

SILICON NITRIDES AND OXYNITRIDES PREPARED IN HIGH-PRESSURE PLASMAS

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The paper deals with preparation of silicon nitride powders with the use of atmospheric-pressure plasma. It compares three basic routes: nitridation of plasma-pyrolyzed SiCl_4 , SiCl_4 ammonolysis, and nitridation of the silicon powder ($4\ \mu\text{m}$) in plasma. For sufficient active nitrogen creation under nitridation conditions as well as for chlorine elimination, the ammonia addition was clearly indicated to be necessary. Direct nitridation yields better product quality but the residence times of 0.1 s are yet short for significant nitridation of plasma-carried powders.

INTRODUCTION

Thanks to the silicon nitride industrial applications, the chemistry of silicon-nitrogen compounds have recently been subject to numerous studies [1–3].

One of the striking disadvantages of commonly used silicon nitride preparation methods is the low reaction rate both in direct nitridation of silicon powder and in carbothermal reduction of silica [4]. It cannot be raised simply by the temperature increase itself because of undesired competitive production of the β -modification at high temperatures. Another inconvenient feature of the aforementioned methods is the source-dependent particle size distribution (mean diameter typically some micrometers).

The difficulties mentioned above can be solved by the methods which make use of vaporized silicon-containing compounds, e.g. SiCl_4 ammonolysis, thermal decomposition of silazanes [5] as well as plasma chemical processes. Two principal ones are:

- a) plasma-assisted ammonolysis of silicon tetrachloride,
- b) direct nitridation of silicon vapours condensing from plasma.

These processes differ from those called CVD in the products that are powdered or fibre-like in this case, as opposed to amorphous films in the CVD. The goal of this paper is to analyse them on the basis of the authors' experimental results.

EXPERIMENTAL SETUP

As the source of plasma, an elongated wall-stabilized arc generator working at atmospheric pressure was used (see Fig. 1, where the complete experimental setup as well as the generator scheme are given). This was a modification of the so called "plasma gun with the step anode" [6]. Nevertheless, the type used here had its interelectrode section of the 6 mm inner diameter (i.d.) electrically isolated from the anode and the additional gas stream, labeled in Fig. 1 as F_2 , played an important role in the gas-dynamic stability of the plasma torch.

Variable channel length l made feasible the absorption of electric energy on various power levels (10 to 27 kW net), which in conjunction with a broad range of gas flows 0.03–0.08 mol/s offers mean specific enthalpies 180 through 450 kJ per mole of the cold hydrogen-nitrogen mixture.

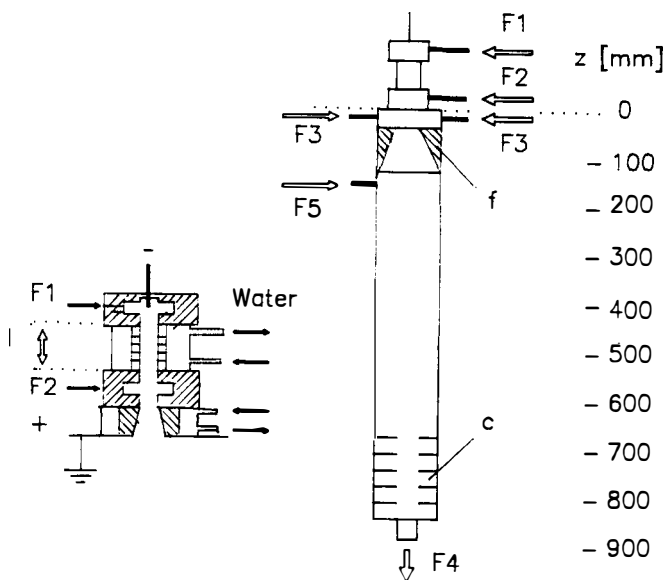


Fig. 1. Schematic diagram of the experimental setup and of the plasma generator.

