applied to the anions, which are assumed to be trapped by the ambipolar potential in the plasma. The conservation equation (in terms of molar concentration \( N_k \) of the \( k \)th chemical species) is written as follows:

\[
\frac{dN_k}{dt} = S_{\text{GB}} + S_{\text{PS}} + S_{\text{DP}}
\]

As mentioned above, clusters with more than 10 silicon atoms are assumed to be formed irreversibly. They do not undergo any chemical reactions and form a source term for the particle growth module. Particles are assumed to grow either by coagulation or by surface reactions of gas phase species. We consider particles in the diameter range 0.2 - 100 nm, which corresponds to a volume range spanning eight orders of magnitude. To ease the calculations for the particle growth we divide the entire volume range into 30 sections on a logarithmic scale. This is the well known sectional approach used in aerosol science [8, 9]. Thus, instead of particles of a particular volume interacting with particles of another volume, the particles in a particular section interact with particles in the same or other sections as well as with the gas phase species. The conservation
The conservation equation for the property \( q_k \) of the \( k \)th section is written as:

\[
\frac{dq_k}{dt} = \dot{q}(1)\delta(k - 1) + \sum_{i,j,k} \beta_{ij,k} q_i q_j + \sum_{j} \beta_{k,j} q_j + \dot{q}_k.
\]  

(4)

where the first term on the right represents the source term due to nucleation of particles and is applied only to the smallest section (section 1). The second term represents a source term due to particles in smaller sections coagulating and entering section \( k \). The third term represents the loss terms due to particles in section \( k \) coagulating with particles in all other sections. We account for the fact that a particle in section \( k \) can collide with a smaller particle and still remain in section \( k \) since the section spans a large volume range. \( \beta_{ij,k} \) represents the collision frequency function between particles of section \( j \) and section \( k \) and is calculated assuming the free molecular regime [10]. The last term in Eq. 4, \( \dot{q}_k \), represents loss due to diffusion, whereas \( \dot{q}_k \) represents the source sink term due to surface growth. This is calculated by first finding the surface reaction rate \( S \) of the gas phase cluster \( r \) in units of \( \text{cm}^2 \text{s}^{-1} \). The volume change \( \dot{q}_k \) in any particular section \( k \) due to surface reactions is then given by:

\[
\dot{q}_{k,s} = \sum_{i\neq j} \sum_{k} \beta_{ij,k} A_k n_i \left( \frac{n_i}{\bar{n}_i} \right) \left( \frac{n_j}{\bar{n}_j} \right) + \sum_{j} \beta_{k,j} A_k n_j - \sum_{i} \beta_{i,k} A_i n_i.
\]  

(5)

where the first term on the right represents gain due to surface reactions between cluster \( i \) and section \( k \) such that the resultant particle remains in section \( k \). \( A_k \) represents the total surface area of all particles in section \( k \). The second term on the right represents surface reactions between cluster \( i \) and a smaller section \( j \) (with total surface area \( A_j \)) such that the resultant particle lies in section \( k \). The last term represents the loss of volume in section \( k \) due to surface reactions leading to the creation of a particle in a larger-size section.

In Eq. 4, the collision frequency function \( \beta_{ij,k} \) and the diffusion coefficient are modified due to charging of the particles. Collisions between particles with opposite charges have a larger collision cross section than neutral particles, whereas collisions between particles with like charges have a smaller collision cross section. We modify the collision frequencies between two sections by calculating the charge distribution over every section. Particles are assumed to be charged by electron and ion currents to the particle. Electron and ion capture by the particle are calculated using the orbital motion limited (OML) theory [11]. The charge distribution is calculated by using a balance equation for every charge state and assuming that the charging is much faster than the coagulation process [12]. In the present model we do not consider photodetachment of electrons from particles due to UV radiation in the plasma, although we previously considered this term [12]. For the diffusion term, only the neutral and positive fractions of particles in any section are allowed to diffuse. The negative fraction is treated similarly to the anions and is assumed to be trapped by the ambipolar potential in the plasma.

