Modeling and Simulation of a Miniaturized Gas Ionization Sensor: Detection of Greenhouse Gases

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Received: 21 January 2013 /Accepted: 14 June 2013 /Published: 25 June 2013

Abstract: Gas ionization sensor (GIS), made of two parallel plates, works on measuring the breakdown voltage of gases that is unique for each gas. The gas breakdown inside the gas chamber occurs due to the ionization of gas molecules by accelerated electron impacts. The acceleration of electrons is very depended on the effective electric field they experience. It is shown that metallic or semiconductor nanowires grown between the two plates improve the sensitivity of the device and breakdown voltages of the gases are considerably reduced. In this work we report the design, modeling, and simulation of a miniaturized GIS based on nanowires. We have developed simulating software based on an open source simulator XOOPIC. The simulation tool is based on combined Particle-In-Cell and Monte-Carlo-Collision approaches. The tool is developed to model and simulate the gas ionization sensor to detect various gases including greenhouse gases with optimized breakdown voltages. *Copyright © 2013 IFSA.*

Keywords: Gas sensor, Particle-in-cell, Monte-Carlo-collision, Green house gases, Nanowires.

1. Introductions

Gas sensors integrated in MEMS with high selectivity, reversibility and durability is highly desirable. In our lab, there is an ongoing research to develop and implement a breakdown ionization gas sensor based on nanowires. This miniaturized inexpensive device is capable of detecting gases in a pressure range of $1 \times 10^{-6} < P < 100$ Torr. The sensor is made of nanowires with high aspect ratio sandwiched between two parallel conductive plates. The role of nanowires is to amplify the electric field inside the gas chamber to lower the breakdown voltages of gases.

The preliminary results of the design and characteristics of the device is reported previously [1-2]. To optimize the structure and functionality of the device in terms of sensitivity, selectivity and to determine the breakdown voltages of gases prior to fabrication of the sensor we have developed a

simulation tool to model and design this miniaturized gas sensor. The software is developed to model the device in terms of the materials, structures, configurations, shape and aspect ratio of nanowires. Our model which is based on combined Particle-In-Cell and Monte-Carlo-Collision approaches (PIC-MCC) provides a platform for further development and optimization of the device. The characteristics of electric fields induced by nanowires with various tip shapes and their interactions were investigated using COMSOL simulation tool. The effects of all other structural parameters to maximize the local electric field were investigated. The results of these studies were previously reported [3] and based on those we designed a device to use in GIS-XOOPIC to determine the breakdown voltages for several gases including greenhouse gases. To verify the results of our simulation, we have compared the results of our work with those we reported using fabricated devices [4, 5].

2. The Device Model and Sensor Structure

Gas ionization sensors (GIS) work based on measuring the unique value of breakdown voltage (V_b) of different gases. It is known that every gas has a unique breakdown voltage in a constant pressure and temperature which acts like a fingerprint for that gas [6-9]. The gas breakdown inside an ionization cell occurs by electron impact ionization mechanism. Free electrons existing in the ionization cell ionize the gas molecules, therefore creates more free electrons and if the process continues, the number of free electrons increases exponentially which results in the flow of a very large current that leads to breakdown of gases.

By applying an external electric field to a two parallel plates a few electrons are forced to leave the shell; therefore they can excite the gas molecules and ionize them. As the voltage increases, electron impact ionization occurs between electrons and lead to increasing the current density until the breakdown happens at V_b . Current density at this region is given by [6-9]

$$J = J_{\text{sat}} e^{\alpha d} / (1 - \gamma(e^{\alpha d} - 1)), \quad (1)$$

where α and γ are the Townsend's primary and secondary ionization coefficients and J_{sat} is the saturation current. " α " represents the number of ionization collisions that an electron made by accelerating for 1 cm in the field direction and " γ " represents the number of electrons which liberated per incident ion at the cathode. " α " and " γ " are the functions of electric field.

The current becomes infinite if the voltage increases up to V_b , which affects " α " and " γ " parameter in a way that current increases hysterically in a region where:

$$1 - \gamma(e^{\alpha d} - 1) = 0, \quad (2)$$

which is known as Townsend criterion and V_b is known as breakdown voltage.

