

Development of Controlled Pitch Nanoarrays for Application in Nanoscale-Based Proportional Counters

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Abstract

Proportional counters (PCs) are a type of gas-filled radiation detection device capable of distinguishing between a wide range of radiation types and energies. In this application, however, these devices are limited by high power consumption and high bias potentials required to operate in the proportional detection regime. Previous work performed with a single carbon nanotube (CNT) anode has shown that nanoscale-based PCs can operate at bias potentials of ~10 V rather than the 1000 V range required for traditional PCs. “Proof of concept” experiments with a single CNT as the anode exhibit a small detection volume and consequently required long count times (24 hrs). To make this a practical detector technology (i.e., decrease the count time), the effective detection volume has to be increased. Experimental data and electric field modeling show that if the pitch (spacing between individual nanotubes) of the arrays is too small, the electric field of the individual nanostructure will collapse and the nanoscale array will behave as a single macro-scale field with the associated high bias potential required to reach the proportional region. Electric-field modeling of the influence of nanostructure pitch on the electric field distribution of these arrays predicted that a pitch of about two-and-a-half times the height of the nanostructure was required to retain the nanoscale electric field. In this work, we report on the fabrication and electrical property testing of nanoscale arrays with a range of controlled pitches. Arrays of differing composition (VACNFs and Si posts) and synthesis routes were produced and characterized. As an indirect measurement of electric field strength, we conducted high voltage breakdown studies under Ar and He atmospheres. The results qualitatively show that the electric field strength associated with the nanoscale arrays is higher than that of a control, particularly at pitches above two-and-a-half times the nanostructure height, as predicted by electric field modeling.

Introduction

Gas-filled detectors are commonly used as radiation detection devices. Depending on the applied potential, these operate as ionization chambers, proportional counters (PCs), or Geiger-Muller detectors. Of these detectors, PCs are capable of detecting a range of radiation types and energies. Traditional PCs require the application of high bias voltages (>1000 V) for operation

and associated step-up amplifiers which carry associated electronic noise and cost. Therefore, the remote deployment of PC detectors is limited by the electronics (i.e., power sources and step-up amplifiers) required to apply high potentials used to bias the PC.

Fabrication of nanoscale materials for use as the anode of a PC should allow for PC operation at much lower potentials due to the increase in electric field associated with a smaller diameter nano-scale anode. For example, the electric field strength, E , for a cylindrical PC of radius, r , can be calculated as:

$$E=V/(r\ln(b/a)) \quad \text{Equation 1}$$

where: V is the applied voltage, a is the anode wire radius and b is the cathode inner radius. From Equation 1 it is clear that as the anode wire radius, a , decreases, E increases. In addition to the lower operating voltage, the same voltage could be used to generate a larger electric field resulting in more electrons being collected, thus increasing the sensitivity of the PC. Other advantages of a nano-PC include reduced platform size and cost, and improved ruggedness.¹

Proof-of-concept work with a single carbon nanotube (CNT) anode has shown that nanoscale-based PCs can operate at ~10 V rather than the greater than 1000 V range required for traditional PCs.¹ However, these “proof of concept” experiments using a single CNT as the anode are, therefore, limited by a very small detection volume and associated long count times (24 hrs). To make this a practical detector technology (i.e., decrease the count time), the effective detection volume has to be increased. Additionally, experimental data generated on tightly packed CNT arrays and electric field modeling demonstrated that if the pitch (spacing between individual nanotubes) of the arrays is too small, the electric field of the individual nanostructure will collapse and the nanoscale array will behave as a single macro-scale field with the associated high bias potential required to reach the proportional region.¹ Electrical field modeling of nanoscale arrays predicted that the pitch needs to be ~2.5 times the nanostructure height in order to avoid the overlapping electric fields.¹

In this work, we report on the fabrication and electrical property testing of nanoscale arrays with a range of controlled pitches. Arrays of differing composition (CNTs and Si posts) and synthesis routes were produced and characterized. As an indirect measurement of electric field strength, we conducted high voltage breakdown studies under Ar and He atmospheres.

