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During the course of this project, we employed and extended our unique capability in template-growth of nanostructured materials, particularly carbon nanotubes. This fabrication capability formed the foundation for further investigations, into the infra-red properties and transport properties of these nanostructures. We were able to fabricate large arrays of identical carbon nanotubes with identical properties, which enabled sufficient signal enhancement to perform novel infra-red spectroscopy studies on the nanotubes. Extensions of our core fabrication method enabled the creation of carbon nanotube arrays on silicon wafers. The importance of silicon as a semiconductor material cannot be overstated, and so the fabrication and measurements of these structures represents an important step toward integrated Si-CNT infrared detectors. The results of this project clearly demonstrate the feasibility of employing ordered carbon nanotube arrays in infra-red detection applications.

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## **Exploration of Highly-Ordered Carbon Nanotube Arrays for Infrared Detection – *final report***

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### ***Summary***

During this project, we pursued and succeeded in the development on a novel method to fabricate highly-ordered carbon nanotube (CNT) arrays and explored the use of CNT arrays in infrared detection applications. We investigated these array films as a new base material for infrared detection with a spectral response that can be tuned over a broad range, through varying the diameter of the tube, and a detection surface area that is not wafer-size limited and conformable to curved surface. Other attributes include high-uniformity, low manufacturing costs, long life-time, high-density and, potential resistance to defect-induced failure.

The main objectives of the proposal were:

1. to grow highly-ordered carbon nanotube arrays on various substrates and investigate in detail the necessary fabrication conditions for controllably producing high-quality arrays of varying dimensions and large ordered domains suitable for infrared detection
2. to investigate and study the infrared properties of these arrays to explore their use in infrared applications such as sensing, imaging.

These objectives have been realized. Moreover, the research has reached a point beyond these objectives where the first room-temperature photovoltaic responses to light pulses in both the visible and mid-IR ranges have been demonstrated in the novel nanotube-silicon heterojunction diode arrays, which by itself is also a new advent in the field of semiconductors.. The results of this project have opened up scientific and technological opportunities associated with carbon nanotube arrays for future space IR sensing and civilian imaging and spectroscopy applications. In particular, the outcomes of this project have a real potential to lead to the development of a new technology for IR detection with a very broad spectral and spatial coverage that is unavailable in conventional IR materials.

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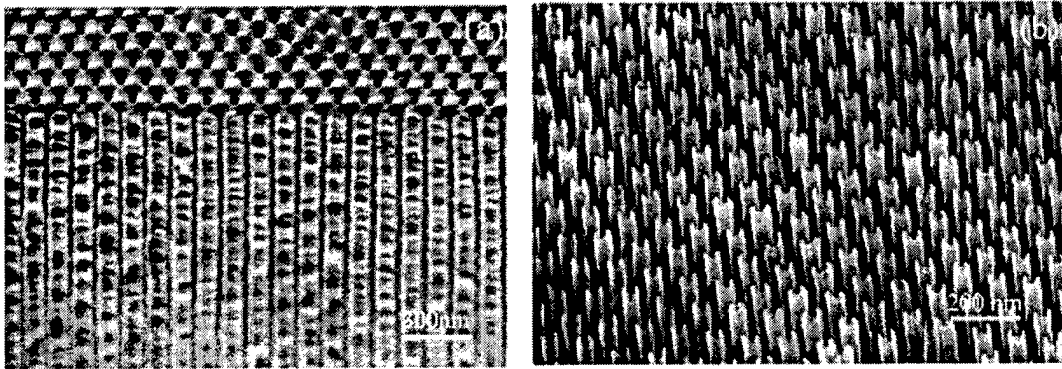
## **Introduction**

Carbon nanotubes, discovered by Iijima in 1991[1], can be semiconducting or metallic, as has been shown both experimentally[2, 3] and theoretically[4]. The semiconducting bandgap—typically in the range of sub 100 meV to a few 100 meV—has been found to be controllable through the tube diameter and chirality in the case of single-walled tubes. This semiconducting behavior and its dependence on diameter make carbon nanotubes an attractive candidate for infrared (IR) detection. However, it is hard to imagine actual IR device implementations using the nanotubes that come in bundles, ropes or other random configurations. Unfortunately, these are the only options for nanotubes produced by conventional methods[4, 5].

Devices for IR detection and imaging, such as focal plane arrays, require large-area, densely-packed detectors in a well-defined array structure with efficient light coupling, high responsivity, good pixel-to-pixel uniformity, low dead pixel count and excellent stability[5]. In addition, to be practical, they must employ a large number of small pixels and be fabricated by a high-yield, low-cost approach. Therefore large-area, ordered and well-aligned high-density arrays of uniform carbon nanotubes were always viewed as valuable, but were not available until our demonstration of a general and extensible nanotemplate method for carbon nanotube array synthesis[6].

