

TOPICAL COLLECTION: ELECTRONIC MATERIALS FOR RENEWABLE ENERGY APPLICATIONS

# Exploration of Gas Discharges with GaAs, GaP and ZnSe Electrodes Under Atmospheric Pressure

# H. HILAL KURT 1,2

1.—Department of Physics, Faculty of Science, Gazi University, 06500 Teknikokullar, Ankara, Turkey. 2.—e-mail: hkurt@gazi.edu.tr

This work reports on the electrical and optical characterization of the atmospheric pressure glow discharge regimes for different semiconductor electrodes made of GaAs, GaP and ZnSe. The discharge cell is driven by DC feeding voltages at a wide pressure range of 0.66-120 kPa in argon and air media for different interelectrode gaps. The discharge phenomena including different stages of discharges such as glow and Townsend breakdown have been examined. In addition, the infrared sensitivities of the semiconducting materials are evaluated in the micro-discharge cell and discharge light emission measurements have been performed. The qualities of the semiconducting electrode samples can be determined by seeking the homogeneity of the discharge light emission for the optoelectronic device applications. Operation of optical devices under atmospheric pressures gives certain advantages for manufacturing of the devices including the material processing and surface treatment procedures. Besides, finite element analyses of the overall experimental system have been performed for the abovementioned semiconductors. The electron densities and potential patterns have been determined on the discharge cell plane between the electrodes. The findings have proven that the electron densities along the plasma cell depend on both the semiconductor type and plasma parameters.

Key words: Atmospheric pressure discharges, semiconductors, 2D electron densities, plasma

# **INTRODUCTION**

Until recently, most plasma experiments have been carried out under vacuum conditions. Recently, atmospheric pressure plasmas have become very important and have achieved great scientific and technological improvements, because they can be used without the need for expensive vacuum systems in many important technological applications such as material processing, sterilization, biomedical application, thin-film deposition, ozone formation and in various practical applications such as surface cleaning, modification and plasma sterilization.<sup>1–7</sup>

Microdischarge plasma cells with semiconductor electrode have enabled the stable operation of nonthermal plasmas at atmospheric pressure and gas temperature a few degrees above room temperature (1/40 eV).<sup>8,9</sup> Indeed, the atmospheric pressure plasmas can be classified in two parts: thermal and nonthermal.<sup>8</sup> Interest concerning atmospheric-pressure glow discharge plasmas has grown rapidly, and it has been found that the breakdown voltage at atmospheric pressures is very high. It is also too difficult to provide stable and uniform gas discharges, even if it is realized. Furthermore, plasma can easily make a transition from the glow discharge stage to arc discharge. At this point, one should prevent the non-uniform arc discharges using the inert gases and homogenous atmospheric pressure discharges that can operate in Townsend and glow modes. The type of the gas discharge

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depends on the external parameters and the stability of the discharge is governed by the semiconductor electrode and the transition from the Townsend discharge to glow discharge that can be developed after breakdown occurs between the electrodes. In the case of Townsend discharge, current density is low and space charge density in the plasma can be neglected and plasma can be accepted as uniform. Atmospheric pressure discharges have been investigated in terms of electrical and optical parameters such as current voltage characteristics (CVCs) and discharge light emissions (DLEs) and plasma parameters like electron distributions along the plasma cell.<sup>10</sup>

When the external applied electric voltage exceeds a threshold value between two electrodes. the charge multiplication occurs exponentially and a gas discharge is ignited and self-sustained discharge develops, which is called a breakdown process. Following breakdown process, secondary electrons contribute to the ionization in the entire discharge range depending on the nature of the cathode material. The breakdown process in gases is an important physical process that expresses the transition of the gas from an insulated state to a conductive state and has a great significance because of its wide applications in electronics and technology.<sup>11</sup> Impact ionization and secondary electron generation are two important factors in order for occurrence of the gas discharge.

