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Numerical modeling of silicon film deposition in very-high-frequency plasma reactor

Koji Satake, Yasuyuki Kobayashi, and Shoji Morita
Advanced Technology Research Center, Mitsubishi Heavy Industries, Ltd.
1-8-1, Sachiura, Kanazawa-ku, Yokohama, 236-8515, Japan
E-mail: satake@atrc.mhi.co.jp

Abstract - **We present a numerical modeling of plasma-enhanced chemical vapor deposition (PECVD) of silicon film from SiH_4 and H_2 gas mixtures in very-high-frequency (VHF) plasma reactor. The model is composed by electron impact, gas-phase, and surface reactions in a well-mixed reactor model. A set of plasma parameters such as electron density, electron temperature and electron impact reaction rates is determined separately by nonequilibrium plasma model and used as inputs for well-mixed reactor models. The gas-phase reactions include electron impact and neutral-neutral reactions. Some of unknown rates of surface reactions are determined using quantum chemical calculations and transition state theory. In well-mixed reactor models, concentrations of each chemical species are calculated in a steady state condition using mass conservation equation uniformed through the reactor. Numerical results of growth rate as a function of plasma reactor operating parameters show good agreement with experimental ones. Finally optimal operating parameters are investigated using our model combined with design of experiments and optimization techniques.**

I.INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μc-Si:H) thin films have a lot of application such as solar cells and thin-film transistors for flat panel displays. Especially μc-Si:H thin film is useful for high-efficiency and stable solar cells, and fast thin-film transistors. Recently hydrogen highly diluted silane gas very-high-frequency (VHF) plasma has been used successfully to grow μc-Si:H thin film[1]-[4]. It is fact that the plasma conditions depending on operating parameters of a reactor determine growth rate and film properties[5]. It is necessary to understand the relationship between plasma reactor operating parameters and deposition phenomena to control both growth rate and film properties. The purpose of the present work is to develop a plasma-enhanced chemical vapor deposition (PECVD) model of mixtures of SiH_4 and H_2 gases, which can predict the film growth from externally controlled operating parameters.

In this study, we are attempting to develop a model that is compact in terms of both computational time and memory storage, while presenting sufficient accuracy to predict film growth over a useful range of reactor operating parameters. Previous PECVD model have been focused on a-Si:H deposition and tended to simplify either gas-phase or surface reaction mechanisms[6]-[8]. Clearly more research is necessary to develop a more accurate and compact model including recent research results of gas-phase and surface reaction kinetics. The calculated parameters such as growth rate, hydrogen content in the film, and surface species are useful to understand the deposition phenomena and predict properties of the films. We emphasize comparisons of model predictions with experimentally measurement growth rates as a means of testing our model and obtaining an appropriate set of reaction-rate parameters to describe this complex deposition system. In addition, our model is effective tool to determine optimal reactor operating parameters.

II.DESCRIPTION OF THE MODEL

Our PECVD model is composed of a series of two linked simulations, schematically as shown in Fig.1. Mainframe of the model is a well-mixed plasma reactor model, AURORA[9], which is one of the application code of the Chemkin-III software package [10],[11] to describe the gas phase and surface reaction kinetics for a given set of reactions. Recently, Meeks and coworkers applied the AURORA software to SiO_2 deposition in the several kinds of high density plasma reactor and showed good agreement with experiment results[12]. Briefly, the model consists of conservation equations resulting from electron energy balance, neutral species energy balance, and individual species mass balances over the reactor volume. In addition, net production and loss rates of each species on the reactor walls and substrate surfaces are included in the mass balances through the set of boundaries. The production and loss rates are weighted by the specified surface area of each wall materials. A steady state solution of the equations by a hybrid method consisted of Newton iteration and time-integration procedures.

In the AURORA software, it is assumed that the plasma conditions are homogeneous and the electron energy distribution function is Maxwellian. In VHF plasma, however, the electrons accelerated in the plasma sheath, which is modulated by the high frequency voltage, become essentially nonequilibrium condition. Consequently, we calculated plasma parameters such as electron density, electron temperature, plasma potential, and electron-neutral reaction rates using the one-dimensional drift-diffusion plasma model that consists of electron energy and charged species mass conservation equations coupled with Poisson's equation[13].

