Application of Mn nano-flower sculptured thin films produced on interdigitated pattern as cathode and anode electrodes in field ionization gas sensor

Hadi Savaloni*, Rojan Savari, Salar Abbasi

School of Physics, College of Science, University of Tehran, North-Kargar Street, Tehran, Iran

A R T I C L E   I N F O

Keywords:
Nano-flower sculptured thin films
Oblique angle deposition
Field ionization gas sensor
Mn
Photolithography
Selectivity

A B S T R A C T

The photolithography method was used for producing interdigitated configurations for cathode and anode electrodes of a field ionization gas sensor in which Mn helical nano-flowers with 3-fold symmetry were deposited using oblique angle deposition together with rotation of the substrate about its surface normal, with each rotation divided into six sections. These sections were alternately rotated at high and low speeds. Three different distances were chosen in the design between anode and cathode electrodes, namely 40, 100 and 200 μm. Physical structure and morphology of electrodes were studied by field emission scanning electron microscope and atomic force microscope analyses.

The breakdown voltage of the system was studied for nitrogen, oxygen, argon, air and carbon mono-oxide gases. Investigations with these gases at different distances between anode and cathode and different gas pressures confirmed Paschen's Law. Results showed that at low pressures, decreasing the gap between electrodes increases the breakdown voltage. With fewer gas molecules between the electrodes the number of interactions between particles is reduced and higher energies are required for ionization of gas molecules. At high pressures, the breakdown voltage is decreased because of an increased number of molecular interactions. The sensor demonstrated good selectivity between the different gases and selectivity was enhanced with increasing gas pressure. A direct relationship was found at low pressures (e.g., 0.1 mbar) between the breakdown voltage and the gas ionization energy while at high pressures (e.g., 1000 mbar) this relationship was reversed.

1. Introduction

Ionization gas sensors work on the bases of breakdown voltage of the gas [1–5]. In order to detect a gas they do not require high temperatures and their response is very fast [6]. They are used as gas detectors in gas analysers such as chromatographs and mass spectrometers [7]. Generally, for ionization of gas molecules a very large electric field (high breakdown voltage) is needed which can be both hazardous and cause high energy consumption. Hence it is important to reduce this by different designs. This can be achieved by modifying the geometry and shape of the sensors or by using sharp-tipped nanostructures. A high electric field is formed at the tip of these nanostructures, which enhances the electron tunneling probability and electron emission current. Numerous studies have been carried out to improve these sensors by the use of different nanostructures [6–17].

Investigations into carbon nano-tubes (CNTs) with a diameter of the order of a few nano-meters have shown high performances of field emission and field ionization. These nano-tubes are used for detection of different gases such as argon and helium as well as the mixtures of different gases. However, they 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 CNTs. During the breakdown process, the strong electric field can change the structure of CNTs and high electric currents break and collapse CNTs. Hence the ionization electric field stability decreases [10,16,18–21]. On the other hand, sensors based on metallic nanostructures such as Au nanowires (NWs) are of high stability and oxygen does not have an adverse effect on them, but they are very costly [6,18,22,23]. Field ionization gas sensors based on Si nano-wires in addition to being cheap, are also easily produced and used, while they also show low breakdown voltages [24,25]. Karaagac and Islam [26] fabricated Si NWs that were covered with a very thin layer of Au using electron-beam deposition technique. This Au layer acted as an enhancer, increasing the density of unoccupied surface states. They pointed out that the increased number of surface states contributes to a higher probability of tunneling of valence electrons from the gas atoms or molecular potential well into
these unoccupied states on Si NWs. It is also shown that metals with higher electron density produce higher electric fields at the tip of sharp nanostructures, hence increasing the tunneling probability during gas ionization processes. In addition to the structural geometry (sharp tips), the gap size between the electrodes is an important parameter, however it must be larger than the electron and ion mean free path to allow collision with gas molecules [27]. In the capacitor-architecture device, it is very difficult to control the electrode gap under 10 μm to gain a safe operation voltage [28]. A few studies of breakdown voltage against distance between electrodes on micron scales have reported a deviation from the Paschen curve for very small gaps [29–34]. As will be discussed further in this work, interdigitated electrodes produced by a lithographic technique provide an ordered region for sensing [35,36]. The photolithographic method creates micro-channels with high structural precision, in which the charge density increases at the sharp edges and corners of these channels resulting in a high electric field being produced at these locations [37]. Photolithography is an accessible technique, currently used for mass production of periodic micro-structures in micro-chips, computer processors and micro-mechanical systems.

