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An E-nose Concept based on Semiconductor-Assisted Field Ionization and Gaseous Discharge on Arrays of Whiskered Nanowires*

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Abstract— **Electronic nose systems employ an array of gas detectors each tailored to respond differently to a range of odors. In the presence of a particular gaseous compound, the responses of sensors form a signature that is analyzed in the signal transduction process. The gas sensing cells operate by a variety of different mechanisms, but generally, catalyst based sensors suffer from issues such as poor specificity, slow response time, and irreversibility. This work introduces a novel approach towards instantaneous and selective discrimination of gases based on their unique ionization properties: electric breakdown voltage and field ionization current-voltage characteristic. Synthesized gold and silicon nanowires, covered with sharp nanoscale whiskers, exhibited anomalously strong discharge and field ionization characteristics at very low bias voltages. The anomalous field ionization phenomenon was attributed to the combination of geometric field enhancement and the presence of localized surface states at the surface of the emitters.**

Index Terms—**Electronic nose, gas sensor, nanowires, field-enhancement, field ionization, electric breakdown.**

I. Introduction

Of late there has been an increasing demand for low-cost portable systems that can mimic the human olfactory system. Commercial electronic nose (e-nose) systems have been available since late 80's providing a plethora of benefits for ubiquitous applications such as environmental monitoring, security systems, food industry, healthcare, and military. The concept of e-nose was introduced by Dodd and Persaud [1]. They showed that a variety of odors can be reproducibly discriminated by a combination of different receptors—metal oxide gas sensors in their case—in a similar fashion to the mammalian olfactory system.

Classical gas sensors built on metal oxide or conducting polymer films fail to offer the specificity demanded by certain applications, for example in detection of hazardous gases, chemical warfare, and other harmful agents. In addition, these detectors could be 'blind' to species with low adsorption toward the active layer such as inert gases. Since high specificity requires strong and irreversible interaction between the sensor and the target gas, there has been a tradeoff between technical realization of high selectivity and reversibility [2]. Even the biological receptors of human nose have a lifetime of a few weeks. In contrast to electrochemical methods, there is no chemical absorption involved in the gaseous field ionization and electric breakdown processes. Therefore, sensors that measure the ionization current-voltage (*I-V*) characteristics of the analyte gas could offer high selectivity, short recovery, and fast response time all together.

Field ionization normally requires application of hundred million volts per centimeter of electric field. Such fields are produced on sharp metallic tips under a bias of a few kilo-volts making it difficult to be utilized in a portable device. However, as it was recently discovered, this is possible at dramatically lower field strengths on the vicinity of sharp gold and silicon nanowire tips grown by customized electrochemical and vapor-liquid-solid methods respectively [3-4]. It is believed that the anomalous low-field phenomena occurs as a result of upward band-bending at the surface of the exposed semiconductor containing surface states, in addition to localized geometrical field enhancement.

This work summarizes attempts and achievements to produce field ionization and electric breakdown of various gases at relatively low bias voltages. Low voltage field ionization and electric breakdown can offer implications for accurate fingerprinting of gases, for instance in biochemical, environmental, and disease sensing applications.

II. Experimental Works

The concept of exploiting electric field amplification on sharp nanostructures to ionize gas species as a detection method is rather new. Zhang et al. [5] for the first time, used a carbon nanotube (CNT) array film at the cathode of a parallel-plate capacitor-like structure, and demonstrated gaseous discharge at relatively low applied voltages. CNTs were grown on a porous silicon substrate to achieve improved adhesion and increased device lifetime. They measured the electric discharge conductance of several gases at atmospheric pressure and showed that they can be separated based on their breakdown voltages. In comparison with the results obtained from flat electrodes without the CNT film, breakdown voltages were reduced several folds while the discharge currents were boosted up about three orders of magnitude.

Later, Modi et al. [6] carried out comprehensive measurements using a similar device with multi-walled carbon nanotubes (MWCNT) at the anode electrode. Locally enhanced electric fields at the sharp tips of individual MWCNTs generate positive coronas followed by electron avalanches or streamers that short circuit the interelectrode gap. These streamers trigger a self-sustained discharge

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between the electrodes that eventually leads to electric breakdown of the gas. Since every gas has a unique breakdown electric field at constant pressure and temperature, the unknown gas type can be 'fingerprinted' by monitoring the breakdown voltage. In addition, the magnitude of the discharge current can be used to determine the gas concentration (Fig. 1a).

