Author

As a bioengineering major, Sohan Weeraratne became fascinated by the number of fields to which he could apply his studies. He decided to focus on radiology and was thrilled to be able to be able to conduct research under Professor Molloi's mentorship. Sohan has become immersed in the vast array of potential radiological nanotube applications and feels honored to have been able to make his own contribution to the field. He plans to continue his research and hopes to pursue graduate studies in medical physics.

Key Terms

- Cold Cathodes
- Doping
- Field Emission
- Hot Cathode
- Nanotubes

Development of Improved TiO_2 Nanotube Field Emission X-Ray Source

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Abstract

X-ray tubes based on carbon nanotubes suffer from limitations in longevity and stable emission, due to carbon's chemical characteristics. Our purpose was to develop a high-performance X-ray tube based on titanium dioxide (TiO_2) nanotubes. TiO_2 nanotubes can be incorporated to increase electron field emission and provide more stable emission. Titanium dioxide is already oxidized and therefore cannot be impeded in ways that carbon can. Also, the metallic features of TiO_2 allow it to withstand heating effects. Our technique used an electrochemical setup comprising an electrolyte solution with a titanium sheet submerged in it to oxidize. TiO_2 nanotube growth requires only a container, electrolyte, platinum electrode, and DC supply. Manipulating key aspects of growth requirements allowed the temperamental parameter breakthroughs we hoped to attain in the field of nanotechnologic X-ray tubes. Chemical doping during growth and after annealing was one of the main strategies we tested, as was altering the concentration of the electrolyte bath for increased conductance. By analyzing our results, we successfully created nanotubes with increased conductivity, density, and overall pattern of growth.

Faculty Mentor

The objective of this study is to develop a high-performance X-ray tube based on a cold cathode titanium dioxide (TiO_2) nanotube. Currently available thermo-emission cathodes have several important limitations. A potential solution to these limitations is to employ an electron source based on a field emission source. Carbon nanotubes have previously been investigated for use as a cold cathode. However, these types of cold cathodes are limited by their short lifetime. The longevity is of considerable importance when considering adoption in a clinical setting. TiO_2 nanotubes show promise to overcome these limitations. A new X-ray tube design using TiO_2 nanotubes may be a significant advance in X-ray technology development and could lead to more miniature X-ray sources.

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Objective

In conventional X-ray tubes, a Tungsten filament is heated to a high temperature in order to extract electrons. These electrons are then accelerated to bombard metal targets, generating X-ray photons (Alivov et al., 2010). Limitations to this heating technique include slow response time, high power consumption, and unsafe working temperatures. Slow response time limits the ability to generate X-ray beams from a fast trigger. The high operating temperatures reduce the metal filaments' lifetime, and the random distribution of electron velocities limits the focusing of the electron beam and the resultant focal spot size (Alivov et al., 2010).

A major objective in the study of X-ray tube-based field emission is to develop a high-performance X-ray tube based on a cold cathode technique. Cold cathode X-ray tubes are currently being investigated as an alternative to thermoionic cathodes for applications such as small animal imaging. As mentioned previously, thermoionic cathodes, or hot cathodes, use temperatures above 2000 °C to allow free electrons to escape the surface. These cathodes require a constant power supply for heating at unsafe temperatures, making them disadvantageous. By incorporating field emission, we seek to achieve electron emission equal to or exponentially greater than thermoionic cathodes with a relatively lower potential needing to be applied. It was first suggested in the 1950s that cold, or field emission (FE), cathodes might overcome the disadvantages of hot cathodes, but electron emission from an FE cathode is unstable under non ultra-high vacuum environments.

Carbon nanotubes have been used previously in efforts to achieve stability under non ultra-high vacuum environments but, although emission stabilizes under these conditions, the carbon nanotube itself remains a problem. Carbon nanotubes have been used for cathode filaments; however, limitations, including oxidation and degradation in conductivity have resulted from carbon's natural elemental characteristics (Chhowalla et al., 2001). Oxidation occurs in vacuums due to leftover gases in the chamber, rendering carbon nanotubes unproductive. Conductance between nanotubes and substrate is poor due to carbon's nonconductive nature as a non-metal.

We propose the use of TiO_2 nanotubes grown by electrochemical oxidation to overcome the limitations caused by using carbon. TiO_2 is a natural oxide, so contact with oxygen is insignificant and does not lead to degradation. Also, TiO_2 nanotubes grow directly from titanium sheets as they oxidize, with titanium's metallic nature ensuring excellent electrical contact between the titanium sheet and the TiO_2 nanotube layer.

