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Regularities of Remote Plasma Enhanced Chemical Vapor Deposition of Silicon Nitride Films

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Abstract—Specific features of remote plasma enhanced chemical vapor deposition processes with inductive and capacitive coupling of power have been analyzed. Experimental results from a study of the physical and chemical regularities of those processes have been considered. Influence of diluting nitrogen with noble gases on growth rate and composition of the deposited films has been discussed. Essential role of argon diluting providing a high concentration of atomic nitrogen in the reacting gas phase required for plasma chemical synthesis of nitride films was demonstrated. Possible approaches to further improvement of plasma enhanced chemical deposition processes have been proposed.

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INTRODUCTION

Low temperature plasma enhanced chemical vapor deposition (CVD) of thin films of various materials is one of the vigorously progressing approach of athermally activated CVD processes [1]. The most widespread sources of low temperature plasmas (LTPs) are low pressure RF and MW discharges. The fairly low energies of heavy particles (~0.04 eV) and high energies of electrons (0.5–15 eV) in such discharges make possible syntheses at fairly low temperatures (450–650 K).

The essence of the plasmachemical synthesis is as follows. A radiofrequency (RF) or microwave (MW) discharge plasma is generated in a gas mixture of required composition, prepared in a reactor at a reduced pressure (10–600 Pa). Ionization, electron excitation, or partial dissociation of the molecules of the starting gas components, which occur in the plasma, form highly reactive atomic and molecular species (free radicals, free atoms, etc.). Homogeneous or heterogeneous reactions between the formed reactive species result in the synthesis of desired compounds.

In a typical plasma enhanced chemical deposition process which is most commonly used in electronic industry, a substrate to be treated is placed onto one of the plane parallel electrodes. A low pressure RF discharge in initiated between the electrodes in an appropriate reaction gas medium. The main disadvantages of such a conventional CVD process are as follows:

– electrically active defects are generated near the surface of the substrate as a result of bombardment by high-energy particles;

– bombardment by charged plasma particles of the growing dielectric film generates charges trapped in the film and increases its porosity;

– inelastic collisions of charged particles present in the low pressure RF plasma with reagent molecules (atoms) form a variety of reactive species and, as a consequence, uncontrolled reactions, thereby making difficult to deposit films of desired composition;

– process parameters (total pressure in the reaction chamber, plasma absorbed RF power, etc.) are interdependent and, therefore, difficult to control individually.

To overcome these problems, numerous studies on plasma assisted CVD of dielectric materials, in particular, silicon nitride and oxide, have been conducted [2]. A version of the CVD process called remote plasma enhanced chemical vapor deposition (RPECVD), in which plasma is generated in the reaction chamber at a distance from the substrate seems promising [3, 4]. The publications on PECVD processes deal primarily with applied issues, whereas their advantages and disadvantages and the influence of process parameters

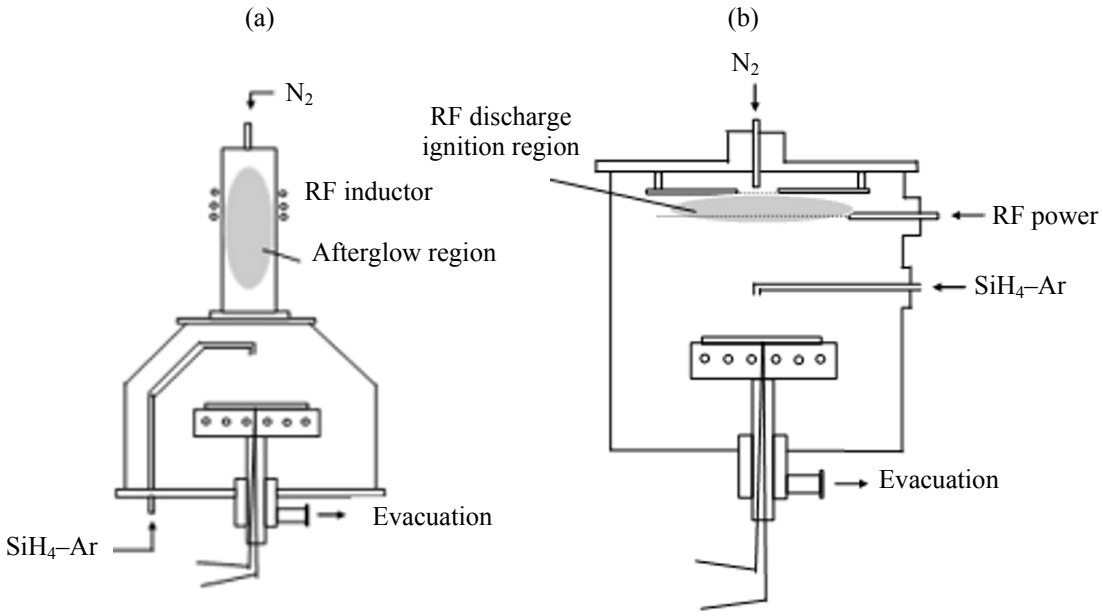

Fig. 1. Schematic diagram of RPECVD reactors with (a) inductively and (b) capacitively coupled plasma.

on the composition and properties of the resulting products have scarcely been discussed.

In the present paper we considered the above issues on an example of the PECVD of silicon nitride films, but the conclusions we draw are general and apply to films of any materials.

Remote Plasma Enhanced Chemical Vapor Deposition

The RPECVD processes have two characteristic features: (1) substrates to be treated are located at some distance from the plasma region and (2) not all gaseous reactants are directly excited by the plasma [3]. In terms of these features, at least two types can be recognized, which differ from each other in nothing more than in the method of coupling of PF power into the reaction system. The most common is inductive coupling of RF power (Fig. 1a). In a setup with capacitively coupled plasma, developed in [5] for deposition of silicon nitride films (Fig. 1b), the discharge region and the substrate in both reaction chambers are spacially separated. Some the initial reactants are introduced into the RF discharge initiation region, where reactant molecules are excited, and then they are transported to the deposition region; other reactants are introduced to the reaction chamber downstream from the discharge region.

Let us find out whether the RPECVD technology allows overcoming the above-mentioned disadvantages of conventional PECVD processes. It was supposed that the main advantage of this method would be minimization of the negative effect of plasma on the surface of the semiconductor and on the deposited dielectric film. However, in view of the fact that the process design does not envision measures for preventing energetic charged particles from the plasma to substrate region, there are no reasons to rule out defect formation both in the semiconductor and in the film that forms.

In the experimental research in [6] we compared the degradation degree of gallium arsenide at different techniques of dielectric film deposition. Thin dielectric films were deposited on test gallium arsenide structures like those commonly used for fabrication of Schottky barrier field-effect transistors but having no gate. Comparison of the saturation currents obtained from the static voltage–current characteristics of these structures before and after deposition of dielectric films showed that the semiconductor surface undergoes no degradation, when the dielectric film is deposited by means of the RPECVD process [6].

