LASER INDUCED GAS BREAKDOWN IN REACTIVE MIXTURES CONTAINING HALIDES OF BORON AND SILICON: DIAGNOSTICS AND MODELING

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1. INTRODUCTION

Plasma-chemical approach is used for synthesis of various gaseous, liquid, and solid substances since 1960th [Vurzel 1970]. Nowadays, the method of plasma enhanced chemical vapor deposition (PECVD) is widely used for production of thin films, protective coatings, carbon-based nanostructures, high purity isotopic materials, biomaterials, and many other products. Plasma for PECVD is typically created in various electrical discharges; e.g. DC and AC glow discharges or discharges operated at audio (10-20 kHz), radio (13.56 MHz), and microwave (2.45 GHz) frequencies. Laser induced plasma (LIP) is rarely used to deposit materials from the gas phase and this work aims at reviving interest to this latter technology and showing its potential.

We run two pilot LIP experiments in reactive gas mixtures. First, LIP is excited in BCl_3 or BF_3 plus H_2 or CH_4 to evaluate the efficiency of deposition of solid boron and boron carbide, materials that are largely used for refractory coatings. Second, we investigate a possibility of synthesis of fluorochlorosilanes SiF_xCl_{4-x} (x = 1, 2, 3) by LIP induced in SiF_4+$SiCl_4$ gas mixtures. Using fluorochlorosilanes with different combinations of F and Cl in the SiF_xCl_y molecule may add flexibility in processes of silicon deposition and etching. The gases used and solid deposits are analyzed by optical emission spectroscopy (OES) and IR and mass spectrometry (MS). We also model the laser induced plasma by performing *static* equilibrium chemistry calculations to see whether desired reaction products are thermodynamically favorable and *dynamic* calculations of the expanding plasma plume to see how and where the products form.

2. EXPERIMENTAL

A sketch of the experimental set-up is shown in **Figure 1**. A Nd:YAG laser (1064 nm, 15 ns pulse width, 800 mJ pulse energy, 5 Hz repetition rate) is focused inside a reactor to create a plasma in the reactive gas mixture. The reactor consists of two coaxial quartz cylinders; it is loaded with gases shown in **Table 1**.

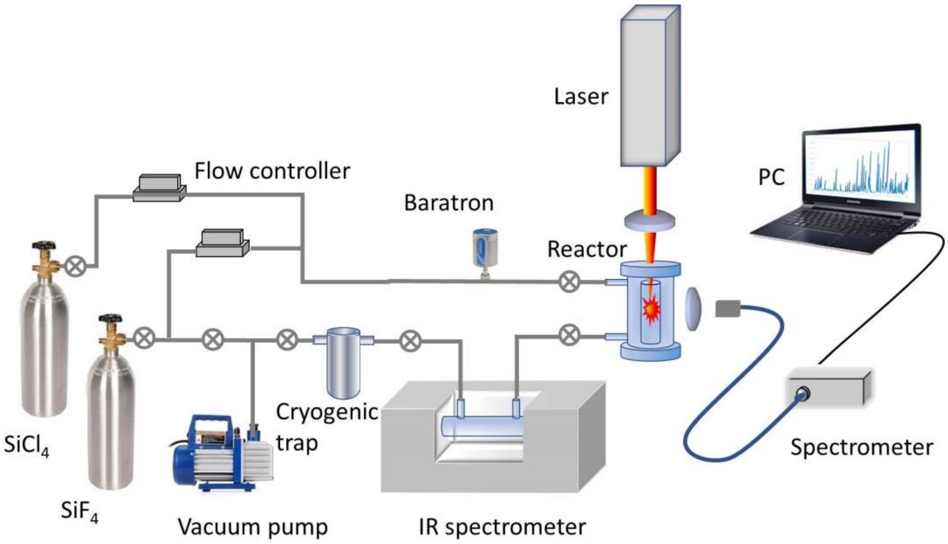

Figure 1. Experimental setup for PECVD with LIP and corresponding diagnostics.

The plasma is analyzed by OES while the gas mixture inside the reactor is analyzed by IR and MS both before and after the laser action. Solid residues that are deposited on the walls of the inner cylinder are studied by the reflectance FTIR.