Using the characteristics that titanium expresses, we demonstrated improvements in X-ray tubes with oxide based nanotubes and combinations of TiO_2 submerged in dopants to increase overall conductivity and emission. Figure 1 shows incorporated nanotubes in an existing X-ray generation setup (Alivov et al., 2010). These newly incorporated nanotubes also increase emission.

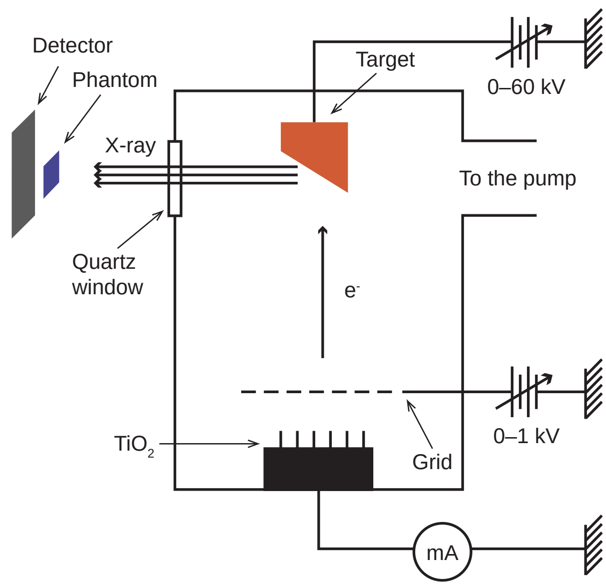

Figure 1

Schematic of the experimental setup used for X-ray generation and imaging using a TiO_2 nanotube field emitter

All data was taken using a Scanning Electron Microscope (SEM) and Energy Dispersive Microscopy (EDS) for analysis of nanotubes and interpretation for future implementation. A typical scanning-electron microscope image of electrochemically grown TiO_2 nanotubes is shown in Figure 2, which demonstrates parameters that help in maximizing emission and conductivity (Alivov et al., 2010).

Approach

Field emission is electron emission induced from materials within high electric fields. This emission from nanostructures occurs at a significantly lower applied electric field due to field enhancement on the top of nanostructures. The parameters that affect field emission efficiency of nanotubes include structural state, density, surface state, and doping level. These parameters individually influence

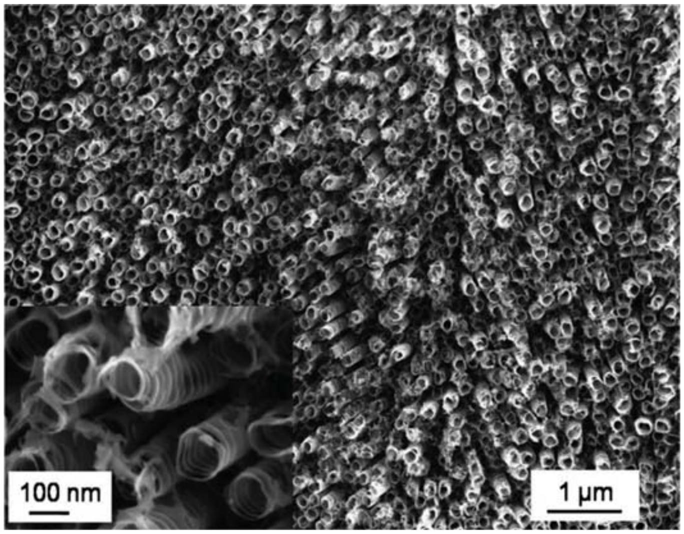

Figure 2

Representative SEM images of TiO_2 nanotubes grown on a titanium sheet by electrochemical oxidation; the insert shows the magnified area

field emission in different ways. Geometric structure factors determine the field enhancement value, the nanotube density determines electric field screening effects, the work function determines the energetic barrier that electrons must exceed to escape the material, and the nanotube conductivity—or doping level—determines the electron supply in nanotubes. These factors can be manipulated to reach a higher conductivity, which would result in higher electron emission efficiency, a goal of much nanotube-based field emission research. These parameters influence the electron current density independently and should be optimized individually, which we have achieved in this study. After achieving maximum optimization of all the parameters, the resulting nanotubes that tested highest in emission efficiency were studied for future use in X-ray tubes designed for small scale imaging such as cardiac imaging or small animal imaging in our lab.

