Design and engineering of ionization gas sensor based on Mn nano-flower sculptured thin film as cathode and a stainless steel ball as anode

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A R T I C L E   I N F O

Article history:
Received 23 July 2017
Received in revised form 4 March 2018
Accepted 28 March 2018
Available online 28 March 2018

Keywords:
Nano-flower sculptured thin films
Oblique angle deposition
Ionization gas sensor
Ball shaped anode
Selectivity
Secondary electron emission

A B S T R A C T

In this work a field ionization gas sensor based on 3-fold symmetry Mn nano-flower sculptured thin film as cathode and a stainless steel ball (SSB) as anode is used. The breakdown voltage of the system was studied for nitrogen, oxygen, argon, air and carbon mono-oxide gases. Investigations for these gases at different distances between anode and cathode (40, 100 and 200 μm), anode (SSB) diameter sizes of 2, 6 and 10 mm and different gas pressures (0.2–1000 mbar) confirmed Paschen’s Law. Results for different anode sizes showed that by decreasing the ball size at high pressures the breakdown voltage decreased, while at low pressures the opposite behavior was observed. For pd values (mbar cm) between 0.025 and 0.2 mbar cm and for different gases studied in this work a good gas selectivity was obtained. Lower breakdown voltages at medium gas pressures are obtained when comparison is made with the published data for different materials (i.e., CNT, Cu, Ag and ZnO) and designs. The effective secondary emission coefficient of Mn nano-flowers and the ratio of the probability of secondary electron emission of Mn to that of other types of cathodes made of different materials showed higher values. These results suggest that Mn can act as a good material in ionization sensors and the nano-sculptured structure designed and engineered in this work can enhance the sensor’s performance.

Nano-structure and morphology of the produced samples were obtained by field emission electron microscope (FESEM) and atomic force microscope (AFM) analyses.

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1. Introduction

Gas sensors can be of high importance in different environmental and industrial applications, including terrorists’ attacks. In general, gas sensors are classified into two basic types, based on their working mechanism; a group based on the chemical absorption process, and a group based on the physical breakdown of the gas [1].

In the first group the absorption of gas molecules on the surface of the sensor change the electrical resistance of the sensing layer. In these sensors, detection of gas molecules is due to the presence of catalysts and sensitive materials such as SnO2 on the surface. However, detection of gases with low absorption energy remains very difficult [2–4]. In order to activate chemical reactions and obtain faster and stronger response they should be operated at >300 °C [1,5,6]. Saturation of surface active sites for absorption is responsible for reduced sensitivity and non-linear operation and is another limitation of these sensors.

The second group of gas sensors is based on the physical ionization of gas molecules. These sensors consist of a closed chamber within which two electrodes acting as cathode and anode are positioned at a certain distance from each other. When a voltage is applied to these electrodes, the electric field in the space between the electrodes causes acceleration of electrons. The inelastic interaction of electrons with the gas molecules ionizes them (if electrons have enough energy for this process). For each gas there is a certain temperature and pressure in which the breakdown voltage occurs (Vb) which is also known as the fingerprint of that gas [7]. The response time of these sensors is very fast, they are very selective and in addition they do not require a high working temperature [4]. However, the usual problems with these sensors are their large size, high power consumption and a high breakdown voltage, which can be hazardous.

In addition to the interaction of electrons with gas molecules for ionization process, a field emission mechanism also influences/affects the formation of ion current and breakdown voltage
of the gas [8,9]. Electron emission occurs where electrons directly tunnel from the cathode into the gas due to the very high electric fields at microscale dimensions and serves as the critical, additional current producing mechanism [10,11]. Go and Venkatraman [12] have published a review article on microscale breakdown and the accompanying phenomena associated with it considering experimental observations, theoretical developments and simulation results which provides thorough information on this process. General, for ionization of gas molecules a very large electric field is needed. This can be achieved by reducing the distance/gap between the two electrodes and/or by using structures with sharp tips, resulting in very strong electric field of 10^8–10^10 V/m [13]. Hence the design of shapes and the geometry of electrode structures in this type of sensors is of importance and the use of porous nanostructures with sharp tips can lead to significant reduction of power consumption and increase in security of the system [14]. A large volume of studies on the enhancement of ionization sensors have been carried out using nanostructures, namely carbon nano-tubes (CNTs) [15–20], titanium dioxide nano-tubes [21], gold nano-wires [4,22,23], silver nano-wires [24], tin nano-wires [25], zinc oxide nano-wires [26,27], titanium dioxide nano-rods [28], and silver zig-zag sculptured nano-structure [29]. The published research on sensors based on semiconductors (metal oxides) show higher stability relative to those based on CNTs but the latter require lower breakdown voltages than the former [15,26]. Metallic nanostructures, because of their higher conductance property relative to semiconductor nano-structures, can have a large population of conductance electrons on the surface of the nano-structure (producing an intense electric field) to interact with the gas atoms in the vicinity of the metal surface. Hence, a higher probability of the quantum tunneling process may occur, due to the change of the electrode shape and electric field distribution. The most studied metals are gold and silver, which are not economically favoured [4,22–24,29]. Manganese is a promising alternative from the transition metals, and is cheap and readily available, being frequently used in metallic alloys particularly in stainless steel and in alkaline batteries as cathode.

In this work a field ionization gas sensor based on helical Mn sculptured 3-fold symmetry nano-flower thin film as cathode, is designed for detection and sensing of different gases (i.e., air, argon, oxygen, nitrogen and carbon monoxide). In this sensor, a stainless steel ball (SSB) is used as anode and the influence of the size of the SSB as well as other parameters such as the distance between the two electrodes and the gas pressure on the response of the system is investigated. The helical Mn sculptured nano-flowers were produced using oblique angle deposition with rotation of substrate and different speeds at different sections of each rotation. Results of this system are compared with the available published data and the reasons for the differences are discussed.