Remote plasma enhanced CVD processes are characterized by less interdependence of process parameters. In a conventional PECVD of silicon nitride films in a SiH_4–N_2 system, even minor variations in the silane flow rate lead to essential changes in the plasma composition due to dissociation of silane and formation of a variety of radical and atoms, such as

SiH_3, SiH_2, SiH, Si, and H [7]. These changes occur directly in the discharge initiation region and, therefore, affect the plasma absorbed RF power. In the case of an RPECVD process, when silane is introduced into the reaction chamber downstream from the discharge region, and also if the chosen gas dynamic conditions allow prevention of backstream diffusion of silane to the discharge region, varying silane flow rate should not affect the plasma absorbed RF power.

Further evidence for a lower interdependence of RPECVD process parameters is provided by the consideration of processes that occur on the surface of the substrate or growing film. As known [1], the real temperature of the reaction surface is determined not only by the heat flux from the heater built-in to, but also by the energy flux delivered to the reaction surface by energetic particles from the plasma zone. Varied plasma absorbed RF power should affect the temperature of the reaction surface and, quite obviously, in an RPECVD process this effect will be weaker.

At the same time, certain RPECVD process parameters are still interdependent, and this interdependence is impossible to obviate by fundamental reasons. For example, varying the total pressure in the reactor, both in conventional PECVD and in RPECVD processes, leads to considerable changes in the plasma absorbed RF power, and, consequently, changes in the composition of the plasma.

The above reasoning leads us to conclude that RPECVD process parameter are characteristically less interdependent, and, therefore, this process is easier to control. At the same time, all disadvantages inherent in conventional PECVD are impossible to overcome completely.

Another disadvantage of conventional PECVD is the occurrence of a number of concurrent reactions in the plasma phase, which form a variety of reactive species (free radicals and atoms) due to inelastic collisions of molecules and atoms of the initial reactants with plasma electrons [8–10]. Obviously, the assortment of plasma particles in RPECVD processes is smaller, as in this case not all starting reactants are directly introduced to the RF discharge region.

In the course of the RPECVD process charged particles (electrons and ions) can be transported from the RF discharge region downstream to the reactant mixing region [11]. These charged species have a wide energy distribution, and this allows synthesis of a variety of reactive radicals from the starting reactant molecules and reactions of the resulting species in the reactant mixing region. The reactive species that form can also be transported with the flow to the deposition region and involved both in film formation and in side homogeneous reactions. Just such mechanism of the deposition process results in an unpredictable composition of deposited films (specifically, uncontrolled incorporation into the growing film of various functional groups, such as NH_j (j = 1–2) and SiH_i (i = 1–3) in the case of the plasmachemical deposition of silicon nitride films [2]). Thus, the disadvantage that is used to be associated exclusively with conventional PECVD has not been overcome in RPECVD processes.

To gain insight into the regularities of RPECVD, we have studied these processes on an example of silicon nitride film deposition in a reactor allowing initiation of both inductive and capacitive low pressure RF discharges. These two methods of coupling do not differ from each other in principle, however, the spacial distribution of electromagnetic fields should affect the energy and concentration of electrons in the plasma. Moreover, knowing their individual features one can extend the range of process conditions. Thus, operation in the capacitive method makes it possible to increase the strength of the electric field and simultaneously localize it in space, thereby decreasing the electrode gap. With an inductively coupled plasma, an opposite possibility, specifically, to extend magnetic force lines without any essential drop in field strength.

In both cases, the initial reactants were silane and nitrogen. If ammonia is used instead of nitrogen, the initial gas mixture is enriched in hydrogen, which leads to its enhanced uncontrollable incorporation into the final product.

Regularities of Inductively Coupled Remote RF Plasma Enhanced Chemical Vapor Deposition of SiN_xH_y Films

An emission spectral study of the composition of an inductively coupled low temperature RF plasma generated in an argon diluted SiH_4–N_2 mixture [12] showed that in the RPECVD of silicon nitride films argon in metastable excited states favors increased concentrations of atomic nitrogen necessary for film formation. This is explained by the fact that the metastable electronic levels of argon atoms at 11.55 and 11.72 eV [13] are close in energy to certain vibrational levels of the $C^3\Pi_u$ electronic level of the N_2 molecule (11.51 eV for v' = 2, 11.74 eV for v' = 3, and ~12 eV for v' = 4). As a result, inelastic collisions of N_2 molecules and metastable argon atoms increases the

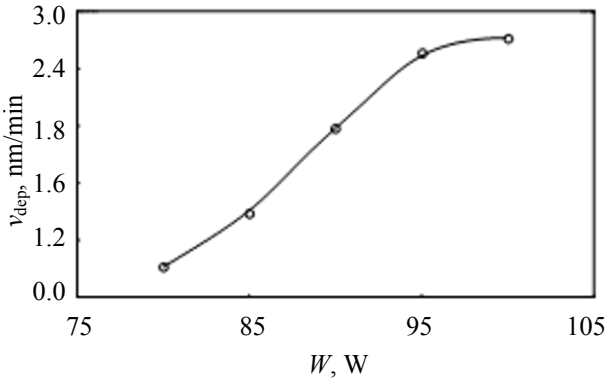

Fig. 2. Dependence of SiN_xH_y film deposition rate on plasma absorbed power (inductive mode). Deposition conditions: total pressure p_{tot} = 45 Pa, substrate (deposition) temperature T_{dep} 570 K, chamber wall temperature T_w = 470 K, nitrogen flow rate Q_N = 170 cm^3/min, and silane flow rate Q_S = 0.4 cm^3/min.

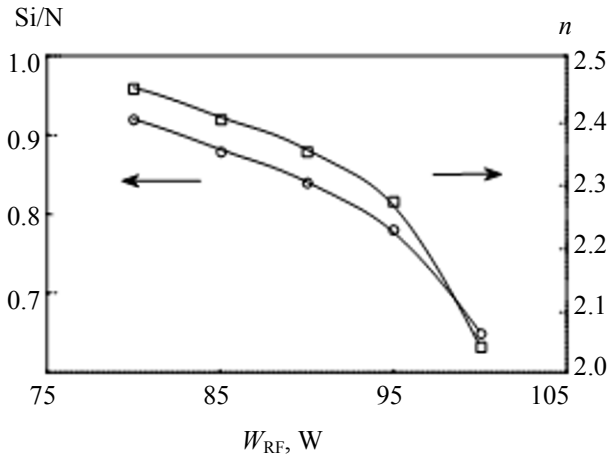

Fig. 3. Dependence of plasma absorbed RF power on the Si/N ratio in and refractive index of SiN_xH_y films. Deposition conditions: p_{tot} = 45 Pa, T_{dep} = 570 K, T_w = 470 K, Q_N = 170 cm^3/min, and silane flow rate Q_S = 0.4 cm^3/min.

probability of the predissociation of molecular nitrogen both directly in the $C^3\Pi_u$ state and with the participation of the $C''^5\Pi_u$ to form nitrogen atoms in ^4S and ^2D metastable states. Furthermore, nitrogen and hydrogen molecules and argon atoms in different excited states were found in the gas medium, as well as atomic nitrogen and Si and SiH radicals formed by a two-step mechanism.

