*Journal of Applied Mechanics and Technical Physics, Vol. 42, No. 3, pp. 427–430, 2001*

# CONDENSATION OF AN ARGON–MONOSILANE MIXTURE IN A FREE JET

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UDC 533.6.011.8:536.423.4

*A mass-spectrometric study of the condensation of pure* Ar *and a* 5% $SiH_4$ + 95% Ar *mixture in a supersonic pulse free jet in a broad interval of stagnation pressures is performed. It is shown that a small content of monosilane in argon leads to the fact that condensation in the mixture begins at lower stagnation pressures than in pure argon; at high stagnation pressures, mixed argon–silane complexes are formed in the flow. The sequence of the stages of cluster formation in the mixture is determined.*

To manufacture solar elements, thin-film transistors, image sensors, and other devices and apparatuses, it is necessary to develop the methods of forming the thin layers of materials over the large areas of substrates with a high rate of their deposition. One of the intensely developed methods of film deposition is the jet method [1–7], which permits one to create thin layers of materials with very high deposition rates over the large areas of substrates. There are several modifications of the jet method whose basic element is a low-density free supersonic jet formed upon adiabatic extension of a gas from a jet source into a vacuum chamber. The jet of gaseous reactants in a gas-carrier is activated thermally, by an electron or photon beam and the discharge or thermal plasma. The active particles formed in the flow ensure the high rate of chemical reactions both in the flow and on the surface. The Si, C, AlN, GaN, etc., films were produced by means of this method.

As is known, upon cooling of a gas caused by its extension, condensation with the formation of small clusters and then with the formation of coarser particles [8] is possible. The presence of clusters and coarser particles, especially in the plasma, exerts a strong effect on gas–phase processes and the processes of film deposition [9–12]. The gas-carrier of silicon from which the main body of silicon-containing films (Si, $SiO_2$, SiC, etc.) forms is monosilane, most often in a mixture with inert gases or hydrogen. The study of monosilane condensation upon its adiabatic extension is of interest.

The goal of the present study is mass-spectrometric measurements of the composition of a molecular beam formed from a supersonic free jet of condensed pure Ar and a 5% $SiH_4$ + 95% Ar mixture.

The work was performed on the complex of gas-dynamic installation LEMPUS of the Novosibirsk State University. To show the presence of clusters, especially mixed ones, a direct method of studying the condensation in free jets, namely, molecular-beam mass spectroscopy, was used [13]. Since the instantaneous flow rate of the gas mixtures under study is high [14], there is the possibility of studying the processes of condensation in a broad range of parameters.

The process of argon condensation in a free jet was first studied to verify the method of diagnostics and compare with the condensation of an argon–monosilane mixture. Figure 1 shows the intensity of signals $I$ of the monomer ions ($m/e = 40$) and dimer ions ($m/e = 80$) measured in a molecular beam separated from the flow of pure argon behind a sound nozzle of diameter $d = 1$ mm versus the stagnation pressure $P_0$. The pressure in a mass spectrometer did not exceed $2\cdot 10^{-5}$ Pa, and the energy of ionizing electrons was 40 eV. The transition to developed condensation is assumed to occur at a pressure corresponding to the maximum of the monomer signal [15]. In this

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0021-8944/01/4203-0427 $25.00