Results of calculations for both the secondary electron emission coefficient of Mn nano-flowers and the ratio of the probability of secondary electron emission of Mn to that of other types of cathodes made of different materials (i.e., CNT, Cu, Au and Ag) showed higher values which implies that not only Mn itself can act as a better material in field ionization sensors but also the nano-structure designed and engineered in this work can enhance the sensor’s performance.

2. Experimental details

2.1. Materials and instruments

Mn and Ag with 99.98% and 99.99% purity were obtained from Merk Co. Glass microscope slides were provided from Bavaria Medico Co. and were cut in 18 x 18 x 1 mm³ pieces and used as substrates. Nitrogen, argon, carbon monoxide and oxygen gases with 99.999% purity were used. An Edwards E19 A3 deposition plant with electron gun source equipped with Sigma Instruments, SQM-160, USA (QMC) quartz crystal monitor was employed for deposition of the helical Mn nano-flower sculptured thin films used as cathode in the field emission gas sensor. The sensor was designed and constructed in our workshop and was equipped with a Pirani pressure gauge. Atomic force microscope (AFM; Scanning probe, model BL 022 NT-MDT) and field emission electron microscope (FESEM; Hitachi S-4100 SEM, Japan) were used for physical structure and morphology analyses of the produced samples.

2.2. Deposition of helical nano-flower sculptured thin films with 3-fold symmetry

Prior to deposition of Ag, all substrates were thoroughly cleaned in an ultrasonic bath with heated acetone and ethanol, respectively. The Edwards (Edwards E19 A3) coating plant was evacuated to a base pressure of 1.5 x 10⁻⁷ mbar. In order to achieve a uniform deposition on the substrates a 30 cm distance between the evaporation source and the substrates was chosen. In this arrangement the vapor source (6 mm in diameter) behaves like a point source with a cosine distribution and because of the 30 cm distance between the vapor source and the substrates it is expected that the vapor has straight trajectories (i.e., no appreciable scattering occurs, due to the large mean free path (~5 x 10⁴ cm [30]). Two stepping motors, which can rotate the substrate holder by the two angles, α and ϕ, control the substrate holder system, with 0.01 /step accuracy and with controlled speed. The movement of the stepper motor for rotation of the substrate about its surface normal (ϕ) and its speed of revolution, as well as facility for dividing each revolution into different sectors, are controlled through interface to a computer in which the related software (in the LAB-VIEW format) is written and installed. All these are domestic made. The substrate holder was a stainless steel disc of 10 cm diameter. The substrates were fixed along four mutually normal radii of the substrate holder disc. Hence, in each run four sets of three samples were produced for use in different analyses and reproducibility check of the samples. The deposition of samples took place in two stages. In the first stage, a 50 nm silver thin film was deposited on the glass substrates at normal deposition angle to the substrate surface. This film acts as a highly conducting base for the sensor. In the second stage, the substrate holder was fixed to a rotating feedthrough as described above, at 80° to the substrate surface normal. Then a helical Mn structure was deposited on the Ag film as the stem of the nano-flower structure with the following parameters; rotation speed of 0.3 rev/min, deposition rate of 0.8 Å/s until a thickness of 180 nm was obtained. On top of this stem, the nano-flower structure with 3-fold symmetry was deposited with two pitches. A deposition rate of 0.5 Å/s was used. Considering that for an N-fold symmetry every revolution of the substrate holder should be divided to 2N sectors, for deposition of 3-fold symmetry nano-flower the smaller sector was chosen as (Φ = 25°) which rotates with a speed of Rₛ = 0.0151 (rev/min) for 277 s, while the other sector was chosen as (Φ = 95°) with a rotation speed of (Rₛ = 0.3 (rev/min) for 53 s. This process was repeated three times until one complete turn (360°) or one pitch of helical structure was fabricated. The total thickness for the stem and the two nano-flower pitches was 280 nm.

2.3. Gas ionization sensor

The components of the gas ionization sensor consisted of a vacuum chamber, pressure gauge, rotary pump, gas inlet needle valve, a stepping motor controlling the movement of electrodes, and a thermometer and a micro-ammeter. The vacuum chamber is a cylindrical Pyrex glass with a height of 14.5 cm and outer and inner diameters of 17 cm and 15.5 cm, respectively. The top and the bot-
tom of this Pyrex glass are closed with two aluminum flanges, each of which contains a facility for differently required connections such as inlet needle valve and electric feedthroughs. The pressure of the chamber was kept constant by the use of an inlet needle valve (Edwards, LVI1OK) for the investigated gas. The Mn samples as described in the preceding sub-section were used as the cathode and a stainless steel ball acted as the anode of the system.

In order to investigate the influence of the distance between the two electrodes, the anode was mounted on a stepping motor so that it could be moved in the z-direction. In addition, in order to make use of the whole area of the cathode for multiple measurements, the cathode could be moved in the x and y directions using two other stepping motors.

3. Theory of gas ionization

In order to draw conclusions from the comparison of other sensors with the sensor presented in this work (Section 5) two theoretical approaches/phenomena may be considered for the gas ionization as described below.

Ionization of gases can be the result of field ionization because of tunneling process and/or the impact process, which depends on the population of electrons and the collision between particles. Field ionization occurs when a neutral atom or molecule is ionized through the tunneling of a valence electron bound by a potential well into the vacuum or unoccupied states of a surface under high applied electric field [31]. In quantum mechanics, this process is explained by assuming that the valence electron of a neutral atom is trapped in a potential well to a depth equal to the ionization potential of an atom (U_j) [32]. By applying an external electric field, the probability of tunneling of an electron trapped in this well increases due to a decreased height. This effect requires a strong electric field, which in turn depends on the geometry of the system and the surface morphology of the electrodes such as presence of sharp tips on the surfaces of the electrodes, the distance between electrodes and the position of gas atoms/molecules relative to the sharp tips on the surfaces of the electrodes. As the electric field becomes stronger, the width of the potential barrier becomes comparable to the de Broglie wavelength of the electron which is trapped in the potential well, hence the probability of tunneling to the vacuum or unoccupied states increases [32]. For a metallic surface, the threshold electric field for the field ionization process is of the order of 2.5 × 10^8 V/cm which can only happen in the neighboring hood of sharp tips [10]. The tunneling process into unoccupied surface states of a sharp metal tip occurs when the energy level of the valance electron bound to an atom (or ionizing particle) is positioned above the Fermi level of the metallic tip [14,33]. The tunneling probability (D) is defined as:

