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INVESTIGATION OF THE EFFECT OF ADDITIONAL ELECTRONS ORIGINATING FROM THE ULTRAVIOLET RADIATION ON THE NITROGEN MEMORY EFFECT

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Abstract. The influence of ultraviolet radiation on memory effect in nitrogen has been investigated. The spectrum of the radiation which passes through the walls of the experimental sample was obtained by the spectrometer. A detailed comparison of experimental results of electrical breakdown time delay as a function of afterglow period with and without ultraviolet irradiation was performed. These studies were done for such product of gas pressure and inter-electrode distance when both breakdown initiation mechanisms exist. The research has shown that ultraviolet radiation leads to the decrease in ion concentration in early nitrogen afterglow due to recombination of nitrogen ions with electrons released from the tube walls and electrodes. Meanwhile, it has been cofirmed that this radiation has a negligible influence on the breakdown initiation in late nitrogen afterglow when a significant nitogen atom concentration is persistent. When the concentration of nitrogen atoms decreases enough, the breakdown initiation is caused by cosmic rays but UV photons have an important influence because of the rise of the electron yield.

Key words: memory effect, electrical time delay, nitrogen, ultraviolet radiation

1. INTRODUCTION

The electrical breakdown time delay in gases is one of the most important characteristics of gas components, which is also known as the delay response. It is defined as a time interval from applying voltage, sufficient enough to initiate the electrical breakdown. Furthermore, the investigation of electrical breakdown time delay can provide useful information about the physical processes that occur in the gas during the operation of electrical devices.

The investigation of electrical breakdown time delay in gas could be performed as a function of different parameters [1], [2]. One of the most important parameters that influences on the mean value of electrical breakdown time delay \bar{t}_d is the afterglow period τ . The dependence $\bar{t}_d = f(\tau)$ is usually known as memory curve. It has been used for qualitative and quantitative analysis of concentrations of positive ions and neutral active

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states remaining from the previous discharge as well as formed during the afterglow period [3], [4]. It has also enabled the estimation of recombination and de-excitation times of the mentioned particles due to their recombination on the tube walls, electrodes and in gas. The particles that come to the cathode play the main role in the initiation of the subsequent breakdown. They induce the secondary electron emission, and if the voltage applied on the electrodes is higher than the static breakdown voltage, secondary electrons created at the cathode can initiate the subsequent breakdown. The previous study showed that Auger neutralization process, in which positive ions participate, as well as Auger de-excitation process for which the molecule metastable state are responsible, play a dominant role in the breakdown initiation in gases at low pressure. Especially in nitrogen, the process of surface catalysed excitation could also be responsible for the breakdown initiation.

Many parameters affect the behavior of the memory curve at low pressures. Some of them are the inter-electrode distance, the material of cathode and tube's walls, the wall's temperature, the applied voltage on the gas tube, the glow current and the glow time. Most of these investigations have already been published. However, the influence of additional electrons which originate from ultraviolet irradiation on the nitrogen memory effect when the product of gas pressure p and the inter-electrode distance d are placed on the left side of Paschen's minimum (the dependence of the static breakdown voltage as a function of the pd product) has not been sufficiently investigated. Practical importance of investigation of this irradiation influence on the discharge in gas-filled electronic components as well as solid system, it could be found in many published papers [5-9]. For this purpose, the aim of this paper is to examine the effect of ultraviolet radiation that comes from the cadmium lamp on the nitrogen memory effect in the presence of vacuum and gas breakdown mechanisms. As for each of the areas of the memory curve depending on the afterglow period length, a different mechanism initiating breakdown is responsible, the influence of ultraviolet radiation for each of them has been individually investigated.

2. EXPERIMENT

2.1. Experimental sample

The cylindrical borosilicate glass (8245 Schott technical glass) tube filled with nitrogen at 6.6 mbar pressure was used as experimental sample and it is shown in Fig. 1. Its volume was about 1 l. It was connected in the circuit with one fixed and one movable iron electrode, so that the inter-electrode distance could be varied by a permanent magnet from the outside. Using this experimental sample allows changing the inter-electrode distance from 0.01 cm to 0.45 cm, while the value of the gas pressure in the tube remains constant. The diameter of spherical electrodes was 1 cm.



Fig. 1 The shape of used experimental samle (1–fixed electrode, 2–movable electrode, 3–rotation shaft from iron)

The tube had to be baked out and evacuated before the nitrogen was admitted in a process similar to that for the production of x-ray and the other electron tubes. After that, the tube was filled with Matheson research grade nitrogen at pressure of 6.6 mbar with the claimed abdundance of impurities such as CO<0.5 ppm, $CO_2<0.5$ ppm, $O_2<1$ ppm, THC<0.2 ppm and $H_2O<1$ ppm. Before the time delay measurements were done, the cathode sputtering with glow current of 0.5 mA was set with duration of a few days. Such value of discharge current was selected to avoid erosion of the cathode during conditioning. Due to the stohastic nature of electrical time delay, each point in memory curves represents the mean value of a hundred measured values. After the breakdown, the current in the tube was 0.5 mA during a glow time of 1 s. This time is sufficient to attain the steady-state discharge conditions in our experiment. It should be noted that the similar experiments were performed by other group of scientists [10] and [11] in which the glow time was the order of milliseconds. The gas sample used in these experiments has the cathode made of gold-plated copper. But, it could be emphasized that the gold provides a relatively stable work function.

