Comparison of different substrates for laser-induced electron transfer desorption/ionization of metal complexes

A A Grechnikov[1,5], V B Georgieva[2], N Donkov[3], A S Borodkov[1], A V Pento[4], Z G Raicheva[2] and Tc A Yordanov[2]

[1]Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of
 Sciences, 19 Kosygin str., 119991 Moscow, Russia
[2]Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences,
 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
[3]Emil Djakov Institute of Electronics, Bulgarian Academy of Sciences,
 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
[4]Energomashtekhnika Ltd, 123 Vernadskogo pr., bl. 2, 119571 Moscow, Russia

E-mail: grechnikov@geokhi.ru

Abstract. Four different substrates, namely, graphite, tungsten, amorphous silicon (α-Si) and titanium dioxide (TiO_2) films, were compared in view of the laser-induced electron transfer desorption/ionization (LETDI) of metal coordination complexes. A rhenium complex with 8-mercaptoquinoline, a copper complex with diphenylthiocarbazone and chlorophyll A were studied as the test analytes. The dependencies of the ion yield and the surface temperature on the incident radiation fluence were investigated experimentally and theoretically. The temperature was estimated using the numerical solution of a one-dimensional heat conduction problem with a heat source distributed in time and space. It was found that at the same temperature, the ion yield from the different substrates varies in the range of three orders of magnitude. The direct comparison of all studied substrates revealed that LETDI from the TiO_2 and α-Si films offer a better choice for producing molecular ions of metal coordination complexes.

1. Introduction
Matrix-free laser desorption/ionization of organic and bioorganic molecules has been a subject of extensive studies in the last decades. This technique is based on using specially prepared substrates absorbing laser radiation as emitters of ions of chemical compounds. The substrate assists the laser-induced desorption/ionization of the analytes preliminary deposited onto the substrate surface, so that this technique is usually referred to as surface-assisted laser desorption/ionization (SALDI) [1]. A variety of inorganic materials in the form of powders, monolithic plates or thin films have been studied as possible substrates for SALDI; it has been found that only a few selected substrates have the ability to promote strongly the ion formation. Among them, graphite and silicon materials have been and still are the most commonly used as ion emitters.

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[5] To whom any correspondence should be addressed.

Most results reported on SALDI have been obtained with basic compounds, which are detected as protonated molecules. The ionization efficiency of protonation strongly depends on the analyte molecules gas-phase basicity of [2]. SALDI ensures the detection of highly basic compounds at an attomolar level (10^{-18} mol) [2], but chemical compounds with low basicity could not be ionized by SALDI. Recently, we demonstrated that laser-induced electron transfer desorption/ionization (LETDI), a novel variant of SALDI [3,4], is applicable for determination of chemical compounds with low basicity. In LETDI, the ionization is based on electron transfer from the excited adsorbed analyte molecule to the substrate. However, understanding of the detailed LETDI mechanism still requires further studies.

In this report, we compare the analytical performance of various substrates, including tungsten, graphite, amorphous silicon (α-Si) and titanium dioxide (TiO_2) films, for the laser-induced electron transfer desorption/ionization of metal coordination complexes. Previous studies recognized the important role of laser-induced surface heating for ion emission in traditional variants of SALDI [5,6].The focus of the present work is on the investigation of the thermal effects on the ionization efficiency in LETDI.

2. Experimental

The scheme of the experimental setup was described in detail in [7]. The setup consisted of a mass spectrometer, a Nd:YAG laser oscillating at higher harmonics and recording equipment.

The mass spectrometer was a laboratory-built, linear, turbopumped time-of-flight mass spectrometer with a 0.70 m flight tube. All measurements were performed in the positive ion detection mode. A diode-pumped Nd:YAG laser (RL02.355, ELS-94, Moscow) with near-diffraction limited beam quality, 0.35 ns pulse duration, was operated at 300 Hz. A frequency-tripling crystal yielded a 355 nm laser pulse of about 50 μJ. The laser pulse energy was varied using an attenuator.

Amorphous silicon (α-Si) films were deposited on monocrystalline silicon by standard RF sputtering of Si in a low-pressure (8×10^{-2} Pa) Ar atmosphere. The thickness of the deposited film was approximately 0.5 mm.

The titanium dioxide TiO_2 films were deposited on monocrystalline silicon by e-beam evaporation of TiO_2 powder (working pressure of 3×10^{-3} Pa). The thickness of the deposited film was approximately 0.35 mm.

The pyrolytic graphite plate and tungsten foil were obtained commercially (Baum-Lux, Moscow).

A rhenium complex with 8-mercaptoquinoline and a copper complex with diphenylthiocarbazone were synthesized according to the well-known procedures [8,9]. Chlorophyll A (magnesium coordination complex with chlorine) was obtained by acetone-based extraction from leaf samples according to the procedure in [10]. The complexes obtained were dissolved in the appropriate solvents and deposited onto the substrates using electrospray deposition.