\[
D = \exp[-6.8 \times 10^{-7}(U_j - 7.6 \times 10^{-4}e^{1/2})^{1/2}] \chi_c.
\]

where the critical distance (\chi_c) for field ionization of the gas atom/molecule may be obtained from;

\[
e\chi_c = (U_j - \Phi),
\]

where, e, E and \Phi are electron charge, the applied field strength, and the work function of the metal, respectively. At distances less than the critical distance, field ionization will not happen [4] as the electron energy level would then lie below the Fermi level in the metal.

In semiconductors, the field penetration into a semiconductor results in band bending that contributes to a degenerate region at the surface [10,33–35]. Hence, the condition of tunneling is modified as:

\[
e\chi_c = U_j - (\Phi + \Phi_h),
\]

where \Phi_h is the additional work function induced by the band bending because of the field penetration and is given by:

\[
\Phi_h = \frac{E_\lambda}{E_F}.
\]

Where \epsilon_r and \lambda are the relative permittivity and the penetration depth of the semiconductor, respectively. \Phi_h is proportional to the penetration depth of the applied electric field. This shows that higher field penetration should lead to more band bending, which in turn contributes to the decrease of the critical distance at which the Fermi energy and the ground state of the atomic electron coincide to trigger the field ionization process. Hence, this decrease in \chi_c because of band bending in semiconductor results in higher tunneling probability and consequently an increased field ionization current with respect to a metallic surface.

The impact ionization process is dependent on the system pressure. At low pressures, the mean free path between collisions is longer than the distance between the electrodes. Hence, although the electrons can be accelerated to ionizing energies, they are unlikely to collide with anything other than the anode. This leads to a very high breakdown voltage at very low pressures.

At very high pressures, the mean free path is very short. This means that the electrons never have enough time to be accelerated to the ionization energy before hitting an atom or molecule. This leads to a high breakdown voltage at very high pressures.

At medium pressures, neither of the above two extremes may occur. The population of atoms and the mean free path of electrons act in such a way that a minimum in the breakdown voltage is obtained. This minimum, of course depends on the type of gas and the material of the electrode.

These processes will be considered in more detail in Section 4 where the influence of different parameters (i.e., gas pressure, distance between the electrodes, and size of the anode (steel ball)) on the performance of the sensor is discussed.

4. Results and discussions

4.1. Structure analysis of the 3-fold symmetry Mn sculptured nano-flowers

Fig. 1(a and b) and (c–e) shows the AFM and FESEM images of the 3-fold symmetry Mn helical sculptured nano-flowers, respectively. The AFM images clearly show the 3-fold symmetry of the grown Mn nano-flowers. The mean diameter and the surface roughness of the observable grains/petals of nano-flowers were measured/analyzed from the 2D AFM image using JmicoVision and Nova software codes and values of 62 nm and 9.4 nm were obtained, respectively. FESEM images of these nano-flowers (Fig. 1) were analyzed using Imaging software. The cross-section of these films (Fig. 1(c) and (e)) shows a helical structure and formation of nano-petals on each pitch. The surface of the sample in Fig. 1(d) also clearly shows the formation of 3-fold symmetry nano-flowers. The Ag bottom layer film and the Mn top layer film thicknesses are indicated using I and II on Fig. 1(e) and values of 50 nm and 280 nm are obtained, consistent with the deposition information.

4.2. Influence of the distance between electrodes on the breakdown voltage

According to Paschen’s law, the breakdown voltage in a uniform electric field is a function of the product of the pressure (p) and the distance between the two electrodes (d) [7]. Considering that \( p \propto nK_BT \) for an ideal gas, then the breakdown voltage should be a
function of \( nd \) (where \( n \) is the gas concentration/density). Hence, by applying the Townsend criteria we have:

\[
V_{\text{breakdown}} = \frac{E_i \cdot d}{e \cdot \lambda \ln \left( \frac{e}{d} \right)},
\]

\[
\lambda = \frac{(k_B T)}{(\sqrt{2} p n r_i^2)}
\]

where, \( e \) is the electron charge, \( E_i \) is the ionization energy of the gas, \( \lambda \) is the mean free path of the gas, \( k_B \) [J/K] is the Boltzmann constant, \( T \) [K] is the absolute gas temperature, \( p \) [Pa] is the gas pressure, and \( r_i \) [m] is the radius of the ionized gas atom/molecule [36].

In Fig. 2(a–o) the response (breakdown voltage) of the sensor for different gases, namely nitrogen, oxygen, argon, air and carbon monoxide and for anodes (SSBs) of different diameters of 2 mm (column I of Fig. 2), 6 mm (column II of Fig. 2) and 10 mm (column III of Fig. 2) and the distance between the two electrodes of 40 \( \mu \)m, 100 \( \mu \)m and 200 \( \mu \)m is given. It can be observed that the behavior of the sensor (breakdown voltage) for all gases, for all anode sizes and all distances between electrodes is consistent with Paschen’s law.

At low pressures, a higher breakdown voltage is observed for all varied parameters. This can be due to low concentration of gas molecules between cathode and anode, hence number of interactions that lead to gas ionization is also low and mean free path of electron is increased (see Section 3). Therefore, at this pressure range, a higher energy is needed for gas ionization and breakdown occurs at higher voltages. This is consistent with the impact theory (Section 3). At medium range pressures used in this work, the concentration of gas molecules is increased, hence the electron mean free path is decreased and the number of interactions is increased. Therefore, a higher number of secondary electrons is produced which lead to lower breakdown voltages. On further increase of gas pressure, higher number of interactions may occur, hence the mean free path of electrons is reduced. Hence, electrons do not have enough time to be accelerated to the ionization energy before hitting an atom or molecule. This leads to high breakdown voltages at very high pressures. In addition, under these circumstances, due to
increased gas molecules concentration a number of gas molecules should be positioned at a distance from the sharp tips of electrode structure less than critical distance ($x_c$) and should hinder (i.e., act as a barrier for) the field ionization [4]. This also leads to higher breakdown voltages.