Breakdown is considered to occur when the Townsend's criterion is fulfilled.<sup>11</sup>

$$\gamma_e(e^{\alpha d} - 1) = 1 \tag{1}$$

Townsend's criteria for avalanche breakdown is as follows:

$$i = i_o \frac{e^{\alpha d}}{\left[1 - \gamma_e(e^{\alpha d} - 1)\right]},\tag{2}$$

where  $\alpha$  is the Townsend first ionization coefficient, which represents the impact ionization and  $\gamma$  is the Townsend second ionization coefficient related to the secondary electron generation in front of the cathode.

The aim of this study is to point out basic physics of the glow discharge operating up to atmospheric pressure and to investigate stable discharge conditions in the case of various cathode materials (GaAs, GaP and ZnSe). This research work provides an analysis of DC discharges in the Townsend and glow modes and also presents theoretical spatial electron distributions for the purpose of understanding the complex physical process behind the microdischarges. The range of stabilization is also investigated for glow discharge operation in argon as filling gas. The plasma instabilities occur due to the high current densities in the active area of the discharge.<sup>12,13</sup> It should be noted that the transition from the stable glow discharge to the unstable glow discharge is due to the increase of the number of secondary electron emissions from the cathode after the breakdown process is conducted by both plasma parameters and semiconductor electrodes. This study may provide important contributions to future work on atmospheric pressure micro-size discharge in that respect.

# EXPERIMENTAL

The experimental setup is sketched in Fig. 1. The discharge cell is situated inside a vacuum chamber. The chamber is pumped to pressure below 0.13 kPa and then filled with argon and air up to the



Fig. 1. Schematic diagram of the gas discharge cell which is the main part of IR image converters: (1) a light source, (2) Si filter, (3) IR light beam, (4) Au contact, (5) GaAs, GaP and ZnSe cathodes, (6) gas discharge gap, (7) mica foil, (8) UV–VIS light beam, (9) transparent conductive SnO<sub>2</sub> contact, and (10) flat glass disc.<sup>12,13</sup>



Fig. 2. 3-D CVCs of Townsend discharge for different electrode spacing d (50–525  $\mu$ m) and for different diameters D of the GaP cathode under strong  $L_2$  IR illumination in Ar. (a) p = 1.99 kPa, (b) p = 4.66 kPa, (c) p = 82.65 kPa, and (d) p = 101 kPa.

operating pressure of 120 kPa. The discharge is generated in air and argon media between two parallel plate electrodes. One of the electrodes is a semiconductor covered with Au contact from one side and the other electrode is a thin film covered glass disc. CVC and DLE have been measured simultaneously. The gas discharge characteristics of plasma are measured by a multimeter (Keithley 199) and digitalized by custom-made software in a PC.

### **RESULT AND DISCUSSION**

The present work deals with an experimental study of Townsend and glow discharge in the air and argon media with the aim of examining the properties of semiconductors at the stable gas discharge conditions up to atmospheric pressures. The effect of interelectrode distance d and gas pressure p on the optical and electrical properties of GaAs, GaP and ZnSe in the case of different infrared illumination intensities have been studied in the plasma-

semiconductor system. CVCs and DLEs have been determined using multimeters and electrometers and also photomultipliers.

In Fig. 2, the current-voltage plots (CVCs) are shown for different cathode diameter D at a pressure range of 1.99–101 kPa in argon gas in the case of various interelectrode distances d at constant illumination intensity  $L_2$ .

The current tends to increase with an increasing cathode diameter D but decreases with an increasing d in Ar. The reason is that the electron densities of plasma are significantly affected by enhanced ionization rates in gas discharge media. The increase in cathode diameters results in the increase on the active area of plasma. The increase in the distance between the electrodes leads to a decrease in the number of electrons that contribute to ionization by reaching the anode from the cathode and also causing a decrease in current density due to losses caused by diffusion of electrons into the cell walls.<sup>14</sup> Figure 2 shows that stable plasma can be