The estimated values of static breakdown voltage U_s for this experimental sample for two values of inter-electrode distance of 0.01 cm and 0.1 cm were 418 V and 386 V, respectively. The electrical breakdown time delay measurements were performed for overvoltage $\Delta U/U_s = (U_w - U_s)/U_s = 50\%$ higher than static breakdown voltage, where U_w is voltage applied on the tube electrodes.

2.2. Experimental setup

Electrical breakdown time delay measurements were performed with an electronic system, whose block diagram is shown in Fig. 2. The used electrical system, from the architecture point of view, consists of three major parts. Those are high voltage power supply, analog subsystem and digital subsystem. For high voltage power supply it is necessary to operate in the range from 100 to 1000 volts within the desired power raring.



Fig. 2 Block diagram of system for electrical breakdown time delay measurement

The measured electrical breakdown time delay values can range from several microseconds to several minutes, while the values of afterglow period set by the system can range from couple of microseconds to several days. Due to the statistical nature of time delay, it is necessary to perform a large number of measurements since the measurement error of time delay mean values decreases as $\sqrt{1/N}$, where *N* is the total number of measurements. The number of measurements in this experiment was a hundred for only one value of the afterglow period. Since the measurement cycle can be set up for

an arbitrary number of different afterglow period values, it can be concluded that the total number of measured timed delay values per experiment can be extremely large. Such large number of data should be stored somewhere in real time and kept for further statistical analysis which the digital subsystem enables.

The used electrical system allowed obtaining the dependence of the mean value of electrical time delay vs. afterglow period, $\bar{t}_d = f(\tau)$ on two different values of interelectrode distance, with and without the presence of UV radiation.

Before discussing the processes that predominantly affect the secondary electron emission process during the afterglow, it is necessary to highlight the progress that was made in measuring the electrical time delay using the improved measurement system. What this system enables is a significant reduction in the value of the afterglow period duration for which electrical breakdown time delay could be measured. Hence, the lowest value of the afterglow period value for which the measurement of electrical breakdown time delay was possible was 3 μ s. Thus, the value of afterglow period for which it was possible to measure electrical breakdown time delay was reduced by three orders magnitude using the improved system, which allowed tracking the decrease in the concentration of the charged and neutral active particles that were passed from the discharge into the afterglow period. Further, this system has enabled sufficiently reliable monitoring the recombination/deexcitation of positive ions and neutral active particles formed during and after discharge based on the process of secondary electron emission which they initiate. The detailed development of the electrical system used to measure the electrical time delay and its electrical scheme could be traced in [12].

2.3. Investigation of ultraviolet irradiation

As a source of ultraviolet radiation the commercial cadmium lamp was used. Before recording memory curves, spectral analysis of the light that comes from the lamp, which goes through the glass tube walls, was performed. A piece of borosilicate glass was placed between the cadmium lamp and the spectrometer in order to ascertain which wavelengths could pass through the gas-filled tube walls. This enabled measuring the light intensity influence in this process.

The instrument used in spectroscopic analysis was Avantes spectrometer Avaspec-3648 [13] which has a useable range from 200 nm to 850 nm. The spectrometer has a diffraction grating with 600 lines/mm and the slit size is 10 μ m, making the lowest resolution between two near lines 0.32 nm. As can be seen, the most intense lines in the spectrum are wavelengths 327 nm, 480 nm and 509 nm. The obtained emission spectrum is shown in Fig. 2, and as it can be seen, the wavelengths larger than 327 nm can pass through the glass walls.

The physical process that occurs when ultraviolet light from the cadmium lamp falls on the cathode surface is the photoelectric effect. Specifically, based on Einstein's relation for the photoelectric effect provided that freed electrons do not experience collisions inside the metal, or if the photons are delivered energy electrons at the cathode surface, the energy of the incident photons will be equal to the sum of the work function cathode material and the maximum kinetic energy of the released electrons.



Fig. 3 Strongest observed lines in the emission spectrum of the cadmium lamp which pass through the borosilicate glass

Therefore, comparing the value of energy corresponding to the wavelength the spectrum resulting lines with a value of the iron work function, the existence of photoelectric effect could be determined [14]. To make it possible, the photon energy from the lamp needs to be greater or equal to the value of the work function of iron, of which the electrodes are made. In the literature, there are inconsistencies in the value of the work function of iron, according to the different authors, varying from 3.5 eV [15] to 4.3 eV [16]. It can be asked how the secondary electrons can be emitted from the cadmium lamp since the work function of iron is slightly greater than the photon energy of the smallest wavelength of the spectrum. It should be noted that the iron electrodes are coated by a layer of iron oxide, which has smaller work function than the iron [15]. Earlier qualitative energy dispersive spectroscopy analysis of the electrode surface confirmed the iron oxide layer stability, and that it cannot be removed by sputtering during the discharges. Because of that, from the spectrum of cadmium lamp lines 327 nm, 341 nm, 346 nm and 360 nm should be taken into account, with corresponding energies 3.79 eV, 3.64 eV, 3.59 eV and 3.45 eV.

