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The influence of the electron structure of atoms shells on characteristics of optical breakdown in metal vapour

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Abstract

By making use of the collision-radiative model that describes the phenomenon of optical breakdown in a metal vapour, the influence of the electron structure of atoms shells on the threshold intensity and breakdown period is analyzed. Two metals to be examined, aluminium and copper, are close in their thermo-physical properties but differ in the configuration of the electron shells of their atoms. General characteristics of optical breakdown, the influence of excitation energies of the neutral atom electron shells, as well as the ionisation potential, and the influence of higher excited states on threshold intensity and breakdown period are analyzed.

1. Introduction

The action of laser radiation of the intensity 10^7–10^9 W/cm^2 on metal targets is accompanied by a number of various physical processes. In the intensive evaporation regimes, the ways these processes go on are largely determined by the possibility of plasma being formed in the evaporated matter [1–3]. The initial stage of plasma formation, the so called optical breakdown, depends on the laser action parameters, namely the irradiation intensity and duration as well as on the target material properties.

Mathematical modelling [4–7] showed that the optical breakdown of metal vapour is governed by the processes of: (a) filling the excited states of electron shells, (b) cascade ionisation of particles.

Metals are characterised by a great number of energy levels in their atoms and ions, with the levels being split and mixed. This circumstance considerably complicates the description of level-by-level kinetics and requires that a large number of excited states should be taken into account. It is clear that at least at the first stage of optical breakdown the electron structure of atoms should play a significant role.

In view of the fact that optical breakdown is the intermediate process between two qualitatively different

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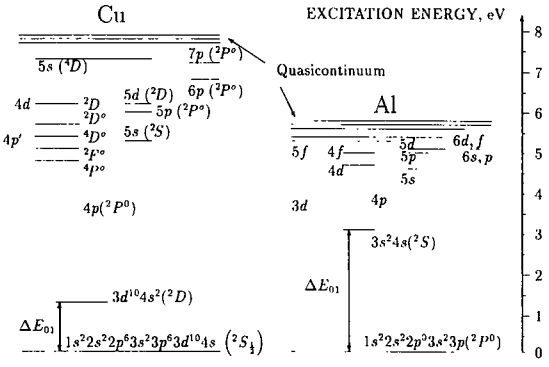

Fig. 1. Scheme of electron levels of neutral Al and Cu atoms.

states of matter (a neutral gas and a plasma) and has a markedly threshold character, two parameters: (a) the threshold intensity G_0 and (b) the time the electron–ion avalanche takes to develop (i.e. the breakdown period t_0) are of great interest to be found and compared with experimental results.

As noted above, electron shells of Al and Cu atoms have significant differences. First of all, in the Al atom, whose ionisation potential is ~ 1.7 eV lower than that of the Cu atom, the resonance 3p level is approximately twice as high as the first excited state 4s ($^2S_{1/2}$) in the Cu atom as shown in Fig. 1. Moreover, this excitation level 4s ($^2S_{1/2}$) in the Cu atom is metastable, i.e. the radiative decay from this state to the ground state is forbidden. At the same time the modelling [4–6] showed that the threshold values of optical breakdown intensity of copper vapour are by two orders higher than those of Al vapour.

2. Mathematical model

Numerical simulation is made on the basis of the mathematical model describing the level-by-level kinetics and cascade ionisation of Al and Cu atoms. The mathematical model is constructed with the following assumptions and restrictions:

(a) the kinetics of the step-by-step ionisation and recombination is considered for neutral atoms only;

(b) photo excitation processes, charge changing processes between atoms and ions, etc. are not considered;

(c) the mathematical model used a finite number of excited states of a neutral atom, Fig. 1. The effect of the upper levels of excitation is taken account of with the help of quasi continuum;

(d) the processes of plasma formation proceeds under the conditions of quasi neutrality.