Experimental

Nanoscale Array Fabrication. Nanoscale arrays with controlled pitches were fabricated at the Center for Nanophase and Materials Science (CNMS) located at Oak Ridge National Laboratory (ORNL). Arrays of both vertically aligned carbon nanofibers (VACNFs) and silicon (Si) posts were produced on boron-doped n-type <100> silicon wafer substrates (Montco Silicon Technologies, Spring City, PA). The boron doping of the silicon wafer results in an electrically conductive substrate for eventual incorporation into a PC device.

VACNF Arrays. The VACNF arrays were produced using electron beam lithography to define a Ni catalyst pattern with controlled pitch followed by plasma enhanced chemical vapor deposition (PE-CVD) to grow the carbon fibers. The process used to grow the fibers has been described in detail elsewhere.² Briefly, a Jeol-6300FS/E electron beam lithography system was used to define the catalyst pattern on a ZEP520A resist. The resist was developed in xylene followed by evaporation of 5-10 nm of Ni. The resist and metal overlayer were then lifted off using acetone. The patterns created by electron beam lithography and metal liftoff were 3x3 mm square cells with 200 nm Ni catalysts having pitches of 1, 2, 3, 5, and 10 microns. The plasma used to grow the VACNFs in the PE-CVD process consisted of an acetylene/ammonia gas mixture at 650 °C. The plasma power was adjusted by controlling the current from 1 to 3 A. The growth time was varied between 1 to 2 minutes.

Si Post Arrays. The Si post arrays were also defined using electron beam lithography to deposit a metal (i.e., Cr) pattern and the nanostructures were developed by removing Si in the gas phase using reactive ion etching (RIE). The electron beam lithography and metal liftoff procedures described above were again used to pattern 3x3 mm square cells with 200 nm Cr dots having pitches of 1, 2, 3, 5, and 10 microns. The Cr dots serve as a mask during RIE, where a SF₆/O₂ plasma is introduced at -110 °C to etch away exposed Si. The SF₆/O₂ plasma generates F* free radicals that react with the silicon to produce highly volatile SiF₄.³ At cryogenic temperatures a SiO_xF_y passivation layer is formed on the sidewalls of the Si post which prevents etching of the sidewalls. Formation of this passivation layer is prevented on the bottom of the Si substrate by ion bombardment.⁴ The total etch time used to create the Si posts was 1 minute.

Nanoscale Array Characterization. The nanoscale arrays were characterized using a field emission scanning electron microscope (FE-SEM).

Electrical Property Testing. A 3.5" (diameter) stainless steel vacuum chamber was used to control the gas-phase composition during the testing of the electrical properties of the nanostructured arrays. Inside the chamber two parallel electrodes (Si wafer with the nanostructured array as the anode and an aluminum plate as the cathode) were separated by a Teflon spacer (Figure 1). The electrodes were connected through one arm of the chamber to a high voltage power supply and the applied potential and current monitored as a function of time.

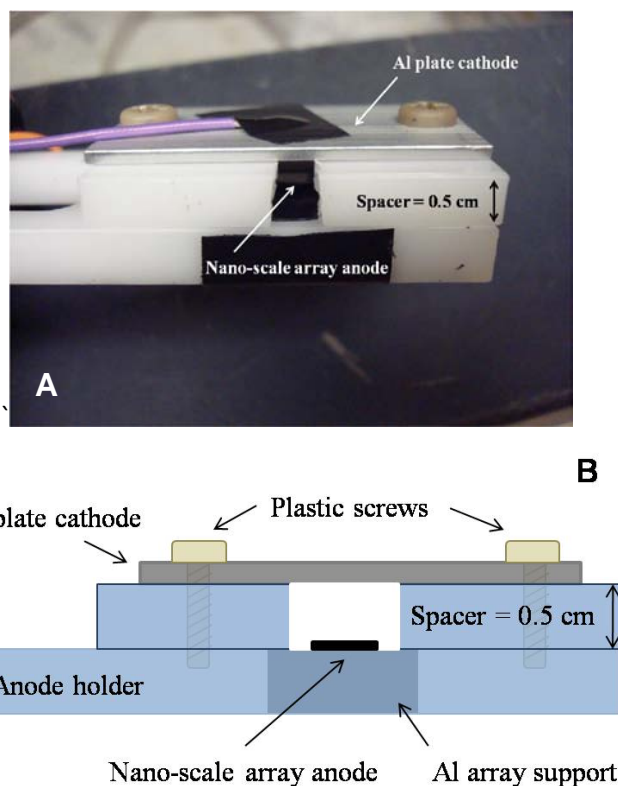


Figure 1. A) Photograph of parallel plate setup. B) Schematic cross-section of parallel plate setup.

