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PHYSICAL
ELECTRONICS

Formula for Determining the Surface Temperature of the Fullerite Consisting of a C_{60}–C_{70} Mixture from a Mass Spectrum

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Abstract—A calculation is used to show that the kinetic energy of particles in the sublimation flux of the fullerite consisting of a mixture of C_{60} and C_{70} that is caused by a pulsed laser beam is significantly higher than the interparticle interaction energy, i.e., $kT \gg E$. This finding is used to deduce a formula to determine the fullerite surface temperature from mass spectrum data on the basis of gas-kinetic equations and the data obtained by the Knudsen method for a fullerene effusion flux. The calculated and experimental results are compared. Specific features are noted for the procedure of measuring the temperature. Examples for calculating the surface temperature for other heating methods are given.

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INTRODUCTION

Surface- or matrix-assisted laser desorption ionization-time of flight (SALDI-TOF or MALDI-TOF) laser mass spectrometry (MS) is used to study the component composition and content in complex structures. This method is based on time-of-flight analysis of the structures evaporated/ionized under the action of a pulsed laser pulse [1].

This method is widely used to analyze organic components [2, 3], superconducting structures, ceramics [4], and (metal) fullerenes [5, 6]. However, the most important parameter of the evaporation/ionization process, i.e., the sample surface temperature (which determines the sublimation, polymerization, and destruction of crystallites and molecules in a structure), remains usually undetermined. If necessary, researchers develop specific techniques to measure or control temperature using additional devices.

The authors of [2, 3] used energy calculations, where they took into account the material and laser beam parameters, to determine the surface temperature during laser mass spectrometry of organic components. The measurements were controlled with the well-known IR thermometer and photometric measurements of a certain region.

Obviously, this brings up the question: How the process of determining the surface temperature can be simplified? More radically, how this problem can be solved using a measured mass spectrum and no additional devices or techniques for measurements?

We assume that the mass spectrum that has the lines of particles from an evaporation flux contains information on the temperature of the surface from which the particles were evaporated. To determine the surface temperature, we calculated the ratio of the data from mass spectra of two particles. As a result of transformation of an expression obtained for an evaporation flux, we found a relation between the surface temperature and the mass spectrum data. Below, we comprehensively describe this technique to determine the surface temperature.

In this work, we study the products of electric arc synthesis (fullerenes) and the mass spectrum of the fullerite made of their mixture, which includes the most stable structures (C_{60}, C_{70}). These objects appear as a result of a sequence of processes with a large number of particles. These processes are as follows: the synthesis of fullerenes in an electric arc discharge, the collection of fullerene soot from the discharge chamber walls, the extraction of fullerenes into a solvent, and the filtration of fullerenes from an amorphous component. As a result, the fullerite that is introduced into a mass spectrometer forms on a substrate after the removal of the solvent. Conditions for the formation of an ion flux from the fullerite surface are created on this surface under the action of a series of laser pulses and an accelerating voltage. This flux is electronically detected as a mass spectrum. These processes are well known [6].

The purpose of this work is to find an analytical relation between the mass spectrum parameters and the temperature of the surface of the fullerite consist-

Coefficients A_j and B_j and the evaporation fluxes of fullerenes C_{60} (I_{60}) and C_{70} (I_{70}) calculated by Eqs. (2)–(4) at a given sample surface temperature

Fullerite C_j	A_j, K [6]	B_j [6]	j-fullerene current I_j (A) at sample temperature T (K)		
			400	500	1000
C_{60}^{*}	8738 ± 472	10.85 ± 0.76	0.793×10^{-14}	0.166×10^{-9}	0.064
C_{70}^{**}	9768 ± 774	11.23 ± 1.49	0.468×10^{-16}	0.321×10^{-11}	0.013

* The temperature range of experimental measurements is 560–990 K.

** The temperature range of experimental measurements is 650–904 K.

ing of a mixture of C_{60} and C_{70} formed by the electric arc method.

For SALDI-TOF MS, we calculate the sublimation of the fullerite placed in a mass spectrometer, e.g., AutoFlex (Bruker, Germany).

THEORETICAL ANALYSIS

The fullerite consists of high-strength but weakly interacting fullerenes and is characterized by noticeable sublimation of fullerenes at ~400 K [7].