The influence of the distance between electrodes is shown in Fig. 2. When the distance between electrodes is reduced the electric field is increased which results in lower breakdown voltage. However, if the electrodes get too close to each other then the number of gas molecules between electrodes decreases leading to fewer inter-
actions, which results in high breakdown voltages. In Fig. 2(a)–(c) for nitrogen gas at pressures, lower than 25 mbar it can be seen that the highest and lowest breakdown voltages occur at 40 μm and 200 μm distances between electrodes, respectively. However, at pressures higher than 25 mbar, the behavior of the sensor is opposite to that at lower pressures and the breakdown voltage increases with distance between electrodes. This is due to the reduction of electric field with increasing distance between electrodes. Hereafter, we may assign the pressure of 25 mbar as a critical pressure at which the response of the sensor for nitrogen gas changes direction. The mean free path of electrons at this critical pressure of nitrogen (Eq. (6)) is 21 μm which can also be assigned as the critical mean free path of nitrogen. The same discussion can be made for oxygen (Fig. 2(d–f)), argon (Fig. 2(g–i)), air (Fig. 2(j–l)) and carbon mono-oxide (Fig. 2(m–e)) which leads to critical pressures of 8, 25, 10 and 8 mbar, respectively. The critical mean free paths values for oxygen, argon and carbon mono-oxide obtained from Eq. (6) are 72, 72 and 90 μm using the above mentioned critical pressures. In case of air which may be considered as a combination of 78% nitrogen and 22% oxygen, the mean free path may be calculated by assuming 0.78(λ\textsubscript{nitrogen}) + 0.22(λ\textsubscript{oxygen}), which yields a value of 53 μm at 10 mbar pressure.

According to Eq. (6) the mean free path for low pressures (e.g., critical pressure) is longer. In addition, at a distance of 40 μm between the electrodes the electric field should be stronger and as mentioned above the number of gas molecules between the electrodes is less than the situation where the distance between electrodes is 100 μm or 200 μm. Hence, the number of interactions leading to the gas ionization is reduced and a higher breakdown voltage is required. At higher pressures, the mean free path is shorter. For shorter distances between electrodes at these pressures a stronger electric field is produced, hence for shorter distances between electrodes (i.e., 40 μm) lower breakdown voltage is obtained relative to 100 μm and 200 μm distances for the electrodes. Furthermore, in Fig. 2 it can be observed that at low pressures the breakdown voltage for argon gas when the distance between electrodes is 200 μm is much lower than that for nitrogen gas. This observation shows the strong influence of mean free path on the breakdown voltage.

4.3. Influence of the geometry and the diameter of anode (SSB) on the breakdown voltage

Fig. 3(a–o) shows the results of breakdown measurements of the sensor for different anode (ball) sizes and different distances between the two electrodes for different gases investigated in this work. All plots in Fig. 3(a–o) show the Paschen’s law behavior.

Results show two opposite behavior at two ends of the diagrams (i.e., low and high gas pressures). At low pressures the highest breakdown voltage is obtained for the smallest SSB (2 mm in diameter) while the lowest breakdown voltage is obtained for the largest SSB (10 mm in diameter). As mentioned before, the opposite effect is observed at the other end (high pressures) of the diagram. These observations can be explained as follows; at low pressures two phenomena may be considered; a) the electric field at the tip of the smaller SSB is stronger than that for the larger SSB, hence it is expected to obtain smaller breakdown voltage, b) the number of gas molecules between the larger SSB and the cathode is higher than that for the smaller. Therefore, a higher probability for ionization is expected for the larger SSB. However, since the gas pressure is the same for both systems then it is possible that the gas molecules between the two electrodes in case of small SSB be closer to the cathode sharp tips and this distance can be smaller than the critical distance (x\textsubscript{c}) (see Section 3, Eq. (1)). Hence, this may cause a barrier for the ionization process. However, in the case of the larger SSB, since the effective area is greater (due to larger diameter of SSB) the distance between the two electrodes for some gas molecules may be greater than the critical distance and smaller breakdown voltages may be required.

At high gas pressures, as mentioned above the behavior of the breakdown process for different SSB sizes is opposite to that of low gas pressures. This may be caused, on one hand, because at the same gas pressure the number of gas molecules available for ionization process is higher for the large SSB. On the other hand, because of high gas pressure, the fraction of gas molecules close to the cathode sharp tips is also higher and produces a stronger barrier against ionization process. In addition, the smaller SSB also produces stronger electric field, hence these two effects act in favor of the smaller SSB, which leads to lower breakdown voltages.

Finally, at the medium gas pressures the above-mentioned processes compete with each other and a minimum is observed for all SSB sizes used in this work; for each gas and for each distance between two electrodes, at a certain gas pressure all show almost the same breakdown voltage.

4.4. Selectivity, detection limit and sensitivity of the sensor

In Figs. 4 and 5 the breakdown voltage is plotted versus pd (result of pressure multiplied by the distance between two electrodes) for different SSB sizes and for different gases used in this work. In Fig. 4 the pd range less than 0.2 mbar cm and in Fig. 5 the pd range greater than 0.2 mbar cm are depicted. At very low values of pd the field ionization gas sensor shows large breakdown voltages and the selectivity of the sensor is very poor [15]. However, at this range of pd (<0.025 mbar cm), it can be seen that by increasing the distance between the two electrodes better selectivity may be obtained (compare results in columns I, II and III of Table 4 in each row at this pd range). At higher pressures up to pd = 0.2 mbar cm good selectivity (distinct breakdown voltage) is obtained for all system variations (i.e., change of SSB size and distance between the two electrodes). In Fig. 6 influence of both distance between the two electrodes and SSB size on the breakdown voltage of all gases investigated in this work and at pd = 0.2 mbar cm for different values of d = 40 μm, 100 μm and 200 μm (i.e., gas concentration of 0.002 moll\textsuperscript{−1}, 0.0008 moll\textsuperscript{−1} and 0.0004 moll\textsuperscript{−1}, respectively) is given. As pointed out above each gas exhibits a distinct breakdown behavior.