3. RESULTS AND DISCUSSION

The experimental results presented in this paper are the follow-up of the recent research presented in [17]. In investigation whose results are presented below, the interelectrode distance was taken as a parameter in tracking the behaviour of the memory curve. In this case the research was done in the persence of ultraviolet radiation. The analysis of the influence of additional electrons originating from commercial cadmium lamp has been performed. The memory curves present in Figs. 4 and 5 are obtained for nitrogen-filled tube, with and without source of ultraviolet radiation for two different values of inter-electrode distance of 0.01 cm and 0.1 cm, respectively. The analysis of the obtained results enables a discussion of the ultraviolet radiation influence as well as the inter-electrode distance to the memory curve behavior. A type of breakdown initiation mechanism also has an influence on the memory curve behavior.



Fig. 4 Memory curves with and without presence of radiation from cadmium lamp for inter-electrode distance of 0.01 cm



Fig. 5 Memory curves with and without presence of radiation from cadmium lamp for inter-electrode distance of 0.1 cm

3.1. Nitrogen memory effect

A special mechanism of breakdown initiation occurs at low pressure values when the inter-electrode distance is less than the electron mean free path ($pd \le 10^{-3}$ mbar cm [18]). Under these conditions the breakdown appears in the so called technical vacuum and it is caused by the existence of an avalanche mechanism which creates free electron and ions. In this case, the breakdown starts in the processes at the electrode, but is significantly

different than γ processes of Townsend's mechanism. There are several ways of the vacuum breakdown initiation, but all are common to evaporation of the electrode material forms a vapor cloud which is still developing breakdown with Townsend's avalanche mechanism [19]. In order to form a cloud of vapor, it is necessary that the electrodes' surface has a large number of micro-spices which should cause a sufficient amount of energy to cause thermal instability. Thermal instability of electrodes could be caused by emission mechanism, by micro-particles accelerated in electrode material, or through the avalanche effect in the adsorbed residual gas layer on the electrode. It can be induced in three ways: the emission mechanism (autoelectron emissions), accelerated micro-particles from electrode materials or avalanche effect in the gas adsorbed layer on the electrode surface.

As a criterion of whether it is a technical vacuum or not, the dependence $U_s = f(pd)$ was monitored for the gas sample used in this experiment, which was published in [17]. The product value of inter-electrode distance 0.01 cm and nitrogen pressure in the tube of 6.6 mbar lies to the left of the Paschen's curve minimum. It corresponds to the most favorable conditions for the gas ionization. In this case it was not pure vacuum breakdown mechanism existence, but for this the value of pd product the combined effect of vacuum and gas breakdown mechanism exists. The presence of vacuum breakdown mechanism leads to the existence of additional electrons in the inter-electrode gap which are otherwise responsible for the secondary electron emission in the plateau region of memory curve.

It is known that the memory curve of nitrogen has three areas [1] which are caused by the existence of different mechanisms responsible for the electrical breakdown initiation in the gas. Using an advanced system for measuring the time delay allows a detailed analysis of the plateau area of the memory curve (short-lived afterglow) which has been done on this occasion. Namely, if the positive ions are present in the gas, their movement towards the cathode is enabled by connecting a voltage to the electrode tubes, where they eject electrons that initiate electrical breakdown in the process of secondary electron emission.

The positive ions could be transferred from the discharge to the short-lived afterglow, but they persist in gas to 10 ms. The discussion in the paper [20] showed that the minimum emissions of 1^{-} system occurred 1-10 ms after the discharge had ceased. On the other hand, the positive ions could be formed during the actual relaxation in the metastable molecule reactions

$$N_2(A) + N_2(a') \rightarrow N_4^+ + e \text{ (or } N_2^+ + N_2 + e),$$
 (R1)

(R2)

$$N_2(a') + N_2(a') \rightarrow N_4^+ + e \text{ (or } N_2^+ + N_2^- + e),$$

with the rate coefficient values of $3.2 \cdot 10^{-12} \text{ cm}^3 \text{s}^{-1}$ [21] and $5 \cdot 10^{-11} \text{ cm}^3 \text{s}^{-1}$ [22].

 $N_2(A)$ and $N_2(a')$ metastable molecules formed in the discharge recombined 1-10 ms after the discharge had ceased [23], [24], so that the number of the reactions (R1) and (R2) decreased with time up to 10 ms. Also, if the electrons are present in the gas, the positive ions could be formed by electron impact on the nitrogen molecules, as well. The electrons in the gas could be found up to 1 ms after the discharge ceased [25]. If a voltage is applied to the electrodes after the relaxation which lasted $\tau \le 1$ ms the electrons would perform ionizing collisions and thus encourage the process of secondary electron emission. Since the mechanism of positive ion creation during the (R1) and (R2) reactions dominates over the electron impact even during the discharge [22], it can be concluded that the same will happen outside the discharge, and the contribution of the process of the secondary electron emission during the afterglow can be neglected.