The nanowires/nanorods structures are very suitable for gas ionization sensors. Their high aspect ratio and sharp tips enhance the electric field locally around the tips and this accelerates the breakdown process due to creation of a corona or conducting filament of highly ionized gas around the tips. The gap between electrodes is bridged by a powerful electron avalanche (promoted by corona), and a self-sustaining interelectrode discharge will be formed at a lower voltage compared to parallel plate capacitors [1-5]. Applied electric field, E_{app} , in a parallel-plate capacitor is uniform in the gap between the plates, but if one of the electrodes is replaced by a protruded surface such as metallic nanowires/nanorods, locally high electric field will be formed at the tip of each structure caused by field enhancement effect [1]. The local electric field around the tips is given by:

$$E_{\text{loc}} = \beta E_{\text{app}}, \quad (3)$$

where $E_{\text{app}} = V/d$ is the applied electric field, and β is the field enhancement factor that relies on the geometry of the device and it is larger in structures with sharper tips and higher aspect ratio [9].

The field enhancement factor (β) has been the subject of many analytical, computational and experimental investigations and several formulas have been obtained to predict a value for it based on the geometrical model for the micro protrusion or nano protrusion [9]. These geometrical models include "hemisphere on a plane", "hemisphere on a post" and "hemi-ellipsoid on plane". For instance, the "hemisphere on a plane" model predicts that for ultrahigh aspect ratio structures, β is almost proportional to the ratio of protrusion length L to tip curvature r_t :

$$\beta \approx 0.7L / r_t, \quad (4)$$

Due to the interaction between electric field components produced at the tip of nanowires, the resultant electric field (a major parameter to lower the breakdown voltage) is affected by the geometry, shape, tips, configurations, materials and the aspect ratio of these nanostructures. These parameters are the subjects of our studies in this work to optimize the design and functionality of the sensor.

The schematic illustration of the device is presented in Fig. 1.

Fig. 1. Schematic illustration of the sensor [1].

The detail structure and fabrication of the sensor based on gold nanowires were previously reported [1-5].

3. Software Description

An open source simulator, XOOPIC is designed based on PIC-MCC to simulate plasmas in a well-defined geometry using a variety of boundary conditions.

Particle-in-cell (PIC) Monte Carlo simulation has become a very effective tool in exploring processing plasmas. A particularly attractive feature of this method is that it allows the simulation of physical processes, which cannot always be observed or reduced directly from laboratory experiments.

The idea of this technique is to simulate the electron motion in k-space using random numbers to account for the random nature of this motion. The free electron flights are interrupted by the scattering process and are resumed again and again, each time from a new starting point in the k-space. The elastic and inelastic particle collisions in the gas chamber are treated using the MCC method. In the particle-push phase of the PIC cycle, each particle is tested to determine whether or not it scatters.

As a starting point we used a uniform distribution of all particles inside of the GIS chamber. The main particle types used in this work are: neutrals, primary electrons, secondary electrons, single charged positive ions and single charged negative ions. Primary electrons are ejected from the nanowires tips, by field emission and move toward the anode. Their position and velocity is affected by the electric field strength, by the collisions with other particles and collisions with the walls. When a primary electron collides with a neutral particle, the collision can be one of the following types:

1. A primary electron elastically collides with a neutral, with no energy lost but a change in the particles velocity occurs.
2. A primary electron collides and ionizes a neutral particle, with energy loss and change into the particles velocity. The neutral atom becomes a single positive charged ion and a secondary electron is released from its orbit.
3. A primary electron collides and excites the neutral particle, with energy loss that changes into the particles velocity.
4. A primary electron collides and attached to the neutral particle. The neutral particle becomes a single negative charged ion.

Fig. 2 shows various electron-gas particle collisions inside the gas chamber.

Fig. 2. Electron-particles collisions inside the gas chamber.

In this work, we have integrated elastic, excitation, ionization, vibrational and electron attachments cross sections into our simulation package. These parameters were collected from available data in the literature [10-21].

Fig. 3 shows steps are taken in one round to calculate the electric charges and current within one time interval of Δt .

Step 1, electrons are accelerated due to the applied potential on the electrodes.

In step 2 collisions between the electrons and gas molecules happens. The probability of the collision is depended on the electrons and ions cross –sections. As the collisions occur the velocity and direction of electrons are changed. The electric charges and the current are calculated at this stage, step 3. In step 4, the new electric field is calculated using Poisson's equations. This new electric field exerts a larger force on the emitted electrons causing higher accelerations and more collision inside the gas chamber. As the process continues, positive and negative charges are accumulated on opposite electrodes until the breakdown happens.

Fig. 3. Classical PIC – MCC schemes.

Since XOOPIC is a 2-D simulator, the nanowire array was modeled by parallel rectangular conductive sheets along the 3rd imaginary dimension (z) with unity length.