The level-by-level kinetics of neutral atoms, dynamics of the charge composition and temperature of different components of the vapour under the action of laser radiation are described by the following system of non-linear differential equations [4–7]:

$$\frac{dN_m}{dt} = \sum_{j=0}^{m-1,m\neq 0} \left(k_{jm}N_j - r_{mj}N_m\right)N_e - \sum_{j=m+1,m\neq M}^{M} \left(k_{mj}N_m - r_{jm}N_j\right)N_e + \sum_{j=m+1}^{M} A_{jm}N_j - \sum_{j=0}^{m-1} A_{mj}N_m - \alpha_m N_m N_e + \beta_m N^+ N_e N_e \quad m = 0,1,\ldots,M-1,M, \tag{1}$$

$$\frac{dN^+}{dt} = \sum_{m=0}^{M} \left(\alpha_m N_m - \beta_m N^+ N_e\right)N_e, \tag{2}$$

$$\frac{dN_e}{dt} = \frac{dN^+}{dt}, \tag{3}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\tfrac{3}{2}N_{\mathrm{e}}T_{\mathrm{e}}\right)=\left(\mu G-\tfrac{3}{2}\delta\right)\left(\upsilon_{\mathrm{en}}+\upsilon_{\mathrm{ei}}\right)N_{\mathrm{e}}-\sum_{m=0}^{M}J_m\left(\alpha_m N_m-\beta_m N^{+}N_{\mathrm{e}}\right)N_{\mathrm{e}}$$

$$-\sum_{m=0}^{M-1}\sum_{j=m+1}^{M}\Delta E_{mj}\left(k_{mj}N_m-r_{jm}N_j\right)N_{\mathrm{e}}, \tag{4}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\tfrac{3}{2}N_{\mathrm{g}}T_{\mathrm{g}}\right)=\tfrac{3}{2}\delta\left(\upsilon_{\mathrm{en}}+\upsilon_{\mathrm{ei}}\right)N_{\mathrm{e}}. \tag{5}$$

Eq. (1) describes the dynamics of concentration variation of neutral particles in the ground ($n=0$) and excited ($0<n\le M$) states. The maximum value of M corresponds to the number of the last discrete state of the neutral atom taken into account in the model (Fig. 1). The first two terms in Eq. (1) account for the reactions of formation and decay of the nth excited state taking place when a neutral atom collides with an electron. The third and the forth terms describe the emergence and decay of the nth level due to spontaneous radiative processes. The last two terms in Eq. (1) account for the reaction of the nth level ionisation by the electron impact and creation of this level owing to the three-particle recombination reaction with the participation of an electron.

Eq. (2) describes changes in the concentration of single-charged ions N^{+}. By the quasi neutrality condition Eq. (3) describing changes in the concentration of electrons in vapour coincides with Eq. (2).

Eqs. (4) and (5) describe the energy balance of the electron component with the temperature T_{e} and the heavy component with the temperature T_{g}. Laser radiation with the intensity G is absorbed by the electron component due to the inverse bremsstrahlung effect (for more details see Ref. [7]).

3. Analysis of the results

Dynamics of optical breakdown in Al and Cu vapour was studied in details in Refs. [4–7]. It was shown that if the initial temperature of vapour is chosen to be $T_{\mathrm{e}}=T_{\mathrm{g}}=0.2$ eV and the laser pulse duration is infinite, the breakdown periods for Al and Cu vapour are comparable and equal to $t_0=3\times10^{-2}$ s and $t_0=10^{-2}$ s, respectively, then the threshold intensities differ by about two orders of magnitude: $G_0(\mathrm{Al})=3\times10^{7}$ W/cm^2, $G_0(\mathrm{Cu})=2\times10^{9}$ W/cm^2.

3.1. Influence of excitation energies of the neutral atom electron shells

To study the dependencies of the main characteristics of optical breakdown on the position of the resonance level in the Al atom, we shall use the simplified scheme of the electron structure of the atom, which in addition to the ground state $3s^2 3p\ (^2P^0)$ also takes into account the first excited state $3s^2 4s\ (^2S)$. Furthermore, when using the model (Eqs. (1)–(5)) we shall vary the resonance level excitation energy from 0 to the values corresponding to the atom ionisation potential I.

Fig. 2 represents the dependence of the threshold intensity G_0 on the resonance level excitation energy of the neutral Al atom at two initial temperatures of the vapour. The dependencies $G_0(\Delta E_{01})$, (where ΔE_{01} is the excitation energy of the first, i.e. resonance level) are indicative of the fact that when the resonance level position is shifted towards the ionised continuum $E_1\to I$, the threshold intensity values are decreased by about three orders. The shift towards the ground state results in a rapid growth of the threshold intensity values. Depending on the initial temperature the maximal increase is about three orders for $T_0=0.3$ eV and about five orders for $T_0=0.2$ eV. The maximum values of G_0 are observed at the excitation energy $\Delta E_{01}\approx0.1$ eV. When the ground and resonance levels are brought closer together, the threshold intensity decreases sharply.