The model includes 15 gas-phase neutral molecules, two kinds of ions, and 40 reactions such as electron-neutral and neutral-neutral reactions. The rates of electron-neutral collision processes including elastic, ionization, excitation, dissociation and attachment was obtained from the plasma model. The steady state and spatial averaged plasma properties, which are electron density, electron temperature, and electron-neutral molecule collision reaction rates, were used as input for the well-mixed plasma reactor model. In compiling the neutral-neutral reaction set, we relied heavily on previous work in the literature[14]. The elementary processes were determined referring to other researchers' investigations[15]. Some of unknown rates of surface reactions were estimated based on transition state theory and *ab initio* calculations. In addition, we adopted the formalism of the Chemkin-III software to describe the reaction mechanism. This formalism defines a surface species as a chemical species on the top-most layer of the solid located at the solid-gas interface. Eleven surface species were considered to describe the adsorption of neutral radicals and reactions between the surface species. Any species in the below the top-most layer is defined to be a bulk species. Three bulk species were introduced to calculate hydrogen content. We introduced 48 surface reactions on the substrate and 10 surface reactions on the reactor wall.

In well-mixed reactor model, all chemical species concentrations are assumed to be uniform throughout the reactor volume. Peclet number, which describes the ratio of species transport to diffusion, is an order of 10^{-2} in our typical operating conditions. Since the number means that species diffusion dominates, the assumption is roughly satisfied.

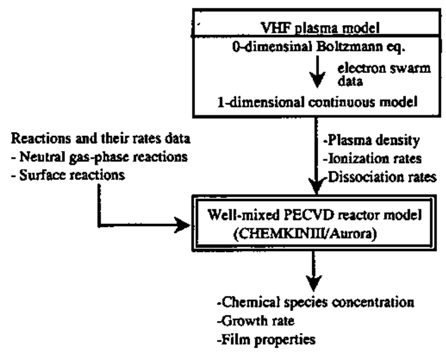

Figure 1: Schema of the PECVD model.

III.RESULTS AND DISCUSSIONS

In this study, we investigated growth rates and film properties obtained from SiH_4 and H_2 mixtures in a capacitively coupled plasma as a function of power (10-70 W), frequency (13.56-100 MHz), gas pressure (300-1500 mTorr), flow rate (300-750 sccm), and ratio of flow rate of SiH_4 gas (0.015-0.03). A substrate temperature was maintained at 450 K. The electrodes are separated by 1 cm and the plasma volume is about 144 cm^3. A substrate sits on grounded electrode. The boundary condition for charged particles in the plasma is that these densities are set to zero at the electrodes.

First of all, 48 plasma simulations were carried out as a function of power, frequency, and gas pressure described above to obtain a set of parameters such as electron density, electron temperature and electron impact reaction rates used as inputs for the well-mixed reactor model, and also plasma potential presented to an objective function. From the results of simulations, we created polynomial regression models of electron densities, plasma potentials, ionization rates, and dissociation rates depending on the three controllable parameters. Typical result is given in Fig.2 where the normalized first-order coefficients called main effects of the three parameters are shown. Plus and minus values mean positive and negative correlation, respectively. We can see that the plasma potential increases with increasing power, and decreases with increasing frequency and gas pressure. The input parameters for the well-mixed reactor model such as electron density, electron temperature and electron impact reaction rates were determined by the regression models.

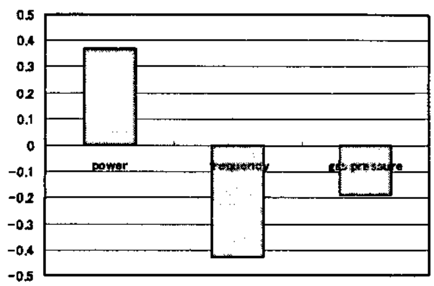

Figure 2: Main effects for plasma potential.

Next the calculated results obtained from the well-mixed reactor model were compared to experimental ones to verify the accuracy of our model. Figure 3 shows the calculated growth rates in comparison with the experimental results as a function of gas pressure and frequency. The calculated results show a good agreement with experimental ones satisfactory. The increase in gas pressure and frequency increases net dissociation rate of SiH_4 molecule and silicon containing radicals which are precursors of silicon growth. Consequently the growth rate has a positive correlation to each parameter.

Table I shows the hydrogen content and the fraction of each hydrogen coverage with and without hydrogen dilution. Hydrogen content decreases in case of hydrogen dilution due to microcrystallization. It is clear that the surface is dominated by monohydrides under hydrogen dilution, by contrast, di- and trihydrides become larger without hydrogen dilution. Higher hydrides such as di- and trihydrides are decomposed to lower hydrides by reacting with a nearby dangling bond. The creation of dangling bonds is enhanced by surface H abstraction due to dilution by. These trends agree with experimental results measured by FT-IR[16]. The well-mixed reactor model coupled with high frequency plasma model has the ability to predict silicon film deposition. The computational time for one case was about 20 s.