The calculations of the vibrational temperature during the discharge showed that the concentration of excited vibrational levels v > 10 had a value of 0.1% concentration of nitrogen molecules in the ground state [4]. A similar trend is predicted if the discharge current is low, which corresponds to the conditions of our measurements. Therefore, it can be concluded that immediately after the completion of the discharge, the concentration of the vibrational-excited nitrogen molecules (v > 10) is high, and the reactions of positive ions creation are possible [26]:

$$N_2(X, v > 24) + N_2(a') \rightarrow N_4^+ + e$$
, (R3)

$$N_2(X, v > 29) + N_2(X, v > 29) \rightarrow N_4^+ + e$$
, (R4)

$$N_2(X, v > 36) + N_2(A) \to N_4^+ + e$$
 . (R5)

After $\tau \sim 10$ ms the emission intensity of 1° system increases. This intensity passes through a maximum value in the interval of 15-20 ms [20]. This maximum results from the growth of the positive ion concentration during the short-lived afterglow. From the aforementioned facts it can be seen that in this range the concentration of $N_2(A)$ and $N_2(a')$ metastable molecules pass through the maximum, which leads to, due to the higher probability of the reactions (R1) and (R2), the increase of the positive ion concentration. However, considering the fact that after 10 ms the positive ions and metastable molecules from the discharge recombine or become de-excited, it can be concluded that the other particles present in the gas are involved in the creation of the positive ions.

It is believed that the formation of $N_2(A)$ and $N_2(a')$ metastable molecules in the shortlived afterglow for the relaxation time $\tau > 10$ ms follows from the reactions

$$N(^{4}S) + N_{2}(X, v \ge 39) \rightarrow N(^{2}D) + N_{2}(A),$$
 (R6)

$$N(^{4}S) + N_{2}(X, \nu \ge 38) \to N(^{4}S) + N_{2}(a'), \qquad (R7)$$

involving $N(^4S)$ atoms and the highly vibrational-excited nitrogen molecules [26]. $N(^4S)$ atoms retain 1% of the nitrogen molecule concentration after the discharge period up to $\tau \sim 10 \text{ ms} - 1 \text{ s}$ [27], which is more than other particles in the gas do.

As for the highly vibrational excited nitrogen molecules, the population availability of the highly vibrational excited levels increases during the short-lived afterglow due to the "pumping up" effect. The calculations of other authors [27] have shown that the concentration of N_2 (X, v > 25) molecules has the maximum value for the afterglow period in order of tens of milliseconds.

This maximum coincides with the maximum of the 1⁻ system emission, so it can be concluded that, in the interval of 10-15 ms, the efficiency of the (R6) and (R7) reactions is the largest in the short-lived afterglow. This leads to an increase in the concentration of $N_2(A)$ and $N_2(a')$ metastable molecules, which, by participating in the reactions (R3)-(R5), cause the increase of the positive ion concentration.

The concentration of highly vibrational excited nitrogen molecules $N_2(X, v > 25)$ rapidly decreases after reaching the maximum, and the relaxation times of the order of 100 ms is already about 50% lower than the maximum, whereas for $\tau \sim 1$ s it is negligible [27]. This decrease significantly reduces the probability of positive ion creation in the previously mentioned processes, so their significance in the process of secondary electron emission is smaller for the relaxation time $\tau > 30$ ms.

Bearing in mind the aforementioned discussion, the $3 \,\mu s < \tau < 70 \,ms$ interval in Figs. 4 and 5, which represents an area of the short-lived afterglow (particularly in Figs. 6 and 7) is investigated in detail. A slightly larger increase in the electrical breakdown time delay value in the 3 μ s < τ < 1 ms interval is caused by the decrease of the positive ion concentration and $N_2(A)$ and $N_2(a')$ metastable molecules being transferred from the discharge to the short-lived afterglow. In this interval, the secondary electron emission is dominated by the positive ions that are either transferred from the discharge or afterglow through reactions of $N_2(A)$ and $N_2(a')$ metastable molecules and highly vibrational excited nitrogen molecules, also transferred from the discharge. Since in the $3 \mu s < \tau < 1 ms$ interval positive ion concentration is the largest for all afterglow periods for which the measurements are performed, the efficiency of the secondary electron emission is the largest in this interval. It is characterized by the lowest values of electrical breakdown time delay on the memory curve of Figs. 4 and 5. The end of the interval 3 μ s < τ < 1 ms coincides with the minimum intensity of 1⁻ system emission in the short-lived afterglow, when most of the positive ions are recombined and the majority of the de-excited electrons and $N_2(A)$ and $N_2(a')$ metastable molecules are transferred from the discharge.

In the next part of the short-lived afterglow (1 ms $< \tau < 70$ ms), the positive ions are also responsible for the secondary electron emission, but almost entirely those incurred during the actual relaxation. At the beginning of this interval the levels' concentration of the highlyvibrational excited nitrogen molecules reaches a maximum, and then the efficiency of the (R6) and (R7) reactions, in which $N_2(A)$ and $N_2(a')$ metastable molecules are formed, is the highest. These molecules, in their mutual interaction in reactions (R1) and (R2) as well as in reactions with nitrogen highly vibrational excited molecules (reactions R3-R5), cause the increase of the positive ion concentration and enhance the secondary electron emission.

The renewed increase in the positive ion concentration caused in such a way is represented on the memory curve of Figs. 4 and 5 by a significantly slower increase in the t_d value during the interval 1 ms $< \tau < 70$ ms than during the interval 3 µs $< \tau < 1$ ms.