It was shown [12] that the starting silane is not directly involved in SiN_xH_y film growth. Silicon hydride radicals react with atomic hydrogen and/or other silicon containing radicals and do not affect the film deposition rate. The formation of silicon nitride films involves silane radicals (Si and/or SiH_2 and/or SiH_3) and atomic nitrogen, whose relative fractions in the reaction mixture determine the growth rate and composition of the deposited films and, consequently, their main properties.

The actual concentration of reactive species in the vicinity of the growing film depends on those process parameters that affect the rate of formation of silane radicals and atomic nitrogen in the plasma and afterglow regions, as well as on their transport conditions to the support surface. In this connection it was natural to expect that the film growth rate would depend on the plasma absorbed RF power which is one of the main parameters of a PECVD process. Actually, when the RF power was increased by 30%, the film growth rate had steadily increased 2.5 times (Fig. 2).

The reagents (silane and nitrogen) have quite different dissociation energies. The minimum energy of electrons in the discharge, required for dissociation of silane to form SiH_n (n = 0–3) radicals is 2.2–5.7 eV [7], whereas the predissociation energy of N_2 to form atomic nitrogen is higher than 11 eV [11, 14]. Varying the plasma absorbed RF power (W_{RF}) usually affects the average energy of electrons in the plasma medium, which should be accompanied by a change in the ratio of silane radicals and atomic nitrogen and, as a result, in the composition of deposited films. The steady decrease of the Si/N atomic ratio in the deposited films, observed as the RF power was increased (Fig. 3) suggests the concentration of nitrogen atoms in the plasma increases more rapidly than the concentration of silane radicals, as evidenced by the measured refractive indices and electrophysical parameters of the films.

Another process parameter which was suggested to strongly affect the concentration of silane radicals in the reaction mixture and, consequently, film growth rate and composition is the starting concentration of silane. However, the experimental results showed that only at low silane flow rates (Q_S) ($\leq$ 0.6 cm^3/min) the film growth rate (v_{dep}) increased as the starting silane concentration was increased (Fig. 4). Further increase of the SiH_4 flow rate to 4.0 cm^3/min decreased the film growth rate. Such pattern of the $v_{dep} = f(Q_S)$ function is explained by the characteristic features of the RPECVD process, namely, low electron concentrations in the deposition region, associated with the recombination reactions that occur as the plasma medium moves from the discharge region, and; consequently, fairly low concentrations of SiH_x

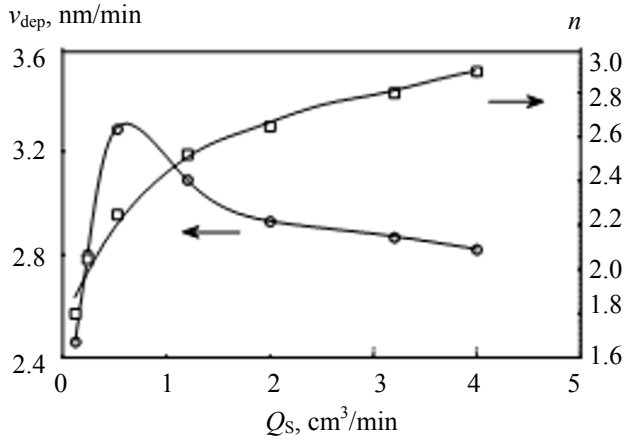

Fig. 4. Dependence of the deposition rate and refractive index of SiN_xH_y films on silane flow rate (inductive mode). Deposition conditions: p_{tot} = 45 Pa, T_{dep} = 570 K, T_w = 470 K, Q_N = 140 cm^3/min, W_{RF} = 95 W.

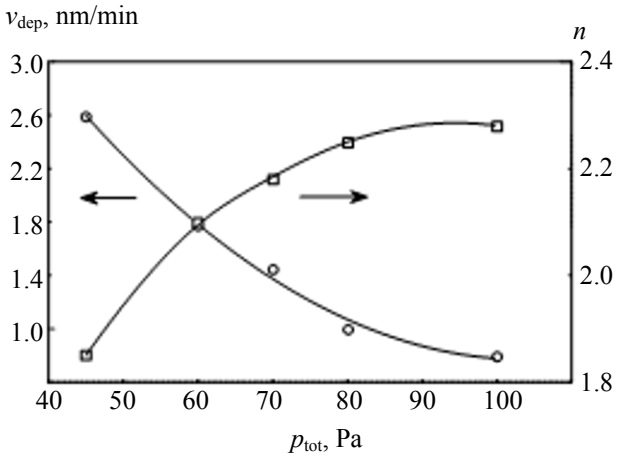

Fig. 5. Dependence of the deposition rate and refractive index of SiN_xH_y films on total pressure (inductive mode). Deposition conditions: T_{dep} = 570 K, T_w = 470 K, Q_N = 60 cm^3/min, Q_S = 0.4 cm^3/min, W_{RF} = 95 W.

radicals formed at low silane flow rates ($\leq$ 0.6 cm^3/min). Under such conditions, homogeneous reactions between SiH_x (x = 0–3) and SiH_4 to form inactive silicon–hydrogen compounds containing several silicon atoms (up to 6–8) [15]. Therefore, the film growth rate steadily increases with increasing silane flow rate. The retardation of film growth with further increase in silane flow rate is associated with acceleration of homogeneous reactions and, as a consequence, depletion of the reaction mixture in the SiH_x radicals involved in silicon nitride formation. At high silane concentrations, formation of powder deposits on the reactor walls is usually observed.

The fact that the refractive index of films steadily increases from 1.6 to 2.8 as the silane flow rate Q_S is increased from 0.1 to 4 cm^3/min (see Fig. 4) suggests that this process parameter has a strong effect on the composition of the resulting films. An increase of Q_S increases the concentration of silane radicals in the reaction medium and, consequently, increases the silane radicals/atomic nitrogen ratio; as a result, the N/Si ratio in the films decreases. At silane flow rates higher than 0.4 cm^3/min, films enriched in silicon and having low specific breakdown voltages and specific resistances are deposited.

The results of study of the effect of the reactor wall temperature T_{wall} on film growth rate proved to be quite informative for understanding factors responsible for film deposition. It was experimentally established that an increase of T_{wall} at constant substrate temperatures T_s and other process parameters leads to a steady increase in the film deposition rate, which is associated with the acceleration of certain processes in the reaction medium.

According to the results of research on the emission of a nitrogen plasma at different reactor wall temperatures [11], which revealed retardation of recombination processes in the plasma, associated with the decrease in particle concentration with heating, we can conclude that the increase in v_{dep} is caused by improved conditions of transport of reactive plasma components involved in film formation to the lower part of the reactor.

Noteworthy, substrate temperature only slightly affects the rate of film growth: The variation of v_{dep} about the average temperature as the substrate temperature was varied in the range 420–570 K was no larger than 10–12%.