The calculations show that the losses due to excitation $k_{01}N_0\Delta E_{01}$ (where k_{01} is the excitation reaction rate for the resonance level, see Eq. (1)) increase exponentially when the resonance level and the ground state come

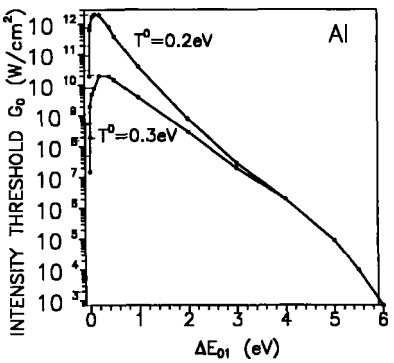

Fig. 2. Radiation intensity threshold values versus excitation energy of Al atom resonance level.

closer together, until $N_0 \gg N_1$. Along with energy losses, decreasing ΔE_{01} leads to increasing the concentration of excited particles N_1. As a consequence, with $\Delta E_{01} < 0.1$ eV, the energy released as a result of quenching (i.e. deexcitation) of the excited states $r_{10} N_0 \Delta E_{10}$ (where r_{10} is the quenching reaction rate) becomes comparable with the energy losses due to excitation $k_{01} N_0 \Delta E_{01}$. Owing to this the energy losses of electron subsystem due to excitation–quenching of the resonance level $Q_E = \Delta E_{01}(k_{01} N_0 - r_{10} N_1) N_e$ are drastically decreased, which results in decreasing the intensity threshold values G_0. When the resonance level is shifted towards the ionisation potential ($\Delta E_{01} > 0.1$ eV), the losses due to excitation are significantly higher than the contribution due to quenching (over the whole range of ΔE_{01}: $0.1 < \Delta E_{01} < I$); moreover, the losses due to excitation decrease because the coefficient k_{01} decreases with growing ΔE_{01}.

It has already been noted that the electron shell structure of the Cu atom differs essentially from that of the Al atom. The principal difference is that the resonance $4s^2$ (^{2}D) state of the Cu atom is metastable. The probability of radiative decay of this state to form an atom in the ground state 4s ($^2S_{1/2}$) is small. Besides, the probability of the formation of an atom in the $4s^2$ (^{2}D) state by collision of the ground state Cu atom with an electron is much smaller than that of the formation of an atom in the excited 4p ($^2P^0$) state. Therefore the transition of the Cu atom into the metastable resonance $4s^2$ (^{2}D) state is favoured not only by collision transitions but also by spontaneous radiative decay of the 4p ($^2P^0$) level. Thus in Cu vapour, threshold values of the radiation intensity G_0 and the breakdown time t_0 are both dependent on the resonance state excitation energy ΔE_{01} and on the excitation energy ΔE_{02} of the 4p ($^2P^0$) state as well.

To find out which of the levels has a greater effect on the threshold intensity G_0 and breakdown period t_0 two series of calculations were performed: in the first series the excitation energy ΔE_{02} of the 4p ($^2P^0$) level was fixed and the excitation energy of the resonance metastable state ΔE_{01} was varied. In the second series the energy ΔE_{01} was fixed and the energy ΔE_{02} was varied. The results of these calculations have shown (Fig. 3) that the excitation energy of the metastable $4s^2$ (^{2}D) state exerts a week influence on the threshold intensity G_0 required for breakdown of Cu vapour to occur; whereas the energy of the 4p ($^2P^0$) state, which is closest to the ground state (the optical transition to this state from the ground one being permitted), exerts a stronger effect on the value of G_0. In addition, the behaviour of the dependence $G_0(\Delta E_{02})$ coincides qualitatively with a similar dependence for Al vapour.

The result obtained indicates that in order to initiate the optical breakdown in vapour of a metal whose atoms have electron shells with small excitation energies, it is necessary to use laser radiation with a higher intensity than that used to initiate breakdown in vapour consisting of atoms with excited state being positioned at higher levels. The presence of metastable levels also makes a contribution into the optical breakdown dynamics.

