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

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A B S T R A C T

The photolitography 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

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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, integrated 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 (vapor incident angle greater than 85°) 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 $18 \times 18\ mm^2$. 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 $Å^{-1}$. 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 2 N sectors. In this work the smaller sector was chosen as $\Theta_L = 25°$ which rotates with a speed of $R_L = 0.0151$ (rev/min), while the larger sector size was $\Theta_H = 95°$ and its speed (R_H) 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

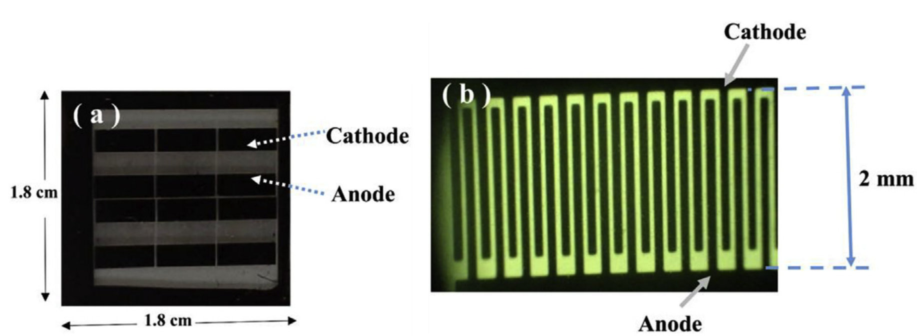

Fig. 1. a) Photograph of the array of interdigitated electrodes, b) optical microscope image of Mn thin film in form of interdigitated electrodes formed on (a).