F_1 - cathode gas flow, F_2 - anode gas flow, F_3 - tetrachlorosilane injection, F_4 - exhaust, F_5 - ammonia injection, l - variable channel length, f - fluidizer, c - cooler.

Mean plasma velocity in the channel approaches the value of 500 m/s (where the value of 4.5 kK represents a reliable minimum mean temperature estimate). It is to note here, that the maximum parameter value can differ substantially from the mean (or average) one. The spectroscopically determined maximum temperature rises as far as 12 kK in this type of plasma gun [7]. The plasma velocity and temperature fall partially down already in the anode nozzle; further on, after having been mixed with cold carrier nitrogen, the mean temperature drops to roughly 4.2 kK, within only a tenth of a millisecond.

The plasma chemical reactor is a cylindrical tube of 50 mm i. d. and variable length. The maximum length of 810 mm corresponds to a dwelling time max. 0.12 sec. (without considering back streams), which is by far much for homogeneous plasma chemical reactions, but may be insufficient for heterogeneous reactions involving the mass transfer between plasma and condensed phase.

The stainless steel mantle of the reactor is a ground for a low heat transfer from plasma to cooling water. Thus, more significant temperature drop within the reaction zone can be accomplished by feeding a cold gas or another quenching agent into the reactor only. The copper cooler, adjacent to the reactor, allows the initial cooling rate of min 10^6 K/s at 2 kK. This value decreases with increasing thickness of powder deposits, but throughout an experiment holds the exit gas temperature below 420 K.

Three chemical systems were studied in experiments:

1. $\text{SiCl}_4(\text{g})\text{—N}_2\text{—H}_2$,
2. $\text{SiCl}_4(\text{g})\text{—N}_2\text{—NH}_3$,
3. $\text{Si}(\text{s})\text{—N}_2\text{—NH}_3$.

A summary of the run conditions for the experiments is given in Table I.

Table I
Summary of the run conditions for the experiments

	$\text{SiCl}_4\text{—N}_2\text{—H}_2$	$\text{SiCl}_4\text{—NH}_3\text{—N}_2$	$\text{Si—NH}_3\text{—N}_2$
reactor length [mm]	850	850	850
displacement of F ₃ [mm]	10	10	10
displacement of F ₅ [mm]	—	150	150
generator voltage [V]	240	160	180
generator current [A]	90	92	92
gas phase comp.:			
N ₂ [mol %]	71.4	41.6	83.6
H ₂ [mol %]	26.6	0	0
SiCl ₄ [mol %]	2.0	0	0.83
NH ₃ [mol %]	0	49.8	16.2
Si(g) [mol %]	0	0	0.74
mean plasma temp. [kK]	5200	5900	5900
mean plasma enth. [kJ.g ⁻¹]	13.9	11.1	10.8

Nitrogen used in all these experiments was evaporated from the liquid-nitrogen tank and was not further purified. The oxygen content in nitrogen varied between 0.01–0.1 vol. %. Hydrogen was technical grade (> 99.5 vol. % purity).

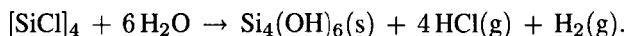
The tetrachlorosilane vapour pressure was maintained by the saturator in the thermostated bath and the $\text{SiCl}_4\text{—N}_2$ mixture (F3) was driven into the reactor at the distance $z = 10$ mm from the anode. Injection of ammonia (F5) was carried out via a lateral tube of 3 mm i.d. mounted at $z = 150$ mm (F5). In the experiments with powdered silicon the whole apparatus was installed vertically, so that the plasma generator was placed under the reactor. A part called “fluidizer” was added between the reactor and the anode to prolong the residence time of silicon in the hot reactor zone. Silicon powder (average particle size $3.8\ \mu\text{m}$ according to Sedigraph measurements) was carried by nitrogen, its typical mass flow rates being 1.6 g/min. This was checked by weighing the powder in the silicon feeder before and after the experiment.