Evidence for the conclusion that transport processes strongly affect film growth rate is provided by a considerable decrease in v_{dep} with increasing total pressure p_{tot} in the reaction chamber (Fig. 5). Pressure has a complex impact on plasma characteristics. First, the total pressure affects the electron energy distribution [16], which determines the concentrations of excited species, radicals, and ions in the reaction medium. As shown in [11], as the pressure was increased above a certain value, the emission lines belonging to plasma components started to steadily decrease, which reflects increasing concentrations of excited species due to energy decrease and increasing electron concentration. Second, the total pressure controls the partial pressures of the starting reactants,

and, therefore, increasing p_{tot} drives homogeneous reactions of silane radicals with the starting SiH_4 [17]. Sufficiently high p_{tot} not infrequently cause polymerization of silane radicals [5, 15], as a result of which by-products deposit on the walls of the reaction chamber as a fine yellowish brown powder. Third, increased pressure hinders electron energy transport to the lower part of the reactor. The above mentioned phenomena all are responsible for decreased concentrations of reactive silicon-containing species and atomic nitrogen in the substrate near-surface region by impairing the conditions of their transport to the reaction surface.

Thus, the available experimental evidence allows us to conclude that the rate of film deposition processes is primarily controlled by the conditions of transport of the reactive components of the plasma medium, involved in SiN_xH_y film formation to the substrate surface.

Regularities of Capacitively Coupled Remote RF Plasma Enhanced Chemical Vapor Deposition of SiN_xH_y Films

The experimental setup for chemical vapor deposition of SiN_xH_y films by means of a remote plasma generated by a capacitive RF discharge is described in [5].

A mass spectroscopy study of the composition of the gas phase on RPECVD film deposition in a setup with capacitively coupled plasma gave the following information [18].

Under the studied deposition conditions, 60–80% of silane dissociate in the plasma to form at least SiH_2 which react in the gas phase and are probably adsorbed on the growing film. The dissociation degree decreases with increasing pressure and is almost independent of the RF power in the range studied.

The Si_iH_j species ($i > 1$) are formed even in the absence of plasma but at support holder temperatures of up to 570 K.

The *m/z* 29 to 31 peak intensity ratio much differs from theoretical, which was also observed in [19]. This is explained by the fact that the signals of silan overlap with Si_2H_2 signals

No formation of particles containing a Si–N bond, like, for example, aminosilanes, was detected in the SiH_4–N_2 gas mixtures. Evidence for homogeneous synthesis of such particles is also lacking from other works, for example, [19]. It remains to believe that the incorporation of nitrogen into SiN_xH_y films occurs as a result of heterogeneous reactions between reactive atomic nitrogen and certain silane radicals on the growing film surface.

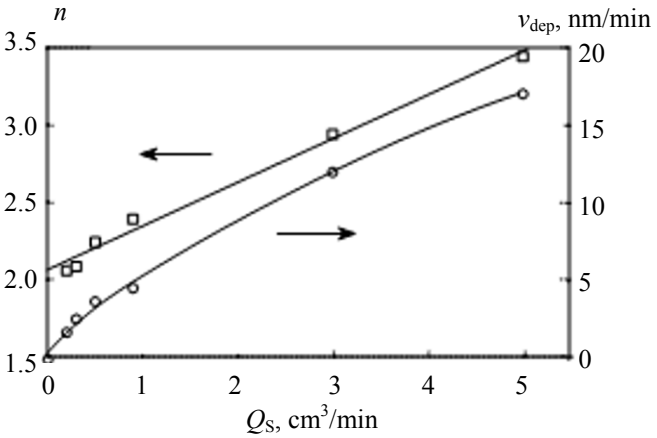

Fig. 6. Dependence of the deposition rate and refractive index of SiN_xH_y films on silane flow rate (capacitive mode). Deposition conditions: W_{RF} = 75 W, T_{dep} = 570 K, nitrogen flow rate through the plasma region Q_N^t = 150 cm^3/min, flow rate of nitrogen diluent of silane Q_N^s = 10 cm^3/min, p_{tot} = 22 Pa.

The above information was taken into account in drawing conclusions concerning the principal physicochemical regularities of film deposition and speculations about the common features of the processes that occur in the two differently designed deposition systems.

It was established that the deposition of silicon nitride films in the SiH_4–N_2 system in the temperature range 400–600 K is made possible by the formation in the plasma medium of atomic nitrogen and reactive silane radicals via collisions between the starting SiH_4 molecules and particles generated in the plasma region. It is quite reasonable to suggest that the rate of film deposition is strongly dependent on silane flow rate. This suggestion is confirmed experimentally (Fig. 6).

The dependence for a capacitive RF discharge differs from that for an inductive RF discharge. A probable reason for this difference lies in the concentration of charged species, first of all electrons (n_e) in the reactor region downstream from the silane inlet. The higher n_e value is associated with a number of reasons. First, the plasma glow region in the case of capacitive coupling is 12 times as large as in the case of inductive coupling. Second, the ratio between the volume of the reactor to its surface area between the plasma and deposition regions in the described system is 7, while the respective value for systems with

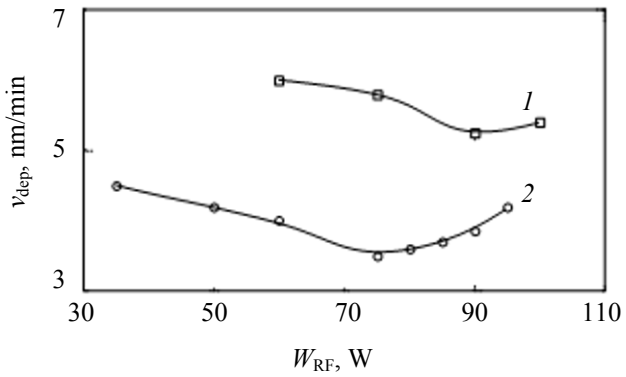

Fig. 7. Dependence of the deposition rate of SiN_xH_y films on scattered RF power (capacitive mode). Deposition conditions: T_{dep} = 570 K, p_{tot} = 22 Pa, (*1*) Q_N^t = 150 cm^3/min, (*2*) Q_N^t = 70 cm^3/min, Q_N^s = 10 cm^3/min, Q_S = 0.3 cm^3/min.

inductive coupling is no more than 3, and this suggests more active recombination of electrons in inductively coupled plasma on the walls of a narrow, long chamber. Third, systems with capacitive coupling are operated at a lower pressure (22 vs 45 Pa), which, too, favors electron transport to the silane inlet region.

The higher electron concentration favors a more complete dissociation of silane. Moreover, conditions unfavorable for homogeneous reactions between silane radicals and SiH_4 to form inactive silicon–hydrogen compounds are created. Therefore, unlike what is observed with inductively coupled plasma, specifically, slowdown of film growth at high silane flow rates (>0.6 cm^3/min), in the case of capacitive coupling much higher film deposition rates take place, implying a high concentration of silane radicals.