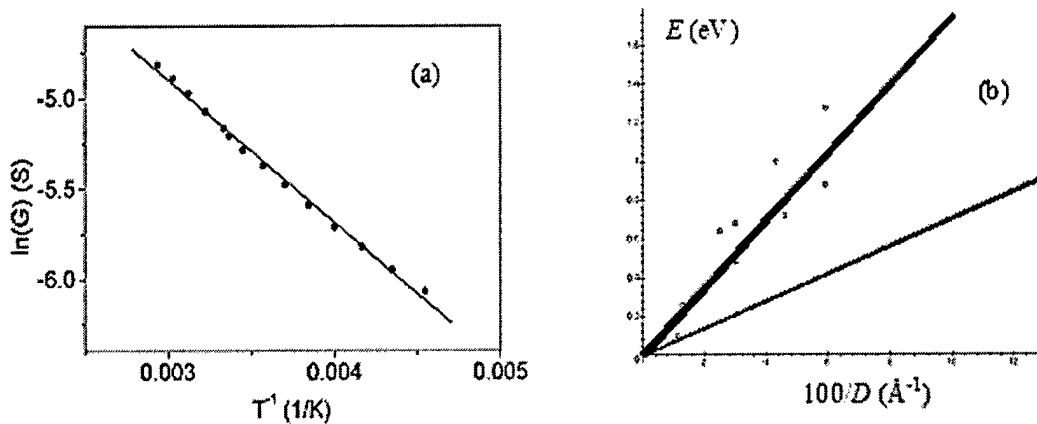
## **Technical introduction**

In this project highly-ordered carbon nanotube (CNT) arrays were fabricated using our newly developed synthesis method and explored for their use in IR detection. The fabrication method is based on using a nanochannel alumina (NCA) template which is formed non-lithographically in the process of anodizing high-purity aluminum, and can be used as a stand-alone film or formed on the surface of a foreign substrate. In this process it has been shown that under certain conditions[7] self-organized arrays of straight and deep pores nanometer-scale in diameter can be formed, as shown in Figure 1(a), and that the pore diameter and periodicity can be varied separately, within certain parameter ranges that are yet to be fully mapped out, while retaining the hexagonal ordering. The carbon nanotubes are grown directly within the pore channels in what is essentially a CVD process with transition metal particles being first deposited in the pore bottom to serve as catalysts. Conventional nanotube fabrication methods produce bundles or random matrices of carbon nanotubes with varying dimensions. In contrast, this method produces highly-ordered, large-area two-dimensional arrays of densely-packed carbon nanotubes with unprecedented uniformity in diameter, length and orientation, as seen in Figure 1(b).



**Figure 1.** (a) Scanning electron microscope image of nanochannel alumina template. (b) Highly-ordered carbon nanotube array formed by thermal decomposition of acetylene within the template channels.

The resultant carbon nanotubes are typically multi-walled and experiments to date have shown them to be semiconducting [8] with a bandgap in the mid to far IR region, that can be varied with the diameter. This is shown in Figure 2(a). This finding for multi-walled CNTs has been independently confirmed using different methods of measurement [9], and is supported by theoretical predictions for multi-walled CNTs [10] as shown in Figure 2(b).

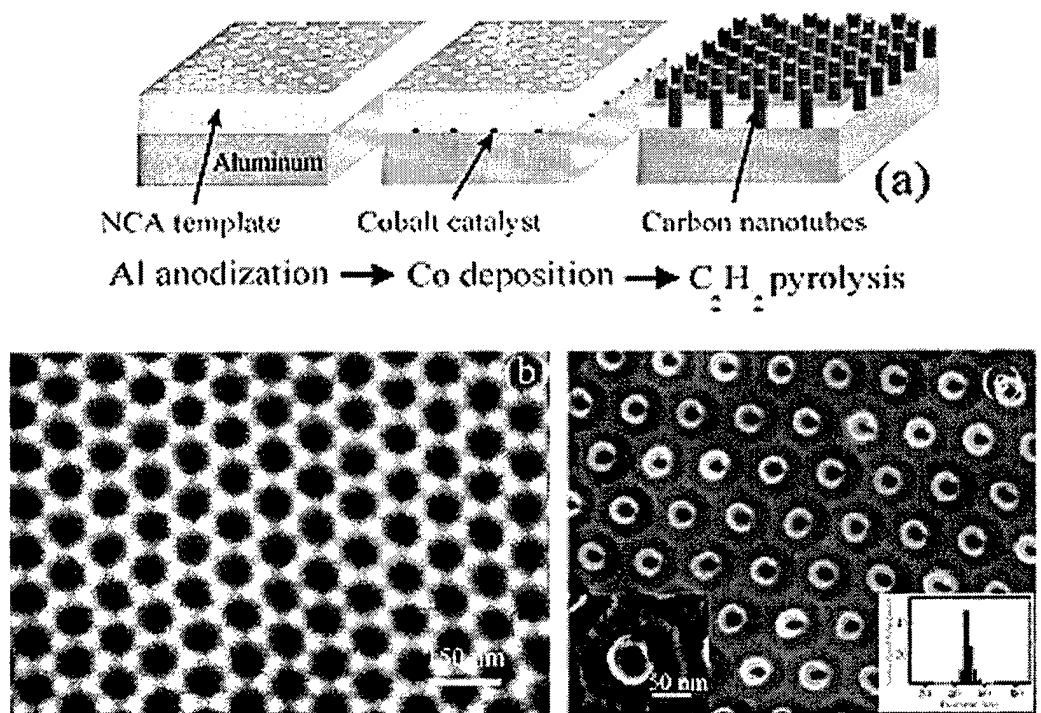


**Figure 2.** (a) Log of nanotube conductance versus inverse temperature, showing semiconducting exponential activation law with a band gap of approximately 135 meV. (b) Dependence of nanotube band gap versus inverse diameter. The thick line is the theoretical result for multi-walled tubes along with tunneling spectroscopy data, while the thin line is the theory for single-walled tubes.

Given that the pore diameter and thus the nanotube diameter can be controllably varied in this approach, this finding has the implications that with essentially the same material and fabrication technology one can design and synthesize IR detectors that respond to different wavelengths in the far-IR to mid-IR range. The CNT arrays produced by this method possess several features which are important for IR applications: The ordering and uniformity of the CNT arrays, a unique feature of this CNT fabrication approach, should improve the signal-to-noise ratio in IR detection by recording and summing coherent signals while suppressing (i.e., averaging out) the random phase and spatial

randomness of thermal noise. The dense packing ( $\sim 10^{10}/\text{cm}^2$ ) of the nanoscale CNTs provides hundreds to thousands of individual CNTs to each pixel of a typical IR detector array, and thus a much desired high redundancy to guard against failure. The independence and isolation, both electrically and mechanically, and weak inter-tube thermal coupling of the CNTs in the array means that defects are confined to individual nanotubes and are unlikely to spread out as in typical IR semiconductors (e.g. HgCdTe, antimonides) which are continuous. The quasi one-dimensionality of the nanotubes suggests a reduced density of states and therefore reduced phonon coupling [11] and higher operational temperatures. In addition, such arrays can be formed on foreign substrates including curved surfaces, lending themselves to potential applications such as "smart skin" functions. Finally, the excellent parallel and vertical alignment of these arrays gives them a large effective detection surface and an intrinsically high detectivity to normal incidence photoexcitation—a distinct advantage over quantum well intersubband detectors.

Our approach for synthesizing CNT IR detector arrays provides a practical cost-effective process for producing large-area IR devices for a variety of applications in future space-, air- and land-based IR sensing and imaging applications. This fabrication approach is summarized in Figure 3.