There is a further increase in the electrical breakdown time delay value due to the fact that having reached the maximum during $\tau = 10 - 15$ ms, the concentration of the highly excited vibrational molecules of nitrogen begins to decline. This, over time, leads to the reduction of the efficiency of the reactions which produce the positive ions. At the end of the 1 ms < τ < 70 ms area, the concentration of the positive ions decreases to a level at which the probability of the secondary electron emission process of their impact upon the cathode becomes very low and then this process begins to dominate neutral active particles. Since the efficiency of these particles in the secondary electron emission is significantly lower than the efficiency of the positive ions, there is a sudden increase in the value of t_d for τ > 70 ms. At the same time, the value $\tau \sim$ 70 ms is the end of the area of the short-lived afterglow time in Figs. 4 and 5.

Most reactions of nitrogen positive ions creation, both by electron impact ionization of neutral molecules, during breakdown and discharge by associative ionization processes, involve metastable molecules and highly vibrationally excited molecules were listed in papers [28]. It could be seen that N^+ , N_2^+ , N_3^+ , N_4^+ ions have a certain role in the process of secondary electron emission from the cathode in early afterglow. Taking into account the published data [28], the concentration of N_2^+ ions is $5 \cdot 10^{10}$ cm⁻³ after discharge ceases, while the concentrations of the other ions are significantly lower. For

this reason, it can be proposed that N_2^+ ions formed in processes (R1) and (R2) have a dominant role in the breakdown initiation in the early afterglow. The drift velocity of these ions can be estimated by expression $v_d = e\lambda U_w/m_i \bar{v} d$ [29], where the mean free path is calculated as $\lambda = kT/\sqrt{2} \pi D^2 p$ (k is the Boltzmann constant, T = 300 K is gas temperature, D is the ion diameter and p is gas pressure), U_w is applied voltage on the electrodes, m_i is the ion mass, d is the inter-electrode distance, e is the elementary charge and \overline{v} is the mean thermal velocity estimated as $\overline{v} = \sqrt{2kT/m_i}$. For nitrogen-filled discharge tube at 6.6 mbar pressure, for present experimental condition, the mean free path is $1.47 \cdot 10^{-5}$ m and the mean thermal velocity is 421.73 ms⁻¹, while the value of the drift velocity for overvoltage of 50% is $6.9 \cdot 10^4$ ms⁻¹. It can be concluded that the drift velocity is higher than the thermal velocity. For these afterglow periods the electrical breakdown time delay is only determined by total time necessary for the ion drift to the cathode and the secondary electron release from its surface. In the case when the drift velocity is lower than the thermal velocity, it is emphasized that the positive ions also play the most important role in the process of secondary electron emission because of their drift motion toward the cathode under the field influence in the inter-electrode gap. Not only the positive ions but the metastable molecules and other neutral active particles as well can cause the secondary electron emission at the cathode. However, when a voltage is applied to the electrode, the diffusion time of these particles to the cathode is considerably longer than the drift of the positive ions, so their direct contribution to this process is negligible provided that the positive ions are present in the gas.

The rapid growth of the electrical breakdown time delay value at the end of shortlived afterglow indicates a change in the mechanism that dominates in the process of secondary electron emission. After $\tau = 15$ ms, the concentration of $N_2(A)$ and $N_2(a')$ metastable molecules and high vibrational excited molecules of nitrogen decreases, consequently the number of positive ions formed the above-mentioned reactions became lower. Because of that, when the concentration of positive ions becomes lower than the concentration of neutral particles in a gas, which can also cause secondary electron emissions, the form of memory curves change, entering the region of rapid electrical breakdown time delay increase, so-called long-lived afterglow. The efficiency of neutral active particles in causing the process of secondary electron emission is much smaller than in the case of positive ions, causing the value of t_d rapidly increased in relation to the plateau memory curve. Earlier investigations [1], [3], [24], [30] confirmed that the nitrogen atoms in ground state $N(^4S)$ remaining from the previous discharge as well as formed after the discharge ceased are the most responsible particle for the secondary electron emission from the cathode in late nitrogen afterglow.

Numerical models, which followed the decrease of nitrogen atoms concentration based on the re-association on the tube walls [3], [4], [24] combined with a model predicts that secondary electron emission is caused by nitrogen atoms, showed a good agreement with the experimental obtained memory curves in the area of sudden increase in t_d value. The decrease of N atoms concentration is inversely proportional to the probability of the secondary electron emission, indicating the t_d value increases. Since their concentration decreases exponentially [4], as well as the decline of the light emitted from the tube after discharge, this downward trend in log scale is shown linearly.