At the same time, like with inductively coupled plasma, as the silane flow rate was increased in the range 0.1–5.0 cm^3/min, the refractive index of the resulting films tended to increase, providing evidence for increasing Si/N ratio in them. The steeper increase of the refractive index of the films with increasing Q_S is likely to be explained by a steeper increase in the concentration of silane radicals in the plasma medium. In the case of inductively coupled plasma, homogeneous reactions that are accelerated by increasing silane flow rate decrease the concentration of radicals, as evidenced by a less steeper $n = f(Q_S)$ curve.

The refractive index of the silicon nitride films with a nearly stoichiometric composition is close to 2.05, and, as follows from Fig. 6, in the experimental system used in the present work they are deposited at Q_N/Q_S ratios higher than 250. Increased relative fraction of silane in the reactor causes enrichment of deposited films in silicon, which is confirmed by the fact that their refractive index increases up to 3.88, specifically to a value characteristic of pure silicon.

Compared to the setup with inductive coupling, conditions of transport of electrons and ions to the deposition region in the setup with capacitive plasma are better and ensure a fairly high silane dissociation degree, even if the plasma absorbed power is not very high and only slightly varies as it is increased [18, 20]; all this explains why the dependence of deposition rate on RF power in the considered system has a different pattern. As seen from Fig. 7, when W_{RF} is increased by a factor of 3, the film deposition rate varies only slightly (within ±12%). The higher deposition rate at a lower nitrogen flow rate through the plasma generation region (curve *1*) is associated with a higher partial pressure of silane.

At the same time, the plasma absorbed power much affects the Si/N ratio in the films, as evidenced by the strong dependence of their refractive index on W_{RF} [5]. The fact that the refractive index of the deposited films steadily decreases with increasing W_{RF} is indicative of a steady decrease in the Si/N ratio, associated with increased concentration of atomic nitrogen in the deposition region.

The positions of minima in the dependences of deposition rate on W_{RF} well correlate with the compositions of the films with a nearly stoichiometric Si/N ratio. This finding suggests that the observed variations in v_{dep} are, most likely, apparent in nature and associated with increasing density of film in view of decreasing concentration in layers of hydrogen preferentially bound to silicon [21]. Further increase of W_{RF} leads to formation of layers with excess nitrogen ($n < 2.05$) and gradual increase in the concentration of nitrogen-bound hydrogen in them, which is accompanied by a sharp decrease in film density and underlies the increase in the apparent deposition rate [5].

As to the effect of the total pressure, it is similar both for capacitive (Fig. 8) and inductive (Fig. 5) coupling. In both cases, beginning with $p_{tot} \approx 40$ Pa, the deposition rate steadily decreases, but the decrease is steeper in the former case, probably, because of the higher concentration of silane radicals owing to better transport of excited species from the discharge region. This predetermines both more rapid film growth and higher rates of homogeneous reaction of silane radicals with the starting SiH_4 gas, which become more

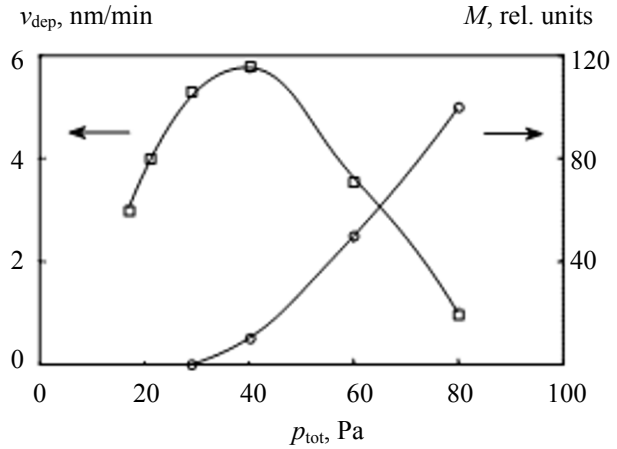

Fig. 8. Dependence of the deposition rate of SiN_xH_y films and the amount of powder deposited on inner reactor walls on total pressure (capacitive mode). Deposition conditions: T_{dep} = 200 K, Q_S = 0.4 cm^3/min, Q_N^t = 60 cm^3/min, Q_N^s = 15 cm^3/min, W_{RF} = 75 W.

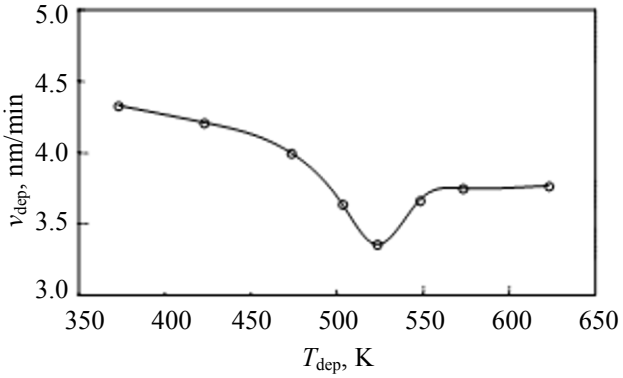

Fig. 9. Dependence of the deposition rate of SiN_xH_y films on support temperature (capacitive mode). Deposition conditions: Q_S = 0.3 cm^3/min, Q_N^t = 150 cm^3/min, Q_N^s = 10 cm^3/min, W_{RF} = 80 W, p_{tot} = 22 Pa.

probable with increasing p_{tot}. The resulting fine yellowish brown powder deposited on the inner chamber walls in quantities sufficient to collect it and quantitatively estimate the increase in the rate of homogeneous reactions with increasing p_{tot}.

The rise of the $v_{dep} = f(p_{tot})$ curve at in the p_{tot} range 18–40 Pa is likely to be explained by the corresponding increase of the partial pressure of silane and the concentration of the radicals formed from it.

Like with inductive RF discharge ignition, the deposition temperature only slightly affects the rate of SiN_xH_y film growth (Fig. 9). When the support temperature is raised from 370 K to 620 K, the deposition rate varies within ±15% around the average value characteristic for a certain combination of other process parameters. As mentioned above, the weak effect of support temperature on film growth rate is characteristic of PECVD processes and usually reveals itself in an inconsiderable (≤ 30%) [22] decrease in the apparent deposition rate of layers due to their densification [23]. The reason for this phenomenon is that the heat energy transferred from the support to reacting species is extremely low compared to the energy transferred from the plasma medium to the support surface as a result of bombardment of the film with energetic plasma particles.

The complicated $V_{dep} = f(T_{dep})$ pattern in the RPECVD process is explained by the fact that the energy flux transferred to the support surface by energetic plasma particles is attenuated by recombination of the latter and becomes comparable with the heat flux from the heater.

At low temperatures (below 520 K), the growth of film is likely to depend upon the energy transferred from the plasma. The layers that form contain a lot of hydrogen [5], primarily, bound to silicon, which reflects the situation that the energy flux transferred to the support surface is insufficient for transformation of chemical bonds.