BCl_3	BF_3	$SiCl_4$
H_2: BCl_3=10:1	H_2: BF_3=3:1	SiF_4
H_2: Ar: BCl_3=10:10:1	H_2: Ar: BF_3=3:4:1	$SiCl_4$: SiF_4=1:2.65
H_2: BCl_3: CH_4=9:1.5:1	H_2: BF_3: CH_4=9:1.5:1	$SiCl_4$: SiF_4=2.65:1

Table 1. Gases used in LIP experiments.

A numerical experiment on the gas mixtures was performed by first calculating the plasma equilibrium composition as a function of its temperature using open source software [CEARUN] and second, calculating plasma dynamic parameters using a hydrodynamic code [Shabanov 2018] and the same open source software embedded in this code.

3. Results and discussion

3.1. Halides of boron

The amount of the deposit enough for further analysis is collected with mixture BCl_3+H_2+CH_4. The deposit is identified as boron carbide and carbon (soot) by the reflectance FTIR technique. No deposit except soot (in methane) is observed for mixtures with BF_3. The OES spectra of gas plasma show efficient formation of BH, BX (X=Cl, F), and C_2 (in methane). The IR spectra of the reaction products after the laser action show the presence of the molecules already identified by OES plus precursors

(BCl_3, BF_3, CH_4), radicals ($HBCl_2$), and new derivatives (C_2H_2, B_2H_6). MS analysis confirms the presence of these molecules.

The results of experiment well agree with the predictions of both static and dynamic simulations. The model does not predict formation of solid boron or boron carbide from mixtures of BF_3 with hydrogen or methane, and same is observed in experiment. For mixtures of BCl_3 with the same gases, condensed phases of B, C, and B_4C form that is detected in experiment and predicted by the model. Some results of laboratory and numerical experiments are reproduced in **Figure 2**.

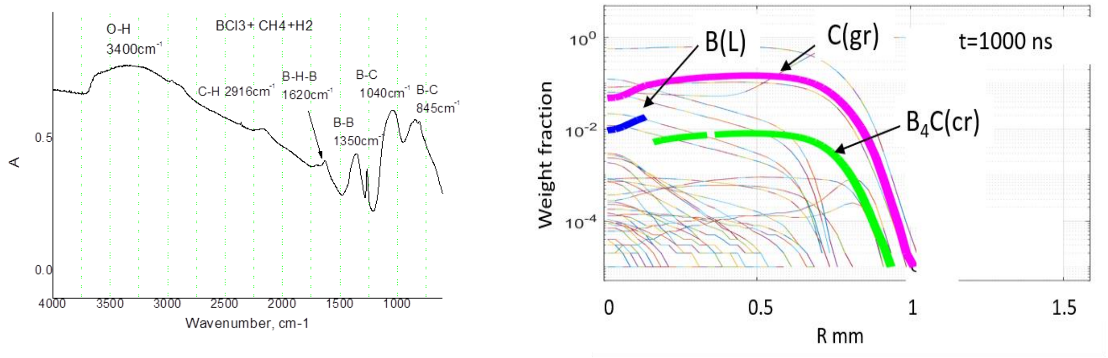

Figure 2. Left panel: IR absorption spectrum of solid deposit from the mixture H_2:BCl_3:CH_4=9:1.5:1. Right panel: dynamic 1D simulation of breakdown in 50% (CH_4+Ar) + 50% (BCl_3+H_2) gas mixture; snapshot of species concentrations at 1 μs of the plasma plume propagation time.

3.2. Halides of silicon

Generation of fluorochlorosilanes in the mixture of SiF_4 and $SiCl_4$ via the reactions 3SiF_4 + $SiCl_4$ = 4 SiF_3Cl (1160 kJ/mole); SiF_4 + $SiCl_4$ = 2SiF_2Cl_2 (307 kJ/mole); and SiF_4 + 3$SiCl_4$ = 4$SiFCl_3$ (71 kJ/mole) is thermodynamically unfavorable due to the positive Gibbs formation energy ΔG_{298} (in parentheses). These reaction products can easily be obtained in LIP after the plasma cools down and formerly dissociated atoms reassemble back into molecules. This is confirmed both experimentally and theoretically. As before, the plasma is analyzed by OES why the reactants and products by IR and MS. Optical emission spectra show the formation of SiCl, SiF, and $SiCl_2$ along with all expected elemental species and their ions. The IR spectra of plasma products reveal strong absorption bands and, hence, efficient formation of sought-after fluorochlorosilanes SiF_2Cl, $SiFCl_2$, $SiFCl_3$, SiF_3Cl, and SiF_2Cl_2 (**Figure 3.**, left panel); the MS measurements convincingly confirm this finding. From IR absorption measurements, a 60% maximum yield of fluorochlorosilanes is estimated for the mixture SiF4:SiCl4=1:1; the dominant specie is SiF_2Cl_2. The same high yield for SiF_2Cl_2 is predicted theoretically based on data generated by ab initio calculations of thermodynamic properties of fluorochlorosilanes. The result of the dynamic simulation for the mixture SiF_4:$SiCl_4$=1:1is exemplarily given in **Figure 3.**, right panel.

