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A mathematical model and simulation results of plasma enhanced chemical vapor deposition of silicon nitride films

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Abstract. We developed a mathematical model of Plasma Enhanced Chemical Vapor Deposition (PECVD) of silicon nitride thin films from SiH\textsubscript{4}-NH\textsubscript{3}-N\textsubscript{2}-Ar mixture, an important application in modern materials science. Our multiphysics model describes gas dynamics, chemical physics, plasma physics and electrodynamics. The PECVD technology is inherently multiscale, from macroscale processes in the chemical reactor to atomic-scale surface chemistry. Our macroscale model is based on Navier-Stokes equations for a transient laminar flow of a compressible chemically reacting gas mixture, together with the mass transfer and energy balance equations, Poisson equation for electric potential, electrons and ions balance equations. The chemical kinetics model includes 24 species and 58 reactions: 37 in the gas phase and 21 on the surface. A deposition model consists of three stages: adsorption to the surface, diffusion along the surface and embedding of products into the substrate. A new model has been validated on experimental results obtained with the «Plasmalab System 100» reactor. We present the mathematical model and simulation results investigating the influence of flow rate and source gas proportion on silicon nitride film growth rate and chemical composition.

1. Introduction
Silicon nitride thin films are used in solar cells, nano- and microelectronics, and other micro-technologies [1]. Plasma enhanced chemical vapor deposition (PECVD) at low-pressure RF glowing discharge is the most applicable technology for silicon film production because a high-quality hydrogenated amorphous silicon nitride (SiN\textsubscript{x}H\textsubscript{y}) can be obtained on large-area surface at low temperature [2]. Chemical composition and physical properties of the deposited films depend on process parameters in a highly non-linear way. It is extremely difficult to predict film properties before deposition, and experiments are expensive and time-consuming. Multiphysics computer simulation is the most efficient way for technology optimization.

The goal of our research is the development of a reliable model and investigation of correlation between process parameters and chemical composition of SiN\textsubscript{x}H\textsubscript{y}. We modeled a real PECVD reactor, and used experimental results and our previous studies [3, 4, 5] to build the chemical kinetics model. For process optimization at the macroscale level we have chosen a continuum modeling approach. Other researchers also used this approach to simulate silicon nitride PECVD from silane (SiH\textsubscript{4}), ammonia (NH\textsubscript{3}), nitrogen (N\textsubscript{2}) and argon (Ar) [6, 7, 8], but they did not consider all four source gases together, as presented in our work. Recent progress in silicon nitride atomic structure investigation by Fourier transform infrared (FTIR) spectroscopy [9, 10] allowed us to develop a new model of surface chemistry mechanism.
2. Mathematical model

A continuum modeling approach is justified at Knudsen numbers $Kn \approx 5\cdot10^{-3}$ calculated for our conditions. The PECVD processes require modeling gas dynamics, heat and mass transfer, electromagnetism and chemical kinetics. Mass conservation law (1) and Navier-Stokes equations for a transient laminar flow of a compressible chemically reacting gas mixture (2) describe the gas dynamics in the process chamber:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0, \quad (1)$$

$$\frac{\partial (\rho u_i)}{\partial t} + \nabla \cdot (\rho \mathbf{V} u_i) = -\frac{\partial p}{\partial x_i} + \nabla \cdot (\mu \mathbf{V} u_i) \quad i = x, y, z, \quad (2)$$

where $\rho$ is density, $t$ is time, $\mathbf{V}$ is velocity vector, $u_i$ is projection of velocity vector on $i$ axis, $\mu$ is the kinematic viscosity. Heat transfer equation can be written as

$$\frac{\partial (\rho h_0)}{\partial t} + \nabla \cdot (\rho \mathbf{V} h_0) = \nabla \cdot (k_{eff} \nabla T) + \frac{\partial p}{\partial t} + S_h, \quad (3)$$

where $h_0$ is enthalpy, $k_{eff}$ is thermal conductivity, $T$ is temperature, $p$ is pressure, $S_h$ is the heat source due to chemical reactions. A model of capacitively coupled plasma (CCP) is based on Maxwellian electron energy distribution function. Electron balance is given by

$$\frac{\partial n_e}{\partial t} + \nabla \cdot \mathbf{J}_e = S, \quad (4)$$

where $n_e$ is electron density, $\mathbf{J}_e$ is electron flux and $S$ is a source of electrons due to chemical reactions. Energy balance in plasma can be written as

$$\frac{3}{2} \frac{\partial}{\partial t} (n_e T_e) + \nabla \cdot \left( \frac{5}{2} T_e \mathbf{J}_e - \chi \nabla T_e \right) = P - P_c \quad (5)$$

where $T_e$ electron temperature, $\chi$ is a constant for electron termodiffusion, $P$ is power adsorbed in plasma and $P_c$ is an energy loss due to electron impact reactions. The spatial distribution of electrostatic potential $\varphi$ is described by the Poisson equation:

$$-\nabla \cdot \varepsilon_r \nabla \varphi = e (\Sigma_i q_i n_i - n_e), \quad (6)$$

where $\varepsilon_r$ is relative permittivity, $q_i$ is charge of ions, $n_i$ is ion density, $e$ is elementary charge. Mass transfer equation for the $i^{th}$ species can be written as

$$\frac{\partial}{\partial t} (\rho Y_i) + \frac{\partial}{\partial x_j} (\rho u_j Y_i) = \frac{\partial}{\partial x_j} J_{ij} + M_i \omega_i, \quad (7)$$

where $\rho$ is density, $Y_i$ is a mass fraction of $i^{th}$ species, $J_{ij}$ is projection of diffusion flux vector on $j$ axis, $M_i$ is molar mass of $i^{th}$ species, $\omega_i$ is chemical reaction rate.

