INTRODUCTION

Silicon nitride films, which are widely used as insulating layers in integrated circuit chips, are usually obtained by chemical deposition from the gas phase (from the mixture of dichlorosilane (DCS) and ammonia) at low pressure—by the so-called chemical vapor deposition (CVD) process. The quality of the films obtained by chemical deposition depends, first of all, on the following main factors: the temperature and pressure in the CVD reactor and the composition of the gas mixture. The choice of the optimal regime of deposition requires a detailed knowledge of the kinetics of gas-phase and surface reactions that determine the film growth process.

Phenomenological models available [1–3] largely fail to satisfy the researcher, because their application involves the definition of a large number of simulation parameters that should be determined experimentally. Since the CVD process occurs at sufficiently high temperatures, a large number of reaction products arise in the gas phase, that, in turn, react with both original reactants and other reaction products. Therefore, it is nearly impossible to determine the optimal parameters experimentally. Moreover, because of the increased requirements for the quality of thin films, in particular, for their strength and adhesive characteristics, one needs an analysis of new deposition regimes in the work chamber of the reactor. Recently, first of all due to the development of computational methods of quantum chemistry, a growing interest has been focused on the study of the film growth in a CVD process by an atomistic description of the whole set of processes, which involves nonempirical ab initio first-principles simulation methods [4–13].

The present paper largely complements and extends the kinetic scheme of reactions in the gas phase that was developed earlier in [4–8, 10, 12]. It includes the reactions of catalytic decomposition of DCS, which have a noticeable effect on the composition of the gas phase, on the kinetics of the processes in the working chamber, and on the processes on the surface of the deposited film. The extended chemical mechanism [13] constructed and proposed in this work is supported by the methods of atomic simulation that involve an ab initio quantum-chemical analysis of gas-phase and surface reactions. This chemical mechanism allows one to adequately describe the kinetics of reactions in the gas phase in a wide range of temperatures, pressures, and ratios of the original components. We develop an effective kinetic model for the whole set of possible reactions, that involves the calculation of the rate constants and concentrations of the gas mixture components. A thermodynamic analysis of the surface coverage by various chemisorbed groups is carried out, and equilibrium surface concentrations are obtained for the main chemisorbed groups. Practically significant conclusions are made about the character of the deposition process and, in particular, about the role of the extended chemical mechanism.

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Nonempirical Simulation of Chemical Deposition of Silicon Nitride Films in CVD Reactors

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Abstract—This work is devoted to the atomistic simulation of chemical vapor deposition (CVD) of thin silicon nitride films from the mixture of dichlorosilane (DCS) and ammonia in CVD reactors. The earlier developed chemical mechanism is substantially extended by including the reactions of catalytic decomposition of DCS, and a self-consistent atomistic model of a CVD process is developed. An extended chemical mechanism is constructed and analyzed that allows one to adequately describe kinetic processes in a gas phase within the ranges of temperature, pressure, and the DCS : NH₃ ratio of original reactants, that are characteristic of silicon nitride deposition. An effective kinetic model is developed that involves the calculation of the rate constants and the concentrations of the gas mixture components. A thermodynamic analysis of the surface coverage by various chemisorbed groups is carried out, and equilibrium surface concentrations are obtained for the main chemisorbed groups. Practically significant conclusions are made about the character of the deposition process and, in particular, about the role of the extended chemical mechanism.
the ratio of the original concentrations of DCS and ammonia, which allow us to make important conclusions about the character of the deposition process and the role of the extended chemical mechanism.

1. CHEMICAL PROCESSES
IN THE GAS PHASE

1.1. Quantum-Chemical Analysis

The main criterion for the choice of the set of reactions important for the chemical mechanism in the gas phase is, first of all, the residence time of the mixture in the reactor under conditions characteristic of the silicon nitride deposition from DCS and ammonia. For instance, in [4, 8–10, 12], a set of first- and second-level reactions was defined that are significant for the chemical deposition of silicon nitride from DCS and ammonia in a flow reactor. For the completeness of the model, in the present paper we analyze an extended set of possible reactions of the first, second, and third levels:

\[
\begin{align*}
\text{SiCl}_2\text{H}_2 + \text{NH}_3 & \leftrightarrow \text{SiH}_2(\text{NH}_2)\text{Cl} + \text{HCl}, \quad (\text{III.3b}) \\
\text{SiCl}_2\text{H}_2 + \text{NH}_3 & \leftrightarrow \text{SiH}(\text{NH}_2)\text{Cl}_2 + \text{H}_2, \quad (\text{II.3a}) \\
\text{SiCl}_2\text{H}_2 & \leftrightarrow \text{SiHCl} + \text{HCl}, \quad (\text{I.3b}) \\
\text{SiCl}_2\text{H}_2 & \leftrightarrow \text{SiCl}_2 + \text{H}_2, \quad (\text{I.3a}) \\
\text{SiH}_2\text{Cl} + \text{SiH}_2\text{Cl} & \leftrightarrow \text{SiHCl}_3 + \text{SiH}_2\text{Cl}, \quad (\text{III.1}) \\
\text{SiH}_2(\text{NH}_2)\text{Cl} + \text{NH}_3 & \leftrightarrow \text{SiH}(\text{NH}_2)\text{Cl}_2 + \text{H}_2, \quad (\text{II.7a}) \\
\text{SiH}(\text{NH}_2)\text{Cl} + \text{NH}_3 & \leftrightarrow \text{SiH}(\text{NH}_2)\text{Cl}_2 + \text{H}_2, \quad (\text{II.7a}) \\
\text{SiHCl}_2 \leftrightarrow \text{SiHCl}_3 + \text{H}_2, \quad (\text{II.4}) \\
\text{SiHCl}_3 + \text{H}_2 & \leftrightarrow \text{SiH}_2\text{Cl} + \text{SiH}_2\text{Cl}, \quad (\text{III.4a}) \\
\text{SiH}_2\text{Cl} + \text{HCl} & \leftrightarrow \text{SiHCl}_2 + \text{H}_2, \quad (\text{I.2a}) \\
\text{SiH}_2\text{Cl} & \leftrightarrow \text{SiHCl} + \text{HCl}, \quad (\text{III.7}) \\
\end{align*}
\]

In the notation of the reactions, the Roman numerals stand for the type of a reaction (I corresponds to decomposition reactions, II to reactions of bimolecular substitution involving ammonia, and III corresponds to reactions involving DCS). Reactions that correspond to different transformation channels for the same system of reactants are denoted by Arabic numerals: 1 corresponds to SiH4, 2 to SiH2Cl, 3 to SiH2Cl2, 4 to SiHCl3, 5 to SiCl4, 6 to SiH3(NH2), 7 to SiH4(NH2)Cl, 8 to SiH(NH2)Cl2, 9 to SiH(NH2)Cl3, 10 to SiH(NH2)2, 11 to SiH(NH2)Cl, and 12 to SiH3(NH2). Reactions that correspond to different channels for the same system of reaction products are denoted by letters (a, b, c), which correspond to the abstraction of the groups H2, HCl, and NH3, respectively. The additional reactions (type III) are numbered by Arabic numerals. For these reactions, the letters (a, b) indicate the insertion of silanes into the Si–H and Si–Cl bonds, respectively.

The activation barriers for a number of forward and reverse reactions, as well as the corresponding reaction heats, are presented in Table 1. Quantum-chemical calculations were performed by the GAMESS [18] and Gaussian [19] software packages. For all the molecular structures, geometry was fully optimized without symmetry restrictions at the MP2 level (i.e., by the self-consistent field method with regard to the electron correlation within the second-order Möller–Plesset perturbation theory) with the use of the standard basis set 6-311G(d, p); the energies of the structure were determined with the use of a multiconfiguration quasi-degenerate perturbation theory (MCQDPT) implemented in a software package [18]. In addition to the data presented in Table 1, the quantum-chemical calculations yield the vibrational spectra of stable molecules and activated complexes.

Notice that reaction (II.3a), which leads to the generation of hydrogen, has been eliminated from the final scheme because it has a higher activation barrier compared with the competing reaction (II.3b), which is accompanied by the release of HCl. For similar reasons, we excluded reactions (II.7a) and (II.8a), which are much slower than the competing reactions (II.7b) and (II.8b), respectively. We also excluded reaction (III.6) from the scheme because of its high activation barrier.

The scheme includes the reaction of catalytic decomposition of DCS:

\[
\begin{align*}
\text{SiH}_2\text{Cl}_2 + \text{HCl} & \rightarrow \text{SiHCl}_2\text{SiH}_2\text{Cl}, \quad (\text{III.4a}) \\
\text{SiHCl}_2 & \rightarrow \text{SiH}_2\text{Cl} + \text{SiCl}_2, \quad (\text{III.9}) \\
\text{SiH}_2\text{Cl} & \rightarrow \text{SiHCl} + \text{H}_2, \quad (\text{I.2a}) \\
\end{align*}
\]