In this work our aim is to fabricate Mn helical nano-sculptured thin films with 3-fold symmetry nano-flower (two pitches and 100 nm thickness) on top of helical nano-sculptured stem/pillars of 180 nm thickness and use them as cathode and anode electrodes of field ionization gas sensor.

It should be mentioned that in recent years, oblique angle deposition (OAD) of thin films as a physical vapor deposition method has provided facilities for production of variety of nano-structures with structural anisotropy which can be controlled by pre-design of the structure [38]. OAD (vapor incident angle less than 85°) and Glancing angle deposition (GLAD) methods together with the rotation of substrate about its surface normal can be used in 3D nano-structure fabrication [39,40]. Sculptured nanostructures fabricated by these methods have a vast area of applications such as optical filters [41], reflectors [42], polarizers [43], sensors [44,45], bioscaffolds [46] and microchannels [47]. Hence, by using the sculptured thin film deposition technique one can control the shape, size and void fraction of the growing structure such as helical nano-flowers produced and used in this work [48–50] while in the conventional (normal angle) deposition these cannot be controlled and films grow according to the structure zone model (SZM) [51–53], where at low diffusion zone tapered structures with voids between them grow. The use of 3-fold symmetry nano-flower has been investigated in our earlier works [48–50] and compared with 4- and 5-fold symmetry nano-flower sculptured thin films and it was found that 3-fold symmetry nano-flowers have higher void fraction and the sharp points (hot spots) can be positioned with controlled gap between them while there is more freedom in choosing the petal sizes when compared with 4- and 5-fold symmetry nano-flowers.

The pattern of anode and cathode electrodes is designed in an interdigitated shape, which forms integrated electrodes. The distance between electrodes is chosen to be 40, 100 and 200 μm. The sensing was performed for different gases, namely oxygen, nitrogen, air, carbon mono-oxide at different pressures.

2. Experimental details

2.1. Materials, fabrication and analyses

The substrates were microscope slides (Bavaria medico, Germany) cut to 18 × 18 mm². They were ultrasonically cleaned in heated acetone and ethanol (99.99% purity obtained from Merk Darmstadt, Germany), respectively. On these glass substrates an array of interdigitated patterns were produced by using photolithography technique with visible light. This was achieved by using a positive type photoresist (AZ 1500-Series: 320–440 nm wavelengths, AZ electronic materials, USA), which breaks the molecular bonds of the photoresist. The photoresist polymer was evenly deposited on the surface of the glass substrate using a spin coater system by placing a drop of photoresist on the glass substrate and spinning it with 3000 rpm for 30 s, then 2000 rpm for 20 s. The sample was then dried in an oven at 110 °C for one minute. A mask which consisted of comb-like interdigital planar electrodes as anode and cathode with different gap sizes of 40, 100 and 200 μm was designed and prepared on a transparent sheet using Corel Draw software (Fig. 1). The mask was placed on the photoresist and was radiated for 17 s. This will loosen the binding of the molecules at the irradiated areas. After this stage the sample was heated at 90 °C for 1 min in an oven. A silver film of 50 nm thickness was deposited on the above mentioned prepared substrate at normal angle to the substrate surface. This film acts as a uniform conducting surface for electrical contacts. Then the Mn helical sculptured thin films were deposited on the Ag film by electron beam evaporation from a graphite crucible at room temperature. This film consists of a helical stem, the top part of it being a helical nano-flower film with 3-fold symmetry, deposited with two pitches. The deposition angle for this sculptured Mn film (both the stem and the nano-flower part) was fixed at 80° to the surface normal of the substrate and the substrate was rotated clock-wise. The deposition of the stem with a thickness of 180 nm took place using a rotation speed of 0.3 rev/min and a deposition rate of 0.8 Å·s⁻¹. On top of this stem, the helical Mn nano-flowers with 3-fold symmetry in two pitches and thickness of 100 nm (thickness of each pitch being 50 nm) were deposited, considering that for an N-fold symmetry each revolution of the substrate holder should be divided to 2N sectors. In this work the smaller sector was chosen as Θs = 25° which rotates with a speed of Rs = 0.0151 (rev/min), while the larger sector size was ΘL = 95° and its speed (RL) was chosen to be 0.3 rev/min.