At higher pd values (Fig. 5) apart from the behavior of the sensor in all system combinations for oxygen gas, the selectivity is decreased as it can be seen in Fig. 7 where data is presented for p = 1000 mbar (i.e., gas concentration of 0.04 moll\textsuperscript{−1}).

In Fig. 8 variation of breakdown voltage with concentration of Ar-air and CO-air mixtures are given for different distances between the two electrodes as well as different SSB diameters. The detection limit of the sensor used in this work can be obtained from this figure by plotting the asymptotic lines to the curves as shown in Fig. 8. Results are summarized in Table 1 where they are also compared with the published data of Modi et al. [15] for Ar-air using carbon nano-tubes as an electrode and Liao et al. [26] for CO-air using ZnO nano-wires as an electrode. It can be seen that results of the sensor used in this work for Ar-air (3.8% (3.8 × 10\textsuperscript{4} ppm)) is higher than that obtained by Modi (1%) and for CO-air (3.2% (3.2 × 10\textsuperscript{4} ppm)) is
lower than that obtained by Liao (5%). This shows that the helical Mn nano-flower sculptured based field ionization sensor as cathode and SSB as anode has a potential for use as a detection system of gases at the percentage level in mixtures with air with fast response (application of the breakdown electric field results in a stable discharge within ~20 μs [7,15]).

A quantitative approach for obtaining the sensitivity of field ionization gas sensor is through a plot of current discharge versus logarithm of gas concentration as shown in Fig. 9. This figure shows the self-sustaining current discharge at breakdown for all gases used in this work (i.e., air, Ar, N₂, O₂ and CO). Linear logarithmic variation is obtained for all gases used over the whole range of
gas concentrations investigated. This behavior of the sensor indicates the self-sustained current discharge generated at breakdown is a characteristic feature of gas concentration for conduction. The sensitivity $C_v/(I_a-I_b)$ of a sensor is described as the ratio of the magnitude of change in response upon exposure to the gases ($I_a$) to that of without exposure to the gases ($I_b$). In Table 2 results of sensitivity of the gas sensor used in this work for the distance between the two electrodes of 100 $\mu$m are compared with those of Modi et al. [15] for 150 $\mu$m distance between the two electrodes (CNTs) and Liao et al. [26] for 100 $\mu$m distance between the two electrodes (ZnO nano-wires). Comparison of the results in Table 2 shows that Modi et al.'s [15] sensor based on CNT nano-tubes has a higher sensitivity than helical Mn nano-flower sensor while it should be noted that their results are for 150 $\mu$m distance between the two electrodes. (This larger distance provides higher number of gas molecules between the two electrodes in Modi's system), but helical Mn nano-flower based sensor shows higher sensitivity relative to that of Liao et al.'s [26] sensor based on ZnO nano-wires. In addition it should be mentioned if results of helical Mn nano-flower based sensor for 200 $\mu$m distance between the two electrodes and SSB diameter of 10 mm compared with those of Modi et al. [15] achieve higher sensitivity.

Hence, considering these facts it may be concluded that the field ionization sensor based on helical Mn nano-flowers discussed in this work for large SSB size (10 mm) shows higher sensitivity than those published in [15,26]. This can be due to higher number of gas molecules present between the two electrodes.

5. Comparison of the results of Mn nano-flower based sensor with other types of sensors

5.1. Comparison with CNT based sensor

The first enhanced ionization sensor was built using carbon nano-tubes (CNTs) [15]. The diameter and the height of CNTs were 25–30 nm and 30 $\mu$m, respectively. The distance between CNTs was 50 nm. The distance between electrodes in the CNTs based sensor was 150 $\mu$m. Modi et al. [15] only obtained very limited data, which can be distinguished in Fig. 10. Results obtained for air in this work for 100 $\mu$m and 200 $\mu$m distances between the two electrodes are compared with the CNTs based sensor containing an Al anode and a multiwall CNTs cathode in Fig. 10.
The differences at low and high pressures, as discussed in Section 4.3 could be due to the shape of the anode used in this work (SSB); by increasing the diameter of SSB lower breakdown voltages were obtained at lower pressures. However, only two points presented for air at high pressures. On the basis of only four measurements in the whole pressure range a fair comparison with the CNTs results is difficult. However, it may be that if a flat anode had been used in this work, like the one used in the CNTs sensor, good agreement or even better results may have been obtained.

5.2. Comparison with ZnO nano-wire based sensor

Field ionization sensors based on CNTs are not stable and durable and when they are exposed to oxygen, they become oxidized, while the heat caused by corona discharge can destroy the sharp tips of the CNTs. During the breakdown process, strong electric fields can change the structure of CNTs and high electric currents cause the CNTs to break and collapse leading to poor ionization electric field stability [26,34,35]. Liao et al. [26] using ZnO nano-wires as anode electrode and a copper plate as cathode electrode showed that ZnO nano-wires have greater stability at room temperature compared to CNTs, although they give higher breakdown voltages [26]. The diameter and the height of ZnO nano-wires in Liao’s work were 150–200 nm and 2 μm. Liao et al.’s [26] results for air and carbon monoxide are compared with those of the Mn nano-flower based sensor of this work in Fig. 11. In case of air (Fig. 11-a) one can see that apart from at very low pressures (∼1 mbar) the Mn nano-flower based sensor shows lower breakdown voltages. This can be due to the smaller size of the Mn grains (nano-flower petals) than the ZnO nano-wire tips which produce stronger electric field. In case of CO gas (Fig. 11b), results are comparable above 4 mbar pressure for the smaller SSBs (2 and 6 mm). Results of 10 mm SSB of Mn sensor are in agreement with those of the ZnO sensor in the pressure range of 1–10 mbar but at higher pressures the behavior of ZnO is better and shows lower breakdown voltages.