Now we shall analyse the change in the breakdown time $t_0(\Delta E)$ versus the excitation energy of the resonance electron state of a neutral atom (Fig. 4).

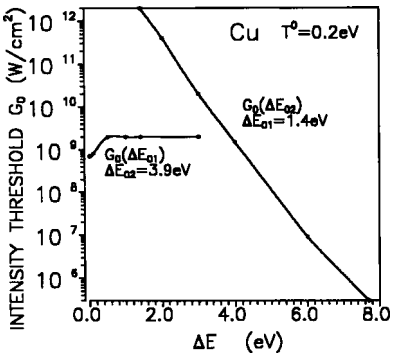

Fig. 3. Radiation intensity threshold values versus excitation energies of Cu atom resonance level (ΔE_{01}) and 4p level (ΔE_{02}).

As shown above, at small resonance state excitation energies, at the stage preceding to the emergence of electron avalanche, the major fraction of the energy of the vapour electron component is spent to excite the resonance state. As a consequence, the resonance level is rapidly populated, but the ionisation rate of this level determined by its binding energy $I_1 = I - \Delta E$ is low. Due to the latter circumstance the electron avalanche develops slowly. With increasing ΔE losses due to excitation diminish. The resonance level is populated not so intensively as in the case of small ΔE, but the ionisation rate grows. In this connection the time taken for the avalanche to develop is decreased and reaches the minimum value at $\Delta E \approx I/2$ (Fig. 4). As ΔE grows above $I/2$, the small excitation rate of resonance state begins decelerating significantly the process of electron avalanche development, regardless of the fact that the ionisation rate of this state grows rapidly. As a result of the mutual action of these two processes breakdown times for Al and Cu vapour are increased as the excited state approaches the ionisation continuum.

It can be seen from Fig. 4 that the minimum t_0 value is reached for the resonance state excitation energy to be about $I/2$. When the initial temperature of vapour increases up to $T^0 = 0.3$ eV, the dependence $t_0(\Delta E)$ does not vary qualitatively.

3.2. *The influence of atom ionisation potential*

Beside peculiarities of the atom electron structure, the atom ionisation potential is an important quantity affecting the optical breakdown parameters. To estimate its influence on the principal characteristics of optical

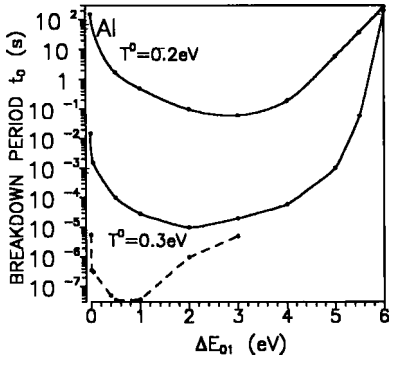

Fig. 4. Breakdown period versus excitation energy of Al atom resonance level. The dashed line curve shows the breakdown period calculated with the higher excited states taken into account.

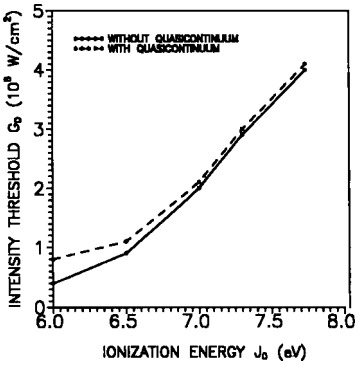

Fig. 5. Radiation intensity threshold values versus the ionization potential value of Al atom. Dashed line curve: simulation with quasi continuum taken into account; solid line curve: without quasi continuum.

breakdown let us perform a simple computational experiment, where the value of the Al atom potential $I = 5.98$ eV will be raised up to that of the Cu atom ionisation potential $I = 7.7$ eV. Conversely, the Cu atom ionisation potential will be lowered down to the value of the Al atom ionisation potential. The increase in the ionisation potential I_{Al} is accompanied by the growth of the intensity threshold values, Fig. 5, and at $I_{Al} = 7.7$ eV the value of G_0 reaches 4×10^8 W/cm^2. This is approximately 5 times lower than is required for breakdown to occur in Cu vapour under the same conditions. Hence, at the same values of the ionisation potentials $I_{Al} = I_{Cu} = 7.7$ eV the intensity threshold values remain essentially different. This is connected with the peculiar electron configurations of the atoms. This conclusion is confirmed by simulation of breakdown in Cu vapour when the ionisation potential I_{Cu} is lowered down to I_{Al}. At $I_{Cu} = 5.9$ eV the threshold values of G_0 are found to be 4 times higher than those for the Al vapour.