Both Ag and Mn were obtained from Merk & Company Inc. with purity of 99.99%. An Edwards (Edwards E19 A3) coating plant with a base pressure of 2 × 10⁻⁷ mbar was used. In order to remove the
irradiated parts of the polymer after deposition of the Mn helical nano-flower sculptured films, the samples were immersed in acetone bath. The remaining pattern on the substrate is the required pattern to be used in the gas ionization sensor.

Fig. 2(a) shows the schematic of the evaporation system showing substrate position and rotation for sculptured thin film growth. The distance between the evaporation source and the substrate was 30 cm. 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 substrate it is expected that the vapor travels in straight trajectories (i.e., there is no appreciable scattering due to the large mean free path (∼103–104 cm [54]). The deposition rate was measured by a quartz crystal deposition rate controller (Sigma Instruments, SQM-160, USA) positioned close to the substrate holder and at almost the same azimuthal angle as that of the substrate. This was calibrated after obtaining the film thickness using a field emission electron microscope (FESEM) and dividing by the deposition time.

The substrates were fixed along six opposite radii of the substrate holder disc. Hence, in each run six sets of four samples were produced for use in different analyses and a reproducibility check of the samples. In addition, the deposition process was repeated a few times and the reproducibility of the results was confirmed.

The substrate holder system is controlled by two stepping motors that can rotate the substrate holder by the two angles, α and φ, with 0.01°/step accuracy and with controlled speed. The movement of the stepper motor for rotation of substrate about its surface normal (φ) and its speed of revolution as well as facility for dividing each revolution to different sectors are controlled through interface to a computer in which the related software (in the LABVIEW format) is written and installed. All these are domestic made [55].

The film thicknesses and column shapes and sizes were measured by field emission electron microscope (FESEM) (Hitachi S-4100 SEM, Japan). The FESEM samples were coated with a very thin layer of gold to prevent the charging effect.

The surface physical morphology and surface roughness of the samples were obtained by means of atomic force microscope (AFM: NT-MDT, SOLVER, Nova Tech) analysis with a Si tip of 10 nm in diameter and in non-contact mode. The Olympus CX21 optical microscope was employed for producing images from Mn thin film in form of interdigitated electrodes.

2.2. Details of gas ionization sensor

The schematic structure of the gas sensor is shown in Fig. 2(b). The vacuum chamber of the sensor is a cylindrical shape Pyrex pipe with outer and inner diameters of 17 cm and 15.6 cm respectively and a height of 14.5 cm, which is capped with two high grade Al flanges. The gas inlet is through a needle valve (LV10K; Edwards) and the pressure is controlled by a Pirani gauge. The pressure during the measurement is kept constant by simultaneous working of the vacuum pump and control of the inlet gas by the above mentioned needle valve. The breakdown voltage for each gas was measured for different gas pressures and different distances/gaps between the two electrodes as explained in the preceding section. Prior to any setup for measurement, the measuring/sensing gas was introduced into the chamber and purged by the vacuum pump three times. This process is required to make sure that sensing is made for the pure gas. A rotary pump was used to pump down the chamber to a pressure of 5 × 10⁻⁵ mbar before letting any gas inside the chamber. The anode and the cathode electrodes were connected to the output of the power supply through an electrical feedthrough mounted on the bottom Al flange.

3. Theory of gas breakdown mechanism

There is always a probability that a gas contains a number of positive and negative charged particles due to cosmic rays, ultraviolet light or a radioactive irradiation. In absence of an electric field, the production and recombination rates of these positive and negative charge carriers are equal, hence balancing each other and the gas is inert. However, when a small electric field is applied to the electrodes, electrons and ions are accelerated in opposite directions resulting in a current density determined by the mobility of the carriers hence the gas exhibits an ohmic behavior. In this region, the rate of recombination of
positive ions with electrons is large and as a result the density of the charged particles and the current decrease [4].

\[
J = (n_i \mu_i + n_e \mu_e) eE
\]

(1)

where, \(J\) is the discharge current density, \(e\) is the electron charge, \(E\) is the electric field, \(n_i\) and \(n_e\) are electron and ion concentrations, and \(\mu_i\) and \(\mu_e\) are the mobilities, assumed to be constant at small fields.