Again it should be mentioned that the use of a flat anode in the sensor of our work should have produced better results at least at low pressures (see discussion in Section 4.3), particularly in the case of air.

5.3. Comparison with Au nano-wire based sensor

Au nano-wire based sensors with diameters of about 180 nm and length of 2–7 μm were reported in [22]. Results (the break-
down voltages) of this sensor for nitrogen, oxygen, argon and air gases are compared with those of the Mn nano-flower based sensors of this work in Fig. 12(a–d) by considering the 100 nm distance between the two electrodes of this work and 132 nm for the Au sensor. At low pressures (<1 mbar) the Au nano-wire based sensor shows lower breakdown voltages than the sensor reported in this work. However, at medium pressures (1–15 mbar, the range reported in [22]) both sets are either comparable or the Mn nano-flower based sensor shows lower breakdown voltages (i.e., for N₂ and Ar are comparable, and for O₂ and air are lower). The difference between the results of these two different sensors may be due to the smaller size of the nano-petals in the present sensor, which are about three times smaller than the diameter of the Au nano-wires, hence producing stronger electric field.

Similar to the above discussions use of a flat anode should have produced similar results at low pressures (particularly in case of air).

5.4. Comparison with Ag graded chiral zig-zag sculptured thin film based sensor

Savaloni et al. [29] used oblique angle deposition and substrate rotation to fabricate Ag graded chiral zig-zag sculptured thin films (GCZSSTF) with a thickness of 2 μm. They used this film as the cathode and an Al plate as the anode in their field ionization sensor [29]. Results of this sensor (only three data points in the medium pressure range) and the Mn sensor reported in this work are compared in Fig. 13 for oxygen, argon and air gases. It can be observed that in all cases the present sensor works at lower breakdown voltages. These observations can be explained on the basis of the size of the nano-petals in the Mn nano-flower based sensor which are about ten times smaller than the Ag grains in the Ag GCZSSTF, which strongly affect the strength of the electric field produced at the tip of these structures hence reducing the breakdown voltage.

Further discussion on the source of differences between our Mn nano-flower based sensor and other sensors reported in the literature should also consider secondary emission from the material used as the cathode.

Secondary emission can be defined as the emission of electrons as result of a material being bombarded by a particle (ion, neutral, metastable neutral, electron) and is determined by the ratio of the number of emitted electrons to the number of incident particles:

$$R = \frac{N_{e,\text{emitted}}}{N_{p,\text{incident}}}.$$  (7)

Here, ion-induced emission due to positive ions produced in the discharge and accelerated towards the cathode by the electric field is the dominant process leading to secondary emission. The potential energy process is the dominant ion-induced secondary emission mechanism (also called the Auger process). When a ‘slow’ ion approaches the surface, creates an electrical potential energy well with a potential barrier of the order of a few atomic radii [37]. An electron with energy of ε_{c,cath} (near the Fermi energy) may tunnel out of the solid surface and become trapped in the potential well hence it interacts with the ion. There are two possibilities for this, namely atom neutralization and Auger emission (ion-induced secondary emission). The probability of the former is much higher than the latter process. Neutralization takes place through capture
Fig. 7. Current versus breakdown voltage at \( p = 1000 \) mbar (different distances between the two electrodes and different SSB sizes) for \( \text{Ar}, \text{N}_2, \text{CO}, \text{air} \) and \( \text{O}_2 \), showing distinct voltages.

Fig. 8. Breakdown voltage of \( \text{Ar} \) and \( \text{CO} \) gases in a mixture with air as a function of gas concentration for different distances between the two electrodes and different SSB sizes.

of electron in an excited state of the positive ion and forms a neutral gas molecule \( (e^-_{\text{cath}} + M^+ \rightarrow M^*) \) (both metastable and short-lived excited states are possible). The energy of this excited state will be the difference between the ion energy and the energy gained from the electron tunneled from the solid surface (i.e., cathode) \([38]\):

\[
E_{M^*} = E_{\text{ion}} - E_{\text{e,cath}}
\]
Fig. 9. Effect of different gases’ concentrations on breakdown current for different distances between the two electrodes and different SSB sizes. The current varies logarithmically with concentration.

Fig. 10. Breakdown voltage versus gas pressure of field ionization gas sensor based on Mn helical nano-flower sculptured thin film with 3-N symmetry cathode and stainless steel ball (SSB) anode is compared with that of the sensor based on carbon nano-tube as cathode and Al plate as anode for air.

This excited state or metastable will relax to the ground state by emission of a photon (recombination radiation) of energy equal to the difference in the excited and ground state:

\[ h\nu = E_M^e - E_M. \]  

In case of Auger emission, the electron is captured in the ground state by the positive ion to form a neutral molecule while there is an energy mismatch between the captured electron \( (\varepsilon_{e1,\text{cath}}) \) and the ground state of the neutral gas molecule as [38]:

\[ \Delta\varepsilon = \varepsilon_{e1,\text{cath}} - E_M. \]  

This energy may be transferred to a second electron in the cathode (this depends on the material of the cathode) with energy of \( \varepsilon_{e2,\text{cath}} \), hence ejecting this electron from the cathode. This process
Table 2
Results of the sensitivity of the helical Mn nano-flower based sensor compared with those of [15] (CNTs based sensor) and [26] (ZnO nano-wire based sensor) for certain values of gas concentrations reported in [15] and [26].