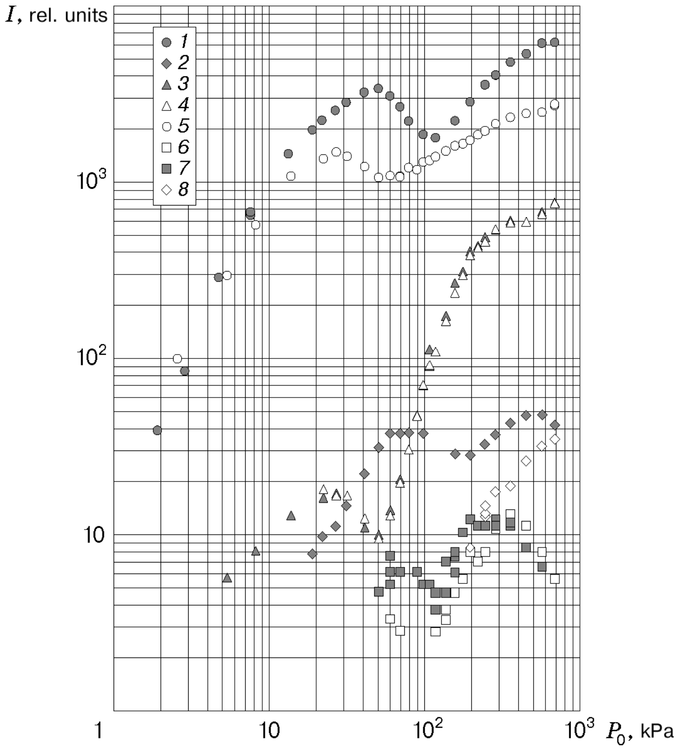

Fig. 1. Intensity of the signals of monomer and dimer ions in pure argon (points 1 and 2) and in a 95% Ar + 5% $SiH_4$ mixture (points 3–8) versus the stagnation pressure for $m/e = 40$ (1), 80 (2), 30 (3), 31 (4), 40 (5), 62 (6), 63 (7), and 80 (8).

case, the maximum is fixed for $P_0 \approx 50$ kPa. It follows from Fig. 1 that dimers appear and, hence, condensation begins at a much lower pressure (of the order of 20 kPa).

One can describe the signal intensity of an argon monomer in a molecular beam as follows. At low pressures, in the absence of condensation, the signal is a linear function of $P_0$. After the onset of condensation, owing to the increase in temperature in the jet, the transition of a part of monomers to clusters and, probably, the skimmer interaction, the signal reaches its maximum and then begins to decrease. The subsequent growth of the signal intensity is due to the process of cluster fragmentation at electron impact. As for a dimer ion of argon, the first maximum is, apparently, explained by the contribution from the dimers formed in the jet and the fragmentation of small clusters, and the repeated growth is also a consequence of the fragmentation of large clusters in this case. The behavior of the curves and the position of the extrema generalized with respect to the parameter $P_0 d^{0.8}$ agrees well with known results [8, 15, 16].

The dependence of the strength of separate signals recorded in a 95% Ar + 5% $SiH_4$ mixture (monomer and dimer of argon, $SiH_2$, $SiH_3$, $Si_2H_6$, and $Si_2H_7$) on the stagnation pressure is obtained under the same conditions. It is necessary to note the same behavior of the signal intensities of the argon monomers in the mixture and pure argon. At low stagnation pressures (lower than 10 kPa), the signals do not practically differ. The difference arises with the onset of condensation. As one should expect, the addition of 5% of monosilane results in the fact that condensation begins at a considerably lower pressure. In addition, the signal of the argon monomers in the mixture is lower than in pure argon under condensation conditions. The signal of the argon dimers in the mixture is recorded at higher stagnation pressures than in pure argon, after the signal of the dimer ions of hydrogenated silicon is generated.

The specific features mentioned above are, apparently, due to the fact that, condensing more rapidly than argon, monosilane contributes to the formation of mixed argon–monosilane clusters. The possibility of occurring such process is shown by Randall and Howard in [17], in which the formation of an $ArSiH_4$ dimer was observed. The transition to developed condensation in the mixture occurs at a pressure of about 25 kPa, which corresponds to the maximum on the curves for monosilane and argon monomers. In the jet of a mixture consisting of a readily condensing impurity and a gas-carrier, a significant part or even the entire impurity can pass to a condensed state at high pressures [16]. In addition, it is known that in a molecular beam, the number of clusters is larger than in a jet because of the different velocity of the transverse scatter of light and heavy particles [18] (in this case, the heavy

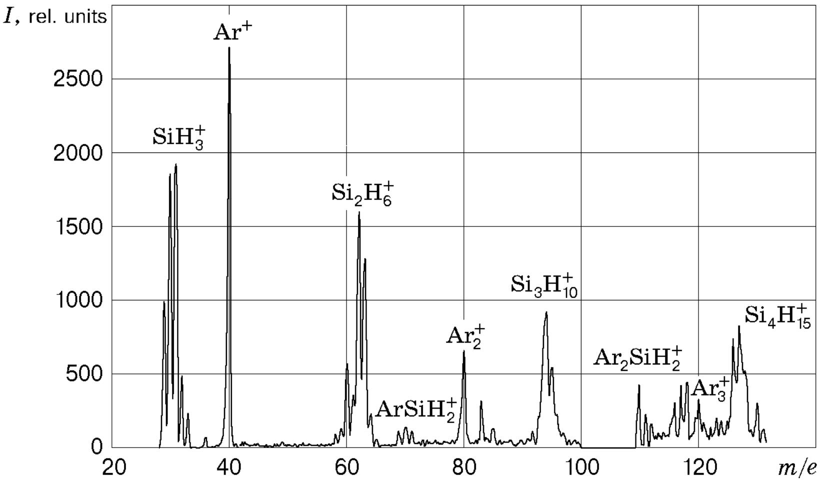

Fig. 2. Mass spectrum of a 95% Ar + 5% $SiH_4$ mixture at $P_0 = 300$ kPa.