The recombination process will be stopped/decreased by an increase in the strength of the electric field. In the absence of recombination processes the rate of ion and electron production is constant. The limiting condition is reached when all ions and electrons reach the electrodes before they have time to recombine and the total number of charges arriving at the electrodes is then equal to the total number being produced. In this stage, the current density does not depend on \(E\), or on the mobilities, and is called the saturation current density, given as [4]:

\[
J = \frac{d e}{dt} \frac{dn}{dt}
\]

(2)

where \(d\) is the distance between the two electrodes and \(dn/dt\) is the total rate of carrier production per unit of volume. By further increasing the electric field, neutrals will be ionized by electron impact, which in turn increases the current. Also, the inelastic interaction of ions with the cathode electrode can produce secondary electrons and with a further increase in electric field, these secondary electrons may ionize more atoms. Hence a chain of ionization processes called electron avalanche may occur. This state of the gas in which the current of charged particles increases exponentially is known as Townsend’s discharge [56]. When the voltage is increased further to the voltage \(V_b\), electrical breakdown will occur.

In this region current is given as [4];

\[
i = i_0 \frac{e^\gamma}{1 - \gamma (e^\gamma - 1)}
\]

(3)

where, \(i_0\) is the current in the saturation region (initial current), \(a\) and \(\gamma\) are first and secondary Townsend ionization coefficients.

The observed breakdown voltage is a specific fingerprint for detection of a particular gas. Townsend’s first ionization coefficient is defined as the number of ionizing collisions, on average, made by one electron per unit drift in the direction of the electric field. The probability of secondary electron emission from the cathode is given as [57];

\[
\gamma \approx 0.016(E_1 - 2\varphi)
\]

(4)

where, \(E_1\) and \(\varphi\) are the ionization energy and the cathode work function.

In gas ionization sensors, the most influential mechanisms on the gas breakdown are the field ionization and the impact process, which depend on the population of electrons and the inelastic 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 tip surface under high applied electric field [58]. According to the Paschau’s law the breakdown voltage is given as [2-4,59];

\[
V_b = \frac{E_i d}{ekln(\frac{2}{\lambda})}
\]

(5)

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

(6)

where, \(e\) is the electron charge, \(\lambda\) is the mean free path of the gas, \(K_B\) is the Boltzmann constant, \(T\) is the absolute gas temperature, \(p\) is the gas pressure, and \(r_i\) is the radius of the ionized gas atom/molecule [59]. The gas breakdown voltage depends on the structure of the system, material, distance between the two electrodes, temperature and gas pressure. The population and the speed of the gas molecules are the main factors/parameters in the impact mechanism. According to Paschen’s law, variation of breakdown voltage with respect to the variation of pressure (at fixed distance between electrodes) is explained as follows.

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 very 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.

In quantum mechanics, the process of field ionization 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 (\(U_i\)) [60]. By applying an external electric field, the probability of tunneling of an electron trapped in this well increases due to a decreased barrier height. This effect requires a very strong electric field, which in turn depends on the geometry of the system and the surface morphology of the electrodes such as the presence of sharp tips on the surfaces of the electrodes, the distance between electrodes and the position of gas atoms/molecules relative to these sharp tips. As the electric field becomes stronger, the width of the potential barrier becomes comparable to the de Broglie wavelength of the electron that is trapped in the potential well, hence the probability of tunneling to the vacuum or unoccupied states increases [60]. For a metallic surface, the threshold electric field for the field ionization process is of the order of \(2.5 \times 10^8\) V/cm which can only happen in the neighborhood of very sharp tips [61,62]. The tunneling process into unoccupied surface states in a sharp metal tip occurs when the energy level of the valence electron bound to an atom (or ionizing particle) is positioned above the Fermi level of the metallic tip [26,63]. The tunneling probability (\(D\)) is defined as [64];

\[
D = \exp \left[-6.8 \times 10^{-7} \left(U_i - 7.6 \times 10^4 E_i \frac{1}{\chi_c^2} \right) \right]
\]

where the critical distance (\(\chi_c\)) for field ionization of the gas atom/molecule may be obtained from Ref. [6];

\[
eE x_i = (U_i - \Phi)
\]

where, \(E\) and \(\Phi\) are the applied field strength, and the work function of the metal, respectively.