The electrical properties of the nanostructured arrays were qualitatively tested by measuring the high voltage breakdown (an indirect measure of electrical field strength) between the array and aluminum plate in parallel plate geometry (Figure 1). Breakdown studies were conducted under He and Ar at atmospheric pressure with an electrode spacing of 0.5 cm. The breakdown potential was experimentally defined as the applied voltage where a continuous current discharge between the plates was observed. Control studies were also conducted with a boron doped Si wafer containing no nanostructure arrays.

Results

VACNF Array Fabrication. Vertically aligned carbon fibers with wide separations were grown from catalyst patterned substrates using PE-CVD (see Figure 2). PE-CVD is needed to form vertically aligned fibers because with conventional CVD techniques the widely spaced individual nanotubes will grow more in a horizontal direction and lay on the surface of the substrate.⁸ However, when using PE-CVD the carbon fibers will grow vertically in the direction of the electric field.^{2,5-7, 9-11}

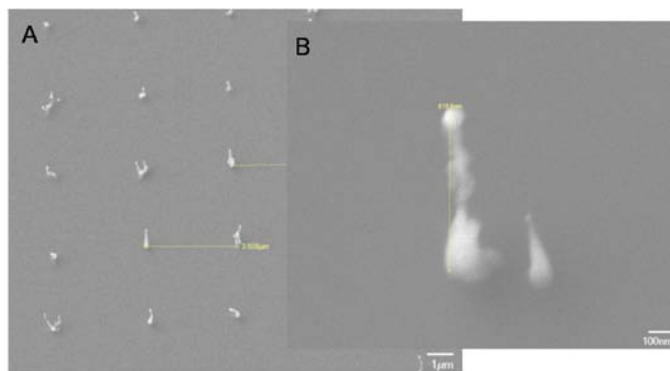


Figure 2. A) 3 micron pitch array of VACNFs, B) close up of a single carbon nanofiber.

In the case of PE-CVD, the metal deposited (i.e., Ni) during the electron beam lithography process acts as a catalytic site from where the carbon fibers grow up from the surface (Figure 2). The VACNFs shown in Figure 2 were grown at a temperature of 650 °C with 60 sccm of acetylene and 100 sccm of ammonia with a 1 minute growth time. These growth conditions yield fibers that are ~1-2 microns in length. As can be seen in Figure 2B, the catalyst tended to break-up during growth leading to the formation of multiple carbon fibers at each catalytic site. Movement of the catalyst during the growth process was also observed resulting in a distortion of the arrays. The distortion of the arrays was most significant with the 1 and 2 micron pitches (data not shown). The gas ratio also proved to significantly affect the morphology of the fibers. When the acetylene flow rate (i.e., the carbon source) was increased to 70 sccm, and all other conditions remained the same as stated above, the fibers appeared less etched, as in Figure 2, however, they appear more conical in shape (Figure 3) due to build up of carbon around the catalyst.⁶

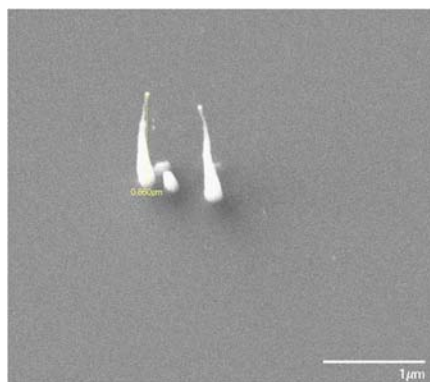


Figure 3. Close up of conically shaped VACNFs.

Si Post Array Fabrication. Uniform Si posts were fabricated using the same electron beam lithography patterning techniques used to grow VACNFs, followed by reactive ion etching (RIE).^{12,13} In contrast to the growth of VACNFs, in RIE the metal acts as a mask as reactive gases are introduced to etch away the exposed Si surface, leaving behind Si pillars where the

metal was deposited (Figure 4). During a 1 minute etch, Si posts with heights of ~2 microns were produced (Figure 4).

