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SCANNING CALORIMETRY IN GAS DISCHARGE PLASMAS

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Abstract: The scanning mode of calorimetry in plasmas is developed to study both kinetic and energetic characteristics of surface chemical reactions and catalytical processes which result in heat release at the surface under plasma exposure. The main goal of scanning calorimetry in plasmas is to determine separately a contribution of each kind of heat transfer to the total heat flux from a plasma to a surface. A heat of reaction of plasma chemical etching the silicon single crystal is measured experimentally by comparison of temperature dependencies of heating rate for two calorimeters having different surface properties.

Keywords: plasma surface interaction, transient temperature, heat of reaction.

1 INTRODUCTION

Mechanisms and kinetics of the most of heterogeneous chemical processes in plasmas are studied not sufficiently, but this topic is of great interest for plasma processing. It is common knowledge that any chemical transformation is attended by heat release or absorption. The heat power is directly connected with the rate of chemical reaction. Transient temperature measurement after discharge ignition can be the basic way to get some information about the interaction of chemically active plasmas with surfaces [1]. Measurement of heat power and its temperature dependence gives knowledge which is inaccessible for any other techniques. An energy transformation is the subject of the calorimetric technique. The novel variant of calorimetry in plasmas is developed to reconstruct the structure of the total heat flux from a plasma to a surface. In this report the experimental study of plasma stimulated exothermic chemical reaction using the differential mode of scanning calorimetry is discussed.

2 SCANNING CALORIMETRY IN GAS DISCHARGES

A key procedure of scanning calorimetry is to determine the temperature dependence of a heat power transferred to the calorimeter which is immersed in a gas discharge plasma. Temperature dependence of an integral heat flux to the surface is determined using continuous temperature scanning and laser measurement of both calorimeter temperature T(t) and its time derivative dT/dt (i.e., heat power heating the calorimeter). Thin plate of monocrystalline semiconductor (Si, GaAs) is used as calorimeter and temperature-sensitive Fabry-Perot cavity for transient temperature measurement. Temperature scanning is realized via heating the calorimeter by plasma itself. The separation of an integral heat flux into components and the identification of their nature are based on the existence of individual temperature dependence of transferred power for every mechanism of heterogeneous relaxation of energy. The explicit form of the dependences of heat fluxes on the calorimeter temperature allows to determine the effects of linear and nonlinear heat sources on the heating rate. The second feature of every mechanism is the limiting stage of heat transfer (generation, diffusion or surface kinetics). Physical background and experimental procedures of this technique were described in detail previously [2,3].

3 EXPERIMENTAL

The study of temperature kinetics of silicon crystal after discharge ignition in CF_4 +O_2 is performed in the cylindrical quartz reactor 20 cm in diameter and 45 cm in length. RF discharge (13.56 MHz) is excited by external electrodes. Gas pressure is 50 Pa, a total gas flow is kept at about 100 sccm. RF power applied to discharge is 260 W. A 0.5-mm-thick silicon single crystal (2.5x2.5 cm) is placed at the reactor axis on the holder which consists of two quartz rodes 1.5 mm in diameter. The radiation of the 5 mW He-Ne laser at wavelength of 1.15 μm is directed to the crystal through the quartz window. This wavelength is in the range of transparency of silicon. Reflected radiation passes back through the same window and is detected with germanium photodiode and registered with PC. A crystal covered with 0.3-μm-thick SiO_2 film serves as inert reference calorimeter since the etch rate of SiO_2 is 30 times less then the etch rate of silicon. The crystals under study have an uncovered surface in part, their covered parts are used to measure the temperature without the crystal thickness variation, it is

necessary to use laser interferometric technique. The mass loss for each crystal is determined by weighing before and after plasma exposure. Experimental setup is schematically shown in Fig.1.