EXPERIMENTAL RESULTS

1. $\text{SiCl}_4 - \text{N}_2 - \text{H}_2$ system

The atomic emission spectroscopical observations revealed distinct emission SiN bands in the $\text{SiCl}_4 - \text{N}_2$ plasma which, however, disappeared after addition of even small concentrations (over 1 mol. %) of hydrogen (via F1) into the plasma gas [8]. Whereas the former arrangement yielded no solid product, the latter one gave a good yield of powder, yet of poor nitridation degree. The result can be explained by the instability of the SiN radicals in the oxidizing medium containing free chlorine in the former case, whereas in the latter one a sufficient silicon condensation rate was not complemented by an excited nitrogen (atomic or molecular) concentration high enough to take up all the temporarily free silicon bonds.

Powders in this experiment were collected both in the reactor and on the filter. Great differences in the chemical composition and morphology were observed. In the reactor hot zone ($z < 200$ mm), the fine powdered amorphous silicon was collected, which exhibited an extreme chemical reactivity. In a lower temperature region ($z > 200$ mm) polymerized products of the SiCl_4 decomposition appeared. These were easily hydrolyzed after their exposure to wet air [9]:



In the reactor zone with $z = 600\text{--}750$ mm a growth of fibrous materials was observed. These include dendritic crystals as well as whiskers. They originate on common roots, bifurcating and ramifying further in submicron needles, which can be (in the consequence of local overheating) terminated by larger round particles (droplets of metallic silicon), as it can be seen in Figs. 2a and 2b. The chemical composition of the fibres varies with their length: at the origin the microprobe (CamScan) revealed Si, Cl, partially even O, in the bodies Si and N only. X-ray diffraction analysis (XRD) confirmed the presence of the crystalline modifications of silicon nitride and silicon in this area (see Fig. 3). The $\beta\text{-Si}_3\text{N}_4$ diffraction pattern agrees with that given in JCPDS tables (No. 33-1110), while $\alpha\text{-Si}_3\text{N}_4$ pattern exhibits a systematic deviation in the interfacial distances -0.65% from the standard (JCPDS No. 9-250). The phase composition was verified by IR spectroscopy, which (on the base of standards) makes possible a qualitative distinction of α - and β -modifications (Fig. 4).

The crystalline fibrous phase ceased at the coordinates $z > 850$ mm and chemically bound nitrogen cannot be detected any more. Powder samples taken from the filter are made up by mixtures of free silicon and nonstoichiometric SiO_x (see also Fig. 4). The oxygen content may reach as high as 27.5% as determined by high-temp. extraction (LECO).

2. $\text{SiCl}_4 - \text{N}_2 - \text{NH}_3$ system

The finely disperse product of SiCl_4 plasma ammonolysis differed substantially from that of preceding case. This confirms a different reaction mechanism as well [10]. Residual content of NH_4Cl in products deposited on the reactor walls increased from 30 mass % (at $z < 300$ mm) up to 60 mass %, as determined by DTA. Lower values were the result of sublimation concurrent with deposition. Most analytical methods (as well as further material processing) necessitate its elimination.

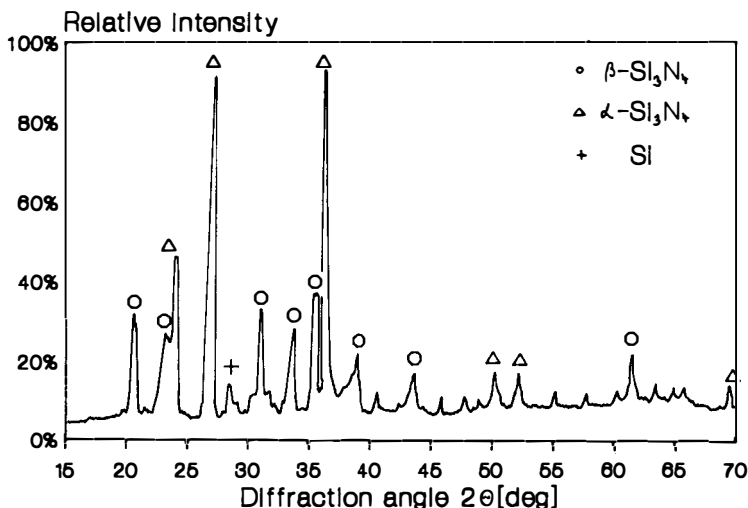


Fig. 3. X-ray diffraction pattern of whiskers grown in the reactor during the $\text{SiCl}_4\text{--N}_2\text{--H}_2$ experiment.