**Figure 3.** (a) Schematic of CNT array fabrication process. (b) NCA template after first anodization showing hexagonal texturing. (c) Highly-ordered CNT array formed using method in (a). Left inset is a close-up of the nanotube in its hexagonal cell. Right inset is a histogram of the nanotube diameter showing narrow size distribution around 47 nm.

## **Project objectives**

As described in the Summary, the primary objectives of this project were:

- to develop a fabrication method to controllably and repeatably produce highly-ordered CNT arrays of high-quality and varying dimensions, on various substrates
- to examine and characterize the electrical and optical properties of CNT arrays under IR excitation
- to initiate the exploration of the device applications of CNT arrays in IR detection

The goal of this research was to demonstrate the feasibility of highly-ordered CNT array films as a new base material for IR detection applications. Although many new exciting questions were opened and remain to be answered through further in-depth investigations, the project goal itself has been achieved. Researchers at Wright-Patterson Air Force Labs were invaluable collaborators with us in this project and contributed significant time and equipment to the effort.

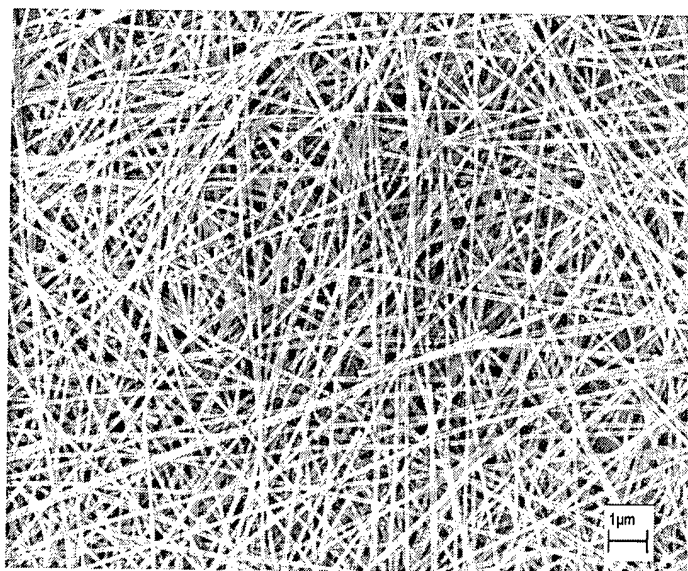
## **Project outcomes**

This project provided valuable results in three main areas: the improvement and refinement of the fabrication methods of the carbon nanotubes, the study of the infra-red properties of multi-wall CNTs, and the study of electronic transport in a hybrid CNT-Si heterojunction system. Improvements in the fabrication methods enabled the subsequent experimental developments in the study of nanotube properties, both in and out of the arrays

### **Studies of infra-red properties of isolated nanotubes**

We performed an infrared optical absorbance study of highly uniform nanotubes grown by chemical vapor deposition in the self-assembled porous matrix in alumina. For unambiguous IR spectral measurement, nanotubes were extracted from their growth template, purified, and evenly dispersed on a reflecting substrate. The findings, which are consistent with previous results from electronic transport studies, reveal that the nanotubes are semiconducting with a band gap of  $\sim 100$  meV. This suggests the potential of nanotube arrays for IR sensor applications. Previous scanning electron microscopy and conductance studies have found that the nanotubes in this array are of a single length and diameter and are essentially identical in their electro-mechanical properties [6, 12]. Moreover, the tubes can be easily accessed electrically and optically, which make them especially attractive for electro-optical device applications. We have performed a variety of transport, optical, STM, SEM and HRTEM studies and characterizations on single extracted and in array nanotubes grown by CVD in alumina matrix and confirmed that nanotubes are identical in their geometric configurations, chemical composition, electronic and optical properties.

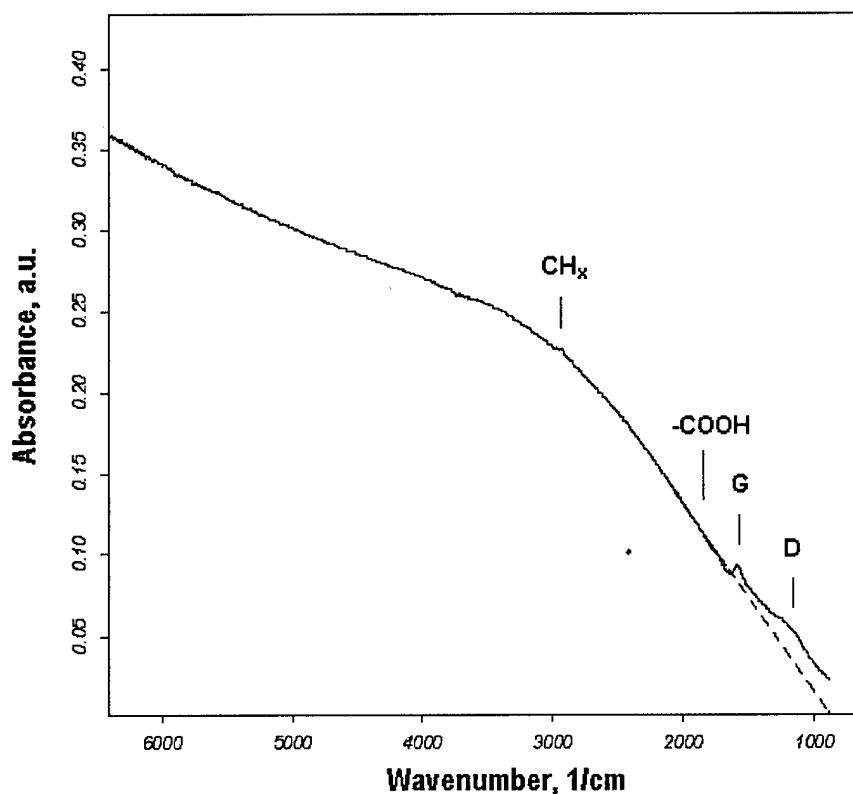
The synthesis is based on a catalyst-assisted CVD process in an aluminum oxide nanopore matrix, as described in [6], with pore diameter of  $\sim 60$  nm and length of  $\sim 20$   $\mu\text{m}$ . Because of the rich spectroscopic properties of the alumina in the IR range of interest, unambiguous IR properties of the carbon nanotubes can be best obtained on freestanding, purified samples. For this reason, the hosting alumina matrix was chemically dissolved by 0.1 M NaOH. After an acid purification step followed by several days of DI water cleansing, CNTs suspended in ethanol solution were evenly placed onto a substrate to minimize any stacking-induced change in their electronic properties. From the SEM image in Figure 4, one can see that a thin mat consisting of residue-free CNTs 60 nm in diameter with a standard deviation of 5% is produced by this approach. An AFM scan of the mat confirmed that no out-of-plane bending (undetectable by SEM) of the tubes is present. This uniformity, unavailable in nanotube ensembles fabricated by any other means, enables the strategy of aggregating the signal for this study.