The observed decrease in the apparent deposition rate with increasing temperature is associated with gradual decrease in the concentration of bound hydrogen [5] in layers and film densification, as evidenced by gradually increasing refractive. The densification of films with increasing T_{dep} is accompanied by gradual alteration of their composition toward stoichiometric. Based on the results in [5], we can suggest that near-stoichiometric SiN_xH_y films are formed at temperatures higher than 525 K. Further increase of the temperature results in that the growth rate steadily increases and, after T_{dep} > 570 K, stops to change. The refractive index and the etch rate of layers [5] in this temperature range vary only slightly, which suggests that the density of the growing film no longer changes. It can be suggested that in this temperature range under the conditions of enhanced energy flux from the heater, a real increase of the deposition rate, associated with either increased mobility of active reacting particles on the surface or increased rate constant of one of surface reactions. Evidence for this suggestion comes from the

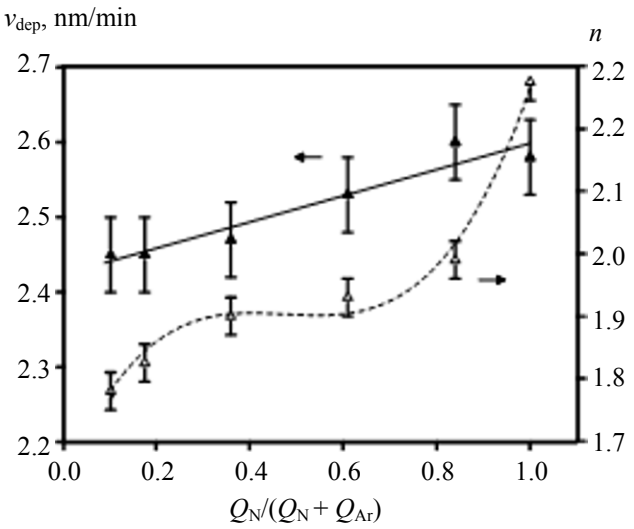

Fig. 10. Dependence of the deposition rate and refractive index of SiN_xH_y films on the $Q_N/(Q_N + Q_{He})$ ratio in the SiH_4–N_2–Ar plasma medium. Deposition conditions: T_{dep} = 570 K, T_w = 470 K, Q_S = 0.4 cm^3/min, Q_N = 13–180 cm^3/min, Q_{Ar} = 0–130 cm^3/min, p_{tot} = 40 Pa, W_{RF} = 95 W.

fact that increasing deposition temperate leads to a slight increase in the concentration of N–H_i bonds (which, as established, are formed on the reaction surface) in layers.

Comparing the results of research on RPECVD of SiN_xH_y films, we can conclude that the mode of RF discharge ignitions only slightly affects the main regularities of the processes. Owing to their design features, CCP reactors have better, compared to ICP reactors, conditions for transport of electrons and ions to the deposition region, as a result of which a higher silane dissociation degree and, consequently, higher deposition rates are observed even at a moderate power.

The above described findings give us strong grounds to present a model of RPECVD of SiN_xH_y films in the SiH_4+N_2 system. Nitrogen molecules are excited or ionized in the RF discharge region due to inelastic collisions with electrons. Part of the N_2 molecules dissociates to form atomic nitrogen primarily by the predissociation mechanism. The excited nitrogen species and electrons are transported downstream to the reactor, where they are mixed with silane and collide with them to form silane radicals SiH_x (x = 1–3) and atomic silicon. The formation of SiN_xH_y films occurs as a result of heterogeneous reactions between silane radicals (Si or/and SiH_2 or/and SiH_3) with atomic nitrogen on the support surface.

Effect of Inert Gas Diluents on Remote Plasma Enhanced Chemical Vapor Deposition of Silicon Nitride Films

The plasma composition was studied by optical emission spectroscopy to show that argon atoms in metastable electronic excited states enhance dissociation of molecular nitrogen. Therefore, it can be suggested that near-stoichiometric silicon nitride films containing no excess silicon are better deposited in the SiH_4–N_2–Ar system. Moreover, inert gas atoms in long-lived metastable states are capable of substantially intensifying energy transfer from the RF discharge region to the reactant mixing and support regions, thereby increasing the concentration of highly reactive species and driving reactions on the support surface.

In this connection, as well as to estimate the degree of similarity between effects in different deposition systems, we undertook an experimental study of the effect of argon and nitrogen dilution of the nitrogen passing through the inductive or capacitive RF charge ignition, on the growth rate of silicon nitride films and their properties [12, 24, 25].

Dilution of Nitrogen with Argon [24]

In the reaction chambers of both the types used, the nitrogen–argon mixture was passed through the RF discharge ignition region. In the case of the inductive mode, the nitrogen flow rate was 10–150 cm^3/min and the argon flow rate was 0–150 cm^3/min, and in the case of the inductive mode, 13–180 and 0–290 cm^3/min, respectively. Varying the nitrogen and argon flow rates in the above ranges we could vary the $Q_N/(Q_N+Q_{Ar})$ ratio in the gas mixture passed through the plasma region in the range 0.1–1.

In the case of inductively induced plasma, argon dilution led to a steady decrease in the film deposition rate; however, the decrease was inconsiderable (Fig. 10): as the $Q_N/(Q_N+Q_{Ar})$ ration was varied over a wide range (0.1–1), the rate varied as little as ±5% around the average value characteristic of the chosen combination of other process parameters. The slight decrease of the film growth rate is most likely associated with decreased concentration of silane radicals, because the dilution of nitrogen with argon decreases the concentration of electrons in the plasma [12].

Fourier-transform IR spectroscopy revealed no oxygen in the deposited layers. It can be suggested that

the decrease in the refractive index with increasing fraction of argon in the gas mixture (Fig. 10) is caused by an increase in the fraction of nitrogen in the layers, which agrees with the results obtained by emission spectroscopy. The increase in the fraction of nitrogen in the deposited layers is probably explained by the increase in the concentration of atomic nitrogen in the plasma medium, associated with the enhancement of predissociation of molecular nitrogen under the action of excited argon atoms. The IR spectral results, too, agree with the suggestion that lowering the $Q_N/(Q_N + Q_{Ar})$ ratio increases the concentration of nitrogen-bound hydrogen and decreases the concentration of silicon-bound hydrogen in the layers. These findings provide evidence for the fact that dilution of nitrogen passed through the discharge region with argon increases the fraction of nitrogen in the films.

It is important to note that if nitrogen is too much diluted with argon, the electrophysical properties of the deposited films are strongly impaired, and they become less denser, probably, due to the decrease content of nitrogen-bound hydrogen. The N–H_j bond formation should stronger distort the amorphous structure of the nitride than the formation of the same quantity of Si–H_i bonds, because blocking of any of the three nitrogen bonds with hydrogen gives rise to a bulkier defect in the nitride structure compared to blocking silicon bonds. Just the lower density of nitrogen-enriched nitride films containing a lot of N–H_i bonds, is responsible for their low chemical stability and unsatisfactory electrophysical characteristics.