To estimate the sublimation process quantitatively, we perform a calculation for one of the mixture components. The following physical constants of the C_{60} fullerite are used [6]: the intermolecular bond length is $L\{C_{60}–C_{60}\} = 2R \approx 10$ Å and the binding energy is $E_0 = 1.6$ eV. At a temperature $T \sim 10^3$ K ($kT \approx 0.086$ eV), a sublimation flux forms from the fullerite surface. The interfullerene distance in this flux is $2R^* \approx 100$ Å, and the fullerene–fullerene interaction energy is determined from the relation $E = E_0(R/R^*)^{\alpha}$, where $\alpha > 4$, since the van der Waals forces appears during the polarization of interacting clusters [8]. After substituting numerical values into this relation, we found that the kinetic energy of C_{60} (and C_{70}) particles in the flux substantially exceeds the pair interaction energy, i.e., $kT \gg E$. Allowing for this finding, we calculate the process of fullerite evaporation.

For simplification, sublimation is represented in the form of a general flux of j fullerenes. The following relationships, which are usual for an ideal gas, are satisfied in the near-surface space of the fullerite: the flux of chaotic (thermal) motion of sublimated particles is $I_j = 0.25en_jv_js$ and the vapor pressure is $p_j = n_jkT$, where n_j is the particle concentration in the gas phase. From these relationships, we obtained the equality $p_j = 4kTI_j(ev_js)^{-1}$, where s is the evaporation surface, k is the Boltzmann constant, T [K] is the fullerite surface temperature, $v_j = [8kT(\pi m_j)^{-1}]^{0.5}$ is the average particle velocity, $m_j = 12n_jm_p$ is the mass of the conventional jth fullerene with n_j carbon atoms, and m_p is the proton mass. After simplifications and the substitution of the numerical values in the sublimation flux of j fullerenes, the pressure is determined from the equality

$$p_j = 8.236 \times 10^{-6} I_j (es)^{-1} (Tm_j)^{0.5}. \quad (1)$$

Equation (1) gives an analytical relation between the sublimation parameters. This is the well-known Hertz–Knudsen equation written for j fullerenes. The further transformations of Eq. (1) are related to the use of the dependence of the partial pressure in the flux on the kind of mixture particles (C_{60}, C_{70}) at a given flux temperature T.

If the evaporation surface area is $s = 10^{-6}$ m^2, we substitute the fullerene C_{60} and C_{70} masses into Eq. (1) and find the partial pressures of the flux components,

$$p_{60} = 63.8 T^{0.5} I_{60}, \quad (2)$$

$$p_{70} = 68.9 T^{0.5} I_{70}. \quad (3)$$

Depending on surface temperature T^* in a mass spectrometer, the fullerene evaporation flux at saturated vapor pressure p_j has the following form, as in the case of other materials [6, 9]:

$$\log p_j = -A_j/T^* + B_j, \quad (4)$$

where constants A_j and B_j for the jth fullerenes (C_{60}, C_{70}) where determined by the Knudsen method of effusion [6]. We assume that the temperature in the fullerene evaporation flux in Eqs. (1)–(3) and the surface temperature of the ion flux, which is formed with the accelerating voltage, in Eq. (4) are the same, $T = T^*$.

For some surface temperatures, we performed calculations and found the currents of fullerene C_{60} and C_{70} ions accurate to 3% at the numerical values of coefficients A_j and B_j [6]. The calculation results are given in the table. It is seen that, at a temperature of 400 K, the ratio of the fluxes of fullerenes C_{60}/C_{70} (I_{60}/I_{70}) is more than two orders of magnitude and that this ratio decreases with increasing temperature.

Using the tabulated data, we determined the logarithm of the ratio of the C_{60} to C_{70} ion current. The results of calculating $\log\{I_{60}/I_{70}\}$ as a function of the surface temperature for three given temperatures are presented in Fig. 1 as line a, which extrapolates the calculation to a wide temperature range. Two points b in Fig. 1 illustrate the experimental data from [10], which will considered in detail in the final section of the work.

According to the calculation results, the points located in line a correspond to equilibrium sublimation. For the points located above or below the equilibrium line, the number of fullerenes C_{60}/C_{70} in the flux exceeds the equilibrium value.

An equation for the line of equilibrium sublimation from the mixture fullerite surface, i.e., line *a*, is analogous to Eq. (4) and has the form

$$\log(I_{60}/I_{70}) = D/T - E, \quad (5)$$

where the thermodynamic coefficients for the mixture fullerite were determined using line *a* in Fig. 1 ($D = 1032$, $E = 0.35$).