Sublimation in pure nitrogen at 900–1000 K for a period of more than 4 hours revealed itself to be the most efficient method. This process gives a guarantee of the suppression of the NH_4Cl concentration below 1 mass % (by IR spectroscopy).

The processed powder was an X-ray-amorphous oxynitride of chemical composition (by LECO): 34.2 mass % nitrogen, 10.8 mass % oxygen, which corresponds to a formula $\text{SiO}_{0.34}\text{N}_{1.25}$. Its specific surface area was $87.5 \pm 10 \text{ m}^2\text{g}^{-1}$. The IR spectrum proved the absence of the crystalline phases (see Fig. 4, curve *f*) as well as the absence of the well developed tetrahedrons SiN_4 , which have the characteristic absorption peaks near 490 cm^{-1} [11].

Oxynitride prepared in this way was thermally treated in the hydrogen-nitrogen gas mixture (9 : 1 by volume, oxygen content less than 10 ppm) at temperature 1670 K for 5 hours. The outcome was a mixture of more than 60 mass % of crystalline α - and β - Si_3N_4 (see Fig. 4) in the mass ratio 92.2 : 7.8 (determined by XRD) and of the rest of the amorphous phase.

3. Si—N₂—NH₃ system

The necessary condition for a complete silicon nitridation is a sufficiently long contact time of silicon and active nitrogen. Under the plasma conditions it may be accomplished by a full evaporation of metallic silicon prior to nitridation process, which takes place at lower temperatures (under the Si_3N_4 thermal stability threshold, which is at atmospheric pressure about 2170 K [1]). The enthalpy surplus in plasma is generally sufficient for this process. Somewhat more complicated is the heterogeneous evaporation kinetics. Krasovskaya [12] has calculated the evaporation degree of the silicon particles of a mean diameter of $50 \mu\text{m}$ under experimental

