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# A New Ecologically Safe Method of the Deposition of Silicon Nitride Layers in a Quasi-Closed Low Pressure Reactor

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## Abstract

In the present work we describe a new method to obtain silicon nitride layers from silicon tetrachloride and ammonium in a quasi-closed low pressure reactor. This method conserves all the merits of the traditional RPD process but possesses some advantages. It is more reagent- and energy-saving. The performance without pumping off excludes the admission of hazardous gases to the environment and solves ecological problems. Kinetic dependencies of the new process and the properties of layers are similar to those obtained earlier by traditional deposition in a reduced-pressure reactor.

## INTRODUCTION

Modern microelectronics has achieved such a perfect state that the number of silicon, oxygen, nitrogen, phosphorus, boron atoms required for the performance of the elements of microcircuits is 12 to 15 orders of magnitude below the Avogadro number. This is a vivid example of precise technologies. However, the prefix *micro-* relates only to the size of the resulting microcircuit. Taking into account modern scale of microcircuit production and the related semiconductor production, it should be noted that in general electronics uses large-scale amounts of chemical compounds and reagents that possess various degrees of ecological danger.

As examples, fluorine compounds can be mentioned that are used in chemical and plasmochemical etching, as well as silane, its derivatives and organometallic compounds that are used in the deposition of semiconductor and dielectric layers. The use of these compounds in flow-type reactors is usually accompanied by the release of toxic compounds into the atmosphere. Besides, as the experience shows, the coefficient of the useful consumption of reagents in these reactors is usually not more than 10 %. So, a very important problem arises to create highly efficient reactors excluding the release of toxic gases into the atmosphere.

In the present work we describe a version of one of the processes that is among the most important processes in the technology of silicon nitride layer production and does not cause the pollution of atmosphere.

Earlier, studying the distribution of growth rates over the equal-temperature zone, we showed in our works [1–3] that the conditions of an ideal displacement reactor are realized. This allows to involve well-established notions of the kinetics of closed systems. We have also shown that the deposition kinetics of silicon nitride layers according to the reaction involving the ammonolysis of silicon tetrachloride at reduced pressure is described as a sequence of two stages. At the first stage, an intermediate product is formed in the gas phase in the interaction of $SiCl_4$ with $NH_3$. The second stage is the transformation of the intermediate product into silicon nitride that occurs on the surface of the growing layer. The scheme proposed was confirmed in [4] where the rate constants of both stages were determined.

The works considered above describe the traditional schemes of silicon nitride layer synthesis. Meanwhile, the interaction of $SiCl_4$ with

$NH_3$ has a remarkable feature. At high temperatures (above 600 °C) the ammonolysis of $SiCl_4$ is described by the equation

$$3SiCl_4 + 4NH_3 = Si_3N_4 + 12HCl \quad (1)$$

Silicon nitride layers are deposited on all the surfaces in the high-temperature zone of the reactor. Hydrogen chloride formed in this process reacts with the excess ammonium to form $NH_4Cl$ that is deposited in the cool zone. The overall process follows the equation

$$3SiCl_4 + 16NH_3 = Si_3N_4 + 12NH_4Cl \quad (2)$$

Usually the transformation degree of $SiCl_4$ into silicon nitride under the conditions of a reduced-pressure reactor does not exceed 10–20 %. The rest silicon tetrachloride is transformed into silicodiimide $SiN_2H_2$. This process has been well studied [5]. At room temperature it is described by the scheme

$$SiCl_4 + 6NH_3 = Si_2N_2H_2 + 4NH_4Cl \quad (3)$$

So, it follows from equations (1)–(3) that both in the hot and in the cool zones of the reactor final products formed during the reaction are present in the solid state. This feature of the reaction of $SiCl_4$ with $NH_3$ allowed to conduct the synthesis of silicon nitride in a quasi-closed reactor. The initial reagents at stoichiometric ratio are admitted at a constant rate into the reactor which has been evacuated preliminarily and after this cut off the vacuum pump. Since the transformation of HCl and $NH_3$ into $NH_4Cl$ [6] and the transformation of the intermediate silicon-containing product into $SiN_2H_2$ [5] occur much more rapidly than the initial reagents are admitted, the deposition of solid products in the cool zone acts as a specific vacuum pump which allows to conserve the required pressure without pumping out for the whole deposition period.

## EXPERIMENTAL

Experiments were conducted in a usual reduced-pressure reactor within the temperature range of 800–900 °C, pressure was varied within 0.5–2 Torr. Since no carrier gas is used for the deposition in the quasi-closed reactor, the flow was measured by a corrosion-proof sensor and controlled by a Teflon leakage valve using the teflon heat expansion principle.