After transformations and the substitution of the numerical values of the coefficients for the fullerite in Eq. (5), we derived Eq. (6). Specifically, when the product of arc synthesis in the form of a mixture of fullerenes C_{60} and C_{70} is sublimated, the fullerite surface temperature as a function of the ratio of the fullerene currents I_{60}/I_{70} in a mass spectrometer is determined from the formula

$$T = 1032/[0.35 + \ln(I_{60}/I_{70})]. \quad (6)$$

Equation (6) has a singularity at $I_{60}/I_{70} = 1$, i.e., when the fluxes are the same. In Fig. 1, this case is indicated by the point of intersection of equilibrium line *a* with the abscissa. This singularity manifests itself at a fullerite surface temperature $T_0 \approx 2950$ K.

The relative error of calculating the temperature was determined using functional dependence (6) and the errors of the arguments according to the relationship [11]

$$\begin{aligned}\delta_T = \{[0.35 + \log(I_{60}/I_{70})]\ln 10\}^{-1} \\ \times [\delta_{60} + \delta_{70} + \delta_1 + \delta_2],\end{aligned} \quad (7)$$

where δ_{60} and δ_{70} are the relative errors of measuring the intensities in the mass spectra of C_{60} and C_{70} fullerenes, which are obtained from the ratio of the absolute error of measuring the peak of a fullerene; $\delta_1 = 2$ ppm is the instrument intensity error according to the specifications of the device [12]; and δ_2 is the error related to the rounding of the parameters in semiempirical formula (6). As is seen from Eq. (7) and Fig. 1, the error of calculating the temperature is lower at a temperature $T < 1000$ K. The substitution of numerical values into Eq. (7) gives the relative error of determining the temperature ($\delta_T \approx 1$–3%).

Formula (6) was deduced and is used to measure the surface temperature of the fullerite made of a mixture of C_{60} and C_{70} fabricated by the electric arc method if the conditions characteristic of an ideal gas are met in the fullerene sublimation flux. When using Eq. (6), it is necessary to take into account that fact that the fullerite made of a mixture of C_{60} and C_{70} represents an open system and consists of components that differ in the evaporation intensity. This specific feature will be considered in more detail further, during an analysis of the experimental results [10].

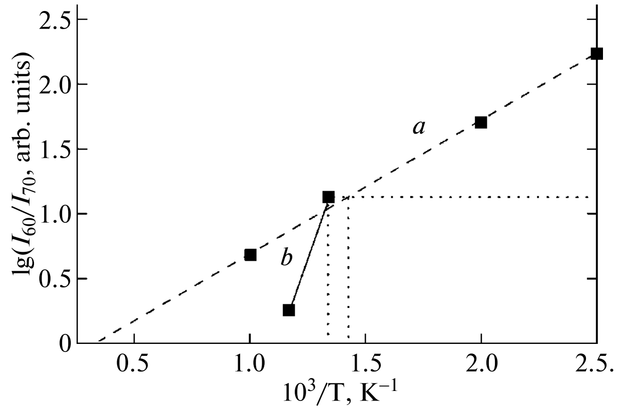

Fig. 1. Ratio of the currents (peaks) of fullerenes C_{60} to C_{70} $\log(I_{60}/I_{70})$ vs. temperature $10^3/T$ (K^{-1}). (*a*) Line plotted from the tabulated data and (*b*) line plotted with the data from [10].

COMPARISON OF THE CALCULATED AND EXPERIMENTAL RESULTS

To test Eq. (6), we use the data on *b* from [10] (this is the only available source that is related to the essence of the process under study), where the mass spectra of a carbon condensate after secondary condensation are presented. The primary condensate was formed during ohmic heating of a graphite (99.99% purity) rod. Secondary evaporation of particles from the layer several microns thick that was deposited by the Knudsen method from a W ribbon was performed under the action of a KrF laser. Ionization and the mass spectrum of a sublimation flux at a temperature of 500 and 600°C were obtained using an ArF laser.

According to the *b* data in Fig. 1 from [10], the ratio of the mass-spectrum peaks at the point obtained at the cell temperature ($T_{\max} = 773$ K) is $C_{60+}/C_{70+} = 12$. As follows from Eq. (6), this ratio of the peaks C_{60+}/C_{70+} is achieved at a temperature $T_1^* = 721$ K, and the experimental temperature is higher than the calculated value by $\Delta T_1^* = 52$ K. The second point for the *b* data from [10] was obtained at a temperature $T_{\max} = 873$ K, which corresponds to $C_{60}+/C_{70}+ = 2.1$. The calculation by Eq. (6) for this ratio of the peaks yields $T_2^* = 1536$ K, and the experimental temperature is higher than the calculated value by $\Delta T_2^* = 663$ K.