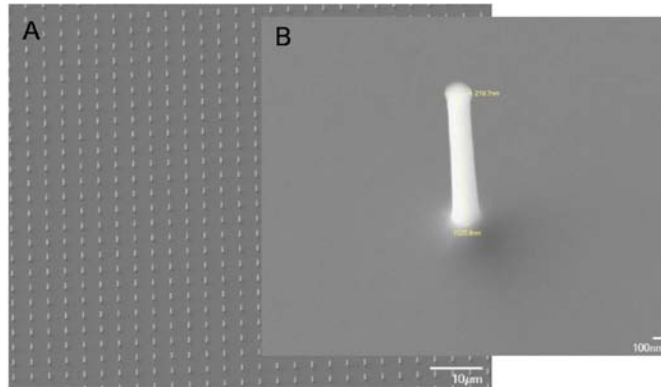


Figure 4. A) 3 micron pitch array of Si posts, B) close up of a single Si post.

In addition to producing Si post arrays with controlled pitch, we have also produced arrays of Si pillars with variable diameters. Figure 5 shows that Si posts with diameters of 3000, 1000, 500, 100 and 50 nm (pitch of 20 μm) can be fabricated. Controlling not only the pitch, but also the diameter of the nanostructured arrays will allow us to test the operating voltage of PC devices and electric field strength as a function of nanostructure diameter.

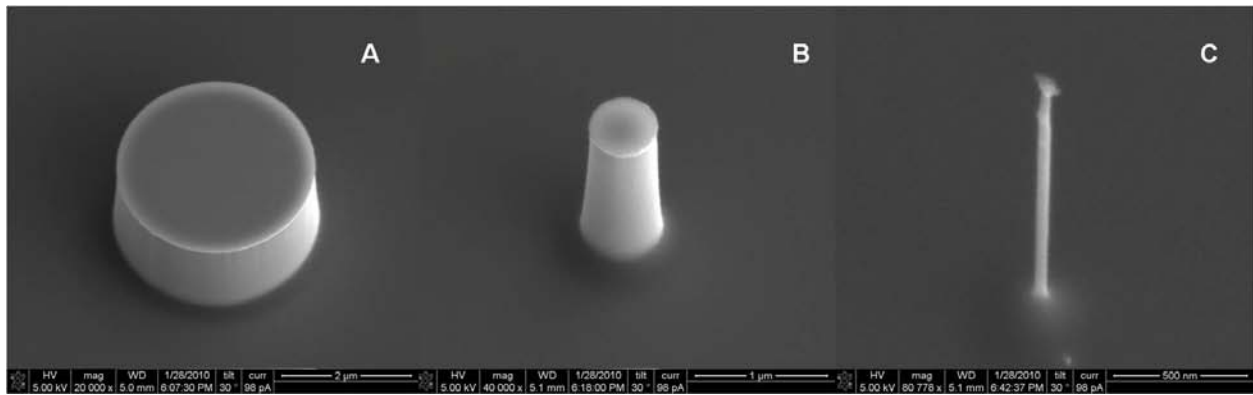


Figure 5. FE-SEM images of Si posts with a diameters of A) 3000 nm, B) 500 nm, and C) 50 nm.

High Voltage Breakdown Studies. A study by Modi et. al. has shown that gas ionization sensors utilizing an electrode with carbon nanotubes (anode) will lead to a decrease in the breakdown voltage between that electrode and a parallel plate configuration.¹⁴ This decrease is attributed to the much higher electric fields at the nanotube tips which results in the formation of highly ionized gas surrounding the nanotube tips, thus leading to a quickening of the breakdown process.¹⁴ In these studies they also found that the carbon nanotube devices could be operated for several hours with no damage to the nanostructures.¹⁴ Similar studies have been conducted with our nanostructured arrays to obtain an indirect measure of the electric field associated with the arrays and to determine if the arrays could structurally withstand applied potentials up to

several kV. Ar and He atmospheres were used to probe the stability of the produced nanoscale arrays at different applied potentials (~ 3500 V for Ar and ~ 1500 V for He).

