

# Diagnostics of Chemically Active Plasma of RF Capacitive-coupled Discharge in $\text{H}_2+\text{SiF}_4$ , $\text{H}_2+\text{GeF}_4$ and $\text{H}_2+\text{BF}_3$ mixtures

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The dependencies of concentration of electrons in chemically active plasma of  $\text{H}_2+\text{A}$  mixtures (where A -  $\text{SiF}_4$ ,  $\text{GeF}_4$ ,  $\text{BF}_3$ ) on  $\text{H}_2/\text{A}$  ratios as well as their emission spectra were investigated in RF capacitive-coupled discharge at a pressure of 1 torr. It was found that with the increase in concentration of fluorides in hydrogen mixture the concentration of electrons decreases; mostly it is observed for  $\text{A}=\text{GeF}_4$  according to its high electron affinity value.  $\text{SiF}$ ,  $\text{GeF}$  and  $\text{GeH}$  radicals as well as atomic hydrogen were registered in emission spectra. The line of  $\text{BF}$  radical is absent.

## 1. Introduction

Determination of internal parameters of chemically active plasma on the basis of volatile fluorides and, in particular, the concentration of free electrons is an actual task due to sufficiently broad practical application of these substances in plasma chemical technologies. For this purpose it is expedient to use the non-contact methods of MW interferometry and emission spectroscopy. At the same time the plasma should be maintained by the discharge of the same type. In this work this approach was used for investigation of chemically active plasma of  $\text{H}_2+\text{SiF}_4$ ,  $\text{H}_2+\text{GeF}_4$  and  $\text{H}_2+\text{BF}_3$  mixtures sustained by RF capacitive discharge.

## 2. Experiment and discussion

Investigations were conducted in RF capacitive-coupled discharge with frequency of 13.56 MHz at a pressure of 1 torr and power of 500 Wt delivered to discharge.  $\text{H}_2/\text{SiF}_4$  ( $\text{GeF}_4$ ,  $\text{BF}_3$ ) ratio changed from 8 to 36. A generator, tuned to the frequency of 35.7 GHz, was used as the source of probing radiation of MW interferometer. The level of power of reference and probing signals was equal to 65 MWt. The emission spectrum of chemically active plasma was investigated in the range of 350 ÷ 800 nm using HR4000CJ-UV-NIR emission spectrometer.

It was found that under the realized experimental conditions the concentration of free electrons of plasma in pure hydrogen plasma was equal to  $n_e = (1.5 \pm 0.04) \cdot 10^{12} \text{ cm}^{-3}$ . While adding the fluorides to hydrogen plasma its decrease is observed which depends on the ratio of mixture components. The lowest value of  $n_e$  takes place for  $\text{H}_2+\text{GeF}_4$  mixture where it is equal to  $(9.8 \pm 0.04) \cdot 10^{11} \text{ cm}^{-3}$  at the ratio of  $\text{H}_2/\text{GeF}_4 = 13.5$ . With this ratio the values of  $n_e$  in  $\text{H}_2+\text{SiF}_4$  and  $\text{H}_2+\text{BF}_3$  mixtures negligibly differ from each other and are equal to  $(1.1 \pm 0.04) \cdot 10^{12} \text{ cm}^{-3}$  and  $(1.2 \pm 0.04) \cdot 10^{12} \text{ cm}^{-3}$ , respectively. The

emission spectra in the same range of reagent ratios were registered for the studied mixtures. Apart from the lines of atomic hydrogen, the lines assigned to  $\text{SiF}$ ,  $\text{GeF}$  and  $\text{GeH}$  radicals were found in the emission spectra of  $\text{H}_2+\text{SiF}_4$  and  $\text{H}_2+\text{GeF}_4$  mixtures. At the same time the line of  $\text{BF}$  radical was not observed in the spectrum of  $\text{H}_2+\text{BF}_3$  mixture. The process of dissociative attachment of electrons is the main channel of energy transmission from electrons into chemical system [1]. Electron affinity is the main molecular parameter characterizing this process. According to quantum-chemical calculations for  $\text{GeF}_4$ , the adiabatic electron affinity  $\text{EA} = 1.46 \text{ eV}$  [2] and for  $\text{SiF}_4$  and  $\text{BF}_3$  the value of  $\text{EA}$  is negative [3, 4] which indicates the absence of "attachement" of electron to these molecules within the framework of the used basis set. Our results conclusively indicate high ability of  $\text{GeF}_4$  molecule to attach the electron. This ability is noticeably lower for the molecules of two other fluorides. Should we assume that after the process of electron attachment the dissociation of molecules follows with formation of corresponding radicals, the fact of absence of the line of  $\text{BF}$  radical in the spectrum of  $\text{H}_2+\text{BF}_3$  mixture can indicate that the "attachement" of electron to  $\text{BF}_3$  is less manifested than in the case with attachement to  $\text{SiF}_4$ .

## 3. References

- [1] H.Massey. Negative Ions. Cambridge University Press. 1976.
- [2] Q.Li, G.Li, W.Xu, Y.Xie, H.F.Schaefer. J.Chem.Phys. **111** (1999) 7945.
- [3] R.A.King, V.S.Mastryukov, H.F.Schaefer III. J.Chem.Phys. **105** (1996) 6880.
- [4] D.J.Grant, D.A.Dixon, D.Camaioni, R.G.Potter, K.O.Christie. Inorg.Chem. **48** (2009) 8811.