**Figure 4.** SEM image of CNTs dispersed on Al highly polished substrate.

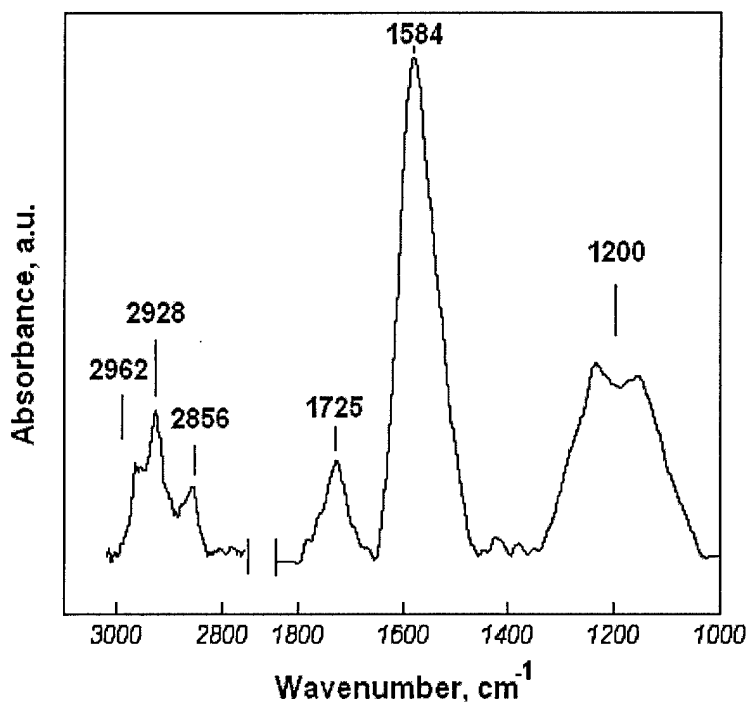
A Bruker micro-FTIR system was employed for the room temperature infrared measurements. To further enhance the weak IR-absorbance signal from the CNT mat, a double transmission + reflection configuration was employed by depositing the CNTs on an electrochemically polished aluminum substrate. The reference signal was collected on a clean area of the same Al substrate. The mid-IR to near-IR absorbance spectrum taken on uniformly dispersed, purified CNTs at room temperature (Figure 5), shows no signatures of alumina, demonstrating that the growth template was completely dissolved. The spectrum exhibits a noticeable onset of absorption at the low frequency range. A simple straight-line extrapolation of the absorption curve toward x-axis yields an absorption edge of  $\sim 0.10$  eV. This value happens to be consistent with that found in the conductance-temperature study of similar nanotubes measured individually and in small

groups [8] and with that of a local-bending theoretical model. This is not surprising since the presence of D and G bands strongly implies that the nanotubes are mostly polycrystalline rather than single crystal. As such, their electronic wavefunctions are unlikely to possess long-range coherence, and their local properties thus dominate. Based on the local bending theory, these multi-walled nanotubes should have a bandgap following  $1/R$  dependence on the tube radius induced by a strong electronic-lattice coupling of states near the Fermi energy [10], as supported by the findings from conductance studies [13, 14]. From the  $1/R$  band gap dependence and electrical conductance vs. temperature measurements on 47 nm diameter CVD-synthesized nanotubes exhibiting a bandgap of 135 meV, one would arrive at an estimate of the bandgap of a 60 nm diameter nanotube to be  $\sim 100$  meV. Defects (D-band) and impurities with energy levels positioned in the bandgap could additionally contribute to its softening. However, the great uniformity in diameter and length help retain the main spectral features. Indeed, the shape of MWNT absorption (i.e., exhibiting a broad slope) is expectedly different from that of SWNTs, which should exhibit distinct interband absorbance peaks positioned in correspondence with their 1D density of states [15, 16]. Also, the electronic configurations of MWNTs, as well recognized in the literature, do not resemble those of SWNTs. Moreover, both the diameter and the wall thickness of our nanotubes are rather large and therefore unlikely to exhibit sharp 1D density of state peaks at room temperature.



**Figure 5.** Typical IR-absorbance spectrum obtained on 60 nm diameter CNTs. Measurements were done using a Bruker-micro-FTIR in 2xTransmission+Reflection configuration at room temperature. Straight line extrapolation of low frequency part yields a band gap value of approximately 0.10 eV.

In the measured IR absorbance spectrum, a prime intensity peak is seen at 1584  $\text{cm}^{-1}$ . This is an IR-active, graphite-like E<sub>1u</sub> mode (also known as the G-band) originating from the  $\text{sp}^2$ -hybridized carbon. A double structured absorbance peak at  $\sim 1200 \text{ cm}^{-1}$  (Figure 6), is a disorder-induced one phonon absorbance band, which has been also observed in neutron irradiated diamonds and in diamonds rich in impurity nitrogen [17]. This lattice mode arises from the disruption of the translational symmetry of the diamond lattice [18]. The analogy between the density of states of the disordered diamond and the nanotubes implies that the disordered regions of CNTs likely consist of disordered  $\text{sp}^3$  bonded carbon, also serving as the nucleation sites for hydrogen. In general, the presence of  $\text{CH}_x$  groups, as evidenced in the IR active bands in the range of  $3000 \text{ cm}^{-1}$ , and non-conjugated carboxylic carbonyl groups, with a peak around  $1725 \text{ cm}^{-1}$ , can assist a number of bio-sensing applications by offering a simple route to nanotube functionalization.