The role of metastable argon atoms in the excitation of molecular nitrogen, as well as, probably, silane should increase with increasing total pressure in the reaction chamber [12]. This effect is likely to be associated that increased pressures enhance excitation of nitrogen and silane molecules with long-lived argon atoms which are present in metastable electronic states and slower recombine at high pressures than electrons. Indirect evidence for this suggestion comes from the fact that when the total pressure was increased by slowing down pumping the chamber, the Si/N ratio in the resulting films increased (probably, because the enhanced recombination processes decreased the concentration of atomic nitrogen in the plasma medium), whereas when the total pressure was increased by gradually adding argon to nitrogen the Si/N ratio decreased [18].

Argon dilution of nitrogen accelerates the deposition process only at fairly low RF powers, when

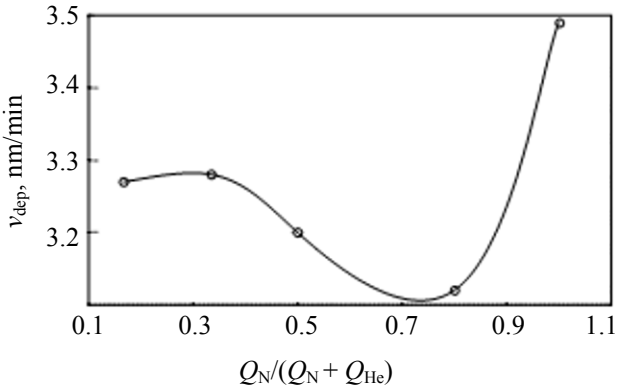

Fig. 11. Dependence of the deposition rate of SiN_xH_y films on the $Q_N/(Q_N + Q_{Ar})$ ratio in the SiH_4–N_2–Ar plasma medium (capacitive mode). Deposition conditions: T_{dep} = 570 K, p_{tot} = 22 Pa, Q_S = 0.3 cm^3/min, $Q_N + Q_{Ar}$ = 150 cm^3/min, W_{RF} = 80 W.

the rate of film formation is controlled by the energy flux at the SiH_4–Ar inlet. In this case, the concentration of silane radicals in the deposition region is fairly low. In the RF discharge region diluent argon atoms are excited to long-lived metastable states and react with SiH_4 molecules to form silane radicals. Increased concentration of silane radicals in the plasma medium accelerates film deposition. As the absorbed RF power is increased, this effect is no longer observed [12].

The experimental results obtained with capacitive discharge ignition provide evidence for the principal conclusions on the role of argon in the RPECVD of silicon nitride films with inductive discharge ignition. In the former case, too, even small argon additives [$Q_N/(Q_N + Q_{Ar}) < 0.9$] in nitrogen increase the concentration of atomic nitrogen in the plasma and, as a result, in the deposited films. However, in the case of capacitive discharge ignition, further increase of the amount of the diluent leads to a deficit of nitrogen in the gas phase and, as a result, enrichment of the film with silicon. Such effect was not observed in the ICP process in view of the lower concentration of silane radicals in the deposition region, which is confirmed by much lower deposition rates. In the latter case, a substantial excess of atomic nitrogen in the reaction medium takes place.

Dilution of Nitrogen with Helium

Helium dilution of nitrogen in the ICP process increases the growth rate of silicon nitride films nearly four times [18], apparently, because helium atoms in long-lived metastable states are actively involved in energy transfer from the plasma region.

In the experiments with capacitive RF discharge ignition we obtained a complicated dependence of film deposition rate on $Q_N/(Q_N + Q_{He})$ (Fig. 11) [25]. In whole, varying the $Q_N/(Q_N + Q_{He})$ ratio over a wide range (0.15–1.0) only slightly affected the deposition rate (≤7%). After a little helium had been added, the deposition rate showed the tendency to decrease. With increasing degree of dilution [the $Q_N/(Q_N + Q_{He})$ was decreased from 0.7 to 0.3], the film growth rate increased but was always lower than in the absence of helium. Note that these results contradict the experimental data described in [26].

The $Q_N/(Q_N + Q_{He})$ ratio is one of the main factors that affect the film composition. Gradual addition of helium to nitrogen [decrease of the $Q_N/(Q_N + Q_{He}$ ratio from 1 to 0.3] decreases the concentration of Si–H_j bonds in the film by about 20% and doubles the concentration of hydrogen bound to nitrogen. Taking into account that the concentration of hydrogen bound to silicon is about an order of magnitude higher than the concentration of N–H_i bonds, we can conclude that helium dilution decreases the total concentration of bound hydrogen in the deposited layers by ~20%. Moreover, as the degree of helium dilution of nitrogen increases, which corresponds to the decrease of the $Q_N/(Q_N + Q_{He})$ ratio from 1 to 0.3, is accompanied by an increase in the concentration of Si–N bonds with simultaneous increase in the concentration of N–H_i bonds and decrease of the Si/N ratio in the films.

The resulting data can be interpreted in terms of the proposed model of the PECVD of films in the SiH_4–N_2 system, taking into account that helium dilution of nitrogen in the case of a low pressure RF discharge increases the average temperature of electrons in the plasma [27, 28], as well as leads to helium atoms in metastable electronic states [$E^*(^3S_1)$ = 19.81 eV, $E^*(^1S_0)$ = 20.61 eV] [28], and, therewith, the radiative lifetime of He^* in the $^3S_1$ state is 150 min. In this connection, in the RPECVD process of silicon nitride film formation in the SiH_4–N_2–He system, the dissociation degree of silane increases due to the higher electron energy with simultaneous increase in the concentration of atomic nitrogen, because the dissociation energy of nitrogen molecules is lower that the energy of metastable helium atoms. Therewith, in view of the long lifetimes of metastable helium atoms (which are orders of magnitude longer than the residence time of gases in the reactor), we can expect enhanced energy fluxes transported to the substrate surface by plasma particles.

Thus, the dilution with helium of nitrogen that is passed through the RF discharge region in the RPECVD of silicon nitride films enriched with silicon (without helium diluent) should give a positive effect, namely, increase the concentration of atomic nitrogen in the reaction medium and creates conditions for preparing films containing no excess silicon.

However, if the deposition of SiN_xH_y films in the SiH_4–N_2 system occurs under conditions suitable for formation of near-stoichiometric films, the introduction of helium results in the synthesis of nitrogen-enriched layers, as evidenced by increased N–H_i concentrations and N/Si ratios (>1.33).

The results obtained in [18, 25] allow us to conclude that the efficiency of helium dilution of nitrogen passed through the RF discharge region varies in a complicated fashion, depending of process conditions and reaction chamber design.

If the deposition rate is limited by the efficiency of transfer of reactive species from the discharge region, the introduction of helium in the plasma-forming medium may favor faster film growth. Probably, this was the case in the work of Tsu et al. [26] who used inductive discharge ignition. If reactive species are transferred from the discharge region in a sufficient quantity, helium dilution has a weak effect, whereas the deposition rate is limited by the conditions of formation and transport of reactive silicon-containing species. Apparently, such conditions took place in a CCP reactor.

