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Gaseous nature of the reaction of Si–N bond formation in self-propagation high-temperature synthesis of silicon nitride by means of an azide method

Nikolai M. Rubtsov,*[a] Boris S. Seplyarskii,[a] Georgii V. Bichurov,[b] Victor I. Chernysh[a] and Georgii I. Tsvetkov[a]

[a] *Institute for Structural Macrokinetics and Materials Science, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. E-mail: nmrubtss@mtu-net.ru*
[b] *Samara State Technical University, 443001 Samara, Russian Federation. E-mail: shs@samgtu.ru*

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Both solid sodium azide and ammonium chloride react with volatile silicon-containing compounds under external initiation; in the reactions Si–N bond forms as evidenced by detecting the emission spectrum of SiN (C–A^{2}P) radicals.

Kinetic mechanisms of processes of solid-phase combustion (self-propagating high-temperature synthesis, SHS), as well as active intermediates, the reactions of which determine the velocity of a combustion wave have been studied.[1] However, information on the mechanisms is important for the development of methods of controlling the synthesis. The work is aimed at the investigation of specific kinetic regularities of the azide method (azide synthesis) of preparation of inorganic nitrides.[2]

It is known that powders of silicon, boron and aluminum nitrides, their compositions, and the products obtained from these materials manifest a number of important chemical and mechanical properties. These are high hardness, higher values of both heat resistance and resistance to corrosive media, low values of temperature expansion coefficients and density compared to metals and alloys.[1,2] A method of the synthesis of nanopowders of refractory nitrides is the combustion of heterogeneous mixtures containing halogen salts of nitrated element [*e.g.*, ammonium hexafluorosilicate $(NH_4)_2SiF_6$] and sodium azide.[2]

Under high temperatures in the front of a combustion wave the halogen salts decompose to form an active element whose nitride is being obtained. Sodium azide has low decomposition temperature; therefore, it also decomposes in combustion front. Active nitrogen formed in the process evidently reacts with the element formed in the breakdown of the halogen salt to give a desired product. It was expected[2] that the nitridation process that occurs using azide method has gaseous key steps involving active atoms and radicals.

The objective of the work is to reveal gaseous nature of the process of Si–N bond formation in azide synthesis with the use of solid sodium azide (NaN_3), solid ammonium chloride (NH_4Cl), and gaseous dichlorosilane (DCS, SiH_2Cl_2) as precursors.

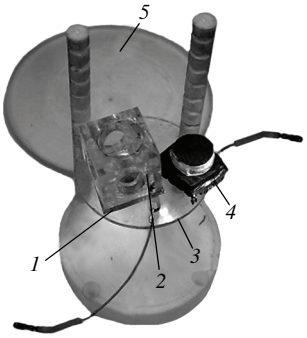

Figure 1 Reaction cell: (*1*) lower titanium electrode; (*2*) Plexiglas skeleton; (*3*) bench insulator; (*4*) upper graphite electrode; (*5*) removable reactor cover.

Experimental procedure allowed recording both formation of solid particles using the scattering of a probe laser beam and optical emission spectra of intermediates of the reaction under investigation. Experiments were performed in a pumped cylindrical quartz reactor. The reaction cell placed in the reactor was composed of upper graphite and lower titanium electrodes fixed in Plexiglas. The Plexiglas skeleton was provided with four orifices for observation, placed in opposition to each other (Figure 1). Thin layer (0.1 g) of the powder of sodium azide or ammonium chloride was placed on the lower electrode.

DCS was initially allowed to bleed into the evacuated reactor up to the necessary pressure. Then, the reaction was initiated with rf discharge (1 W, 5 MHz) at a total pressure of 1–3 Torr or with spark discharge (1 J) at a total pressure of 50–90 Torr. The probe He–Ne laser beam passed through the orifices in reaction cell. The scattering of the probe laser beam with solid particles was recorded through the orifice in the cell located at right angle to the beam by means of a CCD camera. Light emission in the cell due to initiation was focused on the entrance slit of an STE-1 spectrograph with crossed dispersion. Spectra were recorded by means of CCD camera over the interval of 420–900 nm to detect active reaction intermediates. The optical scheme of the spectrograph allowed presenting the spectrum in three intervals (420–540, 500–680 and 620–900 nm) as is seen in Figure 2.

In preliminary experiments, thin layer (0.1 g) of the powder of sodium azide was placed on the lower electrode; DCS was allowed to bleed into the reactor up to 80 Torr. Initiation was performed with a spark discharge. The process described may be considered as a model of preparation of silicon nitride with azide method in the case if gaseous reactions play a decisive role in nitridation process. It was found that the emission spectrum of the spark discharge contains lines of sodium atoms and the band system of electronically excited radicals $C_2(A^3P_g–X^3P_u)$, knocked out of the upper graphite electrode. No evidence for the presence of SiN radicals was obtained. The assignment of the spectrum to C_2 radicals was independently checked by running a spark discharge in the mixture of 80 Torr of DCS and 70 Torr of isobutene (iso-C_4H_8). It is known,[3] that the pyrolysis of isobutene is accompanied by the formation of C_2 ($A^3P_g–X^3P_u$) in a considerable amount. Sodium azide was placed on the