We have also implanted some circuit elements such as the series resistance, R, with the ionization cell. In an actual DC discharge, especially at currents close to the breakdown point, the voltage drop across R becomes important and needs to be considered. Our model also includes the contribution of field-emission from nanowires tips to the discharge process. The nanowires are considered as cathode in our simulations. The nanowires were defined here as both field-amplifying equipotential and field-emitter boundaries with a constant β . Field emission current density from the nanowires tips was computed according to the general Fowler-Nordheim (FN) equation given by:

$$J = \frac{AE_{loc}^2}{\phi_{Au}} \exp\left(-\frac{Bv\phi_{Au}^{3/2}}{E_{loc}}\right), \quad (5)$$

where A and B are the universal FN constants, ϕ_{Au} is the work function/electron affinity of nanowires, and v is the field-dependent correction factor [9].

At certain gas pressure, the minimum voltage that led to formation of an avalanche from the nanowire tips was recorded as the corresponding V_b .

4. Simulation Results

As it is discussed above, the applied field between the two parallel plates will be enhanced largely by placing nanowires between them. Fig. 4 shows the simulated electric field inside a GIS.

Fig. 4. The local electric field from XOOPIC simulation for rectangle nanowire shape.

The enhancement factor is very dependent on the aspect ratio and shape of the nanowires tips as well as the interspace distances between the nanowires. The effects of these structural parameters on the induced

local electric fields between the two parallel plates were studied by these authors and reported previously [22-31]. Devices were designed considering gold, silver, and semiconductor ZnO as the materials for the nanowires.

Due to the discharge current between the two plates, the electron and ion concentrations build up in time. Fig. 5 shows a typical emission of electrons from the tips of the nanowires inside the gas chamber.

Fig. 5. The 2-D model of the device showing avalanche of electrons in the gas chamber at P=1 Torr.

During this process the potential on the cathode electrode is modified due to induced transient currents and the series resistance in the circuit. Eventually at a threshold voltage an avalanche of carriers inside the devices causes the breakdown of the gas. Fig. 6 shows a typical I-t characteristic of the device. A Δt (defined in Fig. 3) = 10^{-14} second was considered in our model and the value of t in Fig. 6 represents the number of cycles of completed MCC calculations. The value of the t obtained at any breakdown is very dependent on the applied voltages. The breakdowns for various gases are only comparable when all happens at the same time of t . However, it is a very time consuming to adjust applied voltage such a way that the breakdown of different gases happens at the same time. For this reason, we have determined the variation of t with respect to applied voltages. This is shown in Fig. 7 for couple of cases. As the curves show there is linear relationship between the applied voltage and the time. Using the extrapolation of these curves, we have obtained the comparable breakdown voltages happened at the same time for gases studied in this work.

In order to verify our simulations results, we have compared the breakdown obtained using the simulation with those obtained using a fabricated GIS based on gold nanowires similar to the designs used in this work. Studies showed that the breakdown voltages obtained using simulation technique for argon gas under various pressure was very close to those obtained experimentally. The results are reported by these authors elsewhere [4, 5].

Fig. 6. Generated cathode current versus time for Ne gas in a device with gold nanowires.

Fig. 7. Typical V_{app} vs t for SF_6 and CO_2 gases. Measurements are done under the same conditions for all gases. The relative breakdown voltages happened at specific time are determined by extrapolating of the curves.

The results of simulations of breakdown voltages for several gases in the modeled GIS devices are tabulated in Table 1. Various nanowires are considered in the designs.

5. Discussion and Conclusion

In this paper we reported the development of a software tool based on the Monte Carlo Collision method to model and simulate the structure of a miniaturized gas ionization sensor based on grown

nanowires on silicon substrate. In this work, we have emphasized to model a device with optimized response time and low breakdown voltages for various gases. We have shown that implementation of nanowires between the two parallel plates enhances the local electric field, responsible for the breakdown voltage. The simulation codes are set to optimize the device parameters for various gases including single atomic gases like Ar, and Ne, as well as greenhouse gases like CF_4 , SF_6 , and NH_3 . To verify our simulation results, we have compared the characteristics of a modeled device with those using experimentally fabricated similar GIS based gold nanowires device.

Table 1. The simulated breakdown voltage at pressure $P = 1$ Torr, $\beta = 500$ and $T = 300$ K.

Nanowire material	Background gas	Breakdown voltage [V]
Ag	Ar	120
	CF_4	195
	NH_3	90
	Ne	140
Au	SF_6	200
	CF_4	222
	Ne	185
	Ar	160
	NH_3	150
	SF_6	270
	N_2	175
	CO_2	215
	CO	177
ZnO	Ar	93
	CF_4	180
	SF_6	170

Acknowledgements

The authors would like to acknowledge support of Natural Science and Engineering Research Council of Canada, and the Faculty of Engineering and Computer Science, Concordia University.

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