An electric field, as depicted in Figure 3, is uniform when the electric field is constant at every point.

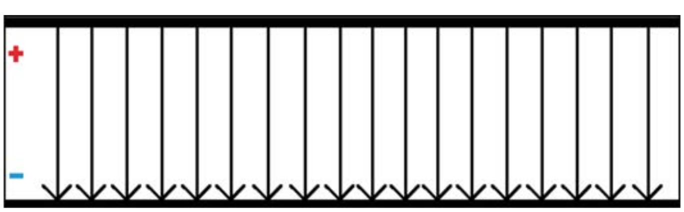

Figure 3

Uniform electric field under normal field emission

This uniform field pattern is weak due to the large distance between electrodes, and high potentials need to be incorporated to obtain any useful field emission. By incorporating nanotubes, we effectively increase the electric field, as demonstrated by the highly concentrated electric field lines shown in Figures 4 and 5.

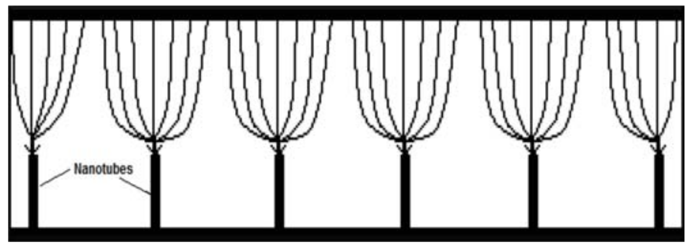

Figure 4

Emission lines under nanotube incorporation

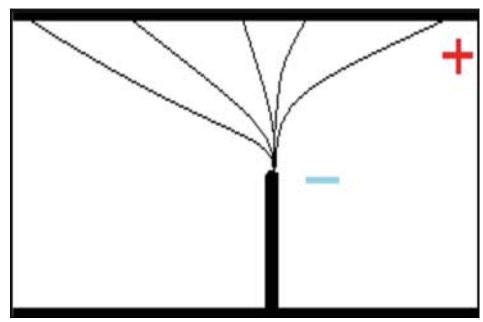

Figure 5

Zoomed in nanotube attracting field lines going from positive to the negative tips

With our newly implemented nanotubes, not only are the positively charged field lines attracted to and concentrated on the tips of the negatively charged nanotube, the distance the field lines travel is also shortened. The mathematical relationship is displayed in Equation 1, which demonstrates the relationship among field emission (E), potential difference ($\Delta\phi$), and distance (d). This equation shows the direct relation of each of these parameters to each other and, thus, the different ways in which field emission may be augmented. Based on this we used our TiO_2 nanotubes to decrease the distance, which increased field emission, providing a secondary option of augmenting field emission without increasing the potential difference to unsafe levels.

$$E = -\frac{\Delta\phi}{d} \qquad (1)$$

Evaluation of the field emission was done using the following simplified Fowler–Nordheim work equation, which was simplified to display linear relationship exemplifying nanotube nature:

$$J = A\left(\frac{\beta^2 E^3}{\phi}\right)\exp\left(\frac{B\phi^{3/2}}{\beta E}\right) \quad (2)$$

where A and B are constants with values 1.5610−6 A/V2 and 6.83103 V eV−3/2 m−1, respectively; E, β, and ϕ refer to the electric field, field enhancement factor, and work function of the TiO_2, respectively. The nearly linear relationship between ln(J/E2) and (1/E) demonstrates the field emission nature of the TiO_2 nanotube cathode. The work function determines the energetic barrier that electrons must exceed to escape the material.

Simulations and experimental studies that seek to manipulate the work equation have investigated the effects of TiO_2 nanotubes' geometrical parameters, array density, doping, and post-growth treatments on electron emission current density, thus creating an easier-to-escape electron environment.

Effect of Structural Parameters

TiO_2 nanotubes' structural parameters include diameter, height, and wall thickness. Overall structure can be controlled during electrochemical growth by strategically determining optimal voltage and electrolyte percentage (Alivov et al., 2009). Few reports have examined field emission from TiO_2 nanotubes, and no systematic studies are available on field emission's dependence on nanotube parameters (Liu et al., 2008; Miyauchi et al., 2006). By challenging the dependence of field emission, we seek to optimize the field emission from TiO_2 nanotubes to achieve the highest field emission current density. As preliminary simulation studies have shown, the field enhancement factor increases linearly with nanotube height and decreases inversely with diameter and wall thickness (Alivov et al., 2010). However, it is important that simulation studies be performed under ideal case scenarios that ignore all other factors. Unknown factors can contribute to the field emission, resulting in deviations from the norm that can seldom be traced.