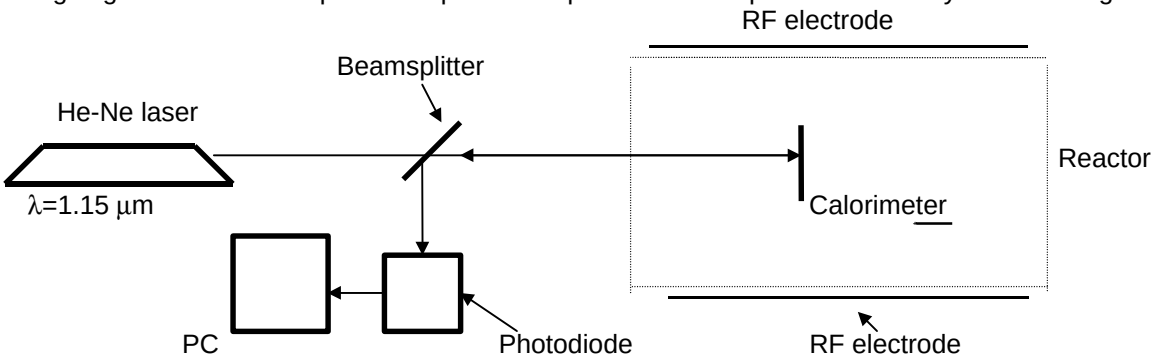

Figure1. Experimental setup for calorimetric measurements in a low-pressure plasma.

When the temperature of calorimeter changes in time after discharge ignition in reactor, the oscillations of the reflectance are observed. These interference oscillations are used to determine the non-stationary temperature T(t) of calorimeter and the time derivative dT/dt at any moment of heating or at any instant temperature. The main characteristics of laser interferometric thermometry of plates made of semiconductors and dielectrics in full detail are discussed in recent review [4].

4 RESULTS AND DISCUSSION

The temporal dependences of temperatures of both chemically inert and active calorimeters in gas discharge in CF_4 +10%O_2 mixture are shown in Fig.2. Heating kinetics for inert calorimeter (lower curve) is described by simple relaxation expression

$$T(t) = T_g - (T_g - T_o)\cdot\exp(-t/\tau) \quad (1)$$

where T_g is the gas temperature in discharge, T_o is the initial temperature of calorimeter, τ is the characteristic time, $\tau = c\rho h/2\alpha$, c is the specific heat capacity of silicon, ρ is the density, h is the thickness of crystal, α is the heat transfer coefficient. Temperature evolution described by Eq.(1) results from the action of heat transfer mechanism involving conductive transport of the energy containing in translational and rotational degrees of freedom of molecules and collisional relaxation of this energy on the surface. Convective heat transfer in our experimental conditions plays no role.

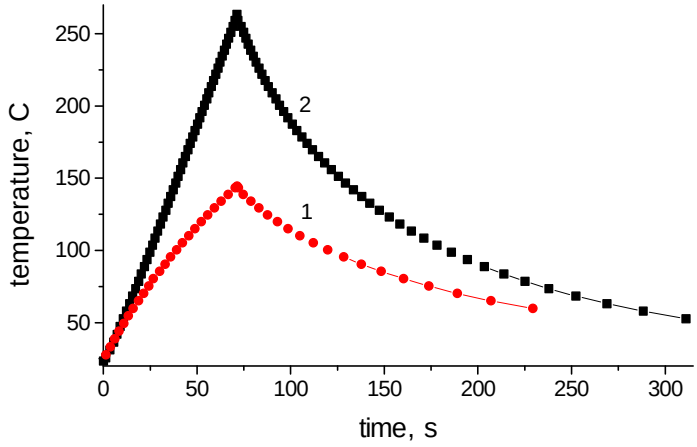

Figure 2. Time dependence of calorimeter temperature after discharge ignition and shutdown (at 70 s).
Both inert (1) and active (2) calorimeters are in a fluorine-containing plasma at 50 Pa. The measures of uncovered surface at the active calorimeter are 1.6x2.5 cm on every side of crystal. The reference (inert) calorimeter is totally covered by SiO_2 thin film for etch protection.

Cooling kinetics of both calorimeters is given by identical expression where T_g equals to the temperature of reactor walls (which is higher than room temperature by approximately 15 to 25 ^{0}C) and T_o is the calorimeter temperature at the moment of discharge shutdown. Some deviations from the simplest relaxation kinetic curve take place at temperatures higher than about 200 ^{0}C due to radiative heat loss which is ignored by expression (1).

Heating kinetics of active calorimeter (upper curve) contrasts sharply with that of inert calorimeter and demonstrates the self-acceleration in time, this phenomenon can be explained as thermal explosion: both reaction rate and heat release increase in temperature due to the positive feedback formation, this results in temporal acceleration of heating rate [5].