The conservation equations for the inlet gas \( \text{SiH}_4 \), the positive ion \( \text{SiH}_3^+ \) and the electrons are written differently from those of the other gas species. The \( \text{SiH}_4 \) density is assumed to be a constant in time (assuming that a continuous influx of \( \text{SiH}_4 \) replenishes the \( \text{SiH}_4 \) lost to clustering and film growth). The positive ion \( \text{SiH}_3^+ \) is also assumed to be constant in time. While it is known that the ion density changes in actual experiments.
these changes are much less pronounced than changes of the electron density. The positive ion density can be considered roughly proportional to the RF power density coupled into the plasma. Finally, the electron density is calculated by enforcing plasma quasineutrality as follows

\[ n_e - n_i = \sum_k n_{k+} + \sum_p k_p n_p \]  \hspace{1cm} (6)

where \( n_e \) and \( n_i \) represent the positive ion and electron concentration respectively. \( \sum_k n_{k+} \) is the sum of all the negative ions considered in the chemical nucleation model and \( \sum_p k_p n_p \) is the sum over all charges on the particles in the coagulation model.

The gas temperature is assumed to be constant in time whereas the electron temperature is calculated by using a global balance for the positive ions.

\[ k_p n_{p+} V = k_r n_i n_e + n_e n_p V - n_e V \]  \hspace{1cm} (7)

where the term on the left-hand side denotes the rate of positive ion production (\( k_p \) is the siliconization rate constant and \( n_p \) the neutral gas density). The first term on the right denotes the loss of positive ions due to recombination with anions (\( k_r \) is the recombination rate coefficient and \( n_i \) is the total ion density). The second term denotes the loss of positive ions to the particles (\( n_p \) is the average attachment frequency to the particles) and the last term on the right denotes the loss of positive ions to the walls. \( V = D_n n_p V \) where \( D_n \) is the ambipolar diffusion coefficient and \( V \) is a typical diffusion length. \( V \) and \( A \) represent the volume and surface area of the reactor. The calculation of the electron temperature is not performed at every time step, but only when the electron concentration changes by a significant amount (10%).

### III. RESULTS

We carried out calculations for SiH₄ inlet gas at a pressure and temperature of 100mTorr (13.3 Pa) and 500K respectively (corresponding to a neutral gas density of \( 1.93 \times 10^{15} \) cm⁻³) and a positive ion density of \( 3.2 \times 10^{4} \) cm⁻³. The chemical reactions were treated using CHEMKIN [13] and SURFACE CHEMKIN [14] and the rate equations for the species were calculated using a modified version of SENKIN [15] that accounted...
Figure 2: Particle size distribution at various times: (a) No surface growth and (b) With surface growth.

for a two temperature system. The coagulation time steps were taken after the chemical kinetics module advanced by fixed intervals. The results presented here do not include the diffusive loss term for the particles.

In Figure 1a and b, we have plotted the time evolution of negative and neutral clusters respectively (all clusters with equal number of Si atoms are represented by a single line). Our calculations show that clustering mainly proceeds through anion-neutral reactions [5]. Due to bottlenecks in this clustering chain, the anionic clusters with four and seven Si atoms reach a higher concentration compared to other clusters. Correspondingly, neutral clusters with five and eight Si atoms also have a higher concentration than the remaining neutral clusters since they are formed preferentially from anions with 4 and 7 Si atoms by neutralization.

Figure 2 shows the particle distribution function at different times. Fig. 2a represents a case where particle growth occurs purely due to coagulation and without surface growth whereas Fig. 2b represents the distribution function with surface growth included. Fig. 2a shows a dip in the distribution function for the smaller sizes. This dip is an artifact of the sectional model - a considerable fraction of colliding particles from the first section enter the third section rather than the second section as a result of which the second section has a lower number density of particles. Surface growth leads to a smoothing of the particle distribution function by increasing the number density of sparsely populated sections. As far as the size of particles is concerned, over the time scales shown in 2, the particle concentrations are high enough ($\geq 10^9 - 10^{10}$ cm$^{-3}$ at $t = 1$s) so that coagulation is the dominant growth term. The effect of surface growth on particle size is seen to be modest.

IV. CONCLUSIONS AND OUTLOOK

As can be seen in Fig 1a, the electron concentration drops by more than two orders of magnitude due to attachment to clusters. This affects the nucleation rate directly and it drops by a similar amount. We have carried out calculations keeping the electron concentration nearly constant. This leads to an increased influx of "nuclei" (due to faster...
clustering) in the coagulation module resulting in substantially large particles after 1s (more than 80 nm). Thus, electron density has a strong effect on the particles. Work is in progress to include the effect of diffusion of particles. A drop in electron concentration increases the neutral fraction of particles, increasing the diffusive losses. Thus, the change in electron concentration significantly affect particle growth. We propose to investigate this effect in the near future.

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REFERENCES