In previous works, larger diameter carbon nanotubes have been reported to have better field emission properties than long and narrow nanotubes (Yoriya and Grimes, 2010; Chhowalla et al., 2001). Specifically, short and stubby nanotubes with diameters of 200 nm exhibited superior field emission characteristics. Therefore, systematic studies are needed to determine which parameters result in the maximum field emission efficiency. The diameter of TiO_2 nanotubes during electrochemical oxidation depends only on applied voltage; it grows linearly and commensurately, normally ranging from 10 to 300 nm as the voltage increases from 10 to 120 V. The nanotubes' height, or growth rate, is determined by the electrolyte composition and can change with the range of 102 to 104 nm/h. Such straightforward control of a key parameter affecting field emission is a promising quality of titanium dioxide for this application.

Design

This project used of an electrochemical setup consisting of a titanium sheet submerged in an electrolyte solution in order to oxidize. TiO_2 nanotube growth requires only a container, electrolyte, platinum electrode, and DC supply (Figure 6) (Alivov et al., 2010). Attempts to manipulate key aspects of growth requirements allowed temperamental breakthroughs from the parameters we accomplished in the field of nanotechnologic X-ray tubes. Chemical doping during growth and after annealing as well as altering the percent concentration of the electrolyte for increased conductance were the main strategies tested throughout the project. By analyzing results, we tested these nanotubes for conductivity, density, and overall growth pattern using different machines to track and learn from patterns attained by repeated testing.

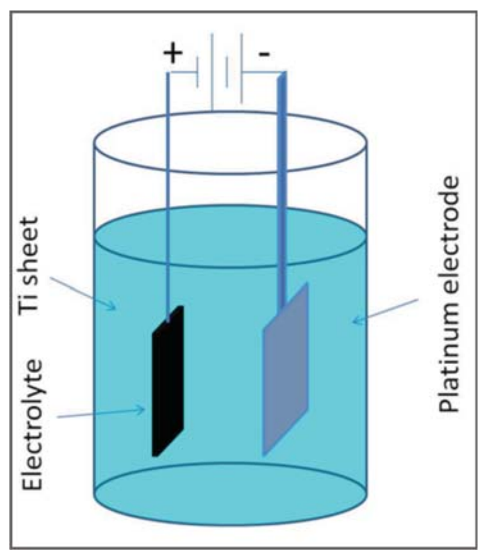

Figure 6
Schematic of the experimental setup for TiO_2 nanotube growth by electrochemical oxidation

Effect of Nanotube Density

Nanotube array density, another factor influencing field emission, arises from electric field screening. High-density nanotube assortments result in higher screening effects, while low-density nanotubes result in proportionally lower effects; therefore, sparser nanotubes are preferred to reduce screening effects and achieve higher field emission gain. Like many other nanotube arrays (including carbon nanotubes), the density of TiO_2 nanotube distribution is hard to control during growth. To date, only a few reports have discussed the development of methods for controlling TiO_2 nanotube density. In particular, preliminary studies show that an increase of ammonium fluoride acid in the electrolyte partially reduces nanotube density. Recently, Yoriya et al. (2008) reported that using diethylene glycol as a solvent in the electrolyte could increase nanotube spacing to some extent; however, the density achieved in this work is far from optimal. We seek, therefore, to perform additional studies aimed at increasing the spacing between nanotubes and establishing reliable methods to control overall density. It is unlikely, however, that nanotube density can be varied to any particular or engineered value during the growth process, and most likely nanotube distribution can only be achieved to certain peak values. We noticed that an increase in ammonium fluoride acid in the electrolyte partially reduces nanotube density and works around this issue. We grew our samples in ethylene glycol and found the optimal percentage of electrolyte to be about 0.7% NH4F. Under 0.7% electrolyte, we found that SEM analysis showed the greatest spacing of about 100μm.