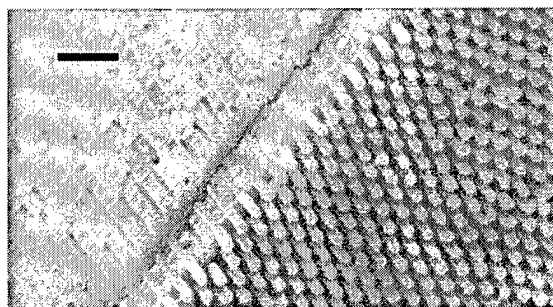
**Figure 6.** A baseline corrected CNT-IR absorbance spectrum clearly demonstrates IR-active peaks centered at 1725  $\text{cm}^{-1}$  (COOH groups), 1584  $\text{cm}^{-1}$  (G band), 1200  $\text{cm}^{-1}$  (D-band). Several peaks at  $\sim 3000 \text{ cm}^{-1}$  range are attributed to  $\text{CH}_x$  groups.

To summarize, infrared optical properties of highly uniform, 60 nm diameter, purified and mono-dispersed carbon nanotubes were investigated. From the IR-optical absorbance data, we found that the CNTs exhibit a narrow optical bandgap on the order of  $\sim 100$  meV, in good agreement both with previous conductance studies and with theoretical models. Together with the ultra-dense packing and perfect parallel vertical alignment over extended areas, these IR properties offer an exceptional platform for mid-IR sensor applications and for easy integration with electronic circuits.

### **Development and transport properties of a Si-CNT heterojunction diode array**

A uniform array of a new type of heterojunction formed between carbon nanotubes and silicon was studied [19]. The heterojunction array was controllably grown with parallel and uniform nanotubes vertically aligned to the silicon substrate using a self-organized nanopore array template. The pronounced rectifying characteristics of the heterojunction were measured with an on-off ratio as high as  $10^5$  at 4 V. The analysis demonstrates a large, type-I band offset at the heterojunction. The charge transport in the nanotubes is found to be dependent on and limited by the dielectric charging and polarization in the alumina matrix containing the nanotubes.

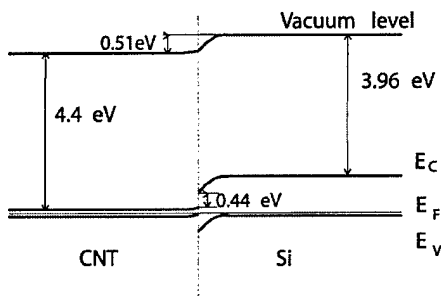
The use of a highly ordered nanopore array template for the growth of the nanotubes was the enabling element of the control and uniformity in this approach, and it came from the ongoing refinement of our method of template-based growth of nanotubes on aluminum substrate [6]. The fabrication process starts with the formation of the nanopore array alumina film by anodizing a layer of Al formed through e-beam evaporation on doped silicon. A very thin Ti layer, approximately 5 nm, is used to ensure good adhesion of the Al film during anodization while permitting the nanopores to perforate through the alumina film to the silicon substrate. Upon completion of the anodization step, an array of uniform and hexagonally spaced nanopores is formed, all normal to the plane and parallel to each other, the same depth and diameter, and available to serve as a template for the nanotube growth. This growth process follows essentially the same steps as in our earlier work on growing nanotube arrays on a freestanding Al plate, as detailed in [6]. A typical array of nanotube-silicon heterojunctions is shown in Figure 7.



**Figure 7.** Typical scanning electron microscopy image of the CNTs grown in the templates. For representation purposes, a part of the template has been plasma etched and a small part of the nanotubes is sticking outside the template. The scale bar is 300 nm.

The electronic properties of the heterojunction between the carbon nanotube and the silicon were examined in detail. A gold electrode film was evaporated on the top surface of the nanotube array at a 45 degree angle to avoid shorting through the nanotubes. The p-type Si (100) wafer with a  $0.01 \Omega \text{ cm}$  resistivity and thickness  $500 \mu\text{m}$  served as the bottom contact in the measurements. The measurements were performed under vacuum and in a cold finger, closed-cycle cryostat using a source measure unit (Keithley 236). The measured I-V dependences at all temperatures exhibited pronounced rectifying behavior with the forward direction at negatively biased CNT electrode, as shown in Figure 8. The rectifying behavior and its polarity are consistent with the data observed at the heterojunction of a carbon nanotube and a silicon nanowire [20].

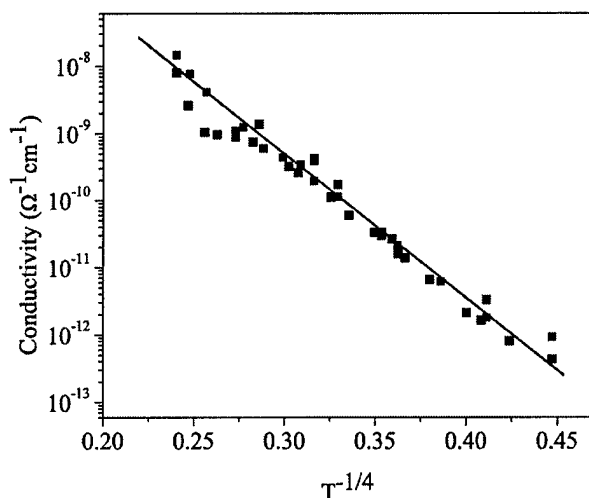
To help understand the underlying mechanisms for the rectifying characteristics and the superior on-off ratio, we start with a band diagram of the heterojunction shown in Figure 8. This band diagram was derived from the work function and band gaps of the two materials, following the Anderson model[21]. The parameters for the silicon were derived from the dopant concentration dependence of the band gap and of the Fermi level as described in [22]. The optical gap of the CNTs was estimated from our optical investigations to be 200 meV, and the work function was assumed to be almost equal to that of graphite with the Fermi level in the middle of the optical gap. With this schematic band diagram in mind, one can readily see that strong rectification and a large built-in voltage of around 0.5 V are expected. Indeed, we have observed photocurrent generation in these samples as well, which are being pursued further for possible infrared applications.