Field ionization may not occur at lower distances than critical distance, because in this case the electron energy lies below Fermi level [6].

4. Results and discussions

4.1. Structure and morphology of Mn helical 3-fold symmetry nanoflowers

The interdigitated pattern used for (see Section 2) sensors having 40 μm distance between the electrodes is shown in Fig. 1(a). Three sets of anode and cathode electrode pairs were prepared on the glass substrate of 18 × 18 mm². Each electrode consists of 15 stripes with 2 mm length and 40 μm width. The optical image (larger scale) of Fig. 1(a) is
shown in Fig. 1(b).

Two dimensional (2D) and three dimensional (3D) AFM images of the helical Mn 3-fold symmetry nano-flower sculptured thin films grown on top of the photoresist polymer patterned on glass substrate are given in Fig. 3(a and b). The 3-fold symmetry of the Mn nano-flowers can be seen in these figures. The mean surface roughness (9 nm) and the diameter of the nano-petals (31 nm) of these films were obtained from the analysis of the AFM images using NOVA and Jmicro-Vision softwares.

FESEM images of the surface and cross section images of these samples are shown in Fig. 4(a–c). In Fig. 4(b) the 3-fold symmetry grown around a defect on the surface of substrate confirms the 3-fold symmetry of the deposited film, while the FESEM cross-section image (Fig. 4(c)) not only shows the growth of the 180 nm stem of these structures, but also vividly distinguishes the two pitches (100 nm) of the grown nano-flower and petals on top of the stem. In Fig. 4(c), I, II and III symbols indicate the 50 nm Ag film, the 180 nm helical stem and the 100 nm helical nano-flower pitches.

4.2. Results of gas ionization sensor

In Fig. 5(a–e) the response (breakdown voltage) of the sensors for different gases, namely nitrogen, oxygen, argon, air and carbon mono-oxide, and for inter-electrode distance of 40 μm, 100 μm and 200 μm is given. It can be observed that the behavior of the sensor (breakdown voltage) for all gases, and for all inter-electrode distance is consistent

Fig. 3. AFM images of helical Mn nano-flowers with 3-fold symmetry. a) 3D image, b) 2D image.

Fig. 4. FESEM images of helical Mn nano-flowers with 3-fold symmetry consisting of 180 nm stem and 100 nm (2 pitches) nano-flower formed on top of 50 nm Ag film: a) surface image, b) surface image showing a defect and the 3-fold symmetry around it, c) cross-section images. I, II and III symbols indicate the 50 nm Ag film, the 180 nm helical stem and the 100 nm helical nano-flower pitches. The circle in figure (b) shows the two pitches of nano-flowers at the top of the film.
with Paschen's law.

At low pressures, a higher breakdown voltage is observed for all varied parameters. This is consistent with the impact theory (Section 3). At the medium range of 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 leads 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. Therefore, 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 concentration of gas molecules 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 [6]. This also leads to higher breakdown voltages.

Comparison of the results in Fig. 5(a–e), shows that for gas pressures less than 3 mbar, an increase of inter-electrode distance leads to a decrease in breakdown voltage for all gases, while at pressures higher than 3 mbar this behavior is reversed. One may then consider 3 mbar as the critical pressure and calculate the mean free path of the gas molecules using Eq. (6) for this critical pressure. The mean free path for this gas pressure is obtained for nitrogen, air, oxygen, carbon mono-oxide and argon, as 174, 177, 191, 239 and 603 μm, respectively. In order to calculate the mean free path for air molecules it was assumed that air consists of 78% nitrogen and 22% oxygen, hence its mean free path should be 0.22λ_{oxygen} + 0.78λ_{nitrogen}. These values show that apart from argon, at this critical pressure the mean free paths are close to 200 μm, which also corresponds to the largest gap chosen between the two electrodes in this work. This fact and the increased number of molecules at this pressure relative to lower pressures between the two electrodes should be responsible for the observed minimum near to this pressure for all gases.