Post-Growth Treatment

The work function determines the energetic barrier that allows electrons to escape TiO_2 nanotubes during field emission. Therefore, reducing the TiO_2 nanotube work function, which is reported to be in the range of 3.9–4.5 eV (Tan et al., 2003; Liu et al., 2008), enhances the electron emission current. Incorporating dopants and other post-growth treatments is known to be an effective way to modify the material work function. Dopants such as nitrogen and carbon have been used frequently and found to increase field emission significantly through their large reduction in the work function (Liu et al., 2008). Using these and other elements, we achieved the highest gain in electron current conductivity and, therefore, perfected a key aspect in maximizing field emission. We also tried to lower the work function by covering our nanotubes with a thin layer of low-work function materials that we simultaneously tested with our newly grown nanotubes.

Effect of Doping

The conductivity of nanotubes directly determines the amount of electron supply in material used during field emission. As a result, a higher electron concentration in the TiO_2 nanotubes is needed to obtain a higher field emission current density. Originally, the conductivity of normal-grown nanotubes is generally believed to be caused by oxygen vacancies within the sample. Depending on the range of growth conditions, initial nanotubes can vary from insulating to semi-metallic behavior ranging from 10^{-4}–10^{8} Ω cm (Alivov et al., 2009). However, the conductivity of TiO_2 crystals caused by oxygen vacancies is known to be unstable due to eventual oxygen diffusion from the surrounding air, which degrades over time. Therefore, a donation of electrons (element doping) should be performed in order to replace titanium or oxygen atoms in their formed crystal lattice. The typical lab donors for TiO_2 are aluminum, nitrogen, carbon, and niobium (Grimes and Ranjan, 2008). Normally, doping of TiO_2 media or lattice can be achieved through several methods: addition of chemical agents during growth, additional post-growth in atmosphere containing the donor element, and direct implantation of donor element ions. Extensive studies have not been done on doping TiO_2 nanotubes with donors grown and controlled by electrochemical oxidation. We performed a number of studies to find effective ways to dope TiO_2 nanotubes with such donors and track these dopants to propose direct relations between them and nanotubes. This goal was pursued primarily through two methods: *in situ* doping that was achieved by dissolving proper chemical compounds in electrolyte during growth and thermal diffusion of appropriate donor element particles from the atmosphere during annealing. Success in this area would offer another parameter control to determine TiO_2 nanotube performance. We successfully used niobium (Nb) as a dopant to increase conductivity as a result of its highly conductive characteristics.

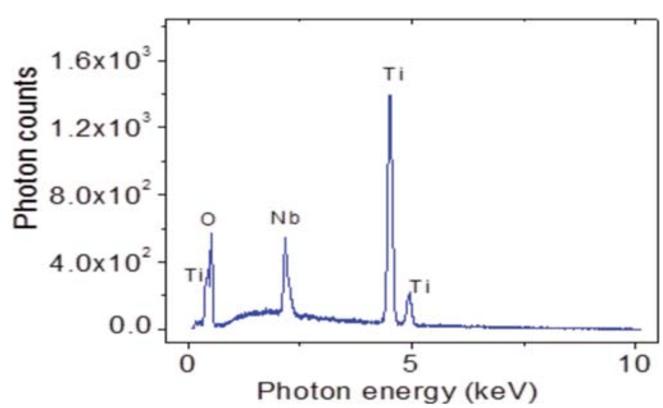

Figure 7

Energy-dispersive X-ray spectroscopy (EDS) analysis of TiO_2 nanotubes grown with niobium dopant; the chart shows that niobium has successfully attached to the sample

Figure 7 shows our EDS analysis nanotubes doped with niobium. Incorporating niobium causes a noticeable amount of reduction of the work function, resulting in increased field emission. We have incorporated niobium in situ and by post thermal diffusion to achieve much longer lasting nanotubes, which we successfully reused many times to obtain stable emission data.

Figure 7

Discussion

By growing TiO_2 nanotubes and incorporating them in a basic X-ray emission schematic, key aspects of emission characteristics were improved to create a safer and more constant electron emission more efficiently. Previous relations to emission required unsafe amounts of electric potential, as was shown in Equation 1. Without these nanotubes, larger distance and unconcentrated field lines require enhancing field emission by maximizing electric potential, the numerator in the equation. Not only did our nanotube incorporation enhance field emission, we also developed a protocol to grow these nanotubes efficiently.

Our results clearly indicate that clustered TiO_2 nanotube arrays have much greater field emission properties than unincorporated nanotubes and regular nanotube arrays. This effect was explained by significant reduction of electric field screening effects in such spaced cluster arrays. We believe that, although these results prove beneficial to the contribution of TiO_2 nanotubes to field emission, they can be significantly improved by further optimization of clustered TiO_2 nanotube fabrication.

Acknowledgements

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