The MWCNT ionization sensor showed some degree of sensitivity in monitoring gas mixtures without first separating the constituents by chromatography. Figure 1b shows the curves of breakdown voltage as a function of the component gas partial concentration, in Ar–air and NH_3–air admixtures. It can be seen how the relative pressures of Ar and NH_3 modulate the breakdown voltage of pure air. For over certain partial concentrations (e.g. above 50% for Ar), the breakdown voltage of the mixture approaches that of the pure analyte. As the relative concentrations decrease, the breakdown voltages increase to the value for pure air.

These results indicate that the electric breakdown induced on nanotubes is affected by the relative concentration of gases in air at the percentage level, and therefore show promise for room temperature detection of odorants mixed with air. The researchers however, did not comment on the lifetime of their MWCNT sensor. Since corona discharges are difficult to control and can generate excessive heat that destroys sharp and slender CNTs, it is expected that the nanotube ionization sensor would exhibit a short life time. As an alternative to CNTs, the functionality of freestanding gold nanowires incorporated into a similar capacitor-like cell was studied [7]. Vertically-aligned gold nanowire arrays were grown electrochemically by replicating the nanoscale pores of anodic alumina templates. The ceramic template was dissolved selectively, leaving behind forest of gold nanowires. The output characteristics of the gold nanowire and the MWCNT devices were similar (Fig. 2a and 2b). In both cases the breakdown voltages were not affected by a large range of gas concentration. However, at concentrations below 10^{-5} moles per liter (mol l^{-1}) the breakdown voltages of the gold nanowire device followed Paschen's law and increased. It was suggested that even though individual CNTs have sharper tips and therefore exhibit a higher field enhancement factor, they are more densely packed compared to gold nanowires, as a result, the overall field enhancement factor becomes smaller due to the strong tip-to-tip electrostatic interaction.

Further, we developed an electrochemical method to grow gold nanowires terminated with atomic scale whiskers (Fig. 3a) and showed that these structures exhibit very strong field emission [8-9] and field ionization [3] properties. Figure 3b shows the curves of breakdown voltage of a few gases as a function of gas concentration, with whiskered gold nanowires as the cathode. It can be seen that gaseous breakdown voltages were reduced about an order of magnitude as compared to the smooth gold nanowire device. Enhanced electron filed emission from the whiskers trigger primary ionizations in the gap. Highly dense plasma formed at the vicinity of gold nanowire tips is provoked by bombardment of positive ions that are generated in the gap in collision with field-emitted electrons. The plasma then expands into a streamer leading to an instant breakdown. Note that maintaining a high selectivity and breakdown at low voltages is a tightrope walk.

With whiskered gold nanowires at the anode, when the alumina template was not completely removed, field ionization occurred at considerably low voltages. Figure 4 compares the field-ion *I-V* curves of a metallic field-ion source [10] to those of our whiskered gold nanowires [3]. Three orders of magnitude reduction in the onset voltage for field ionization is noticeable. Interestingly, computations showed that the field enhancement factor of gold nano-whiskers were not sufficient to generate local field strengths sufficient to trigger field-ionization. It was, hence, suggested that field ionization takes place by tunneling into the surface states of the residual amorphous alumina on the whiskers at low electric field strengths. The magnitude of the field-ion current at a fixed voltage, as well as the field ionization threshold voltage are signatures of the unknown analyte.

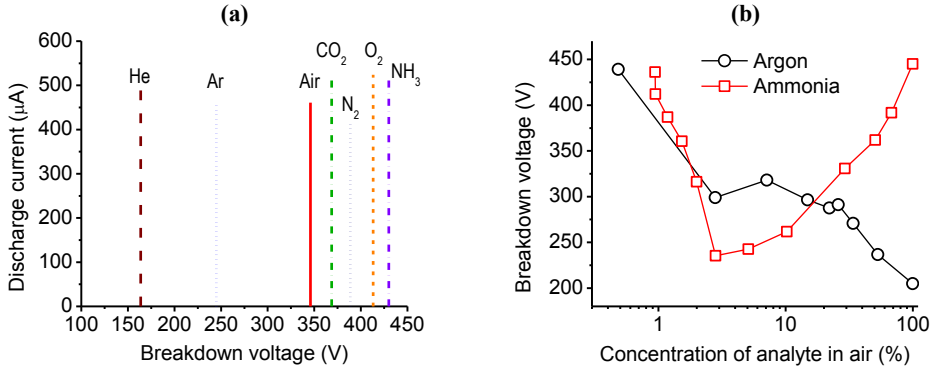

Fig. 1. a) Breakdown voltages and the corresponding discharge currents of several pure gases at room temperature and atmospheric pressure, measured by the MWCNT device. b) Breakdown characteristics of Ar-air and NH_3–air gas mixtures. Breakdown voltage of Ar increases with decreasing its partial concentration almost over the entire range. At 1% Ar, the breakdown voltage becomes identical to that of pure air. For NH_3, the curve displays a Paschen-like characteristic. Graphs are adapted from [6].