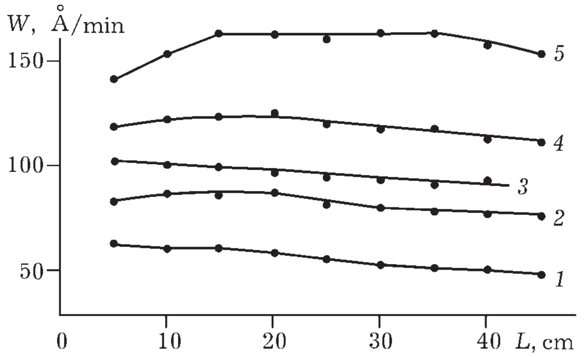

Fig. 1. The distribution of growth rates over the reactor length at 840 °C and different pressures. The initial flow of $SiCl_4$ and $NH_3$ was 1.3 and 7 l/h, respectively.

## RESULTS AND DISCUSSION

Figure 1 shows the distribution of deposition rates over the equal-temperature zone for different pressure in the reactor (the ratio between initial reagents is close to the stoichiometry). Process rate was independent of flow rates which confirms the reactor being ideal displacement one.

Figure 2 shows the dependencies of growth rates in the centre of the zone on the total pressure and on initial $SiCl_4$ concentrations (calculated for the temperature of experiment). Two deposition regimes with different gas flow

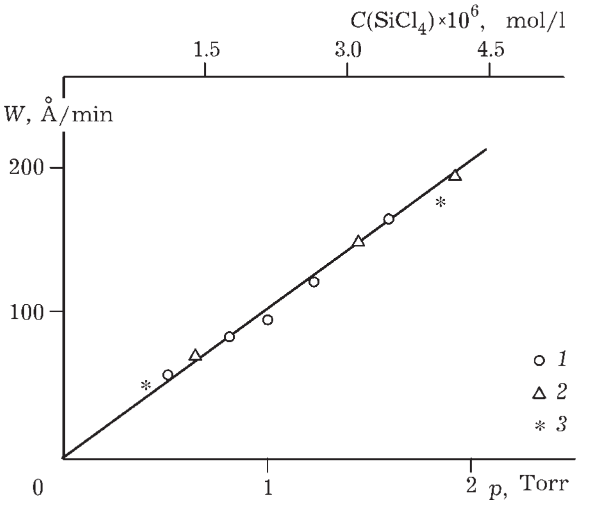

Fig. 2. Dependence of deposition rates on pressure ($SiCl_4$ concentration) at 840 °C for the initial flow of $SiCl_4$ and $NH_3$, l/h: *1* – 1.3 and 7; *2* – 1.65 and 10, *3* – in the standard process with a vertical position of plates.

rates were involved to build up Fig. 2, as well as the data on the growth under traditional process conditions with $NH_3$ taken in excess and argon as carrier gas. One can see that a linear dependence of the rate on $SiCl_4$ concentration is conserved, as that described in [1–3].

The distribution of deposition rates over the zone that is shown in Fig. 3 was determined with vertical position of plates (the distance between the collars being 3 mm) which allowed to obtain thickness scattering less than 5 % at a 100 collars load. The uniformity of thickness over the plate was not worse than 0.7 %.

Refractive index determined by means of laser ellipsometry was 1.96–2.00 and corresponded to the values characteristic of silicon nitride.

IR absorption spectra exhibited, along with the main band at 800 $cm^{-1}$ corresponding to Si—N bonds, also the absorption band at 3340 $cm^{-1}$ corresponding to the vibrations of N—H bonds. Hydrogen content was estimated quantitatively as described in [7]. For the films synthesized at 840 °C, the concentration of hydrogen chemically bonded to nitrogen was $6 \cdot 10^{21}$ $cm^{-1}$.

In order to study the electrophysical parameters of layers, we used the $Si-Si_3N_4-Al$ structures. Figure 4 shows voltametric characteristics of silicon nitride layers obtained in a quasi-closed reactor in the interaction between silicon tetrachloride and ammonium, as well as between $SiH_4$ and $NH_3$ in hydrogen flow at 900 °C, and the layers obtained by means of plasmochemical method from monosilane and ammonium at 200 °C. The comparison of the data presented in Fig. 4 shows that silicon nitride obtained from $SiCl_4$ and $NH_3$ is not worse, judging from its electrophysical properties, than the nitride from monosilane and ammonium in hydrogen which is used in technology. The breakdown field as determined from voltammetric curves was 6 MV/cm. The dielectric constant was determined from volt-farade characteristics to be 8.5.