Summarizing the results of the cited research we can conclude that argon and helium dilution have a similar effect on the silicon nitride film deposition process, which depends on the chosen process conditions and RF discharge ignition mode. Argon much stronger drives formation of atomic nitrogen than helium.

Improvement of Remote Plasma Enhanced Chemical Vapor Deposition Processes

Remote plasma enhanced chemical vapor deposition offer a number of serious advantages over traditional PECVD technologies. At the same time, this approach fails to overcome all disadvantages inherent in PECVD processes.

In particular, the problem of interdependence of process parameters (while much less pressing than in the conventional process) is impossible to solve, because it relates to the very essence of the process.

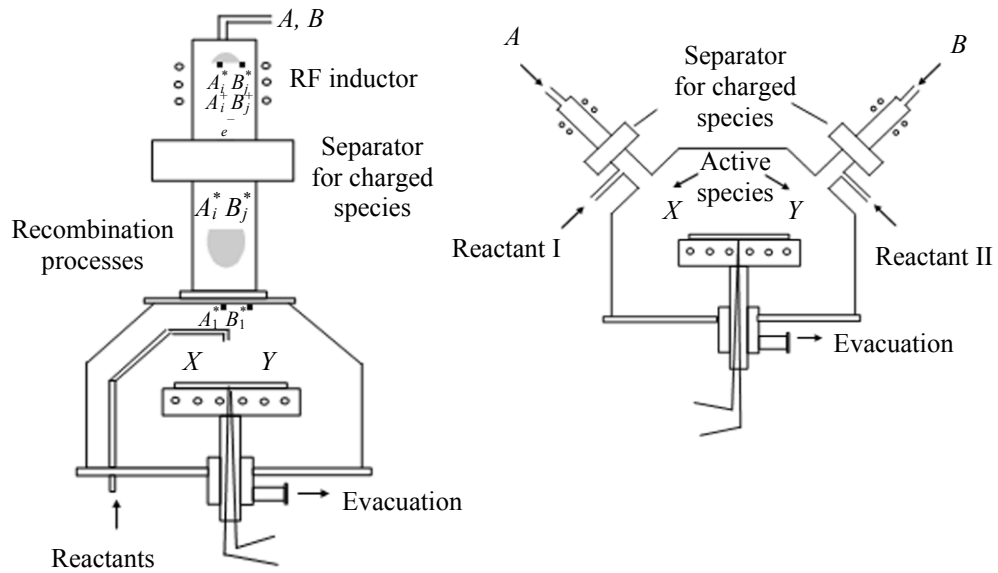

Fig. 12. Schematic diagrams of "ideal" RPECVD processes. (*A, B*) Gases used for generation of neutral excited molecules, (*X, Y*) chemically active species (involved in the synthesis of the deposited substance) formed by reactant reactions with the neutral excited species coming from the discharge region.

The diversity of chemical transformations can be overcome by preventing transport of charged species from the plasma region to the reactant mixing and film deposition region. In the latter case, the chemically active species, but only those required for film growth, can be formed not only in the RF discharge ignition region, but also as a result of inelastic collisions of reactant molecules introduced downstream from the discharge region with neutral excited species coming from the plasma region. Ideally, the energies of the neutral excited species should be equal to the energies required for selective formation from reactant molecules of reactive species involved in film growth. Separation of charged species from neutral can be performed by means of electric and magnetic fields. In an improved RPECVD system, the RF discharge region serves as a source of neutral excited species with discrete energies.

Even neutral excited species of the same type (for example, nitrogen molecules), which are generated in the plasma, are generally characterized by a certain range of discrete energies corresponding to their electronic excited states, whereas for film formation a much narrower range of chemically active species is required. The required species can be isolated based on the difference in their lifetime. Short-lived species are the first to recombine as the gas flux is moving from the discharge region along the reaction chamber, whereas longer lived species reach remote regions of the reactor. Taking this into account, one can locate the reactant inlet at an appropriate distance from the discharge region. If several reactants are necessary for film formation, and the neutral species with an energy required to excite one of them induce undesirable dissociation of another reactant, a reactor with two chambers for separate preparation of reactive species should be used (Fig. 12).

Even though the described process design may prove difficult to realize in practice, it seems quite promising. There is a risk that the electrons formed by the recombination of excited neutral species by the Penning mechanism will reach the reactor region downstream from separators for charged particles [9]. However, the electrons formed by this mechanism generally have low energies which are impossible to increase in the absence of electric and magnetic fields. Such electrons can initiate exclusively excitation, dissociation, or ionization processes requiring fairly low energies. For example, they can contribute much with SiH_4 as the starting reactant, because many reactions involving silane and its radicals require energies ranging from 2 to 5 eV [7]. However, such energies are insufficient in many cases.

In view of the considered process scheme, a problem concerning the nature of species that could be used for energy transfer from plasma to starting

reactant molecules. Obviously, such particles should be long-lived and chemically inert toward the other reactants and apparatus material, have energies which, in an ideal case, coincide with the energies required for forming free radicals and atoms from reactant molecules. Apparently, the atoms of inert gases, such as argon and helium, as well as stable molecules of other gases (for example, nitrogen) in long-lived metastable electronic states can be used as neutral species.

To find out whether metastable excited argon atoms can be used for generation of energetic species involved in SiN_xH_y film formation in a RPECVD system with inductively coupled plasma, we performed experiments in which only argon was passed through the RF discharge region, while nitrogen (flow rate 40 cm^3/min) was fed to the reactor together with a SiH_4–Ar mixture (flow rate 6 cm^3/min). The gas-dynamic conditions were chosen so that the afterglow region did not reach the reactant inlet. As a result, near-stoichiometric silicon nitride films with good dielectric and electroinsulating characteristics [specific breakdown voltage (6–7) × 10^6 V/cm, specific resistance (5–8) × 10^{14} Ω cm, dielectric constant ~6, tan $\delta \leq 0.002$)] were synthesized.

Thus, our experimental results not only gave evidence showing that long-lived metastable argon atoms play an important role in the formation of atomic nitrogen and silane radicals required for silicon nitride deposition, but also demonstrate a principal possibility of the use of argon as a neutral energy carrier if an "ideal" PECVD scheme is realized.

CONCLUSIONS

Remote plasma enhanced chemical vapor deposition processes are a step forward in the development of plasmachemical technologies: They are free of certain disadvantages characteristic of plasmachemical technologies traditionally used in electronics. The RPECVD technology is simpler compared to conventional PECVD, even though it has a more complicated mechanism involving several consecutive stages, and every stage of the RPECVD process is important to understand for its practical realization. Thorough investigation of the physicochemical regularities of the processes is the only way to gain insight into the combination of process parameters ensuring the fabrication of films with a desired complex of properties.

A possible way to improving the RPECVD process is to isolate from the plasma flux neutral excited species having the discrete energies required for forming energetic species involved in the synthesis of the deposited film from the starting reactants.

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