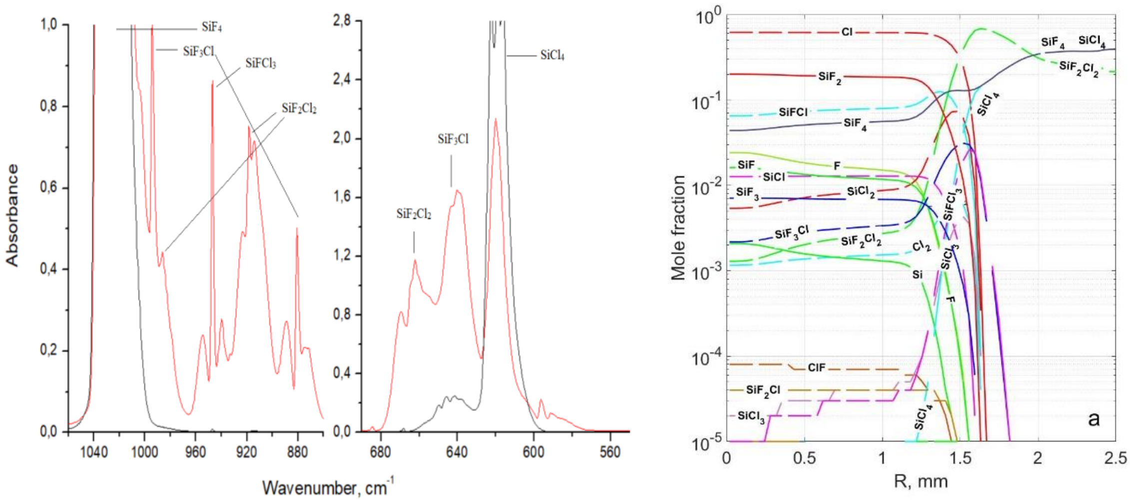

Figure 3. Left panel: IR absorption spectra of mixture $SiCl_4$:SiF_4=1:1 before (black) and after (red) the 40 min laser irradiation. Right panel: dynamic 1D simulation of breakdown in SiF_4: $SiCl_4$ = 1:1 gas mixture; snapshots of the plasma composition after the 5.0μs propagation time.

4. Conclusions

For the BX_3-containing systems (X=Cl, F), the creation of solid deposits of B, BH_3, and C (in mixtures with methane) is observed by LIP excited in the reactive gas mixtures BX_3+H_2 and BX_3+H_2+CH_4. The dynamic calculations of the expanding plasma plume predict coexisting condensed phases of boron, boron carbide, and graphite in mixtures with BCl_3. The maximum concentration of the condensed species is reached in peripheral plasma zones. Overall, the calculations and experimental results imply that PECVD-LIP can be a promising technique for efficient conversion of gaseous precursors into solid elemental constituents and their compounds.

For the SiX_4-containing systems (X=Cl, F), gaseous fluorochlorosilanes SiF_3Cl, SiF_2Cl_2, $SiFCl_3$ can efficiently be synthesized by LIP induced in SiF4+SiCl4 precursor gas mixtures. It is found that the total yield of fluorochlorosilanes in LIDB plasma comprises 60%, with ~30% of SiF_2Cl_2. The equilibrium chemical model adequately predicts the composition of LIP. The dynamic calculations of the expanding plasma plume also agree with experiment and show that fluorochlorosilanes form in peripheral plasma zone and show high sensitivity toward the mixture stoichiometry and plasma temperature.

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6. REFERENCES

[Vurzel 1970] F. B. Vurzel, L. S. Polak, *Ind. Eng. Chem.*, 62 (1970) 8.

[CEARUN] https://cearun.grc.*nasa*.gov (accessed on 15 October 2020).

[Shabanov 2018] S. V. Shabanov, I. B. Gornushkin, *Appl. Phys. A*, 124 (2018) 716.