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Fig. 3. 3-D CVCs of Townsend discharge for different electrode spacing d (50  $\mu$ m–525  $\mu$ m) and for different diameters D of the semiconductor cathode under strong  $L_2$  IR illumination in air for GaP electrode. (a) p = 3.73 kPa, (b) p = 4.66 kPa, (c) p = 73.32 kPa, and (d) p = 82.65 kPa.

obtained in the cell with GaP cathode up to atmospheric pressures in argon media. This proves that our system can be used as a large-area ultraviolet light source under non-thermal and large-scale uniform discharge. Microdischarges are represented by their size in microns, and a great deal of effort is devoted to obtain those systems that produce such kind of plasmas and to produce stable plasmas up to high pressures motivated by numerous applications of microdischarges, such as UV light sources, sensors and microreactors.<sup>15</sup>

Figure 3 shows the graphs obtained for air discharge under the same conditions in Fig. 2. The current values in the air media are greater than those in the argon media and are in the order of  $10^{-4}$  A. Argon has advantages in comparison with air, because it is a noble gas and more stable, and because it has oxidation in the material due to the oxygen content in the air content and therefore, it has instabilities in the CVC graphs. Air consists of a mixture of nitrogen, oxygen and other gases that electrons attach to the atomic nucleus. During the breakdown process in a plasma cell, some of the negatively charged electrons break away from the parent atoms and molecules, leaving them positively charged particles. The negatively and positively charged particles act separately under applied voltage and the movement of the charged particles causes an electric current.<sup>16</sup>

However, current and gas discharge values are lower in the argon media. Further, in the same experimental conditions, breakdown is achieved at lower voltages in the argon environment when breakdown values are compared in the case of D = 18 mm and  $d = 240 \ \mu$ m. We have found that a plasma cell can be operated up to 82.65 kPa in an air environment compared to argon, and it is clear that the stability zone is narrower in air when the curves are compared to that of Ar. This result reveals that it is possible to obtain stable atmospheric pressure



Fig. 4. The change of maximum current with respect to the pressure at different cathode diameter *D* and interelectrode distance *d* for a GaAs electrode. (a) For 50  $\mu$ m, (b) for 100  $\mu$ m, (c) for 143  $\mu$ m, and (d) for 323  $\mu$ m in the case of weak illumination intensity  $L_1$ .

plasmas in the argon up to higher pressures (101 kPa). Nevertheless, microdischarges at air media have been found to resemble Ar discharges in many respects such as current instabilities in the lower pressures under the same operating conditions.

GaAs is a compound semiconductor belongs to the III–V group elements to be formed by direct bandgap semiconductors with a zinc blende crystal structure in the periodic table and used for IR detectors in the near-IR region and also used in the field of LEDs, optical communications and control systems, solar cells, and especially for the high speed application such as fast electronic switching in optoelectronics.<sup>17–20</sup> The interactions between plasma and semiconductor influence the system characteristics. We have focused on the materials which show sensitivity against IR illumination and on the charge transport mechanism that are controlled by their behavior. We also introduce the

availability of these materials in the IR converter system as IR detectors.

If the gap distance increases, the maximum current values will decrease. For fixed electrode spacing d and fixed IR illumination intensity  $L_1$ , the variation of the maximum current with respect to the pressure is shown in Fig. 4. When the maximum current graphs are examined, it is seen that the optimum diameter value is D = 22 mm since our system can work in a wider range of stability at this cathode diameter.

ZnSe has great importance due to the use in high resolution thermal imaging systems, and it can operates up to 20  $\mu$ m. ZnSe is an II-VI inorganic mineral compound semiconductor that has been used for IR Windows in the range of (8–14  $\mu$ m).<sup>19,20</sup> The current value changes depending on the illumination intensity in the plasma system. When there is no illumination over the ZnSe cathode, the minimum current is reached as shown in Fig. 5.

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Fig. 5. Current versus voltage curves as a function of illumination intensity under dark, weak  $L_1$  and strong  $L_3$  for various gas pressures in argon media. (a) For 5.86 kPa, (b) for 8.79 kPa, (c) for 101 kPa, and (d) for 120 kPa in the case of a ZnSe electrode.