Also, according to Eq. (6), at pressures lower than the critical pressure the mean free path increases while the number of gas molecules between the electrodes is reduced, hence the number of impacts between the particles is decreased, which leads to higher breakdown voltages. This is illustrated in Fig. 6. One should also note that at shorter inter-electrode distances the electric field increases, which should result in lower breakdown voltages. However, it seems that the competition between these two effects has resulted in high breakdown voltages for all gases used in this work at lower than 3 mbar (critical pressure) gas pressure. As mentioned above, at higher pressures the behavior of the sensor is reversed and an increase in inter-electrode distance leads to an increase in the breakdown voltage. The decreased electric field in this case should be responsible for this observation. At higher pressures, the mean free path is smaller and the weaker electric field in sensors with larger inter-electrode distances should result in an increased breakdown voltage. Furthermore, in Fig. 5 it can be observed that lowest breakdown voltages are obtained for argon gas and the minimum occurs over a wide range of pressure. The mean free path for argon, as reported above, is the longest of the gases used in this work and in addition argon is an inert gas with the highest ionization energy of these gases. This may demonstrate the influence of the mean free path on the results but a more detailed study of the breakdown voltage of inert gases compared to other gases is required, both from the experimental and theoretical point of view.

### 4.3. Selectivity and resolution of the sensor

Considering that there is a unique breakdown voltage for each gas at a certain temperature and pressure, gas ionization sensors are very selective when compared with other types of gas sensors. The selectivity of other sensors at low gas concentrations is low, because the impact of electrons and the population of gas molecules leads to low ionization current [65]. Hence, one of the major aims in developing these sensors was the enhancement of their selectivity and resolution at low pressures. In Fig. 7(a–c) the breakdown voltage of the sensor for different gases examined in this work and for different inter-electrode distances is plotted in the pressure range of 0.1 mbar–1000 mbar. In general, a good selectivity is obtained for all gases above 1 mbar gas pressure.
measured in this work, however the selectivity is enhanced with increasing gas pressure.

Comparison of the results obtained for different inter-electrode distances (Fig. 7(a–c)) show that a better selectivity is achieved with larger inter-electrode separation. This can clearly be seen when the results of nitrogen gas and air (78% nitrogen and 22% oxygen) are compared. Dharwal et al. [34] also reported similar results when they measured the breakdown voltages for these two gases at atmospheric pressure.

At low pressures as the pressure decreases the number of molecules decreases which leads to reduction of number of impacts between particles, hence one may suggest that the dominant mechanism in breakdown voltage at very low pressure range is the influence (strength) of electric field. In Table 1 the results of breakdown voltages obtained for different gases used in this work at 0.1 mbar pressure and their ionization energies are given. It can be observed that at this gas pressure the breakdown voltage is increased with higher gas ionization energy. This is in agreement with the prediction of Eq. (5). In order to estimate the ionization energy of air one may use the same assumption mentioned in Section 4.2 that the air consists of 78% nitrogen and 22% oxygen, hence the ionization energy should be a 78% (Ei-nitrogen) + 22% (Ei-oxygen) = 14.9 eV, which is consistent with the values for other gases given in Table 1.

The breakdown voltages obtained at the highest pressure (1000 mbar) for all gases are also given in Table 1. Results show that the breakdown voltage decreases with increasing gas ionization energy, which is opposite to that observed at lowest pressure discussed above. This observation suggests that at high pressure the dominant mechanism is the impact one. This may be due to nonlinear electric field at the tip of Mn nano-structures, along the helical columns of these structures and in between them, which leads to movement of particles in different directions and a scattering phenomenon. These lead to a recombination effect that results in an increase of breakdown voltage. Hence, as mentioned above at these high pressures the impact process is dominant and with regard to the gas ionization energy values the breakdown voltage behaves in opposite direction.

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

Garazzetti et al. [66] used Al electrodes in form of microelectromechanical system (MEMS). The thickness of Al thin film was 8 μm which was sputtered on fused silica substrate. On top of the Al film a 10 μm layer of Clariant’s AZ9260 photoresist was deposited for pattern formation which was achieved by etching using inductively coupled plasma. They produced electrodes with distances of 10–500 μm. Garazzetti et al. [66] results for nitrogen and argon are compared with the results of this work for corresponding distances between the two electrodes (i.e., 40, 100 and 200 μm) in Figs. 8 and 9, respectively.