3. Results and discussion

The four studied substrates have different UV absorptivity, thermal conductivity and specific heat capacity. Thus, the first step of the thermal effects investigations was to determine the dependencies of the surface temperature on the fluence of the incident laser radiation for each substrate. Because of the small size of the laser-induced heated area and the short lifetime of the state with high temperature, the experimental determination of the surface temperature under laser irradiation is a complex and laborious task. An easier approach for estimating the surface temperature consists in numerically solving the problem of heat conductivity with a space and time distributed heat source. This approach is well known to yield good agreement with the experiments [11-13].

The parameters necessary for calculations were determined as follows. The absorption of radiation by the material is described by Bouguer's law:

$$I(z)=I_0 \exp(-\alpha z) , \tag{1}$$

where $I(z)$ describes the change in the incident radiation intensity with the depth z; z is directed normally to the irradiated surface; α is the absorbance. The temporal dependence of the laser pulse power W is described as:

$$W(t,z) = W_0 exp\left(-\left(\frac{t-2\tau}{\tau/2}\right)^2\right) exp(-\alpha z). \qquad (2)$$

The normalization condition for a given surface energy density F_0 is specified as

$$F_0 = \iint_0^\infty W(t,z) dt\, dz = W_0 \frac{\tau}{2} \frac{\sqrt{\pi}}{2} erfc(-2) \frac{1}{\alpha} . \qquad (3)$$

So, the normalization factor is:

$$W_0 = F_0 \frac{4\alpha}{\tau \sqrt{\pi} erfc(-2)} \quad . \qquad (4)$$

Because the depth of laser radiation absorption by the materials studied is much smaller than the linear cross-sectional dimensions of the laser spot focused on the surface, in calculating the surface temperature we used the approach of a one dimensional model of heat fluxes. The equation of non-steady-state heat conduction in this model takes the form

$$c_p \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(\lambda \frac{\partial T}{\partial z}\right) + f , \qquad (5)$$

where c_p is the heat capacity; λ is the heat conductivity; ρ is the density of the material; $f = f(z,t)$ describes the heat source, which is determined by equation (2), the normalization condition (3) and by taking into account the amplitude reflection coefficient:

$$f = (1-R)W(t,z) , \qquad (6)$$

where R is the reflection coefficient, which can be found using Fresnel equations.

The optical and thermophysical properties, based on which one can formulate the conditions for solving a non-steady state problem of heat conductivity, are known for the substrates studied [11-17]. The FlexPDE V5.0.2 software package was used for calculations.

Figure 1 shows the calculated dependencies of the maximum surface temperature on the laser radiation fluence. It is seen that the maximum temperature grows linearly as the fluence is increased. The slopes of the curves are quite different for the different materials. This means that different laser energies are needed to achieve the same temperature at the surfaces of the α-Si, graphite, tungsten and TiO_2 substrates.

Figure 2 shows the time dependencies of the surface temperature, calculated for fluences corresponding to a maximum temperature of 1000 K.
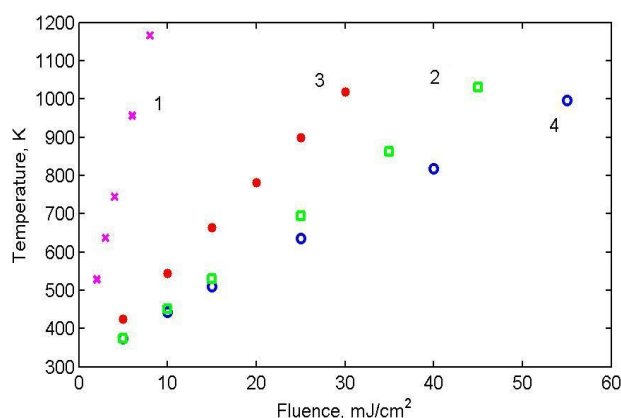
It is seen that the temperature of the surface reaches its maximum nearly at the end of the laser pulse, but the characteristic cooling time is different for the materials studied.

To compare the ionization properties of LETDI substrates, a Re complex with 8-mercaptoquinoline, a Cu complex with diphenylthiocarbazone and chlorophyll A were used as test analytes. Quinolines and thiocarbazones, common organic reagents, are widely used for highly efficient separation and preconcentration of metal element traces, while chlorophyll A is one of the most important bioorganic compound. For all
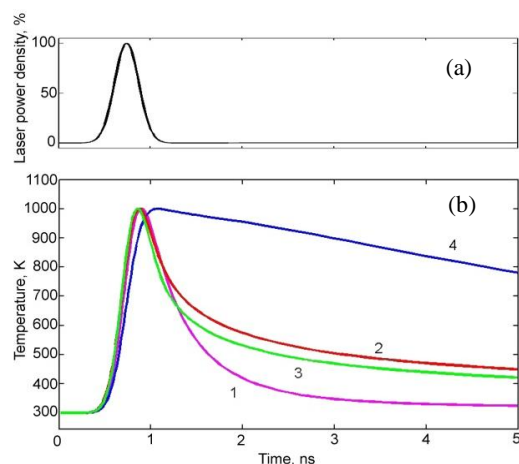

Figure 1. Calculated maximum temperature of the surface versus the laser radiation fluence: 1 − α-Si film, 2 − graphite, 3 − tungsten, 4 − TiO_2 film.