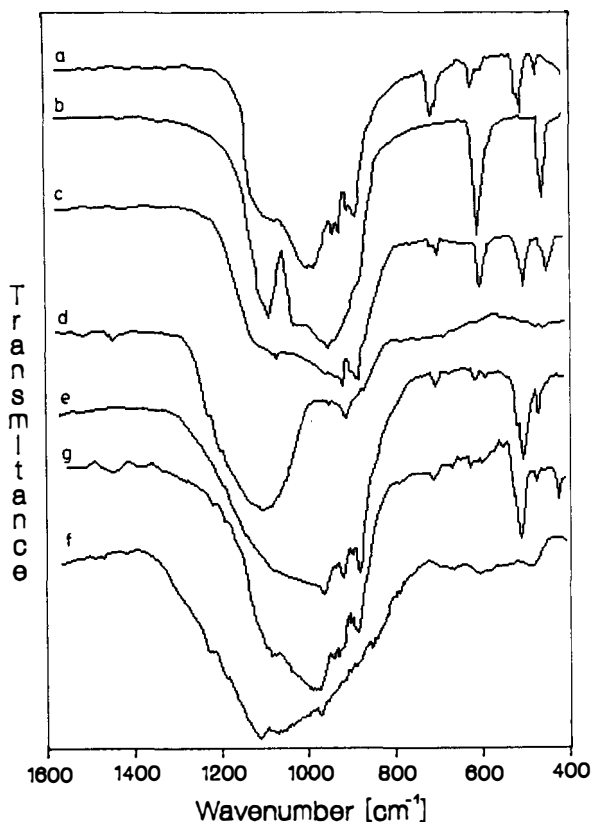


Fig. 4. IR absorption spectra of the standards and of the synthesized materials:
 a) α - Si_3N_4 standard, b) β - Si_3N_4 standard, c) whiskers grown in the reactor $\text{SiCl}_4\text{--N}_2\text{--H}_2$ experiment), d) product on the filter ($\text{SiCl}_4\text{--N}_2\text{--H}_2$ experiment),
 e) whiskers grown in the reactor ($\text{Si--NH}_3\text{--N}_2$ experiment), f) product of the SiCl_4 plasma ammonolysis, g) product of the SiCl_4 plasma ammonolysis after the heat treatment (1400°C , 4 hours, $\text{N}_2\text{--H}_2$ gas mixture).

conditions scaled up by one order (the mean enthalpy being comparable), to 40 mass %. However, estimates based upon other sources [13, 14] which model our conditions, incl. different particle size distribution, give more optimistic results. In accordance with our experiment, only a small part of approx. 5 mass % remains unevaporated. Our microscopic observations indicate that this fraction corresponds to the tail fraction of coarse source particles.

Addition of ammonia via F5 input into the decaying plasma (the so called afterglow) has several positive consequences. The gas temperature substantially falls down, while the arising nitrogen atoms and NH radicals play a dominant role in silicon nitridation [15].

The powder samples taken from the reactor show two distinct phases: a lower polycrystalline silicon layer of thickness almost 1 mm and an upper fibrous struc-

ture of α - Si_3N_4 needles (the structure has been indicated by IR spectroscopy and proved by XRD method). A quantitative elucidation of the IR spectrum of the needles (plotted in Fig. 4, spectrum e) showed the bound nitrogen content was 35 ± 5 mass %. No bound nitrogen was found in the deeper layer (by IR).

High-temperature extraction measurements (LECO) made possible to evaluate the mean mass concentration of Si_3N_4 in the sample, defined by formula

$$X_{\text{Si}_3\text{N}_4} = \frac{n_{\Sigma}}{n_{\text{Si}_3\text{N}_4}},$$

where $n_{\text{Si}_3\text{N}_4}$ denotes the bound nitrogen mass fraction in the nitride phase (0.35 in this case) and n_{Σ} is the total nitrogen molar fraction in the sample as a whole, determined by LECO. The dependence of $X_{\text{Si}_3\text{N}_4}$ vs. z is given in Fig. 5 together with the specific surface area of 5 samples. The curves show that under $z = 350$ mm, the nucleation of free silicon prevails over its nitridation.

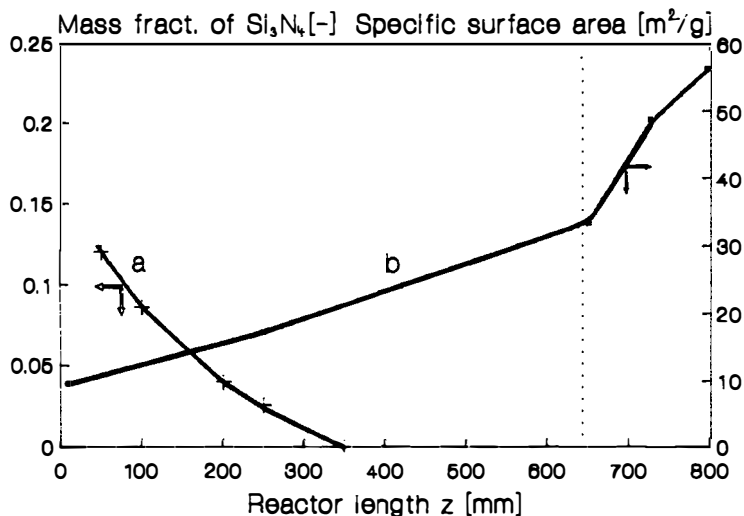


Fig. 5. Reaction degree (a) and specific surface area changes (b) of product along the reactor.

DISCUSSION

A good chemical quality of silicon nitride fibres in the stationary (anchored) phase is the consequence of a relatively long contact time between growing fibre tip of slowly condensing silicon and active nitrogen carrying plasma passing by.