Ito et al. [67] used two Pt electrodes separated by a 1–40 μm gap on a substrate fabricated by lithography confirmed the Paschen’s law. Results for argon gas obtained in this work are compared with their results for the inter-electrode gap of 40 μm in Fig. 9. Similar comparison is made in Fig. 9 using results reported by Mariotti et al. [68] who used SnO2 parallel-plane electrode configuration for the inter-electrode gap of 100 μm.

In both cases (i.e., Figs. 8 and 9), it can be seen that the helical Mn 3-fold symmetry nano-flower sculptured thin films sensor shows lower breakdown voltages than those reported for different systems and materials. This is more pronounced in the case of nitrogen gas and in particular at 200 μm distance between the two electrodes (Fig. 8).

The electronic structure data of both Mn and Al are given in Table 2. The electron density of Al is higher than that of Mn, however the sharp tips in the Mn 3-fold symmetry nano-flower should produce a stronger electric field with increased probability for tunneling process. The tunneling process into an unoccupied state of the sharp tip in the metal surface occurs when the ground state of valence electron bound to an atom (ionizing particle) is above the Fermi level of the metallic tip [26]. The Fermi energy of Mn is lower than that of Al (Table 2), hence we may suggest that the probability of tunneling process for Mn is higher than that of Al. However, fermi energy of Mn is higher than that for Pt and SnO2, hence the same argument does not apply in these cases.

According to Eq. (4) and the data in Table 2, the observed lower
breakdown voltages for Mn relative to those of Al, Pt and SnO2 may be explained on the bases of its lower work function which leads to higher secondary emission probability and sharp tips in its structure which results in higher tunneling probability.

Finally, in Fig. 10 the results of this work on Mn helical nano-flower structure is compared with the only available Mn nano-wire results available in the literature [13]. It should be mentioned that results of Mn nano-wire belongs to a different type of sensor called facing electrode configuration in which Mn nano-wires were used as anode electrode and a copper plate as cathode electrode. It can be seen that the breakdown voltages obtained by the Mn helical nano-flower sensor in this work are lower than the results of the sensor based on Mn nano-wires thin film.

5. Conclusions

The field ionization sensor based on interdigitated electrodes in shape of helical Mn 3-fold symmetry nano-flowers (two pitches of

<table>
<thead>
<tr>
<th>Gas</th>
<th>Ar</th>
<th>N2</th>
<th>Air</th>
<th>CO</th>
<th>O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_{breakdown}(V) in 0.1 mbar</td>
<td>591 ± 8 570 ± 9 562 ± 6 565 ± 7 545 ± 9 534 ± 10 510 ± 9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V_{breakdown}(V) in 1000 mbar</td>
<td>263 ± 9 270 ± 7 275 ± 9 280 ± 10 560 ± 8 560 ± 7 573 ± 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionization energy (eV) [69]</td>
<td>15.8 15.6 14.0 12.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
100 nm thickness) on top of 180 nm helical stem was designed and fabricated. The distance between electrodes were chosen as 40, 100 and 200 μm. Response of the sensor was obtained for different distances between the two electrodes, and different gases (i.e., air, oxygen, nitrogen, carbon mono-oxide, argon) as well as a wide range of gas pressures (0.1–1000 mbar). All measurements showed results in accord with the Paschen’s rule. Selectivity of the sensor under different measurement conditions showed that there is a reasonably good selectivity for all gases above 1 mbar gas pressure measured in this work. In addition, the selectivity is enhanced with greater distance between the two electrodes. It is shown that by reducing the number of molecules (lowering the gas pressure (0.1 mbar); eliminating the impact factor) the breakdown voltage is directly related to the ionization energy of the gas molecule. However, at the other end of the gas pressure range (1000 mbar) the recombination process due to collision of particles and scattering process reverses this relationship. Hence, at low pressures the field ionization mechanism and at high pressures the impact mechanism are the dominant process in the breakdown voltage of a gas.

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