It has been shown earlier [31], [32] that the long-lived Lewis-Rayleigh afterglow lasts up to several hours and it can also been confirmed that the source of the energy for the glow is the recombination of the nitrogen atoms in the ground state. It was concluded that $N(^4S)$ atoms are present a very long time in the afterglow and their concentration deceases mostly by surface recombination on the tube walls [3]. In addition, they could be also recombined in the gas and on the electrodes. The final product of their recombination is $N_2(A)$ metastable state. It can be reach via the following reactions:

$$N(^{4}S) + N(^{4}S) + M \to N_{2}(B) + M$$
, (R8)

where *M* is the atom at the cathode surface, and by the spontaneous de-excitation process of $N_2(B)$ molecules,

$$N_2(B) \to N_2(A) + h\nu. \tag{R9}$$

 $N_2(A)$ metastable state formed in this way [33], transferring the energy to the cathode via the collision. As the work function of iron, is lower than the $N_2(A)$ metastable state energy of 6.2 eV, it can induce the secondary electron emission that determines the value of the electrical breakdown time delay in the late nitrogen afterglow. This process of nitrogen atom recombination on cathode surface is the surface-catalyzed excitation [34]. This is the process of heterogeneous catalysis which is significant for this research, when the adsorbate and the substrate are in different phases, i.e. in gaseous and solid. In order to achieve heterogeneous catalysis, at least one of the reactants needs to be adsorbed and modified into the shape that has got a high affinity for the reactions. And on that way the secondary electrons are produced for breakdown initiation in the late afterglow.

For $\tau \approx 3.10^3$ s and $\tau \approx 7.10^3$ s the memory curves without presence of additional radiation from Figs. 4 and 5 reach the saturation for the inter-electrode distance of 0.01 cm and 0.1 cm, respectively, i.e. the mean value of the time delay slightly changes with the afterglow time increase. It should be emphasized that in the saturation district of memory curves, the concentration of nitrogen atoms decreases to so low value that the cosmic ray becomes responsible for the breakdown initiation. When the applied voltage on the tube is higher than the static breakdown voltage, the electron-ion pairs form in gas and they could initiate the breakdown. Then, it is highly probable that electrons are released from the cathode due to the impact of cosmic radiation. They form the avalanche which leads to the breakdown causing the electrical time delay decrease. Since the flux of cosmic ray during the experiment was approximately constant, the number of the electron-ion pairs created in unit time is approximately constant and the electron yield is also approximately constant. Because of that, the mean value of time delay is constant for the given value of overvoltage. These conclusions are in agreement with the results shown in Figs. 4 and 5. It is important to emphasize that the cosmic ray permanent exists during the experiment. But, for shorter afterglow period when the positive ions and the considerable concentration of $N(^{4}S)$ atoms are present, the role of the cosmic ray in the breakdown initiation is negligible in relation to the secondary electron emission initiated with these particles.

3.2. Influence of ultraviolet radiation

The analysis of the obtained experimental results also enables a discussion of the ultraviolet irradiation influence to the memory effect in nitrogen at 6.6 mbar pressure when the combined

vacuum and gas breakdown initiation mechanism exist. It is clearly observed from Figs. 4 and 5 that ultraviolet radiation, which comes from the lamp, has influence on the electrical breakdown time delay. In some regions of the memory curve the impact is slight, but noticeable. In the area of rapid growth of the mean value of electrical breakdown time delay, the influence of ultraviolet radiation is negligible. The obtained values of \tilde{t}_d were slightly less. The presence of additional electrons from UV irradiation causes the memory curves to reach the saturation earlier and they decrease the \tilde{t}_d values for about the order of magnitude. It should also be noted that some influence of ultraviolet radiation is felt in the plateau area of the memory curve. Because of that, this part of memory curve has been specially presented in Figs. 6 and 7 for both values of inter-electrode distance.



Fig. 6 Ion part of memory curves with and without presence of radiation from cadmium lamp for inter-electrode distance of 0.01 cm



Fig. 7 Ion part of memory curves with and without presence of radiation from cadmium lamp for inter-electrode distance of 0.1 cm

It can be seen from these figures that the plateau length is not changed due to the ultraviolet irradiation. However, for both values of inter-electrode distance the plateau height increases. This increase is caused by the electron yield growth in the interelectrode gap due to the liberated electrons from the cathode by ultraviolet irradiation, which was more pronounced in the presence combined vacuum and gas breakdown. In this case, it should be noted that for further electron yield growth, the presence of the vacuum breakdown mechanism is responsible. These additional electrons induce the process of recombination the part of positive ions formed immediately after the finish of the discharge until the end of the plateau. Meanwhile, these ion-electron recombinations proceed through the following processes:

$$e + N_4^+ \to N_2(X) + N_2(X), \tag{R10}$$

$$e + N_2^+ \to N(^4S) + N(^4S),$$
 (R11)

$$e + N_2^+ \to N(^4S) + N(^2D).$$
 (R12)

The rate coefficients of these reactions are $2 \cdot 10^{-6} (300/T_e)^{0.5} \text{ cm}^3 \text{s}^{-1}$ for (R10) and $2 \cdot 10^{-7} (300/T_e)^{0.5} \text{ cm}^3 \text{s}^{-1}$ for processes (R11) and (R12) [35].

As a result, when an operating voltage is applied on the electrodes, fewer ions per second arrive to the cathode surface when the gas tube is irradiated. Then, the breakdown probability of electron occurrence decreases, causing a rise in the mean value of electrical breakdown time delay.

