Network visualization and entropy estimation of complex silane plasma chemistry using numerical calculation of rate equation set

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Abstract: A chemical process in typical molecular plasma is complex because hundreds of reactions take place sequentially and simultaneously with spontaneity. Our previous studies revealed that networking of reactions is effective for both visualization of its complexity and following analysis based on methods of complex network science. In this study, keeping on with this network visualization, we propose that quantities of entropy are powerful to clarify its properties between diverse reactions and their spontaneous interactive changes.

Keywords: molecular plasma, complex network, numerical calculation, entropy.

1. Introduction

Plasma that includes molecules and is used in various industrial fabrication tools and reactors for thin-film deposition, dry etching, and so forth [1], typically exhibits complex chemical features. The complexity in such lowtemperature plasma chemistry is fundamentally due to the large number of species in its gaseous phase, like molecules, atoms, radicals, polymers and their charged ions in addition to electrons. Among these species, there are many kinds of reactions in two-body or three-body collisions, other than simple decompositions of molecules and molecular radicals [1,2]. One type of these various reactions is hardly observable as an isolated single event and many of them take place sequentially and simultaneously. In our previous studies, to characterize this mixed ensemble, we used networks or graphs in which nodes are species with edges that link the nodes and represent interactive reactions [3-5], and their topology shows statistical properties of scale-free networks [4,5] and is the basis for dimensionality reduction [4].

Unlike these previous studies, here we replace simple edges that shows presence of reaction pathways with weighted edges based on chemical kinetics, and the resultant network visualization reflects equivalent approaches to numerical calculations with time evolutions in iterative steps [6,7]. It follows that the results shown here are quantitative visualization of reaction complexity. To make use of experiences in our previous study [5], we perform this for SiH₄ low-temperature plasma in which electron temperature is high enough to electron impact dissociation while keeping gas temperature at a low level. Then, we newly introduce the concept of entropy to evaluate the network topology as a quantitative measure of reaction diversity and spontaneity. Actually, the reaction system studied here is non-reversible and non-equilibrium, thev can do non-expansion work in then а thermodynamical point of view [8].

2. Method

Before network visualization, we perform typical numerical calculations of time-varying densities of gaseous species in SiH4 plasma in a zero-dimensional model based on finite difference method [6]. We input all datasets of rate constants for reactions listed in Ref [7], and additionally the model includes diffusion flux to reproduce roughly equivalent conditions to experimental reactors. When species B is the counterpart in a given reaction collision of A, where k is the rate constant, both quantities of density (like [A] for species A) and reaction frequency which are in the form of k[B] are recorded in the calculation. The hypothetical characteristic size of the reactor Λ is 0.1 m and we set diffusion flux in the particle balance equation for [A] as $D[A]/\Lambda^2$ with the diffusion coefficient $D = 6.0 \times 10^{-2} \text{ m}^2 \text{s}^{-1}$ equally for all species. Electron density was constant at 2×10^{15} m⁻³, and gas temperature assumed here was 500 K. Gas pressure was set to fix constant SiH₄ density. After the calculations, we confirmed rough consistency of our numerical results with those in Ref. [7]; the model in Ref. [7] is one-dimensional, with higher accuracy to experiments than in our model, but this rough consistency validates our results shown here in a certain level that is necessary for the following analyses.

When we visualize reaction networks, a node of the graph represents species in the gas phase (like A or B) and reactions as edges which include information of a reaction frequency for each pathway as its width (for instance, for the edge from node A and for the reaction $A + B \rightarrow C + D$, the width is k[B]).

To estimate dispersity and networking of this reaction system, we use Shannon entropy, proposed and used in information theory [9], defined as (in units of bits)

$$H = -\sum_{\mathrm{I}} x_{\mathrm{J}} \log_2 x_{\mathrm{J}} , \qquad (1)$$

where this summation is over all species (J), and x is molar fraction with $\sum_J x_J = 1$. This form of the equation is also found as Boltzmann entropy for perfect gas mixtures at constant pressure and temperature in a thermodynamical point of view [8]. In both cases, the quantities of entropy imply disorder or ambiguous finding of species in a system. We also calculate Shannon conditional entropy [9], given as (in units of bits)

$$H(\mathbf{K}|\mathbf{J}) = -\sum_{\mathbf{K}} \sum_{\mathbf{J}} x_{\mathbf{J}} q(\mathbf{K}|\mathbf{J}) \log_2 q(\mathbf{K}|\mathbf{J}).$$
(2)

 $q(\mathbf{K}|\mathbf{J})$ is production probability of species K, provided that the reactant is J, and $\sum_{\mathbf{K}} q(\mathbf{K}|\mathbf{J}) = 1$ for each species J. From Eq. (2), $H(\mathbf{K}|\mathbf{J})$ indicates ambiguity in selection of next reaction paths, which is weighted by existence probabilities (x) of all species.



