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Ultra-low breakdown voltage and origin of $1/f^2$ noise in metallic nanorod arrays

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Abstract

The application of a dc voltage to an array of copper nanorods causes field evaporation of atoms from the tips, resulting in their progressive sharpening and a further increase in the local field. The process is self-limited by the build-up of space charge on the nanorod tips. From an analysis of the conductance noise recorded across the nanorod array, we show that the conduction mechanism bears a strong analogy with the stick–slip problem in sliding friction. The in situ sharpening results in an unprecedented lowering of the breakdown voltage of air by over 90%, as compared to plane parallel electrodes.

1. Introduction

A gas conducts electricity in the presence of an electric field larger than the breakdown voltage. Devices based on gas discharge phenomena are ubiquitous in everyday applications (spark plugs, fluorescent lamps, plasma displays) and industry (arc welding, gas sensing, decomposition of toxic gases), while the underlying physics has been studied for well over a century [1–3]. Since the breakdown voltage of air [4] at STP ($V_B$) is rather large, $(3.13 \times 10^6$ V m$^{-1}$), many attempts have been made to reduce it, for example by heating the electrodes (thermionic emission), ionizing the gas by UV [5], and using needle (as against parallel plate) discharge. An extreme example of needle discharge is to employ a multi-walled carbon nanotube (MW-CNT) array as an electrode [6, 7], the expectation being that the large electric fields at the extremely sharp CNT tips would lead to a lowering of the effective breakdown voltage. Apart from a possible lowering of $V_B$, the dynamical processes that accompany the electrical discharge from the nanometer-sized tips of nanotubes and nanorods have not been investigated until now. We show that a large enough electric field at the tip of a nanorod would cause a field evaporation of the atoms, resulting in a progressive sharpening of the tips towards an atomically sharp state [8], which leads to a further enhancement in the local field and electrical discharge (across a spark gap) at progressively lower voltages. Such a cascading process is self-limited by the build-up of space charge at the tips.

We show in this paper that such alternate cycles of rapid electrical discharge followed by a quiescent period during which the space charge decays relatively gradually is analogous to the well-known stick–slip problem in sliding friction. The ‘stick’ state corresponds to the phase during which the space charge diffusion occurs, while the ‘slip’ state corresponds to the relatively sudden electrical discharge. We investigate the possible stick–slip nature of the electrical discharge in an electrode consisting of a parallel array of mutually isolated metal nanorods through a study of the electrical noise characteristics of the system. In an array with a statistically large number of nanorod elements, the random discharges from different nanorods in the array soon reach a dynamic equilibrium, yielding a steady value of the breakdown voltage. The mechanism of the electrical discharge from a nanorod array and its equivalence with the stick–slip phenomenon have not been investigated or suggested previously. More significantly, we show that the in situ sharpening of the nanorods leads to a remarkable lowering of the effective breakdown voltage. Sustained electrical conduction is shown to occur in air under ambient pressures, at values as low as $V_B \approx 10$ V. The corresponding value of $V_B$ for plane parallel electrodes (with otherwise similar geometry) is $\approx 500$ V. According to the available literature, the lowest air
breakdown voltage recorded so far, using MW-CNT electrodes, was 128 V for a spark gap of 90 μm [9]. Further, Modi et al [7] have shown that there is very little decrease in \( V_B \) as the spark gap is reduced to 20 μm.

2. Experimental details

The copper nanorod (Cu-NR) array was grown in commercially available porous anodic alumina (PAA) templates (Whatman Anodisk 13) with a diameter of 12 mm and a thickness of 60 μm, containing parallel, cylindrical pores with an average diameter of 200 nm. One side of the PAA template was completely covered with an ≈200 nm thick coat of evaporated silver, to form a fully encapsulated working electrode for the subsequent electrolytic growth of Cu-NRs within the pores of the template. The counter electrode was a 99.9% copper plate. The backplated silver layer not only serves as the cathode but also provides a stable substrate for the growth of the nanorods. The diameter of the electrodeposited wires is controlled by the pore size of the PAA template, while the wire length is restricted by the template thickness. During electrodeposition, an ≈50 μm copper layer gets deposited over the silver side of sample, and acts as an electrode in the discharge device described later. We optimized the electrodeposition potential such that the metal NRs get deposited within the PAA nanochannels and not on its surface. Growth was stopped just before the NRs reached the top of the template surface. The as-prepared Cu-NRs within the alumina template display a uniform dark red color, and do not show ageing or oxidation at least for up to two months.