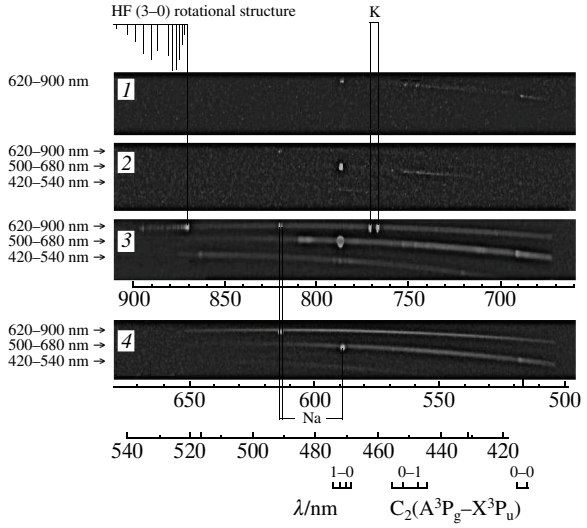

Figure 2 Emission spectra of spark discharge and rarified flame: (*1*), (2) spark discharge in the system solid NaN_3–DCS (80 Torr); (*3*) reference spectrum of the initiated ignition of 10% iso-C_4H_8 in O_2 in the presence of 2% CF_2Cl_2 at total pressure of 80 Torr (it was used for wavelengths calibration), rovibrational structure of HF (3-0)[6] band is clearly defined in the spectrum; (*4*) spark discharge in the system solid NaN_3–DCS (80 Torr) + iso-C_4H_8 (70 Torr). Sodium atom doublets at 589 and 820 nm are clearly defined in the spectra.

lower electrode. In the experiments lines of sodium atoms and much more intense bands of C_2 radicals caused by the pyrolysis of isobutene were observed in the emission spectrum of spark discharge (Figure 2).

Therefore, under spark initiation, the reaction of silicon-containing radicals with active nitrogen was not detected.

However, as is seen in Figure 3 (spectrum *4*) under conditions of rf discharge in 1.5 Torr of DCS over NaN_3 the band system of electronically excited SiN radicals (C–A^2P)[4] is observed in emission spectrum. It means that the reaction of active intermediates of DCS pyrolysis with active nitrogen formed in

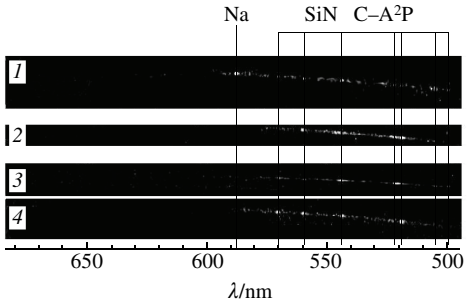

Figure 3 Emission spectra under initiation of the systems DCS + NH_4Cl and DCS + NaN_3 with spark and rf discharges. (*1*) DCS (70 Torr) + NH_4Cl, spark discharge; (*2*) DCS (1.5 Torr) + NH_4Cl, rf discharge, the spectrum was recorded immediately after switching on a discharge; (*3*) DCS (1.5 Torr) + NH_4Cl, rf discharge, the spectrum was recorded 2 min after switching on a discharge; (*4*) DCS (1.5 Torr) + NaN_3, rf discharge.

decomposition of NaN_3 occurs; the reaction results in Si–N bond formation.

It is known that the plasma enhanced reaction of gaseous monosilane (SiH_4) and ammonia (NH_3) is widely used in semiconductor technology to produce silicon nitride films.[5] Therefore, in the following experiments, ammonium chloride as an alternative to sodium azide was used for nitrogen source. In the experiments under spark initiation the formation of intensive clouds of superdispersed particles detected by light scattering was observed for each specific spark discharge. Note that the intensity of laser beam scattering was many times higher than for the use of sodium azide as a nitrogen source. It means that the concentration of solid particles formed is markedly significant. It was found that the emission spectra of both the spark discharge and rf discharge contain weak lines of impurity sodium atoms and the band system of electronically excited radicals SiN (C–A^2P) (Figure 3, spectra *1*–*3*). Therefore, under conditions of both spark and rf discharges (in case of NH_4Cl as nitridation agent), the reaction of the silicon-containing fragments of DCS with nitrogen-containing intermediates occurs under external initiation, giving rise to formation of Si–N bonds as evidenced by detecting the emission spectrum of SiN (C–A^2P) radicals. However, kinetic mechanisms of the reactions for the two nitrogen sources (NaN_3 and NH_4Cl) are most likely to be different.

The investigations performed demonstrate fundamental possibility of gaseous mechanism of nitridation of the volatile silicon-containing compound at room temperature involving Si–N radicals; therefore, the formation of silicon nitride by means of azide method may occur in gaseous phase providing the synthesis of nanopowders. Ammonium chloride shows higher nitridation ability than sodium azide. It means that the role of reagents containing ammonium group under real conditions of azide synthesis is important on the initial stages of the process at lower temperatures. Evidently, the means of initiation of the azide synthesis may have marked influence on the composition of gaseous products and intermediates.

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