The rise in the gas temperature after discharge ignition is 4 or 5 orders of magnitude shorter than the heating of calorimeter. When the discharge is withdrawn, the decay-time for gas temperature is in a matter of milliseconds, whereas the crystal temperature decreases in the cource of a few hundred seconds. Because of this, the transient heating or cooling kinetics for calorimeter is registered under steady-state conditions in reactor. Heat fluxes from plasma and heat release in exothermic processes do not depend explicitly on the time. There is for our conditions, so-called quasistationary process, the only explicit dependence of any heat sources on the surface temperature. So, heat balance equations for both inert (i) and active (a) calorimeters under plasma conditions may be written as

$$D_i \equiv c\rho h\cdot(dT_i/dt) = 2\alpha(T_g - T_i) - D_R \qquad (2)$$

$$D_a \equiv c\rho h\cdot(dT_a/dt) = 2\alpha(T_g - T_a) - D_R + H\cdot\delta\cdot Z\cdot\exp(-\Delta E/kT_a) \qquad (3)$$

where D_R is the power density (W/cm^2) of thermal radiation, which is practically identical for both calorimeters due to small thickness of oxide film as compared with emitted wavelengths at temperatures under study; H (J/g) is the heat of reaction; $\delta = \Delta S/S_0$, ΔS is the area of uncovered etched surface, S_0 is the total area of calorimeter surface; Z (g/s·cm^2) is the pre-exponential factor in the rate constant; ΔE is the activation energy and k is the Boltzmann's constant. Instead of $H\cdot\delta\cdot Z\cdot\exp(-\Delta E/kT_a)$ we will use further the more simple $H\cdot(dm/dt)$, where m (g/cm^2) is the mass of unit area of calorimeter.

Graphical representation of equations (2) and (3) is given in Fig.3 and Fig.4 as temporal and temperature dependences of heating and cooling rates for both calorimeters. By determining time derivative dT/dt from transient temperature T(t), it is possible to plot the dependence of dT/dt on the time as well as on the calorimeter temperature (the last representation is similar to the well known coordinate-momentum plane widely used in mechanics).

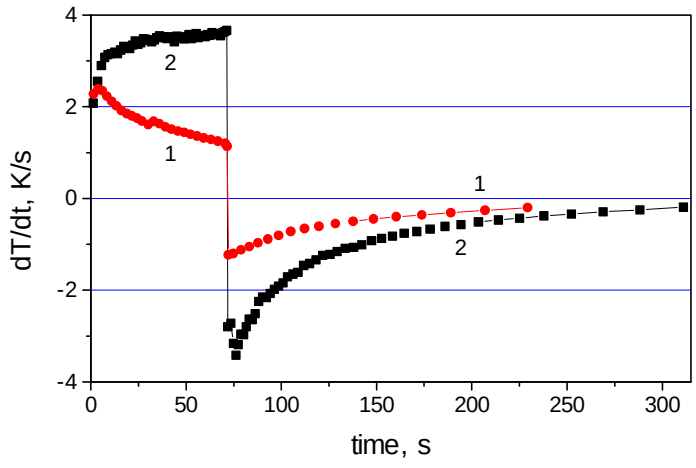

Figure 3. Temporal dependence of heating (dT/dt > 0) and cooling (dT/dt < 0) rates of inert (1) and active (2) calorimeters in CF_4 +10%O_2 plasma (up to t = 70 s) and in a gas after discharge shutdown when the sudden drop in gas temperature takes place.

Differentiating the experimental curve $T_i(t)$ and using a least-square curve-fitting program, we obtain $dT_i/dt \approx 2.47 - 8.9\cdot10^{-3}\cdot T_i(^0C)$, K/s and $D_i(T_i) \approx 0.196 - 6.86\cdot10^{-4}\cdot T_i(^0C)$, W/cm^2. From this data it is easily to determine the neutral gas temperature in our weakly ionized plasma $T_g \approx 280$ ^{0}C, characteristic time for calorimeter heating $\tau \approx 112$ s, and heat transfer coefficient $\alpha \approx 3.4\cdot10^{-4}$ W/cm^2·K. As the conditions under study correspond to the continual heat exchange between gas and calorimeter ($Nu\cdot Kn << \gamma$ [6], where Nu is the Nusselt's number, Kn is the Knudsen's number and γ is the

accomodation coefficient for thermal accomodation of energy of translational degrees of freedom), surface properties have no effect on the heat transfer coefficient α. The value of α determined for inert calorimeter may be used also for active calorimeter. Temperature dependence of radiative heat loss is determined using a cooling kinetics and separation of total heat removal into two parts connected with molecular thermal conductivity (linear item) and thermal radiation (nonlinear item).