3. Results and discussions

Figure 1(a) shows a scanning electron microscopy (SEM) image of a small part of a typical Cu-NR array. The rods are approximately 200 nm in diameter and 60 μm in length, uniformly covering an area of 1 cm diameter with a density of \( \approx 10^{14} \) NR m\(^{-2} \). X-ray diffraction data show that the growth axis of the Cu-NRs is parallel to the [111] axis of Cu. In the device used, they remained embedded in the PAA template, but the template was partially etched out to obtain the SEM image. To study the discharge characteristics, we fabricated a simple device (figure 2). The Cu/Ag backplate of the Cu-NR-embedded PAA formed the negative electrode, while the positive electrode was a pure copper plate separated by an insulating spacer (an annular ring of polyester film of known thickness) from the exposed front end of the Cu-NR surface. The device current (I) across the air gap was measured as a
function of the applied dc voltage (V). When the potential across electrodes separated by an air column exceeds $V_B$, there is a sharp increase in the current, signaling the production of a secondary electron cascade by ionization of the gas molecules. To determine the effective reduction in the breakdown voltage due to the Cu-NRs, the corresponding value of $V_B$ was also measured on replacing the Cu-NR electrode in each case by a plane Cu plate.

Figure 3 shows the $I-V$ characteristics for a typical discharge device based on a 200 nm diameter Cu-NR array for different values of spacer thickness (d). The figure shows the stable discharge characteristic obtained after several (usually 3–6) voltage cycles. For $d = 80 \mu m$, electrical breakdown at ambient pressure was found to occur in a plane parallel electrode geometry (between flat copper plates) above 1000 V, while it occurred at around 100 V when one of the flat electrodes was replaced by a nanorod array. The decrease in the breakdown voltage was even more spectacular for thinner spacers. Thus, for $d = 12 \mu m$, $V_B$ is $\approx 500 V$ for flat electrodes, but less than 10 V for nanorod electrodes. This is by far the lowest breakdown voltage reported in the literature.

The dependence of the observed breakdown voltage on the spacer thickness for both bulk and nanorod-based electrodes is shown as an inset in figure 3. It is important to point out that, during the initial voltage cycles, the nanorod devices typically show electrical breakdown at values close to the corresponding ‘bulk’ value. There is a progressive reduction in $V_B$ with voltage cycling, until it settles down to the values shown in figure 3, usually within 3–6 cycles. We show that this is due to a progressive sharpening of the nanorod tips during the initial discharge cycles. After such ‘conditioning’, $V_B$ settles down to a stable and reproducible value.

The steady decrease in $V_B$ with voltage cycling suggests some type of structural modification of the nanorods. Such a possibility was investigated by studying high-resolution cross-sectional scanning electron micrographs of the nanorod-embedded PAA templates (after cleaving) at different stages of voltage cycling. From a comparison of the structure of individual nanorods in the as-prepared state (figure 1(b)) and after voltage cycling (figure 1(c)), it is evident that repeated electrical discharge does lead to sharpening of the nanorod tips. It is logical to assume that the consequent increase in the local electrical field results in a decrease in the breakdown potential. This is corroborated by our observation that if the nanorods are subjected to sulfuric acid etching, even the initial values of $V_B$ are substantially lower.

An interesting feature of the discharge from nanorod arrays (with respect to bulk electrodes) is that the current rises relatively slowly with increasing voltage in the breakdown region. This can possibly be attributed to the fact that the number of nanorods participating in the discharge process increases with increasing voltage, unlike the abrupt nature of conduction in bulk electrodes. The small difference in the gradient of the $I-V$ characteristics in the breakdown region during different discharge experiments may be related to the exact sequence in which the nanorods start discharging, and further experiments are required to understand such details.

Preliminary observations indicate that 200 nm silver nanowires also show a substantial reduction in the breakdown voltage, which indicates that this effect is not restricted to copper nanowires alone. To obtain an estimate of the operational life of the nanowire-based discharge device, we operated a typical Cu-NW device (200 nm diameter) in constant voltage (50 V) mode for over 220 h. During the entire period, the current remained in the 50–100 $\mu A$ range, which indicates that the device properties did not degrade with time. The operating voltage in this degradation study was deliberately set much higher than the breakdown voltage ($\approx 10 V$), because the sample damage, if any, should be higher at larger voltages.