<table>
<thead>
<tr>
<th>Gas (analyte)</th>
<th>N₂</th>
<th>O₂</th>
<th>Ar</th>
<th>CO</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Currents (µA) obtained for gas concentrations</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2 \times 10^{-3} \text{ mol}^{-1}</td>
<td>0.04 \text{ mol}^{-1}</td>
<td>3.2 \times 10^{-3} \text{ mol}^{-1}</td>
<td>0.04 \text{ mol}^{-1}</td>
<td>2.4 \times 10^{-5} \text{ mol}^{-1}</td>
<td>0.04 \text{ mol}^{-1}</td>
</tr>
<tr>
<td>328</td>
<td>420</td>
<td>425</td>
<td>520</td>
<td>357</td>
<td>460</td>
</tr>
</tbody>
</table>

Fig. 11: Breakdown voltage versus gas pressure of field ionization gas sensor based on Mn helical nano-flower sculptured thin film with 5 N symmetry cathode and stainless steel ball (SSB) anode is compared with that of the sensor based on ZnO nano-wires as anode and Cu plate cathode for: (a) Air and (b) Carbon monoxide gas.

\[ E \text{ ion} = E \text{ cat} + \phi \text{ } \text{ (Eq. 11)} \]

The excess energy can be written as:

\[ \Delta E = E \text{ ion} - E \text{ cat} \text{ (Eq. 12)} \]

and the excess energy will have an energy of:

\[ \Delta E = \epsilon \text{ e} - E \text{ cat} \text{ (Eq. 13)} \]

\[ \Delta E = \epsilon \text{ e} - E \text{ cat} \text{ (Eq. 13)} \]

\[ \epsilon \text{ e} = \Delta E - E \text{ cat} \text{ (Eq. 14)} \]

\[ \epsilon \text{ e} = \Delta E - E \text{ cat} \text{ (Eq. 14)} \]

\[ \epsilon \text{ e} + M \text{ f} - e + M \text{ f} \text{ (Eq. 15)} \]

\[ \epsilon \text{ e} + M \text{ f} - e + M \text{ f} \text{ (Eq. 15)} \]

\[ E \text{ ion} = \epsilon \text{ e} + M \text{ f} - e + M \text{ f} \text{ (Eq. 16)} \]

\[ E \text{ ion} = \epsilon \text{ e} + M \text{ f} - e + M \text{ f} \text{ (Eq. 16)} \]

\[ \epsilon \text{ e} = \Delta E - E \text{ cat} \text{ (Eq. 17)} \]

\[ \epsilon \text{ e} = \Delta E - E \text{ cat} \text{ (Eq. 17)} \]

Hence, the condition for emission of Auger electron: \( \Delta E > E \text{ cat} \text{ (Eq. 18)} \)

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This means that the electron energy of the emitted electron is \( E \text{ ion} \text{ (Eq. 19)} \)

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If this condition is satisfied then the maximum kinetic energy of the emitted electron is \( |e| \text{ (Eq. 20)} \)

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Thus, the condition for Auger electron emission \( \Delta E > E \text{ cat} \text{ (Eq. 21)} \)

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Hence, the condition for Auger electron emission \( \Delta E > E \text{ cat} \text{ (Eq. 21)} \)

\[ \epsilon \text{ e} = \Delta E - E \text{ cat} \text{ (Eq. 22)} \]

\[ \epsilon \text{ e} = \Delta E - E \text{ cat} \text{ (Eq. 22)} \]

\[ \epsilon \text{ e} + M \text{ f} - e + M \text{ f} \text{ (Eq. 23)} \]

\[ \epsilon \text{ e} + M \text{ f} - e + M \text{ f} \text{ (Eq. 23)} \]

\[ E \text{ ion} = \epsilon \text{ e} + M \text{ f} - e + M \text{ f} \text{ (Eq. 24)} \]

\[ E \text{ ion} = \epsilon \text{ e} + M \text{ f} - e + M \text{ f} \text{ (Eq. 24)} \]
case when the ionization energy of the gas is higher and the work function of the cathode material is lower.

Therefore, in comparing the operation of different electrodes used as cathode and in particular in the present work namely Mn nano-structured electrode (cathode) with other types of cathodes discussed in the preceding sections one may use the ratio of the probability of secondary electron emission of Mn to that of other types of cathodes as:

$$ \frac{P_{\text{Mn}}}{P_{\text{other}}} = \frac{E_{\text{ion}} - 2\phi_{\text{Mn}}}{E_{\text{ion}} - 2\phi_{\text{other}}}. $$

(18)

If this ratio is greater than unity it will indicate that secondary electron emission from the Mn nano-structured cathode is higher than the other material used as cathode and under the same conditions one should achieve lower breakdown voltage. In Table 3 characteristics of Mn and this ratio are compared with all other types of cathode materials discussed in the preceding sections. It can be seen that all the materials in this table have larger work function than Mn, which lead all to values greater than unity for the $P_{\text{Mn}}/P_{\text{other}}$ ratio. Hence, one may conclude that not only Mn itself can act as a better material in ionization sensors but also the nano-structure designed and engineered in this work has enhanced the sensor’s performance.

Considering that secondary electrons are emitted from cathode due to ion bombardment, one may use different methods and models to evaluate the secondary electron coefficient as effective coefficient from experimental data under the assumption that electron emission by ions is the only means of electron production from the cathode [39]. The process of emission by ions is one of the main causes of electron emission. However, it is not the only process and it cannot be considered as the dominant cause. In order to determine the effective coefficient, one may use the experimentally measured breakdown voltage [40,41]. In this calculation the evaluation of the effective coefficient, $\gamma$, depends on the primary ionization coefficient, $\alpha$, which expresses the number of single ionizing collisions by an electron in unit distance. Both $\alpha$ and $\gamma$ appear in the self-sustaining condition for a homogeneous electric field [42].

$$ \alpha d = \ln \left( 1 + \frac{1}{\gamma} \right). $$

(19)
Table 3
Characteristics of different types of materials used as cathode in different published sensors including the sensor based on Mn nano-flower type of this work.