Meanwhile, the particles driven by plasma have an efficient contact time for approx. one tenth of a second and this is apparently too short to yield substantial degree of nitridation.

High oxygen content in the disperse product of SiCl_4 ammonolysis may have two basic reasons: a) high oxygen content in the source chemicals, which in co-operation with high affinity of silicon to oxygen leads to an appreciable enrichment of the product with oxygen, b) ultra-disperse state with large specific surface area and extremely small particle diameters (down to 10 nm), generally exhibits higher energy of adsorption [16], and lower apparent activation energy for the reaction of the adsorbed species with the substrate. The powder can almost instantaneously take up a mono-layer of oxygen and/or water vapour, which later on hydrolyzes subsurface layers of the silicon nitride-like compound and tends to a transformation of the nitride bonds to oxidic ones. A product of 80 m^2/g has an average particle diameter 23 nm and a monomolecular layer on its surface represents already 4.7 mass % of oxygen. The distinction between both forms of oxygen in the final product is not quite unambiguous. It seems to be feasible by the high-temperature oxygen extraction in combination with precise IR absorption spectroscopy measurements.

CONCLUSION

The studies on silicon nitride synthesis in the high pressure plasma afterglow, conducted in the Institute of Plasma Physics, showed its feasibility. Since the presumption of a sufficient concentration of active nitrogen species in a hydrogen-nitrogen high-pressure afterglow appeared not to be fulfilled, addition of ammonia was necessary. Nevertheless, this makes the process very close to those not using plasma. This particular plasma synthesis seems to be furthermore too expensive for a unit production. The industrial use of prepared fibrous products is, moreover, doubtful. As it makes use of gas/solid transitions it offers still advantages in the preparation of uniformly doped powders for technical purposes (e.g. engineering ceramics).

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NITRIDY A OXYNITRIDY KŘEMÍKU PŘIPRAVENÉ VE VYSOKOTLAKÉM PLAZMATU

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Dohasínající dusíkovodíkové plazma bylo použito k pyrolýze a nitridaci SiCl_4 a volného křemíku. V uzavřeném reaktoru s dobou setrvání 0,1 s byly připraveny materiály s různým stupněm nitridace, závislejícím především na expozici aktivnímu dusíku. Tomu odpovídá vyšší stupeň nitridace u zakotvené fáze (produktu na stěnách reaktoru) a při přidavku bezvodého amoniaku do reaktoru.

Při použití tetrachlorsilanu jako suroviny vznikal v reaktoru vláknitý materiál (whiskery) o průměru vláken pod $1 \mu\text{m}$ a délce několik stovek μm , který je směsí α - a β -modifikací nitridu křemíku s minoritní příměsí volného křemíku.

Nitridací disperzního křemíku za přítomnosti amoniaku vznikal v zakotvené fázi α - Si_3N_4 . Doba kontaktu unášené fáze s aktivním dusíkem je pro dosažení vysokého stupně nitridace nedostatečná.

Připravené materiály byly podrobeny chemické analýze metodou vysokoteplotní extrakce, fázové složení bylo zkoumáno infračervenou absorpční spektroskopií a rtg. difraktometrií. Metody vykazují uspokojivou shodu výsledků a indikují zvýšenou reaktivitu amorfních ultradisperzních materiálů produkovaných jako unášené fáze.

Obr. 1. Schéma experimentu a nákres generátoru plazmatu. F_1 - průtok katodou, F_2 - průtok anodou, F_3 - dávkovač SiCl_4 resp. Si, F_4 - výstup plynů, F_5 - dávkovač NH_3 , l - proměnná délka kanálu, f - fluidní lože, c - chladič.

Obr. 2. SEM fotografie vláken Si_3N_4 vyrostlých v reaktoru během experimentu s SiCl_4 - N_2 - H_2 .

Obr. 3. Rentgenový difraktogram vláken vyrostlých v reaktoru během experimentu s SiCl_4 - N_2 - H_2 v porovnání se standardy JCPDS.