4. CONCLUSION

On the basis of the above considerations, the following brief conclusion is given. Fundamental research of nitrogen discharge and afterglow is very important because of their different applications. The investigation of influence of ultraviolet irradiation on memory curve behavior has also been published. This effect is a consequence of the production of electrons from the cathode by light from the cadmium lamp. The spectral analysis of the light that comes from the lamp, which goes through the glass tube walls, was performed using Avantes spectrometer Avaspec-3648. It was obtained that ultraviolet irradiation had a noticeable influence in the plateau region and saturation of the memory curve, while a deviation of time delay is insignificant in the region of its rapid increase. Namely, in early nitrogen afterglow ultraviolet irradiation increases the values of time delay, due to the dominant effect of ions enhanced electron-ion recombination. Otherwise, in far late nitrogen afterglow the ultraviolet radiation decreases the time delay values because of the growth in total electron yield. The obtained results have shown that the memory curves in the region of very long afterglow period values are very sensitive to ultraviolet radiation. Because of that, a strict control of environmental radiation during the measurement was necessary to be performed in order to reduce the errors in tracking the kinetics of positive ions and neutral active particles in nitrogen afterglow. The most important process related to positive ions and nitrogen atoms creation/quench are mentioned. In addition, it was represented that the additional electron yield caused by influence of vacuum breakdown initiation mechanism has also a dominant role and that it was responsible for the decrease of t_d value. This phenomenon is more pronounced in the presence of the vacuum breakdown mechanism at the lower value of inter-electrode gap.

The ability to detect weak effects of ultraviolet radiation on the memory effect has reaffirmed that the used time delay measurement technique is very sensitive to the change of particle concentration in gas. Earlier, it was found [3] that the used method could detect nitrogen atom concentration nearly 10^8 cm⁻³. It was determined by the level of a natural charge production between the electrodes.

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References

- M. M. Pejović, E. N. Živanović and M. M. Pejović, "Kinetics of ions and neutral active states in afterglow and their influence on the memory effect in nitrogen at low pressures", J. Phys. D: Appl. Phys., vol. 37, pp. 200-210, 2004.
- [2] N. T. Nesić, M. M. Pejović, M. M. Pejović and E. N. Živanović, "The influence of additional electrons on memory effect in nitrogen at low pressures", J. Phys. D: Appl. Phys., vol. 44, p. 095203(9pp), 2011.
- [3] V. Lj. Marković, Z. Lj. Petrović and M. M. Pejović, "Surface recombination of atoms in a nitrogen afterglow", J. Chem. Phys., vol. 100, pp. 8514-8521, 1994.
- [4] N. Nešić, G. Ristić, J. Karamarković and M. M. Pejović, "Modelling of time delay of electrical breakdown for nitrogen-filled tubes at pressures 6.6 and 13.3 mbar in the increase region of the memory curve", J. Phys. D: Appl. Phys., vol. 41, p.225205, 2008.
- [5] K. Bergmann, G. Schriever, O. Rosier, M. Müller, W. Neff, and R. Lebert, "Highly repetitive, extremeultraviolet radiation source based on a gas-discharge plasma", *Applied Optics*, vol. 38, pp. 5413-5417, 1999.
- [6] J. G. Kim, H. J. Cho, S. K. Park, S. H. Lee, B. G. Choi, J. Y. An, Y. I. Cheon, Y. H. Jeon, T. Ishigaki, K. Kang and W. S. Yoo, "Investigation of unexpected residual effects of ultraviolet based measurements of SiO₂/Si interface by photoluminescence", *ECS Solid State Lett.*, vol. 3, pp. N11-N14, 2014.
- [7] N. Philip, B. N. Saoudi, M. C. Crevier, M. Moisan, J. Barbeau, J. Pelletier, "The respective roles of UV photons and oxygen atoms in plasma sterilization at reduced gas pressure: the case of N₂-O₂ mixtures", *IEEE Trans. on Plasma Sci.*, vol. 30, pp. 1429-1436, 2002.
- [8] A. M. Anpilov, E. M. Barkhudarov, Yu B. Bark, Yu V. Zadiraka, M. Christofi, Yu N. Kozlov, I. A. Kossyi, V. A. Kop'ev, V. P. Silakov, M. I. Taktakishvili and S. M. Temchin, "Electric discharge in water as a source of UV radiation, ozone and hydrogen peroxide", J. Phys. D: Appl. Phys., vol. 34, pp. 993-999, 2001.
- [9] Xin Miao Zhao, J. C. Diels, Cai Yi Wang, J. M. Elizondo, "Femtosecond ultraviolet laser pulse induced lightning discharges in gases", *IEEE Journal of Quantum Electronics*, vol. 31, pp. 599-612, 2002.
- [10] A. V. Phelps, Z. Lj. Petrović and B. M. Jelenković, "Oscillation of low-current electrical discharges between parallel-plane electrodes. III. Models", *Physical Review E*, vol. 47, pp. 2825-2838, 1993.
- [11] Z. Lj. Petrović and A. V. Phelps, "Temporal and constriction behavior of low-pressure, cathodedominate argon discharges", *Physical Review E*, vol. 56, pp. 5920-5931, 1997.
- [12] M. M. Pejović and M. M. Pejović, *Electrical breakdown of gases: measuring systems and experimental research*, University of Niš: Faculty of Electronic Engineering, 2009, in Serbian.
- [13] Avantes spectrometer Avaspec 3648, datasheet. [On Line]. Available at http://www.wacolab.com/avantes/ spectrometers14.pdf.
- [14] Y. Smirnov and N. Yudin, Nuklear Physics, Moscow: Nauka, 1980.
- [15] V. S. Fomenko, Emissionny Svoystva Materialov, Spravochnik, Kiev: Naukova Dumka, 1970, in Russian.
- [16] N. A. Ashcroft and N. D. Mermin, *Solid State Physics*, New York: Holt, Riehart and Winston, 1976.
- [17] E. N. Živanović, "Influence of combined gas and vacuum breakdown mechanisms on memory effect in nitrogen", *Vacuum*, vol. 107, pp. 62-67, 2014.
- [18] J. M. Meek and J. D. Craggs, *Electrical breakdown of gases*, New York: John Wiley and Sons Inc., 1978.
- [19] A. Pedersen, "On the electrical breakdown of gaseous dielectrics-an engineering approach", *IEEE Trans. Electr. Insul.*, vol. 24, pp. 721-739, 1989.
- [20] D. Blois, P. Suppiot, M. Bary, A. Chapput, C. Foissac, O. Dessaux and P. Goudmand, "The microwave source's influence on the vibrational energy carried by N₂(X) in a nitrogen afterglow", J. Phys. D: Appl. Phys., vol. 31, pp. 2521-2531, 1998.