3. Model of chemical kinetics in plasma

The model of chemical processes in plasma describes reactions in the bulk and on the surface. For the gas phase processes we considered 24 species: source gases Ar, N$_2$, NH$_3$, SiH$_4$, ions N$_2^+$, NH$_3^+$, NH$_4^+$, Ar$^+$; molecules and radicals H, NH$_2$, NH, SiH$_3$, SiH$_2$ H$_2$ Si$_2$H$_4$; aminosilanes H$_2$Si(NH)$_2$, HSi(NH)$_2$, HSi(NH)$_3$, Si(NH)$_2$, Si(NH)$_3$, Si(NH)$_4$; excited state of argon Ar* and electron e$^-$. The model of 37 bulk chemical reactions is based on [7, 8]. The cross-sections of electron impact reactions are taken from [11].

A deposition model consists of three stages: (1) adsorption to the surface, (2) diffusion along the surface to the next reactant and (3) embedding of products into the substrate. We considered the most stable species that can be adsorbed on the surface: H$_2$Si(NH)$_2$, HSi(NH)$_2$, HSi(NH)$_3$, NH$_2$, Si(NH)$_2$, SiH$_2$, SiH$_3$. Sticking coefficients defining the probability of adsorption were taken from [7, 8]. The surface reaction model was developed based on the experimental data of Fourier transform infrared spectroscopy (FTIR) [9, 10]. An example of the spectrum decomposition into the Gaussian components is shown in Figure 1. It was found that silicon nitride films are composed of four functional groups with chemical bonds Si$_3$–Si–N, H$_2$–Si–N$_2$, SiH$_3$N$_4$ and H–Si–N$_3$. We suggested 7 reactions between the adsorbed components producing these molecular groups and found reaction rates by matching the simulation results with experimental data. Another 14 reactions describe adsorption to the surface and ions neutralization.
4. Implementation and results

A finite volume method on a regular rectangular computational mesh was used for solving equations (1)-(7) by the CGS-Pre iterative solver. 20 time steps were performed in each RF discharge cycle with a maximum of 500 numerical iterations per time step. Typical simulation time was 18 hours per experiment. We simulated a two-dimensional geometry of «Plasmalab System 100» PECVD reactor by Oxford Instruments Plasma Technology. The frequency of CCP discharge was 13.56 MHz, power 20 W, temperature 350 ºC, and pressure 0.65 Torr.

We carried out two series of experiments: In the first one we varied the total gas flow rate, keeping the ratio of source gases constant. In the second series we varied the flow rate of silane-argon mixture under the constant flow rate of other gases: 600 sccm of N\textsubscript{2} and 20 sccm of NH\textsubscript{3}. An example of 2D distribution of electron density in a simulated PECVD reactor is shown in Figure 2. A comparison of simulation results with experimental data is presented in Figures 3 and 4.

Maximum discrepancy between the simulated deposition rate and experimental data is less than 5%, but further model fine-tuning is still possible. Two important observations can be made: (1) The deposition rate grows a little (by 10%) with a four-fold increase in the total gas flow rate at fixed source gas proportion. (2) The influence of silane flow rate is non-linear, with a maximum of deposition rate at 200 sccm. At lower silane flow rates, the deposition rate is lower because there are fewer silicon atoms for producing aminosilanes. At higher flow rates, low deposition rate is explained by higher film density and possibly by higher silane formation and removal by the flow.

Chemical composition of the films in the second series is shown in Figures 5 and 6. Simulation results are in good agreement with the experimental data. The Si\textsubscript{3}−Si−N fraction increases with growing SiH\textsubscript{4} flow rate (Figure 5), thus increasing the Si/N ratio (Figure 6). The Si\textsubscript{3}N\textsubscript{4} and H\textsubscript{2}−Si−N\textsubscript{2} fractions depend non-linearly on the silane flow rate, thus allowing to find process parameters that provide certain film properties.
5. Conclusions
We developed and validated a mathematical model of plasma enhanced chemical vapor deposition (PECVD) of hydrogenated silicon nitride SiN$_x$H$_y$ thin films. The model is based on Navier-Stokes equations for a transient laminar flow of a compressible chemically reacting gas mixture, together with the mass transfer and energy balance equations, Poisson equation for electric potential, electrons and ions balance equations. A new model of surface chemistry has been suggested, based on the latest experiments and spectral analysis of films deposited under different process conditions. The model correctly predicts the deposition rate and film chemical composition, thus it can be used for optimization of PECVD technology.

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