**Figure 8.** Band diagram of the CNT-Si heterojunction.

A closer examination of the I-V characteristics reveals several important details of the electronic processes occurring in our devices. The reverse current manifests a linear voltage dependence, indicating that its origin is mostly due to current which does not flow across the junction (parallel shunt current). A likely source of the leakage is the anodized alumina hosting the CNTs. The conductivity of the anodized oxide is expected to be relatively low, as was understood through earlier experiments, but was clearly not

low enough in comparison with the strong reverse current blocking effect of the CNT-Si heterojunction. The Ohmic behavior of the reverse current allows us to directly determine the conductivity of the alumina template. The temperature dependence of the reverse conductivity agrees very well with a model of hopping conduction of localized electrons in disordered insulators; this is shown in Figure 10.



**Figure 9.** Temperature dependence of the conductivity derived from the reverse bias part of the characteristics.

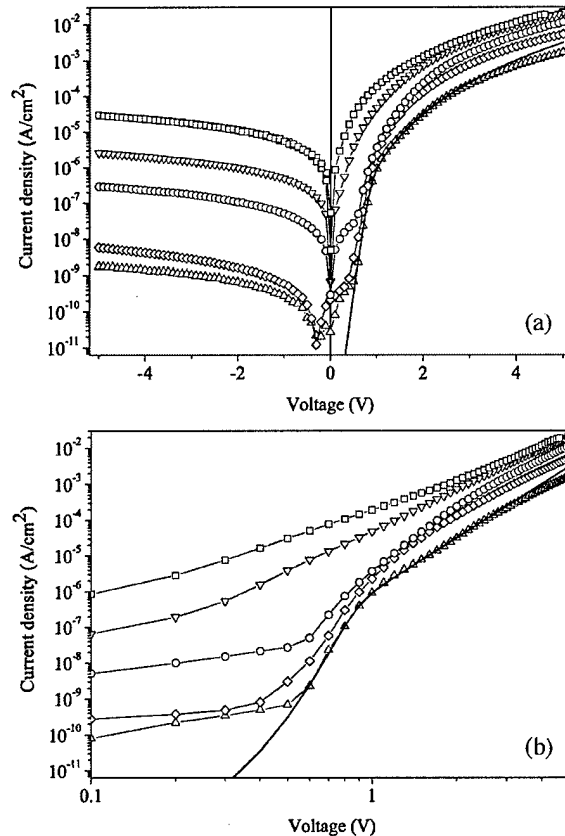
The current through the alumina also governs the forward current in the low voltage range at very low temperature. The processes of charge trapping and release in the alumina cause the shift of the zero crossing point at low temperature from the zero voltage and the observed hysteresis.

The above analysis is valuable for understanding conduction mechanisms in the anodized alumina, which is important for understanding the behavior of this composite system. However, it also shows that the reverse current does not provide much information about the CNT-Si heterojunction, which is even more important to us.

The transport properties of the heterojunction can be studied by analyzing the forward current. The I-V curves in Figure 10(a) exhibit an exponential behavior only at temperatures below 80 K. At higher temperatures the forward current follows a power law dependence, as illustrated in the log-log plot in Figure 10(b). The curves can be fitted with a combination of exponential and power law. The exponential part is typical of current flow across a heterojunction, while the power law dependence is characteristic of space charge limited current. Generally, the latter appears if the transient time of the charge carriers is smaller than the dielectric relaxation time. Such transport is not related to the contact or the heterointerface but to the bulk of the contacting materials. The bulk and the junction regions are connected in series and the current in the device is therefore

determined by the rate-limiting mechanism. This suggests that the injection at the heterojunction at room temperature delivers many more carriers than the rest of the “bulk” material can carry without changing the local field.

The power law  $I \sim V^n$  in Figure 10(b) at room temperature is approximately  $n = 4$ . A power law of  $n > 2$  indicates the existence of distribution of charge carrier traps. A characteristic feature of space charge limited current in the presence of traps is strong temperature dependence [23]. This is, however, not the case in Figure 9. Such an apparent contradiction can be explained by assuming a change in the trap distribution with temperature. An additional factor is the temperature change of the band gap as well as the filling of traps at increased electric field. This level of complexity is, of course, beyond the reach of the I-V models. However, we were able to estimate certain material parameters in our work. We observed that that when a portion of the trap state distribution is filled, it ceases to exert its effect on the transport and thereby alters the effective trap density and the related characteristic constant. This can explain the very narrow trap distribution observed at low temperatures.



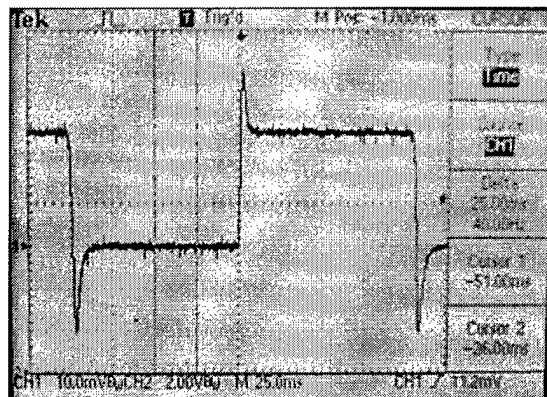
**Figure 10.** Current voltage characteristics of the CNT-Si structures at different temperatures: squares, 300 K; down triangles, 210 K; circles, 90 K; diamonds, 40 K; and up triangles, 17 K. The same data are plotted

in parts (a) and (b) of the figure but in different axes scales. The line represents simulation with a combination of exponential and power law.

We cannot determine with the I-V measurements what the current injection mechanism at the heterojunction is—diffusion, thermionic emission, tunneling through surface states—but independent of the exact type, the forward current is dominated by hole injection in the CNTs from the silicon, given the very large barrier blocking the electron injection at the junction. Hence, the parameters we have determined have to be related to the hole transport. The high conductivity of the silicon wafer and the results of the control electrical measurements suggest that the silicon part of the structure is not rate limiting to the transport. We therefore arrive at a point from which it seems logical to suspect that the nanotubes are where the space charge limited transport takes place. It is widely known that defects in nanotubes are the rule rather than exception, especially for nanotubes synthesized in the relatively low temperature chemical vapor deposition processes. However, considering the high conductivity and high charge carrier mobility [24], the low band gap (due to the relatively large diameter), the low filling factor (low volume), and the low thermal expansion coefficient of the nanotubes, the nanotube part also appears unlikely to be able to host a concentration of unfilled traps that changes with temperature and is sufficiently high to greatly limit the forward current.