However, the maximum current value is obtained when the intensity of illumination is the largest  $(L_3)$ . Because of the intensity of the illumination, the resistance of the semiconductor varies and gas breakdown occurs at lower voltage values. When the intensity of illumination is increased, the resistance of the semiconductor decreases and accordingly the current increases.

Gas breakdown is essentially a threshold period. This means that breakdown occurs if the electric field exceeds a value that characterizes a particular set of conditions. When the magnitude of the voltage or electromagnetic radiation is gradually increased over the discharge interval, no change in the discharge emission can be noticed. If ionization suddenly increases at a certain value of the voltage or intensity, the system senses a current and a glow.

The ZnSe cathode has been illuminated homogeneously with an IR light beam in which a Si filter only passes IR light as shown in Fig. 6. The light emission from the gas discharge cell has been measured using a computerized photon counting unit. The photomultiplier tube has high sensitivity in the UV region; the DLE from the gas discharge cell is also in this region. A glass filter has been used to pass the region of 330–700 nm to destroy the IR leak in the system.

Figure 6 shows the CVCs and DLEs up to 120 kPa in the case of different IR illuminations. Much more attention must be given to the material properties and also must be focused particularly on the lightmaterial interactions and to provide enhanced resolutions in the system. On the other side, in order to achieve optimal plasma conditions, it has been necessary to investigate stable glow discharge in a wide pressure range as shown Fig. 6. The ability to measure and analyze plasma current and discharge light emissions with high spatial resolution is of key importance to optoelectronic device applications based on plasma-semiconductor technology. If one of the electrodes is made in the form of a photodetector plate with a resistance greater than  $10^6 \ \Omega$  cm, the gas discharge current is distributed across the entire electrode surface, causing a gas discharge to emit light. The homogeneity of the light



Fig. 6. DLEs with respect to the illumination intensity (dark, weak  $L_1$  and strong  $L_3$ ) for various gas pressures in argon media and constant  $d = 50 \ \mu m$ . (a) For 8.79 kPa, (b) for 101 kPa, (c) for 108 kPa, and (d) for 120 kPa in the case of a ZnSe electrode.

emission depends on the resistance distribution of the photodetector plate; the light emission intensity is proportional to the discharge current. Local changes in the resistance of the photodetector plate cause local changes in current and gas discharge light emissions. The current and DLE depend on the local parameters of the semiconducting plate, so the inhomogeneities in the semiconductor plate can be viewed from irregularities in the current and light emission as shown in Fig. 7.

Generally, the atmospheric pressure gas discharges becomes stable in which the current fluctuations cannot be seen.<sup>21,22</sup> Occasionally, under certain conditions, discharge may display instabilities and nonlinear behavior.<sup>23–29</sup> During the plasma process, positive charges accumulate on the semiconductor cathodes that reduce the voltage across the discharge gap and leads to current fluctuations. Typical CVCs of the discharge are presented in Fig. 7 together with the DLEs (Fig. 8). In our experiments, we have been able to provide stable discharges of high pressure up to 120 kPa as long as the power supply was able to provide an increasing applied voltage for small interelectrode distance  $d = 50 \ \mu\text{m}$ . An increase of the gap distance d (330  $\mu$ m) leads to a sudden appearance of a current and discharge instabilities as shown in Fig. 8.

When the radiation-voltage graphs are compared to current–voltage graphs, it is seen that these graphs are parallel, but the  $U_{\rm B}$  breakdown values are not equal to each other. The current values are very small (4 × 10<sup>-6</sup> A) for the dark Townsend discharge as can be seen from the current voltage characteristic for p = 13.33 kPa in Fig. 7. Since the current is very low, the radiation intensity (DLE) of the gas is also very low.

Gas discharge light emission has attracted interest in technical systems in order to improve the knowledge of the gas discharge physics and to solve

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Fig. 7. CVCs with respect to the pressure in the case of dark, weak  $L_1$  and strong  $L_3$  illumination intensity in argon media and constant  $d = 330 \ \mu m$ . (a) For 13.33 kPa, (b) for 101 kPa, (c) for 108 kPa, and (d) for 120 kPa in the case of a ZnSe electrode.

the practical problems associated with the use of such discharge.