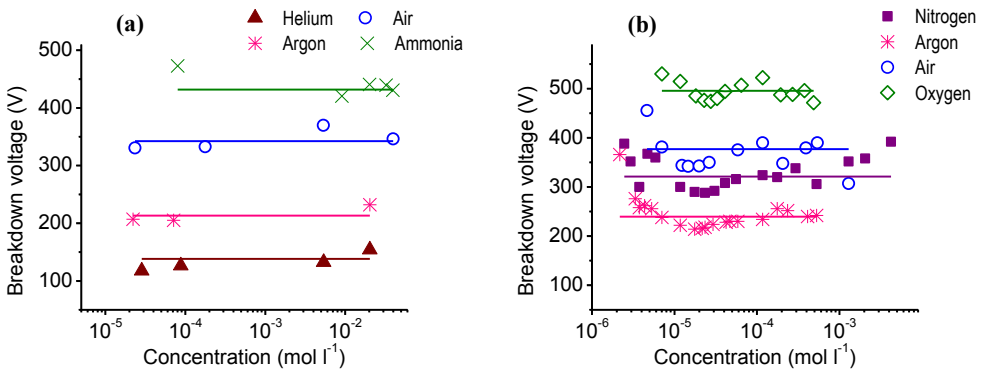

Fig. 2. Effect of gas concentration on the breakdown voltages using the a) MWCNT device [6], and b) the gold nanowire device [7].

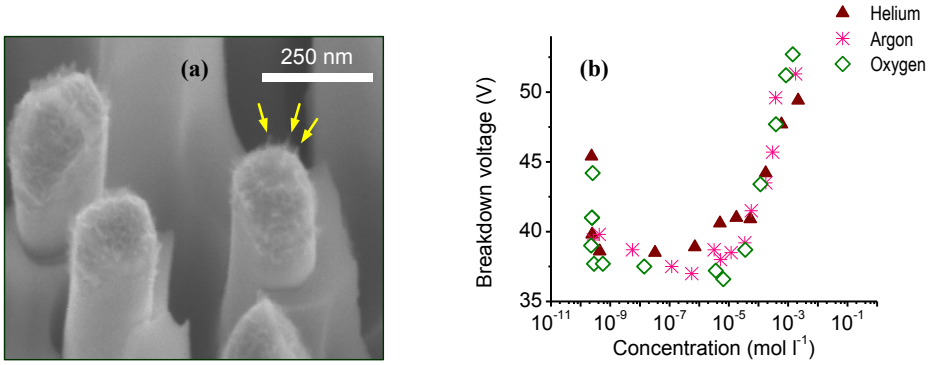

Fig. 3 a) SEM snapshot of gold nanowire tips terminated with sharp whiskers. b) Breakdown voltages of He, Ar, and O_2, measured with these nanowires at the cathode.

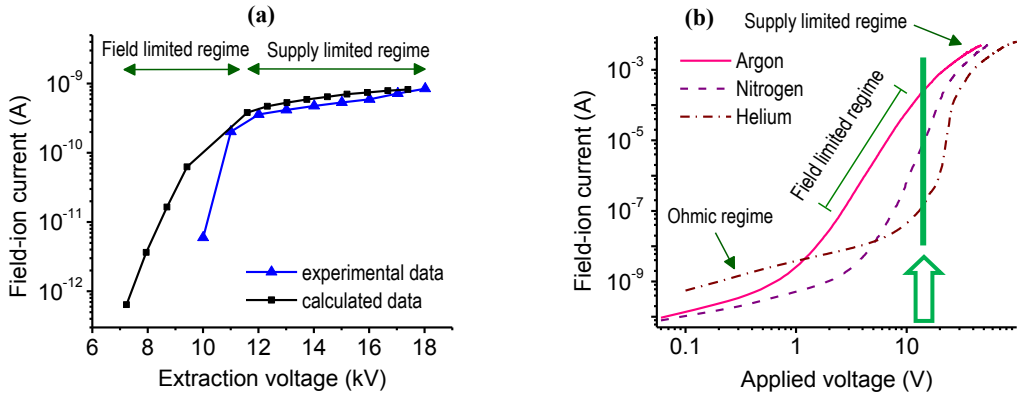

Fig. 4 a) Experimental and calculated *I-V* characteristic of H_2 – Ir gas field-ion source at 300 K, adapted from [10]. b) *I-V* curves of field ionization of Ar, N_2, and He on whiskered gold nanowires. Notice the three order of magnitude reduction in the required extraction voltages and the distinct current amplitudes of three elemental gases at a constant bias.