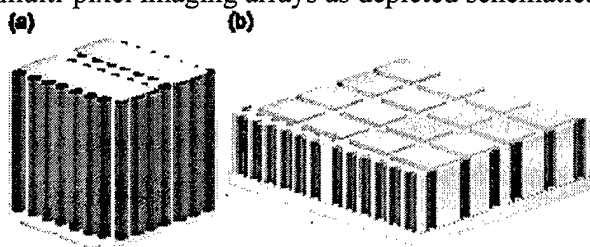
This apparent dilemma can be resolved by considering once again the role and characteristics of the alumina template. The oxide is known to be highly defective from prior works and from the reverse current analysis above, and its conductivity is dominated by hopping processes through traps. It has a much greater thermal expansion coefficient than nanotubes; therefore, its trap state distribution will respond to temperature changes. Because of the close physical contact between the alumina and the nanotubes, a trapped charge in the alumina directly and greatly affects the charge transport in the nanotubes. A similar effect has been observed and semiquantitatively characterized in a nanotube field-effect transistor consisting of a nanotube on top of a SiO<sub>2</sub>-Si substrate [24]. In this particular case, the SiO<sub>2</sub>-Si serves as a back gate, and charge injected in the SiO<sub>2</sub> due to the large local field associated with the large curvature of the nanotube is found to induce a slow drift of the transistor characteristics. Similarly in our case, because of the nanodimensions, and thus the sharp curvature at the side wall and the ends of the nanotube, a much larger local field can result from a given voltage than in a planar gate setting, which enhances the voltage dependence of the trap state filling. Therefore, when all is considered, the alumina matrix seems to be playing much more than a passive mechanic role of hosting the nanotubes, and it is most likely the limiting factor in the electronic performance of this new form of heterojunction. This is rather encouraging—despite the poor electronic properties of the surrounding alumina matrix, the measured performance of the nanotube-silicon heterojunction is already approaching that of the silicon based diodes perfected over decades of persistent efforts. Strategies to improve or to replace the alumina matrix do exist. Examples include thermal annealing or post-growth selective etching followed by re-deposition of high quality

dielectric in the space between the nanotubes. When developed over time and deployed, these techniques can lead to further improvement of this new form of heterojunction.



**Figure 11.** Real-time response of CNT-Si detector demonstrates the potential of these nanostructured materials in room temperature (300K) infra-red detection.

We demonstrated real time photovoltaic measurements of CNT-Si heterojunction detectors for infra-red detection, as shown in Figure 11. These structures work in both thermal and photon detection modes, and cover a very wide spectral range (1–20  $\mu\text{m}$ ). This enables multi-“color” cells to coexist in a single pixel using the same basic material—nanotubes—and differing only in diameter. These devices also offer the usual advantages of our carbon nanotube arrays: dense packing and adjustable length—adjustable and high absorption; vertical alignment, nanoscale and cylindrical symmetry—ideal for normal incidence detection of any polarization; temperature insensitive absorption coefficient due to strong bonding; and low 1-D phonon density of states leading to low phonon coupling to ambient thermal noise. This discovery enables the development of multi-pixel imaging arrays as depicted schematically in Figure 12.



**Figure 12.** (a) CNT IR detector configuration using crossed top and bottom electrodes for XY addressing. (b) CNT IR detector array with transparent bottom electrode and square grid pixel array for readout.

In summary, the demonstrated formation of a CNT-Si heterojunction structure is promising not only as a candidate for building logic structures but also as a platform for ultrahigh density integration of such logic gates in a quasi-3D packing form—that is, vertical device orientation and lateral integration. The two-dimensional periodic lattice of

the nanotubes enables additional possibilities. Their periodic arrangement and high refractive index difference relative to the alumina matrix can be used as a photonic band gap material. Suitable arrangement of the template can even allow the design of Bragg gratings while preserving the junction behavior in the orthogonal direction. The potential application as an optical modulator is apparent, considering the interdependence of Bragg grating properties, refractive index change, and charge injection.

### ***Conclusions***

During the course of this project, we employed and extended our unique capability in template-growth of nanostructured materials, particularly carbon nanotubes. This fabrication capability formed the foundation for further investigations, into the infra-red properties and transport properties of these nanostructures. We were able to fabricate large arrays of identical carbon nanotubes with identical properties, which enabled sufficient signal enhancement to perform novel infra-red spectroscopy studies on the nanotubes. Extensions of our core fabrication method enabled the creation of carbon nanotube arrays on silicon wafers. The importance of silicon as a semiconductor material cannot be overstated, and so the fabrication and measurements of these structures represents an important step toward integrated Si-CNT infrared detectors. The results of this project clearly demonstrate the feasibility of employing ordered carbon nanotube arrays in infra-red detection applications.

### ***Publications and Dissemination of Results from this Project***

#### **Publications**

A. Rakitin, C. Papadopoulos and J.M. Xu, "Electronic Properties of Amorphous Carbon Nanotubes", *Phys. Rev. B.* 61, 5793-5796, 2000.

J.M. Xu, (Invited) "Highly Ordered Carbon Nanotube Arrays and IR Detection", *Infrared Physics & Technology*, 42, 485-491, 2001.

J. Liang, H. Chik, A. Yin, and J.M. Xu, "Two-dimensional Superlattices of Nanostructures: Nonlithographic Formation by Anodic Alumina Membrane Template", *J. Appl. Phys.*, 91(4), 2544-2546, 2002.

I. Levitsky, J. Liang, and J.M. Xu, "Highly ordered arrays of organic-inorganic nanophotonic composites", *Appl. Phys. Lett.*, 81(9), 1696-1698, 2002.

J.M. Xu, (Invited), "Carbon Nanotube IR properties and applications", *Proc. SPIE*, vol 4823, 88-95, 2002.