Breakdown studies were conducted with blank boron doped Si wafers and both the VACNF and Si post arrays at all pitches in He at atmospheric pressure. Under these conditions, the blank boron doped Si wafer gave a breakdown potential of 1450 ± 30 V. The electric field associated with the nanostructures should be much higher than that of the blank boron doped Si wafer at the same potential, resulting in a lowering of the potential required to cause electrical breakdown between the array and Al plate. The arrays of Si posts with pitches (i.e., spacings) of 1, 2, 3, 5, and 10 microns gave breakdown potentials of 1450 ± 10 , 1410 ± 10 , 1410 ± 10 , 1280 ± 20 , and 1240 ± 20 V, respectively. The arrays of VACNFs with pitches of 1, 2, 3, 5, and 10 microns gave breakdown potentials of 1340 ± 20 , 1330 ± 10 , 1180 ± 10 , 1240 ± 30 , and 1190 ± 10 V, respectively. While an explanation for the reduction in breakdown potential for the VACNFs relative to the Si posts is not currently known, the behavior is consistent with the materials effect shown on the microscale for carbon fibers and tungsten metal by Pruitt.¹ These data are plotted in Figure 6, showing a lowering in breakdown potential with the Si post arrays having pitches greater than 5 microns, while all of the VACNF arrays show a lower breakdown potential. The greatest potential decrease with this material is seen with the 3, 5, and 10 micron pitches, a result which is consistent with the electric field modeling that predicted a spacing of at least 2.5 times the length of the nanostructure was required to preserve the electric field strength associated with the nanostructure.¹

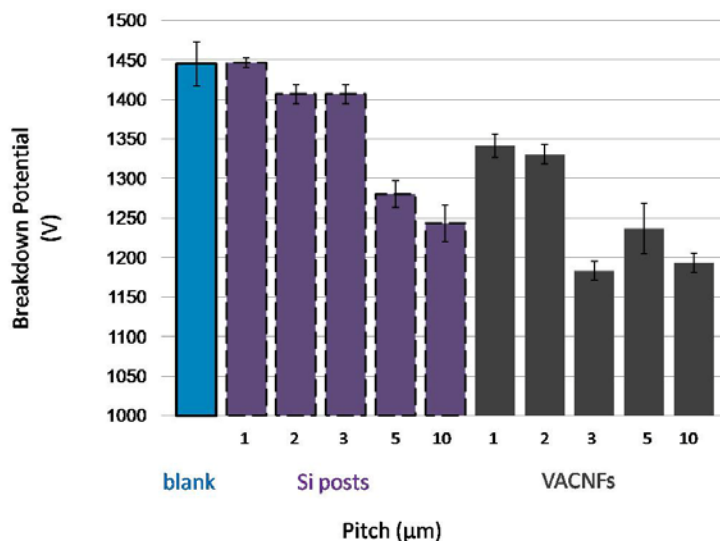


Figure 6. Graph of breakdown potential in He at 1 atm and 0.5 cm electrode spacing for blank boron-doped Si wafers (blue/solid outline), boron-doped Si wafers with nano-scale Si posts (purple/dashed outline), and boron-doped Si wafers with VACNFs (gray/no outline). Error bars are one σ of the 3 measurements taken with the same array.

FE-SEM images of the nanostructured arrays were collected after high voltage breakdown studies to evaluate the stability of the nanostructures after application of high potentials. The arrays that were subjected to breakdown in He resulted in no visible damage to the nanostructures (Figure 7A and B). Note that in Figure 7A there is a scratch at the top of the array, which was visibly present before breakdown studies were conducted. In contrast, high voltage breakdown studies were also conducted in Ar with a 3 micron pitch Si post array, where damage to the array can be seen in FE-SEM images. The damage is shown in Figure 7C as light spots on the array. Close up images of this area (Figure 7D) reveal that the nanostructures and Si surface are significantly damaged. Ar has a characteristically higher breakdown potential, therefore, breakdown occurred at 3580 V, compared to 1410 V in He, and resulted in the destruction of the Si posts. Stability studies of the VACNFs have not yet been conducted in an Ar environment.