Obr. 4. IC absorpční spektra standardů a připravených materiálů: a) α - Si_3N_4 standard, b) β - Si_3N_4 standard, c) vlákna vyrostlá v reaktoru na pozici $z = 675 \text{ mm}$ v experimentu SiCl_4 - N_2 - H_2 , d) materiál usazený na filtru (SiCl_4 - N_2 - H_2), e) vlákna vyrostlá v reaktoru na pozici $z = 150 \text{ mm}$ v experimentu (Si - N_2 - H_2), f) materiál připravený amonolýzou SiCl_4 , g) materiál připravený amonolýzou SiCl_4 po tepelném zpracování (1400°C , 5 hodin, N_2 - H_2 atmosféra).

Obr. 5. Změna stupně přeměny (a) a velikosti měrného povrchu produktu (b) v závislosti na z v experimentu Si - NH_3 - N_2 .

НИТРИДЫ И ОКСИНИТРИДЫ КРЕМНИЯ, ПРИГОТОВЛЕННЫЕ В ВЫСОКОНАПОРНОЙ ПЛАЗМЕ

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Догорающую азотоводородную плазму использовали для пиролиза и азотирования SiCl_4 и свободного кремния. В закрытом реакторе с выдержкой 0,1 с были приготовлены материалы с разной степенью азотирования, зависящей прежде всего от экспозиции активного азота. Этому соответствует более высокая степень азотирования у неподвижной фазы (продукты на стенах реактора) и при добавке безводного аммиака в реактор.

При использовании тетрахлорсилана в качестве сырья образовался в реакторе волокнистый материал (вискеры) параметром волокна ниже $1 \mu\text{m}$ и длиной нескольких сот μm , который представляет собой смесь α и β видоизменений нитрида кремния с миноритной примесью свободного кремния.

Азотированием дисперсионного кремния в присутствии аммиака образуется в неподвижной фазе α - Si_3N_4 . Время взаимодействия уносимой фазы с активным азотом оказывается для достижения высокой степени азотирования недостаточным.

Приготовленные материалы подвергались химическому анализу с помощью метода высокотемпературной экстракции, состав фаз исследовался при помощи абсорбционной ИК спектроскопии и рентгенографической дифрактометрии. Методы выделяют достаточным совпадением результатов и обнаруживают повышенную реактивность аморфных ультрадиспергированных материалов, получаемых в виде уносимой фазы.

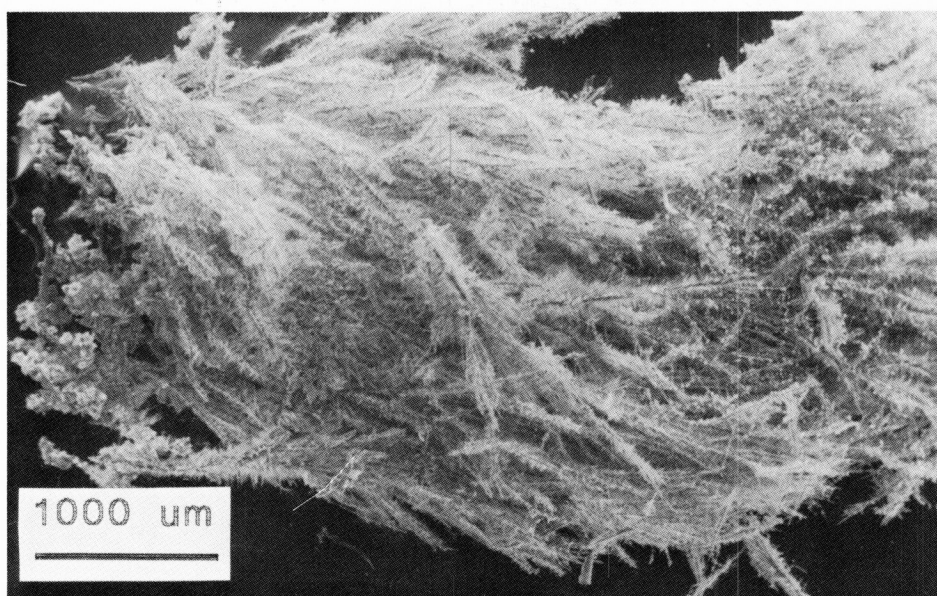
Рис. 1. Схема эксперимента и изображение генератора плазмы: F_1 – проток катодом, F_2 – проток анодом, F_3 – дозатор SiCl_4 или Si , F_4 – выход газов, F_5 – дозатор NH_3 , I – переменная длина канала, f – взвешенный слой, c – холодильник.