Figure 2. (a) time dependence of the laser pulse power density; (b) calculated time dependencies of the surface temperature at laser radiation fluences corresponding to a maximum temperature of 1000 K: 1 – α-Si film, 2 – graphite, 3 – tungsten, 4 – TiO$_2$ film.

these metal complexes, LETDI mass spectra were recorded and identified. It was found that each of the substrates studied produces ions of analytes. In general, mass spectra obtained from different substrates are similar to each other. All mass spectra are dominated by the molecular ions for the most abundant peaks. Additionally, mass spectra of chlorophyll A and a Cu complex with diphenylthiocarbazone include one peak of metal-containing fragment ions. The LETDI mass spectra are relatively "clean" with low chemical background, except for the peaks corresponding to the ions of sodium and potassium. As examples, figure 3 and figure 4 show mass spectra of the Cu complex with diphenylthiocarbazone obtained from α-Si and graphite.

In order to reflect better the LETDI performance of the four substrates, the ionization efficiencies of the LETDI process from different
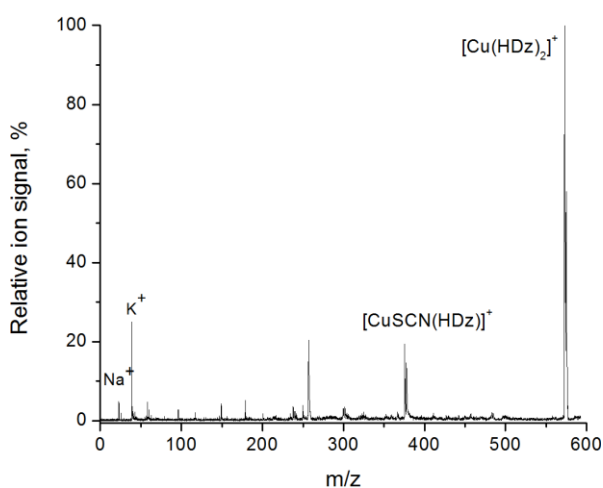

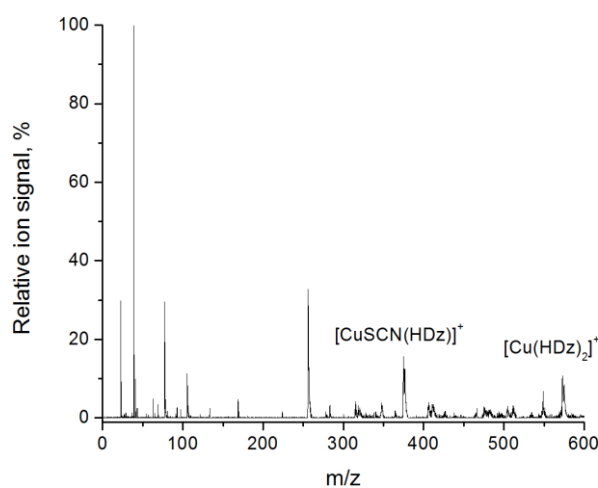**Figure 3.** LETDI mass spectrum of Cu complex with diphenylthiocarbazone (H$_2$Dz) obtained from α-Si.

Figure 4. LETDI mass spectrum of Cu complex with diphenylthiocarbazone (H$_2$Dz) obtained from graphite.

Table 1. Comparison of the ionization efficiencies of the LETDI process from different substrates.

Substrate	Analyte		
	Re complex with 8-mercaptoquinoline	Cu complex with diphenylthiocarbazone	Chlorophyll A
tungsten	1	1	1
graphite	8	7	5
α-Si	5×10^2	5×10^2	4×10^2
TiO$_2$	10^3	5×10^2	7×10^2

substrates, but at the same maximum temperature, were compared. The results obtained for the temperature of 1000 K are presented in the table 1. The ionization efficiency from tungsten was taken to be 1. It is seen that at the same temperature, the ion yield from different substrates varies in the range of about three orders of magnitude. Tungsten exhibits the lowest ionization efficiency, while TiO_2 film provides the highest efficiency. Also, α-Si films can be successfully used as an ion emitter.

Obviously, the efficiency of LETDI is the product of the probabilities of two processes: the probability of ionization of the analyte molecule and the probability of desorption in the form of molecular ion under the action of the laser pulse. All materials studied absorb efficiently UV radiation and transfer the laser energy to the thermal energy. The observed great difference between the materials in the ability to produce the molecular ions of the investigated metal complexes suggests that the efficiency of LETDI is determined by the ionization stage; more specifically, by electron transfer from the molecule. However, the thermal desorption step can limit the yield of ions with high molecular weights.

3. Conclusions

Based on the results of surface temperature calculations and the experimental study of the efficiencies of ionization of metal complexes from various substrates, it was concluded that the efficiency of the LETDI process is determined mainly by the ionization stage.

The direct comparison of the four common SALDI substrates, namely, graphite, tungsten, amorphous silicon and titanium dioxide films, for laser-induced electron transfer desorption/ionization of metal complexes reveals that titanium dioxide and amorphous silicon offer a better choice for producing molecular ions of metal complexes.

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