Note that the authors of [10] gave the maximum; the real temperatures are likely not to correspond to these temperatures, since the cell temperature changed during measurements. Our estimation given below also indicates this specific feature, and the real deviations of the calculated values from the experimental temperatures are $\Delta T_1 < 52$ K and $\Delta T_2 > 663$ K. These deviations are related to the fact that relatively high evaporation of the light component (C_{60}) of the spectrum as compared to component C_{70} takes place

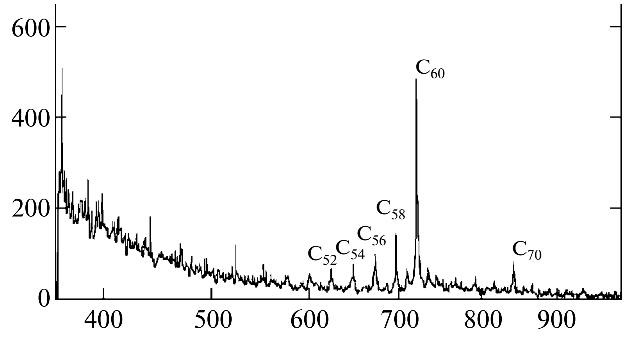

Fig. 2. Mass spectrum of electric arc discharge fullerenes formed during the action of a 5-kV Ar^+ ion beam [12].

when the sample surface temperature specified in an experiment is stabilized. Therefore, the ratio of the currents in the denominator of Eq. (6) decreases, which leads to a fictitious increase in the temperature to be determined, and the difference between the calculated and experimental results increases (this difference is larger at a high temperature).

Using the data on *b*, we performed an estimating calculation. According to Eq. (6), the fullerene C_{60} sublimation intensity at a temperature of 773 and 873 K is 1.25×10^{15} and 23×10^{15} particles/s. The sublimation flux from the fullerene C_{70} surface at the same temperatures is 0.125×10^{15} and 3.4×10^{15} particles/s, respectively. The calculation showed that the fraction of C_{60} in the sublimation flux is significantly higher than that of C_{70}. At every next measurement in the sublimation flux, the fraction of C_{60} decreases and the fraction of C_{70} and the calculated temperature increase. In measurements, it should be taken into account that a 10-μm-thick layer of fullerite C_{60} on an area $s = 1$ mm^2 contains $N = 1.44 \times 10^{15}$ particles at its usual molecular density [6].

For temperatures of 773 and 873 K, the ratios of the sublimation intensities are $I_{60}/I_{70} = 10$ and 6.76, respectively, and the points corresponding to these temperatures fall in line *a* of Eq. (6) for equilibrium sublimation.

CALCULATIONS FOR OTHER HEATING METHODS

The results of time-of-flight mass spectrometry of the mixture fullerite upon heating by an ion or electron beam are presented in [13]. Figure 2 shows the time-of-flight mass spectrum of the mixture fullerite formed by the electric arc method. This mass spectrum was obtained during the action of a beam of positive argon ions Ar^+. In Fig. 2, the ratio of the fullerene peaks is $\{C_{60}/C_{70}\} = 7.3$. With allowance for the analysis of the data in [10] performed earlier and Eq. (6), this ratio is reached at a surface temperature $T_{Ar^+} \le$ 850 K.

To study the mass spectrum of the fullerite, we also used an electron beam. The ratio of the fullerene peaks here is $\{C_{60}/C_{70}\} \approx 50$, which corresponds to a sample surface temperature $T_e \le 500$ K according to Eq. (6).

Using an MX-1320 mass spectrometer, the authors of [14] heated the substrate of the mixture fullerite by an electric current. A mixture fullerite sample was formed on the substrate in the form of an Au filament 0.3 mm in diameter from several drops of a benzene solution of arc synthesis fullerenes. The sample was heated after the solvent was removed according to a certain technique. The sample temperature was determined from the electric current used to heat the substrate. The experiments on the Au filament showed that the ratio of the fullerene currents C_{60}/C_{70} calculated by Eq. (6) for a temperature $T \approx 400$ K is close to the temperature determined experimentally.

CONCLUSIONS

Equation (6) was deduced using physical laws (ideal gas, gas-kinetic equations, Hertz–Knudsen equation) and the well-known physical parameters of the material (intermolecular bond length, binding energy in crystallite) and was experimentally supported.

According to this equation, the evaporation flux depends on the surface temperature and is independent of the heating method and the substrate material.

The proposed technique of determining the surface temperature has advantages for studying nanolayer samples. The relation between the components of such samples changes substantially in every following measurement. The advantage of the suggested technique consists in the fact that the measurement of the sample surface temperature does not need an IR device the readings of which are to be corrected with allowance for photometric equilibrium for a given material surface.

Some of the materials from this work were presented in abstract [15].

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