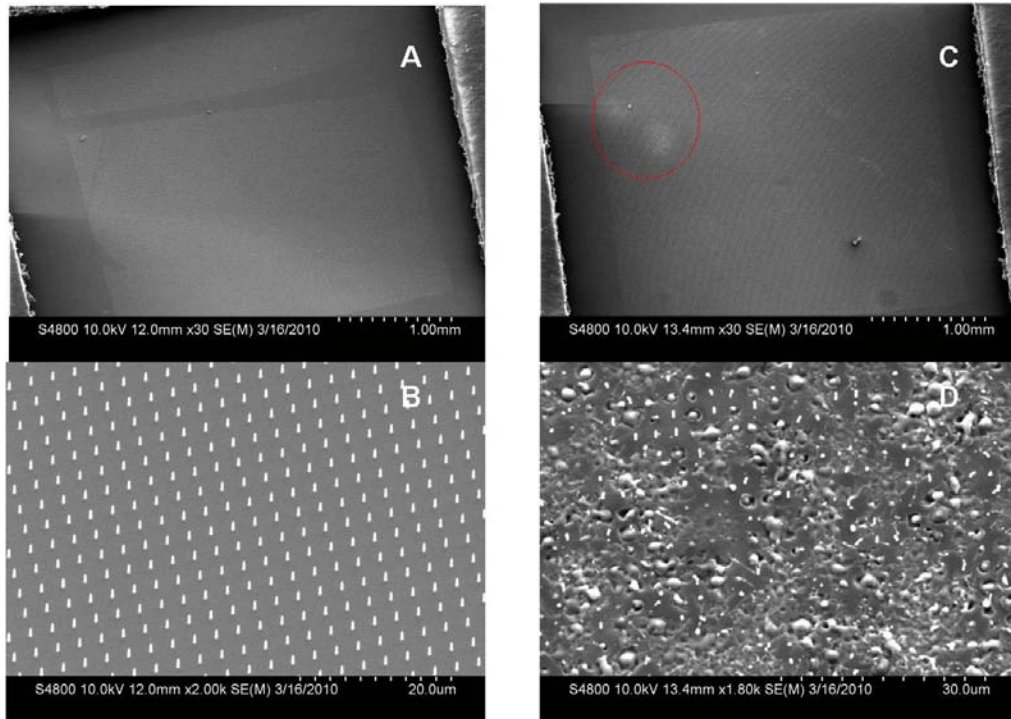


Figure 7. FE-SEM images of Si post arrays (3 micron pitch) after HV breakdown studies in He (A and B) and Ar (C and D). Note that the damaged area of the array in C has been circled.

Conclusions

We have demonstrated that nanostructured arrays with controlled pitch can be fabricated using electron beam lithography to deposit a catalyst for carbon nanofiber growth or a mask for Si post etching. The nanostructures for both types of arrays produced had heights of 1-2 microns, diameters of 200 nm and pitches of 1, 2, 3, 5, or 10 microns. In addition, we have also demonstrated that controlled arrays can be produced with varying nanostructure diameter.

High voltage breakdown studies indicate that the nanoscale arrays should exhibit the required electrical properties (e.g., retention of the nanoscale electric field and mechanical stability) needed for use as a detector material in PCs. The lowered breakdown voltage exhibited by the nanoscale arrays is indicative of a higher electric field associated with the nanostructures, thus suggesting that a radiation detection device based on these materials would display a lower operating voltage than traditional PCs. Although the VACNFs were not perfectly aligned and showed defects, the breakdown potentials were lower at all pitches compared to the Si posts. This implies that the electric field resulting from the carbon nanostructures is higher than that of the Si posts. This further indicates that when PC testing begins we should expect to see some materials effects in regards to the operating voltage.

With preliminary electric field testing of the nanostructured arrays complete, future work will include setting up proportional counting equipment/electronics and testing of the nanostructure arrays as an anode material in PCs. The arrays will be exposed to a gamma source of known activity and the pulse rate versus operating voltage will be measured to determine at what potential the PC operating voltage is reached. PC experiments will be conducted with both material types (VACNFs and Si posts) at the various pitches and diameters (Si posts only) fabricated in this work.

Acknowledgements

This work was supported by the SRNL LDRD program and a NNSA Next Generation Safeguards Initiative (NGSI) postdoctoral fellowship. The authors would like to thank Scott Retterer, Dale Hensley and the rest of the staff at the CNMS located at ORNL for their assistance in fabrication of the nanoscale arrays. We would also like to thank Bob Eakle and Don Pak for engineering design and fabrication.

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