The basic characteristics of DC discharges have great importance for exploring and improving the properties of atmospheric pressure DC gas discharges. Therefore, finite element analysis is very fundamental in the field of plasma physics to describe the nature and physical background of the different dynamic phenomena.<sup>28</sup>

To understand electron densities in the plasma process, electron density distributions for GaAs, GaP and ZnSe have been obtained by a theoretical simulation programme at the same gas pressure. As the band gaps of the materials decrease, the electrons acquire enough energy to excite and ionize gas atoms in the system. In addition, bigger ionization rates are achieved for narrow band gap materials. The electrons in microplasma cell are accelerated to higher energies in the interelectrode distance, and the magnitude of max electron density is around  $6.247\times10^{22}\,m^{-3}$  for GaAs,  $1.7\times10^{21}\,m^{-3}$  for ZnSe and 2.11  $\times$   $10^{21}\,m^{-3}$  for GaP.

It is clear from Fig. 9 that densities of the electrons vary for different cathode materials. The figures show that electron distribution occupies a larger area for GaAs and GaP cathodes as compared to the ZnSe cathode across the whole discharge gap.

#### CONCLUSION

In this study, there has been presented an experimental and theoretical investigation of atmospheric pressure discharges motivated by numerous applications under DC Townsend and glow discharge modes in the case of GaAs, GaP and ZnSe cathodes, and also there are discussed the mechanisms leading to the current filaments in the gas discharge system. It has been shown that the homogenous DLE in the gas discharge range can act as a large area UV light source when the gas pressure and the electric field are high enough, and



Fig. 8. DLEs with respect to the pressure in the case of dark, weak  $L_1$  and strong  $L_3$  illumination intensity in argon media and constant  $d = 330 \ \mu m$ . (a) For 13.33 kPa, (b) for 101 kPa, (c) for 108 kPa, and (d) for 120 kPa in the case of a ZnSe electrode.

when the semiconductor system is excited by IR light. The result of our extensive experimental work has a great importance in the implementation of our presented device (IR image converter with semiconductor electrode) at the atmospheric pressures. At the same time, this device uses micro-emulsions that occur in small volume cells containing various materials and complex structures. These discharge characteristics strongly depend on the geometry of the plasma cell. For this reason, it is important for the optimization of the cell to know the relation between the geometric parameters and the characteristics of the discharge up to atmospheric pressures. Furthermore, increasing the sensitivity and resolution of large-scale gas discharge cell with a semiconductor cathode has been tried by determining the regions where the current and discharge emission are stable.

In order to increase the sensitivity and resolution, it is necessary to understand the gas discharge characteristics of the systems with semiconductor cathodes in detail with the aim of the determination of the optimum discharge conditions. These features are key parameters for designing gas discharge systems. The effect of the gas environments on the discharge characteristics and the behavior of the current have been investigated. In addition, we have acquired the spatial distributions of discharge plasma by computational simulation for GaAs, GaP and ZnSe electrodes. 2-D electron density plots demonstrate that the largest electron density for a GaAs electrode and the lowest electron density for a ZnSe electrode have been obtained. There exists a small plasma region for ZnSe, while larger plasma regions for GaAs and GaP are formed. The calculation results have showed that the simulation gives information adequately on the fundamental properties of the discharge such as spatial electron distributions. As a conclusion, our system can operate up to atmospheric pressure or higher pressures such as 120 kPa at the optimal discharge conditions. Thus, we can use our system as a large area UV light source up to high pressures, especially for a ZnSe cathode.



Fig. 9. 2-D spatial electron distributions at 66.66 kPa (a) for GaAs electrode, (b) for ZnSe electrode, and (c) for GaP electrode. *d* shows the interelectrode distance between the electrodes and *D* is the diameter of the gas discharge cell.



Fig. 9. continued.

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