<table>
<thead>
<tr>
<th>Cathode Material</th>
<th>Fermi Energy (eV)</th>
<th>Work Function (eV)</th>
<th>Electron Density ($\times 10^{28}/m^3$)</th>
<th>Electronic Structure</th>
<th>$\rho_{\text{em}}/\rho_{\text{filter}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>10.9</td>
<td>4.1</td>
<td>16.5</td>
<td>$3s^2 3p^6 3d^5 4s^2$</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>CNTs</td>
<td>5.0 [48]</td>
<td>4.6–4.9 [49,50]</td>
<td></td>
<td>sp²</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>Cu</td>
<td>7.0</td>
<td>4.53–5.10</td>
<td>8.4</td>
<td>3d$^{10}$ 4s$^1$</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>Ag</td>
<td>5.49</td>
<td>4.26–4.74</td>
<td>5.86</td>
<td>4s$^2$ 4p$^6$ 4d$^{10}$ 5s$^1$</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>Au</td>
<td>5.53</td>
<td>5.1–5.47</td>
<td>5.9</td>
<td>5s$^2$ 5p$^6$ 5d$^{10}$ 6s$^1$</td>
<td>&gt; 1</td>
</tr>
</tbody>
</table>

Fig. 14. The effective secondary emission coefficient of the Mn nano-flowers as determined from the experimental Paschen curves for different SSB anode sizes and compared with other types of cathode materials. Column (I) shows results of calculation for the whole range of experimental data for pd while column (II) shows the valid section of this data (between two vertical dashed lines in column I) according to Eq. (20) where the equilibrium condition for electron drift velocity is reached.
The primary coefficient assumes validity when equilibrium conditions for electron drift velocity are reached [42]. The generalized form of $\alpha$ can be expressed in form of,

$$\alpha = A \exp \left( \frac{-Bp}{E} \right) ,$$  \hspace{1cm} (20)

where $A$ and $B$ are constants of the gas being used [43,44].

Combining Eqs. (19) and (20) and considering that before and at breakdown the electric field is uniform along the discharge axis (i.e., $E = V/d, V$ is the electrode voltage),

$$\gamma = \frac{1}{\exp(\frac{Apd}{E}) - 1} = \frac{1}{\exp(\frac{Apd}{V})} - 1.$$  \hspace{1cm} (21)

This equation may be utilized to calculate the secondary electron emission coefficient from the measured breakdown voltage(s).

Results of our calculations for different experimental conditions carried out in this work are presented in Fig. 14, where column (I) in this figure shows results of calculation for the whole range of experimental data for $pd$ while column (II) shows the valid section of this data (between vertical dashed lines in column I) according to Eq. (20) where the equilibrium condition for electron drift velocity is reached [42]. In addition, the available results (valid in the range mentioned above) from the published data for different cathode materials discussed in the preceding sub-sections (only one result from Ag and one data point from ZnO in case of air and one data point from Ag in case of Ar gas) are also included in these figures for comparison. It can be seen that we have obtained high values of effective coefficient for nitrogen gas and air where results for Ar and oxygen gases although do not show large values but when compared with the reported published data within the valid range for systems different from the one used in this work they are higher [41,43–47].

6. Conclusions

Mn helical sculptured nano-flower shaped thin films with 3-fold symmetry were fabricated and used as cathode electrode in the field emission gas sensor. Stainless steel balls (SSBs) of different diameter sizes (i.e., 2, 6 and 10 mm) were used as anode electrode of the sensor. This type of anode which is used in this work for the first time not only provides strong electric field but also provides facility for multiple measurements on the surface of the cathode by two dimensional movements of the cathode surface.

Response of the sensor was obtained for different geometrical configurations (change of parameters) namely, size of the anode (SSB), distance between cathode and anode, and different gases (i.e, air, oxygen, nitrogen, carbon mono-oxide, argon) as well as a wide range of gas pressures. All measurements showed results in accordance with the Paschen’s rule.

1) Investigation of the influence of the diameter of the stainless steel ball used as anode electrode showed that for smaller balls for which the electric field should be intensified and lead to lower breakdown voltages, opposite effect is observed. This is related to the smaller number of gas molecules between two electrodes. At high pressures, where higher number of gas molecules may exist between the two electrodes, this observation can be due to the short distances (less than the critical distance required for ionization of gas molecules from the tip of the cathode nano-structures).

2) At low pressures and for large distances between electrodes Paschen’s rule predicts lower breakdown voltages, by decreasing the diameter of the ball although the electric field is strengthened but due to the fact that for larger anodes (SSBs) a larger number of gas molecules and larger range of distances between the electrodes are available, hence the breakdown voltage is decreased.

3) The sensor designed and produced in this work showed good selectivity for all gases used in this work particularly at medium range gas pressures (i.e., 0.02–0.2 mbar).

4) The detection limit of the helical Mn nano-flower based sensor is better than that reported for ZnO nano-wire based sensor (i.e., 5%) and for large SSB (10 mm in diameter) can be better than CNT’s as electrode, while it also shows good sensitivity.

5) Comparison of the Mn nano-flower based sensor in this work with other sensors based on carbon nano-tubes (CNT), Au nano-wires, ZnO nano-rods, graded chiral zig-zag shaped nano-sculptured silver thin films (GCZSSTF) showed that at medium gas pressures the present sensor works with lower breakdown voltages.

6) Results of the secondary electron emission coefficient calculated for the Mn nano-flowers using the measured breakdown voltages, and the ratio of the probability of secondary electron emission of Mn to that of other types of cathodes made of different materials (i.e., CNT, Cu, Ag and Au) showed higher values. Both of these results show that not only Mn itself can act as a better material in field ionization sensors but also the nano-structure designed and engineered in this work can enhance the sensor’s performance.

Acknowledgements

This work was carried out with the support of the University of Tehran and the Iran National Science Foundation (INSF). HS is grateful to the Centre of Excellence for Physics of Structure and Microscopic Properties of Matter, Department of Physics, University of Tehran for partial support of this work.

References