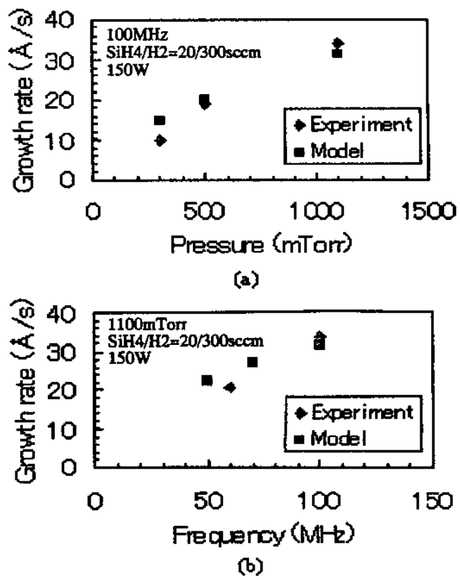

Figure 3: Growth rates as a function of power and gas pressure.

Table I: Hydrogen content in the film and fraction of hydrogen coverage in the case of 300 mTorr, 100 MHz, and 150 W.

	SiH_4/H_2=20/300	SiH_4/H_2=320/0
H content	11.60 %	23.80 %
Si-H	95.00 %	77.50 %
Si-H2	1.00 %	17.60 %
Si-H3	4.00 %	4.90 %

We also carried out optimization of reactor operating parameters using our PECVD model. The range of parameters is describing above. A multiobjective function is defined as

$$f = -GR + V_p + H_c \rightarrow \min \qquad (1)$$

where GR is growth rate, V_p is plasma potential, and H_c is hydrogen content, respectively. The optimizing procedure were performed in two steps as below. In the first step, 60 simulations were conducted using design of experiments (DOE) with Latin hypercubes to examine the correlation between the objectives and the operating parameters. In the second step, optimal parameters were determined by sequential quadratic programming (SQP) coupled with simulated annealing (SA) to minimize the objective function as shown in (1).

Figure 4 shows the main effects obtained from DOE which is the response of the growth rates depending on each operating parameter with keeping the others at mean values. The growth rates increase with increasing power and gas pressure, in contrast, the influence of SiH_4 ratio and flow rate on the rates is not sufficient in the parameter ranges considered. Using this result of each objective value, we can understand the correlation with the operating parameters. Table II gives the objective values and the operating parameters at an optimum resulting from optimization. Although increase in power is effective for increase in growth rates, that increases plasma potentials causing ion damages of thin films. In this optimization, plasma potentials are decreased by increase in frequency, on the other hand, growth rates are increased by increase in gas pressure to suppress ion damage at higher growth rates. Changing weights of each objective or introducing constraints for each one in the function (1), desirable operating parameters can be obtained.

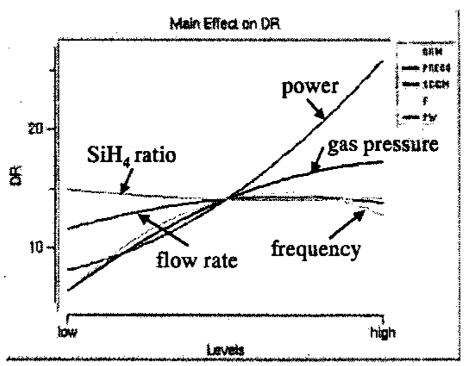

Figure 4: Main effects for growth rates. Low and high on the horizontal axis mean lower and upper values of operating parameters described in the text.

Table II: Objective values and operating parameters at optimal point.

Objectives			
GR (Å/s)	H_c (%)	V_p (V)	Eq.(1)
6.0	5.6	19.4	19.0

Operating parameters			
	Lower	Optimum	Upper
Power (W)	10.0	10.8	70.0
Frequency (MHz)	13.56	89.96	100.00
Gas pressure (mTorr)	300.0	1027.0	1500.0
Flow rate (sccm)	300.0	658.8	750.0
SiH_4 ratio	0.015	0.023	0.030

IV.CONCLUSIONS

The PECVD model presented herein can predict the μc-Si:H deposition from SiH_4 and H_2 gas mixtures in a VHF plasma reactor in a small computational time. The calculated growth rates show good agreements with experimental ones. It is possible to investigate optimal reactor operating parameters by means of combining our model with DOE and optimization techniques.

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