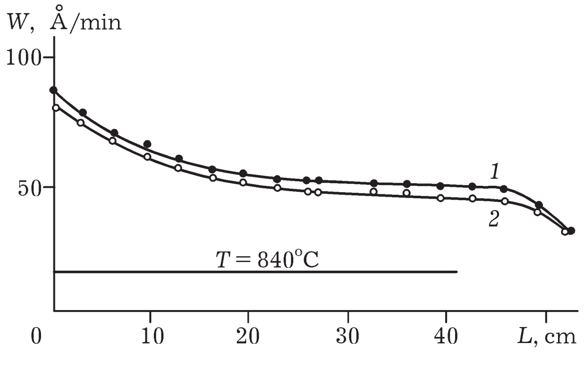

Fig. 3. The distribution of growth rates in a quasi-closed reactor for a vertical position of plates at a distance of 3 mm at 840 °C and 1 Torr pressure. The flow rates of $SiCl_4$ and $NH_3$, l/h: 1.65 and 10 (*1*), 1.3 and 7 (*2*), respectively.

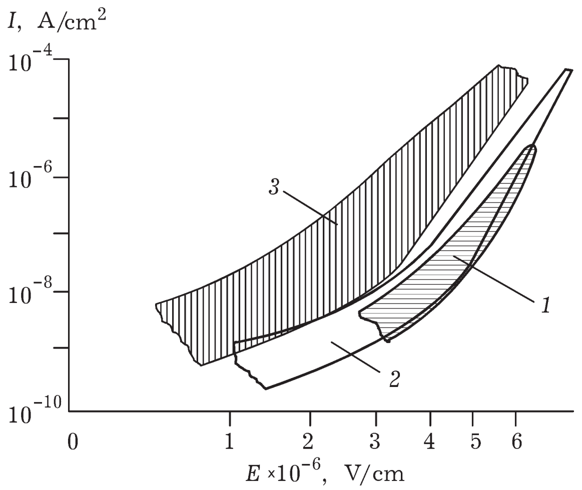

Fig. 4. Voltammetric curves for the $Si-Si_3N_4-Al$ structures: *1* – silicon nitride obtained in the present process; *2* – silicon nitride from $SiH_4 + NH_3 + H_2$; *3* – silicon nitride synthesized in plasma at 200 °C.

In order to check the possibility to use $Si_3N_4$ layers in LOCOS technology, a 100 nm thick nitride layer was deposited onto silicon dioxide layer 45 nm thick. After photolithography with respect to $Si_3N_4$, oxidation in water vapour was performed at 1000 °C for 7 h (till the oxide thickness was 1 μm). The test procedures demonstrated high stability of silicon nitride layers towards oxidation and showed that these layers can be used in LOCOS process.

## CONCLUSION

The investigation of the kinetics of silicon nitride layers growth in a quasi-closed reactor showed that the process does not differ from the traditional deposition in a reduced-pressure reactor and conserves all the advantages of the latter including good uniformity of film thickness over the plate and from one plate to another. The method proposed for the preparation of $Si_3N_4$ layers in a quasi-closed cycle is reagent-saving (since no carrier gas and excess ammonium are used). Besides, its realization is not accompanied by the release of hazardous substances that could pollute the atmosphere.

Recently a new method was reported for the synthesis of microcrystal silicon in a closed cyclic process from the plasma glow discharge in monosilane with hydrogen [8]. After a thin layer of amorphous silicon was deposited, the reactor was disconnected from the pump. When the film was kept in $H_2$ discharge, silicon crystallization occurred.

## REFERENCES

1 O. I. Semyonova, L. A. Nenasheva and S. M. Repinsky, *Izv. AN SSSR. Neorgan. mater.*, 17 (1981) 1223.
2 O. I. Semyonova, L. A. Nenasheva and S. M. Repinsky, *Ibid.*, 20 (1984) 791.
3 S. M. Repinsky, in A. V. Rzhanov (Ed.), Silicon Nitride in Electronics, Elsevier, Amsterdam, 1988, p. 19.
4 O. I. Semyonova and L. A. Nenasheva, *Izv. AN SSSR. Neorgan. mater.*, 25 (1989) 56.
5 M. Billy, *An Chime*, 4 (1959) 795.
6 M. Luria and B. Cohen, *Atm. Environment*, 14 (1980) 665.
7 I. P. Chernov, N. V. Shadrin, Yu. P. Chavantsev *et al.*, *Thin Solid Films*, 88 (1982) 49.
8 S. Koynov, S. Grebnev, P. Radojkovye *et al.*, *J. Non-Cryst. Solids*, 198–200 (1996) 1012.