TABLE 1

| Monomers | Dimers | Trimers | Tetramers | Pentamers | Mixed clusters | |
|---|---|---|---|---|---|---|
| $Ar^+$ | $Ar_2^+$ | $Ar_3^+$ | $Ar_4^+$ | — | $ArSiH_2^+$, | $ArSiH_3^+$ |
| $SiH^+$ | $Si_2H_4^+$ | $Si_3H_{10}^+$ | $Si_4H_{14}^+$ | $Si_5H_{18}^+$ | $Ar_2SiH_2^+$, | $Ar_2SiH_3^+$ |
| $SiH_2^+$ | $Si_2H_6^+$ | $Si_3H_{11}^+$ | $Si_4H_{15}^+$ | $Si_5H_{19}^+$ | $Ar_3SiH_2^+$, | $Ar_3SiH_3^+$ |
| $SiH_3^+$ | $Si_2H_7^+$ | — | — | — | $ArSi_4H_{13}^+$, | $ArSi_4H_{14}^+$ |

TABLE 2

| Type of components | Fraction of components, % | Type of components | Fraction of components, % | Type of components | Fraction of components, % |
|---|---|---|---|---|---|
| Silane: | | Argon: | | Argon–Silane: | |
| monomer | 55.0 | monomer | 27.10 | $ArSiH_n^+$ | 0.25 |
| dimer | 8.45 | dimer | 0.65 | $Ar_2SiH_n^+$ | 0.42 |
| trimer | 1.60 | trimer | 0.17 | $ArSi_3H_n^+$ + | |
| tetramer | 2.45 | tetramer | 0.21 | $Ar_3SiH_n^+$ | 1.70 |
| pentamer | 2.00 | — | — | — | — |

particles are clusters). Therefore, the abrupt increase in the signals of the monosilane monomers after reaching the minimum is caused by the fragmentation of clusters. The growth of the curve of the argon monomer after reaching the minimum is also caused by the fragmentation of clusters, since otherwise the signal intensity should decrease owing to the stronger effect of the skimmer interaction. The source of argon dimers is likely to be the fragmentation of mixed clusters and large argon clusters.

In the present work, in addition to the indicated ions, a number of silicon-containing argon and mixed ions were detected. Figure 2 shows the ion mass spectrum obtained at $P_0 = 300$ kPa in the range of mass numbers $m/e = 28$–$132$ (in Fig. 2, the signal amplitudes corresponding to $m/e = 41$–$100$ and $m/e > 108$ are increased by tenfold and twentyfold, respectively). Together with argon and monosilane monomers and argon clusters and clusters of the silane series (clusters of hydrogenated silicon), there are mixed silane–argon clusters in the spectrum. The basic components of the clusterized gas mixture activated by electrons are listed in Table 1. The most intense signals correspond to the Ar, $SiH_2$, and $SiH_3$ monomers and the stable splinters of the clusters.

The mass fractions of the components of the gas mixture under conditions of the formation of large clusters ($P_0 = 300$ kPa) are given in Table 2. The ratio of the intensities of argon and monosilane monomers, which corresponds to the initial composition of the mixture ($I_{\mathrm{Ar}}/I_{\mathrm{SiH}_n} \approx 20$) in the absence of condensation, decreases considerably with the development of condensation, reaching the value 0.5 at high pressures. This result shows, first, the expel of a great part of argon monomers from the jet axis because of condensation-heat release and, second, the possible difference between the binding energy of the molecules of different types in the mixed clusters.

The measurement results obtained in the present study allow us to assume the following mechanism of cluster formation in the mixture. At the first stage, monosilane is condensed in a flow. Then, with growth of the acceleration pressure argon begins to be condensed on the monosilane clusters, which serves as the condensation cores, thus forming an "argon coat" around the silane core. As a result, mixed cluster argon–monosilane ions appear in the fragments and the ratio between the argon and monosilane splinters changes. With further rise in the pressure $P_0$, when the impurity components of the mixture turns out to be in a bound state, the condensation of a gas-carrier (argon) begins, which leads to the appearance of the cluster splinters of pure argon.

This work was supported by the Russian Foundation for Fundamental Research (Grant No. 00-03-33021a), the Ministry of Industry, Science and Technologies of the Russian Federation (Grant No. 06-05), and the Ministry of Education of the Russian Federation (Grant No. ZN-217-98).

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