Рис. 2. SEM фотосъемки волокон Si_3N_4 , образовавшихся в реакторе во время эксперимента с SiCl_4 - N_2 - H_2 .

Рис. 3. Рентгеновская дифрактограмма волокон, образовавшихся в реакторе во время эксперимента с SiCl_4 - N_2 - H_2 в сопоставлении со стандартами JCPDS: $\circ$ β - Si_3N_4 (Nr. 33-1110), $\triangle$ α - Si_3N_4 (Nr. 9-250), $+$ кремний (Nr. 5-565).

Рис. 4. ИК абсорбционные спектры стандартов и полученных материалов: а) α - Si_3N_4 стандарт, б) β - Si_3N_4 стандарт, с) волокна, образовавшиеся в реакторе в положении $z = 675$ мм в эксперименте SiCl_4 - N_2 - H_2 , d) материал, осевший на фильтре SiCl_4 - N_2 - H_2 , e) волокна, образовавшиеся в положении $z = 150$ мм в эксперименте (Si - N_2 - H_2), f) материал, приготовленный амонизацией SiCl_4 , g) материал, приготовленный амонизацией SiCl_4 после термической обработки (1400°C , 5 часов, N_2 - H_2 среда).

Рис. 5. Изменение степени превращения (а) и размера удельной поверхности продукта (б) в зависимости от z в эксперименте Si - NH_3 - N_2 .



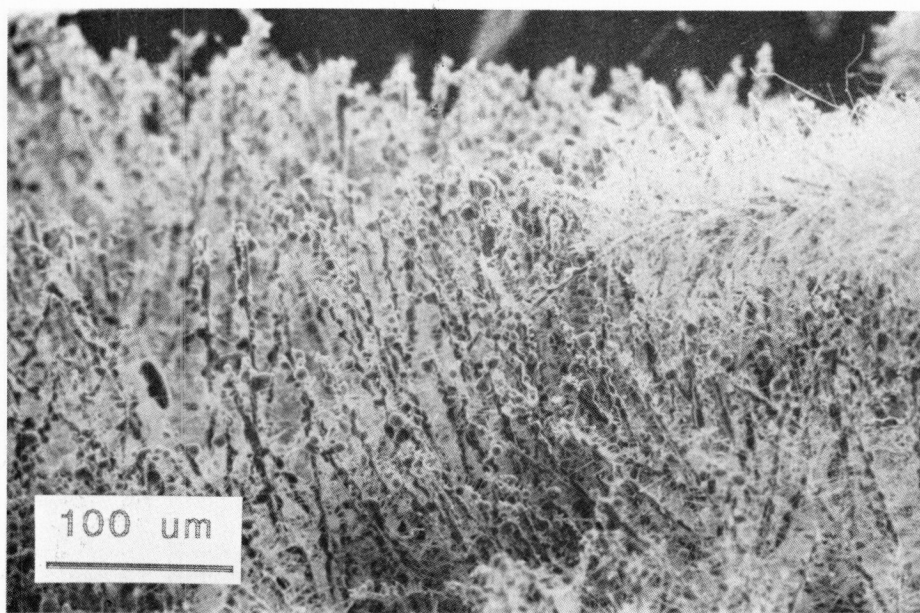


Fig. 2. SEM picture of the Si₃N₄ whiskers grown in the reactor during the SiCl₄—N₂—H₂ experiment.