3.3. The influence of higher excited states

Formally speaking, any atom or ion has infinite numbers of discrete excited states, since the value of the first quantum number n is not limited in the Coulomb field. In real models the number of excited states must be finite. An awkward question arises, however, as to the number of excited states to be taken into account, since a general rule limiting their number is not available. Therefore, when solving concrete problems one should bear in mind which properties of the medium are examined and what contribution to these properties is made by high excited states, along with that made by free electrons. Taking into account that beginning from a certain state with the first quantum number n_*, the properties of bound electrons are similar, in the context of macroscopic analysis, to those of free electrons, it is reasonable to associate them with the continuous spectrum. So the states with quantum numbers $n > n_*$ will be considered in conjunction with continuous spectrum. By analogy with Ref. [8] they will be named the quasi continuum.

Figs. 5 and 6 represent the results of calculations of the radiation threshold intensity and the breakdown period for Al vapour without account of the quasi continuum (solid line) and with account of it (dashed line).

The influence of quasi continuum on characteristics of optical breakdown is manifested much as that of introduction of excited states, beside the resonance level, into the collision-radiative model. Introduction of the quasi continuum raises the intensity threshold values G_0 by about 2 times and decreases the avalanche development time by 2.5 times. As the ionisation potential increases up to 7.7 eV the influence of quasi continuum is diminished, Figs. 5 and 6. This is connected with the fact that the calculations were carried out with a constant number of excited states and, when the value of I_{Al} was increased, a noticeable energy gap was formed between the last excited level and the ionisation continuum. The quasi continuum exerts the highest influence on the neighbouring excited states. This indicates that in optical breakdown simulation the number of

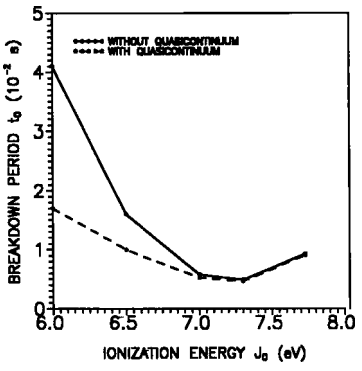

Fig. 6. Breakdown period versus the ionization potential value of Al atom. Dashed line curve: simulation with quasi continuum taken into account; solid line curve: without quasi continuum.

levels to be taken into account could be $n \leq 10$. The influence of higher levels can effectively be accounted for with the help of the quasi continuum model.

4. Conclusions

The closer to the ground state the excitation levels are, the higher the values of the radiation threshold intensity G_0 and the shorter the avalanche development period t_0 will be. The fact that in an atom there are only highly excited states $\Delta E_{0N} \approx I/2$ requires moderate values of the intensity G_0 and relatively long duration of laser action for the breakdown to occur.

Comparative analysis of optical breakdown in Al an Cu vapour showed the following:

(a) Optical breakdown threshold values for the Al vapour are about two orders lower than those for the Cu vapour. This is accounted for by the two reasons. The first one is that in Al atom excited states are positioned comparatively high. Thus, the first 4s level has the energy $\Delta E_{01} = 3.14$ eV $> I/2$. The second reason is connected with a lower ionisation potential $I_{Al} < I_{Cu}$. In the Cu atom the first $4s^2$ (^2D) level is located much closer to the ground state $\Delta E_{01} = 1.5$ eV $< I/2$. Despite that this level is metastable, its action, together with that of the 4p ($^2P^0$) level, raises significantly the breakdown threshold.

(b) Higher excited states of the atom have a significant effect on the electron avalanche development process in vapour, decreasing the optical breakdown time by several orders and increasing the intensity threshold values.

(c) Introduction of the quasi continuum procedure makes it possible to restrict the number of excited states to be considered ($n \leq 10$) with the accuracy in determination of optical breakdown characteristics being the same.

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