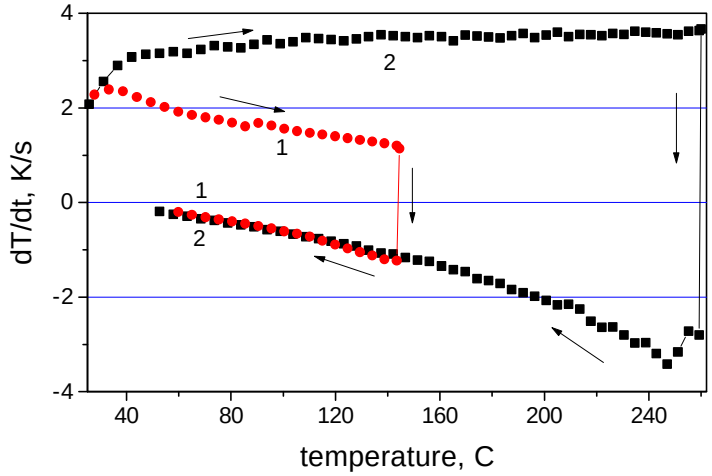

Figure 4. Temperature dependence of heating (dT/dt > 0) and cooling (dT/dt < 0) rates of inert (1) and active (2) calorimeters in CF_4 +10%O_2 plasma (up to t = 70 s) and in a gas after discharge shutdown. Trajectories for both calorimeters in cooling mode are almost identical.

The resulting expression for the heat of reaction is given by

$$H = \frac{\Delta E}{\Delta m} = \frac{\int_0^t [D_a - 2\alpha \cdot (T_g - T_a) + D_R]dt}{\int_0^t (dm/dt)dt} \qquad (4)$$

where ΔE (J/cm^2) is the energy density transferred to the calorimeter due to plasma chemical reaction on the surface, and Δm is the mass loss of crystal after its exposure to plasma. The dependence of mass loss on the parameter $\delta = \Delta S/S_0$ has a linear form with the slope $dm/d\delta \approx 3.85$ mg (Fig.5).

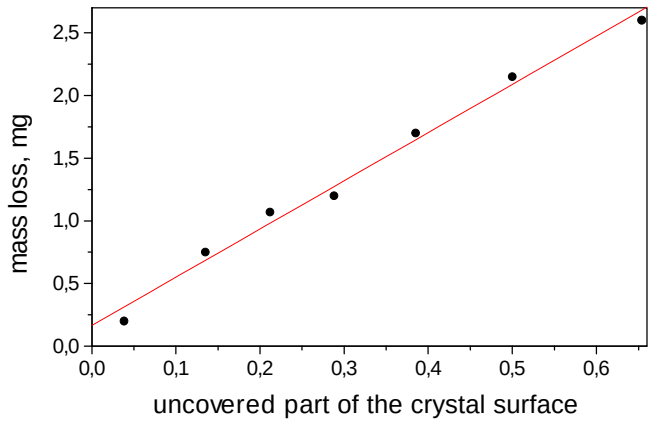

Figure 5. Mass loss due to single silicon crystal plasma etching for 0.47-mm-thick calorimeters (2.5x2.5 cm) with different parts of surface uncovered by protective oxide film. The residence time of calorimeter in the plasma is 70 s.

The dependence of additional heat energy E with respect to inert calorimeter on the parameter δ has also a linear form with the slope $dE/d\delta \approx 95.5$ J. Using data presented in Fig.5 and Fig.6, we obtain the

value of heat of reaction H = dE/dm ≈ 24.8 kJ/g for /100/ oriented P-doped (n~10^{15} cm^{-3}) silicon crystal. The specific heat of etching reaction may be defined as the energy released when the single silicon atom is removed from the surface to the discharge and equals to H_0 =H·m_0 ≈ 7.1 eV, where m_0 is the mass of silicon atom.

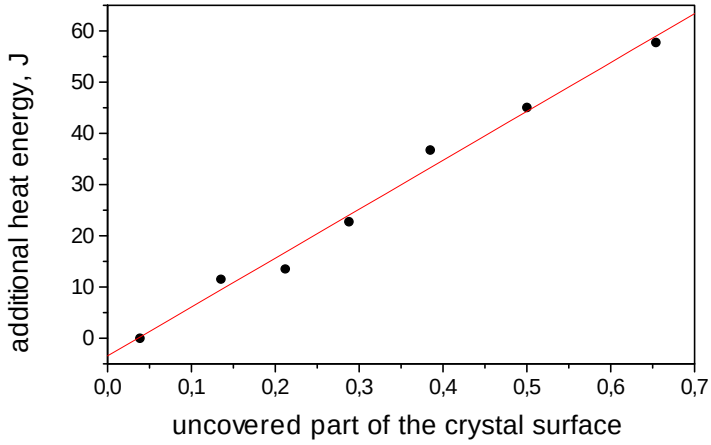

Figure 6. Additional heat released in exothermic chemical reaction and absorbed by 0.47-mm-thick calorimeters (2.5x2.5 cm) with different parts of surface uncovered by protective oxide film. Exposure time is 70 s.