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- [21] B. F. Gordiets, C. M. Ferreira, M. J. Pinheiro and A. Ricard, "Self-consistent kinetic model of low-pressure N₂-H₂ flowing discharges: II. Surface processes and densities of N, H, NH₃ species", *Plasma Sources Sci. Technol.*, vol. 7, pp. 363-378, 1998.
- [22] B. F. Gordiets, C. M. Ferreira, V. Guerra, J. Loureiro, J. Nahorny, D. Pagnon, M. Touzeau and M. Vialle, "Kinetic model of a low pressure N₂-O₂ flowing discharge", *IEEE Trans. Plasma Sci.*, vol. 23, pp. 750-68, 1995.
- [23] E. Eslami, C. Foissac, A. Camparague, P. Supiot and N. Sadeghi, "Vibrational and rotational distributions in N₂(A) metastable plasma", In Proceedings of the XVI Europhysics Conference on Atomic and Molecular Physics of Ionized Gases (ESCAMPIG) - 5th International Conference on Reactive Plasmas (ICRP) Join Meeting, Grenoble, France 2002, European Physical Society, vol.1, p.57.
- [24] V. Guerra, P. Sa and J. Loureiro, "Kinetic modeling of low pressure nitrogen discharge of the postdischarge", Eur. J. Appl Phys., vol. 28, pp. 125-152, 2004.
- [25] P. Supiot, O. Dessaux and P. Goudmand, "Spectroscopic analysis of the nitrogen short-lived afterglow induced at 433 MHz," J. Phys. D: Appl. Phys., vol. 28, pp. 1826-1839, 1995.
- [26] A. A. Matveyev and V. P. Silakov, "Theoretical study of the role of ultra-violet radiation of the nonequilibrium plasma in the dynamics of the microwave discharge in molecular nitrogen", *Plasma Sources Sci. Technol.*, vol. 8, pp. 162-178, 1999.
- [27] P. Sa, V. Guerra, J. Loureiro and N. Sadeghi, "Self-consistent kinetic model of short-lived afterglow in flowing nitrogen", J. Phys. D: Appl. Phys., vol.37, pp. 221-231, 2004.
- [28] J. Levaton, J. Amorim, Souza, D. Franco and A. Ricard, "Kinetics of atoms, metastable, radiative and ionic species in the nitrogen pink afterglow", J. Phys. D: Appl. Phys., vol. 35, pp. 689-699, 2002.
- [29] Von Engel A, Ionized Gases, Oxford: Clarendon, 1965.
- [30] Z. Lj. Petrović, V. Lj. Marković, M. M. Pejović and S. R. Gocić, "Memory effects in the afterglow: open questions on long-lived species and the role of surface processes", J. Phys. D: Appl. Phys., vol. 34, pp. 1756-1768, 2001.
- [31] W. Brennen and E. C. Shane, "The nitrogen afterglow and the rate of recombination of nitrogen atoms in the presence of nitrogen, argon and helium", J. Phys. Chem., vol. 75, p. 1552, 1971.
- [32] J. Berkowitz, W. A. Chupka and G. B. Kistiakowsky, "Mass spectrometric study of the kinetics of nitrogen afterglow", J. Chem. Phys., vol. 25, p. 457, 1956.
- [33] G. Cernogora, C. M. Ferreira, L. Hochard, M. Touzeau and J. Loureiro, "Vibrational populations of N₂(A³Σ_u⁺) in a pure nitrogen glow discharge", J. Phys. B: At. Mol. Phys., vol. 17, pp. 4429-4437, 1984.
- [34] G. G. Manella, R. R. Reeves and P. Harteck, "Surface catalyzed excitation with N and O", J. Chem. Phys., vol. 33, p. 636, 1960.
- [35] I. A. Kossyi, A. Y. Kostinsky, A. A. Matveyev and V. P. Silakov, "Kinetic scheme of the nonequilibrium discharge in nitrogen-oxygen mixture", *Plasma Sources Sci. Technol.*, vol. 1, pp. 207-220, 1992.