Fig. 1. Visualized chemical reaction network of lowtemperature SiH₄ (33.3 Pa) plasma at 4 ms. The red arrows suggest reaction paths linked to SiH₃ as both reactants and products.

3. Results and Discussion

Figure 1 displays the total network of this chemical system at 33.3 Pa of SiH₄ at physical time t = 4 ms. From Fig. 1, for instance, we can easily find one of the main production paths for SiH₃ is

$$SiH_4 + H \rightarrow SiH_3 + H_2, \tag{3}$$

in addition to simple decomposition of SiH₄ by electron impacts. The directed edge from H to SiH₃ was not observed at the very initial phase ($t \sim 0 \text{ ms}$), and this kind of visualization gives us useful suggestions not only for scientific analysis but also technological tuning of parameters.

Figure 2 shows time evolutions of Shannon entropy in various gas conditions. In all cases, entropy increases for this calculation time period due to progresses of decomposition and following reactions, leading to diversity in finding increasing number of species in observation space. To take a closer look, two upward phases of entropy are found in all cases. In the first phase, SiH₄, the initial reactant, is decomposed into various species, which results in very rapid changes in time (< 1 ms). In the second phase, product species of SiH₄ decomposition become reactants for emerging reactions

[5], leading to slower increase of entropy. The case of 3.33 Pa is somewhat particular, since the details in the result indicate that this increase of entropy corresponds to that of vibrational states of SiH₄ and H₂ production.

Figure 3 shows time evolutions of Shannon conditional entropy in various cases. First, we can classify them into two groups. In higher pressure cases, the quantities are higher, whereas they remain in a low level if the pressure is low or H₂ dilution is applied. In this second group, SiH₃ is dominant radicals, favourable for high-quality thin film deposition. The cases in the first group will be beneficial when we select them for polymerization or nano-particle formation. Second, interestingly, unlike the cases of Shannon entropy, the conditional entropy in each case seems to be saturated after 8 ms, or in some cases, decreases inversely. Assumed that this conditional entropy is not the sign of reaction spontaneity but a possible measure for the selection range of energy consumption paths, we can conclude that the complexity enhancement of information flow may stop before the thermodynamical state reaches equilibrium.

This approach based on entropy estimation gives us newly unveiled points of view that differ from the previously developed methods in the category of plasma chemistry. From the literature of thermodynamics and related physical chemistry [8], positive changes of entropy indicates that spontaneous reactions take place, which potentially yield non-expansion (internal) work; this *work* possibly includes the achievement by plasma chemical reactors that is possible only by plasma processes. Further investigation on entropy increments with external and internal parameters will lead to macroscopic merits of plasmas, with our knowledge of details in microstructure that is clarified in network visualization.



Fig. 2. Changes of Shannon entropy in various gas conditions. H₂ dilution in SiH₄ was performed at 33.3 Pa, and the indicator "pp1:2" means partial pressures of H₂ is doubled from SiH₄.



Fig. 3. Changes of Shannon conditional entropy in various gas conditions. Again, the indicators "pp1:2" and "pp1:1" mean H₂ dilution rates for SiH₄.

4. Conclusion

Molecular reaction system in low-temperature plasma is complex, but their quantitative analysis based on numerical calculations can result in informative visualization of this system in network topology. To estimate its complexity with species diversity and reaction spontaneity, we perform calculations of Shannon entropy and Shannon conditional entropy, and they work well to clarify several aspects of events that are veiled or unclear otherwise. There have been several other types of entropy developed in information theory and in thermodynamics, and introduction of these quantities will further enhance our understandings of complex low-temperature plasma.

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6. References

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