By the use of expression (4) we obtain H = 23 ± 2 kJ/g averaged over 6 experiments with different δ in the range from 0.14 to 0.65. Temperature dependence of heat release rate in chemical reaction is determined using the Eq.(3) and shown in Fig.7 for two studied crystals with different values of δ.

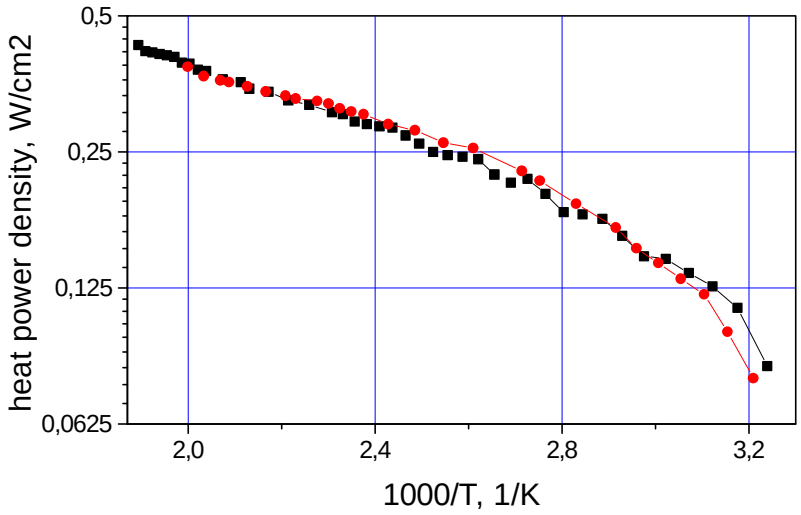

Figure 7. Temperature dependence of heat power density (watts per unit area of uncovered surface) released due to the exothermic surface chemical reaction between fluorine atoms and silicon crystal in CF_4 +10%O_2 plasma at 50 Pa. Curves for crystals with δ =0.5 and 0.65 are shown.

This dependence is plotted in Arrhenius' coordinates and consists of two approximately linear sections: the first is located in the region from 10^3/T ≈1.9 to 2.7 K^{-1} and characterized by the activation energy of ΔE ≈ 0.06 eV, and the second at 2.7 to 3.2 K^{-1} has a value ΔE ≈ 0.13 eV. Pre-exponential factor Z is also determined from the plotted data.

The value of the heat of reaction determined experimentally is essentially less than the enthalpy ΔH of exothermic reaction Si + 4F → SiF_4 which is equal to approximately 55 kJ/g at 25 ^{0}C [7] and H_0 ≈16 eV/atom. This discrepance probably results from non-equilibrium conditions in plasma surface chemical interaction or non-isothermal measurement mode in our experiment. To determine the

temperature dependence of heat of reaction in scanning regime, it is necessary to measure accurately the instant mass loss $\Delta m(t)$ of calorimeter and heat power released due to chemical reaction.

Analogous result was obtained previously [1] in our experiments on the etching of polymer film in oxygen plasma: heat of this exothermic reaction measured with scanning calorimetric technique was almost 2 times less than the enthalpy of complete oxidation of polymer with the formation of H_2O and CO_2. Since there are no identical measurements in chemically active plasmas elsewhere, it is now impossible to compare experimental data of different laboratories and techniques.

5 CONCLUSION

So, scanning calorimetry gives the possibility to determine experimentally some basic (both kinetic and energetic) parameters of plasma chemical reaction on the solid surface. As a first approximation, there was no attention in consideration made above to additional endo- and exothermic processes connected with chemical reaction under study. It is necessary in the future to estimate an energetic role of: a) excited particles desorbing from the surface, b) entropy change when a solid matter is transformed into a gas, and c) the thermodynamic work of the produced volatile compounds opposite the external pressure. Full-scale knowledge on the value of different effects of a plasma on the heat balance of solids immersed to the fluxes of charged, excited and chemically active particles are absent now. Development of scanning calorimetric technique and its application to investigate some commonly used chemical processes in plasma surface interaction is of interest for plasma processing and is now under way. An attempt to transfer the goals and methods from classical calorimetry [8] into non-equilibrium multicomponent plasma and adaptation of measurement technology to research the kinetics and mechanisms of heat exchange seems to be a promising problem.

6 ACKNOWLEDGEMENTS

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