Similar anomalous field ionization behavior was observed on branching silicon nanowires grown using a two-step vapor-liquid-solid (VLS) technique with SiH_4 as the precursor. Figure 5a shows the SEM micrographs of these nanowires. Although the magnitude of the measured ion current was smaller than what would be expected from metallic emitter with the same tip geometry, it was shown that field ionization has been triggered at drastically lower fields [4].

Figure 5b shows the instantaneous response of these nanowires to few gas species. Corresponding field-ion currents were measured while the nanowires were biased at +2 V. For each gas the ratio of the stabilized ion current to its partial pressure, $S = I/P$, is defined as a measure of its sensitivity. The table in the inset shows the values of S normalized to that of nitrogen.

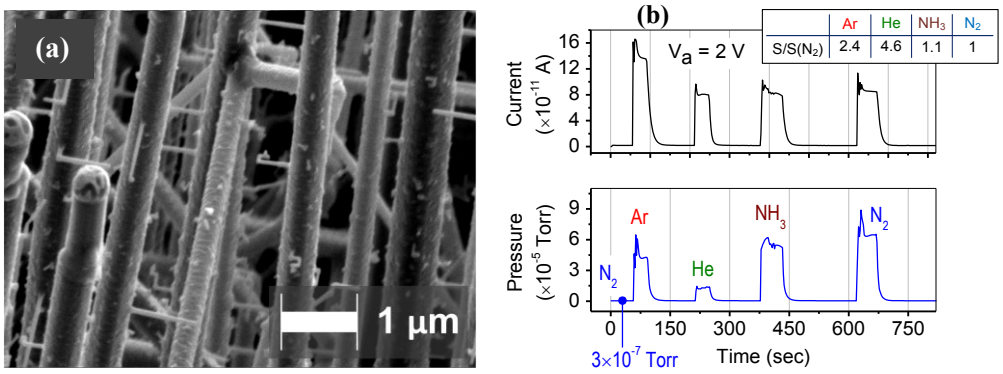

Fig. 5. a) Branching Si nanowires synthesized by a two-step VLS method. b) Ionization currents of Ar, He, NH_3, and N_2 measured in an N_2 background on undoped nanowires at a bias of 2 V. The table in the inset shows values of *S* normalized to that of N_2.

III. Conclusions and Future Work

Vertically aligned nanowire arrays were incorporated as field-amplifying elements to reduce the gaseous breakdown voltages. Non-uniform electric fields generated at the nanowire tips, not only hasten the breakdown process, but also decrease the dependence of the breakdown voltage on gas concentration. Such a characteristic is desirable for an ionization sensor because discrimination of different gases can be performed irrespective of their pressure.

Although unintentional incorporation of impurities in semiconductor nanowires usually has an adverse effect on their electrical properties, it was shown that the surface states associated with such impurities can be beneficial by offering low-power field ionization. In preference to conventional gas detectors, nanowire based field ionization receptors can be employed as a rapid, sensitive, and selective sensing method in e-nose systems. However, as reported earlier [4], there are a number of open questions associated with the properties of semiconductor nanotips that need to be addressed to achieve controlled field ionization properties. Those include, the know-how of growing sharp nanostructures with narrowest possible distribution of tip curvature and composition at the same time, and the type and density of surface states involved in the field ionization processes. Systematic measurements and analysis such as photoemission spectroscopy are required to quantify the position and density of gold-induced surface states on silicon nanotips.

One of the major challenges of using field ionization tips for gas detection applications is their sensitivity to the background atmosphere. Usually the chemicals of interest, the volatile organic compounds (VOC), are part of a complex background such as water vapor. These background species can be ionized easier than VOCs, whereas, the human olfactory epithelium has developed no receptors for water vapor; because it is everywhere in the ambient atmosphere [2]. Separation methods such as micro gas chromatography columns have been developed to separate all the constituents of a sample gas at the sensor input [11], in price of increased response time and device complexity. Additional research work is needed to eliminate the crosstalk caused by the undesired background gas without the use of extra hardware.

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