The physical nature of the electrical discharge from the nanorod array was further studied by analyzing the characteristics of the conductance noise. A constant current (100 nA) was driven through the device and the time dependence of the voltage fluctuation (noise) was recorded for over a day. A fast Fourier transform of the time series data was then carried out to obtain the frequency dependence of the power spectrum (figure 4). The low-frequency noise follows the ubiquitous $S_f = 1/f^{\alpha}$ behavior. However, it is quite clear from figure 4 that the values of the exponent ($\alpha$) observed for flat electrodes and nanorod-based electrodes are distinctly different. While the noise from the bulk copper electrodes exhibits (approximately) an $S_f = 1/f^{3/2}$ behavior, typical of percolative systems in the ballistic (Sharvin) regime [10], the nanorod-based electrodes produce $S_f = 1/f^2$ noise, typical of a discontinuous process. In this context, it is significant that $1/f^2$ noise has been previously associated with the physics of various phenomena related to ‘stick–slip’ dynamics [11].
power spectra of such processes, often associated with self-organized criticality, typically reveal $1/f^\alpha$ behavior.

More information about the dynamics of the electrical discharge from nanorod arrays can be obtained from the time series data (figure 4, inset), which clearly indicates comparatively slow rises but rapid falls in the resistance or voltage at constant current. It is easy to show that such a spectrum can be obtained by a superposition of saw-tooth curves (sloping rise, sharp fall) with random phases. Physically, such a situation could arise in the following manner. Let us consider a nanorod that has been sharpened by several current–voltage cycles such that the field at the tip is just high enough for electrical discharge to occur. Discharge will be accompanied by the formation of ion pairs in the gas and a rapid decrease in the resistance. The process is self-limited by the accumulation of a space charge on the nanorod tip, which will impede further discharge. The gradual dissipation of the accumulated charge corresponds to the slowly increasing part of the resistance noise, followed by the next discharge. Our analysis of the noise data appears to indicate that such a process can be considered to be generically similar to the stick–slip phenomenon, with the slow dissipation of the space charge and the subsequent rapid discharge corresponding, respectively, to the ‘stick’ and ‘slip’ states. We also point out that, in the above scenario, the observation of a steady (and ultra-low) breakdown voltage is essentially a characteristic of the nanorod array, as the nature of the electrical discharge from individual nanorods is expected to show a rather chaotic time dependence.

The rapid increase in current in the nanowire-based devices is indeed due to electrical discharge and cannot be ascribed to field emission alone. This is proved by our observation that at a fixed bias voltage (say, 30 V) above $V_B$, the discharge current decreases with decreasing pressure. Had the process been ascribable to field emission alone, the current should have increased. In general, $V_B$ is expected to show a nonlinear dependence on the product of the inter-electrode separation ($d$) and the gas pressure ($p$), described by the well-known Paschen law [12], which predicts that the absolute minimum value of $V_B$ is $\approx 380$ V for air at atmospheric pressure with an electrode with optimal separation. For smaller values of $p \times d$, $V_B$ increases again since the charge carriers do not have enough kinetic energy to ionize the gas molecules. In the present case, the self-sharpened tips probably enhance the local electric field and produce field induced currents, triggering a spark discharge. Normally, secondary processes such as electron impact excitation and ionization, ionization from metastable gas ions, etc, cause electrical breakdown long before such high fields as required for field emission ($\approx 10^8$ V m$^{-1}$) are reached. The ultra-low breakdown voltages observed by us for metal nanorods, could not earlier be obtained with MW-CNTs, presumably because in situ sharpening was not as effective for such structures with a limiting diameter as with nanorods that can be sharpened—in principle—to a single atom. In contrast, a careful study has shown that MW-CNTs can be sharpened down to a diameter of only about 4 nm [13].

In conclusion, the conductance noise shows $S_N \propto 1/f^\alpha$ behavior with $\alpha \approx 2$ for the nanorod-based device, while $\alpha \approx 1.5$ for plane parallel electrodes with the same separation. The observed noise characteristics appear to suggest that electrical conduction occurs in a metal nanorod-based discharge device in the form of sporadic, random bursts from different nanorods and shows features reminiscent of the stick–slip phenomenon associated with sliding friction. The in situ self-sharpening of the nanorod tips (which is substantiated by high-resolution scanning electron microscope data) gives rise to an ultra-low breakdown voltage for air at atmospheric pressure. Electrical discharge in such nanorod-based devices can be sustained for long periods at an applied voltage as low as 10 V, a fact that could be of great significance in designing low-power discharge devices of many types.

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