R. Hull, R. Martel, J.M. Xu, (invited) "Nanoelectronics: some current aspects and prospects", *Intl. J. of High Speed Electronics*, "Frontiers in Electronics Future Chips", eds. Y-S Park, M.S. Shur, W. Tang, World Scientific, 147-158, vol 26, 2003

J. Liang, H. Chik, and J.M. Xu, (Invited) "Non-lithographic Fabrication of Lateral Superlattices for Nanometric Electro-Magnetic-Optic Applications", IEEE, J. of Selected Topics of Quantum Electronics, 8(5), 998-1008, 2003

C. Papadopoulos, B. Chang, A. Yin, and J.M. Xu, (Invited), "Engineering Carbon Nanotube via Template Growth", Intl J. Nanoscience, vol 1(3/4), 205-212, 2003

C. Papadopoulos, A. Rakitin, and J.M. Xu, "Carbon Nanotube Self-doping", Phys. Rev. B., 67, 033411, 2003.

J.M. Xu, (invited), "Nanotube Electronics – Non CMOS Routes", Proceedings of IEEE, Special Issue on Nanoelectronics and Giga-scale Systems, 91(11), 1819-1829, 2003.

H. Chik and J.M. Xu, (invited) "Nanometric Superlattices –Fabrication, Properties, and Prospects", Materials Science and Engineering R 43 (2004) 103–138

Z. Xia, L. Riester, W. A. Curtin, B. W. Sheldon, J.Y. Liang, B.H. Chang and J. M. Xu, "Direct observation of toughening mechanisms in carbon-nanotube ceramic matrix composites" Acta Materialia, 52, 931-944, 2004.

A. Yin, H. Chik, J.M. Xu, "Post-growth processing of carbon nanotube arrays – enabling new functionalities and applications", IEEE Trans. On Nanotechnology, 3(1), 147-151, 2004.

M. Tzolov, B. Chang, A. Yin, D. Straus, G. Brown, J.M. Xu, "Electronic transport in a controllably grown carbon nanotube-silicon heterojunction array", Phys. Rev. Lett., 92(7), 075505, 2004.

M.B. Tzolov, B. Chang, D. Straus, A. Yin, and J.M. Xu, "Carbon Nanotube-Silicon Heterojunction Diode Array – Integration on Silicon and Rectifying Characteristics" MRS 2003 Extended Summary, 2004.

### **Conference papers**

J.M. Xu, (invited) "Carbon Nanotube Arrays & Nonlithographic Fabrication for Future Electronics", Proc. Of 1999 Intl. Semicond. Dev. Research Symp., Dec. 3, 1999.

J. Li, C. Papadopoulos, and J.M. Xu, "Fabrication of Large-Scale Hexagonally Ordered Array of Parallel Carbon Nanotubes for Electronics Applications", May 3, 195th Electrochemical Society Meeting, May 2-6, 1999, Seattle.

J.M. Xu, (Invited) "Carbon Nanotube Arrays as an Emerging IR Base Material", QWIP-2000, July 27-29, 2000, Dana Point, CA.

P. H. Siegel, T.H. Lee and J. Xu, "The Nanoklystron: A New Concept for THz Power Generation," JPL New Technology Report, NPO 21014, March 21, 2000

P. H. Siegel, T.H. Lee and J. Xu, "The Nanoklystron: A New Concept for THz Power Generation," JPL New Technology Report, NPO 21014, March 21, 2000.

F. Noca, B.D. Hunt, M.E. Hoenk, D. Choi, R. Kowalczyk, R. Williams, J.M. Xu, R. Koumoutsakos, "Nanotube-based Sensors and Systems for Outer Planetary Exploration", Innovative Approaches to Outer Planetary Exploration 2001-2020, 4083, 2001.

B. Hunt, M. Bronikowski, D. Choi, L. Epp, M. Hoenk, D. Hoppe, B. Kowalczyk, F. Noca, E. Wong, J.M. Xu, "Nanomechanical Resonators Based on Carbon Nanotubes", May 12-17, 2002, Maui, Hawaii

L. Chen, A. Yin, J.S. Im, A.V. Nurmikko, J.M. Xu, and J. Han, "Optical Characterization and Device Fabrication of Lateral Patterned InGaN Blue Light Emitting Media on 50nm Scale", Conf. On Lasers and Electro-Optics, 2002, May 20-23.

W. Curtin, B. Sheldon, J.M. Xu, "Experiments and Modeling of Carbon Nanotube Ceramic Composites", 2002 ASME.

B. Hunt, M. Bronikowski, D. Choi, L. Epp, M. E. Hoenk, D. Hoppe, R. Kowalczyk, F. Noca, R. Williams, E. Wong, J.M. Xu, D. Adam, and R. Young, "Nanomechanical Resonators Based on Carbon Nanotubes", Nanoscale/Molecular Mechanics Meeting, Hawaii, May 2, 2002.

J. Liang, H. Chik, and J.M. Xu, "Non-lithographic Fabrication of Nanometric Superlattices", ECS 204th Meeting, Oct 12-16, Orlando, FL., 2003.

M. Tzolov, J.M. Xu, "Carbon Nanotube-Silicon Heterojunction Diode Array – Integration on Silicon and Rectifying Characteristics", extended summary, MRS Fall Meeting, Dec. 1-5, 2003, Boston.

A. Polomska, C.K. Young, G.T. Andrews, M.J. Clouter, A. Yin, and J.M. Xu, "Brillouin Light Scattering from Ordered Carbon Nanotube Arrays", 2004 Canadian Association of Physicist Congress, June 15-17, 2004.

#### **Invited Talks at Meetings and Seminars**

J.M. Xu, "Nanotubes and Nonlithographic Nanofabrication", Motorola Corp. Res. Labs, Phoenix, AZ., January. 9-12, 2000.

J.M. Xu, "Nanotube Arrays and Nonlithographic Nanofabrication for Future Electronics", IEEE EDS/LEOS Distinguished Lecture, IEEE North New Jersey Section, NJIT, Feb.2, 2000.

J.M. Xu, "Next Generation Nanotubes and Device Applications", Aoyama Gakuin University, Tokyo, Japan, March 8, 2000.

J.M. Xu, "Nonlithographic Nanoelectronics", Aoyama Gakuin University, Tokyo, Japan, March 6, 2000.

J.M. Xu, "Next Generation Carbon Nanotubes", Canadian Institute for Advanced Research Nanoelectronics Program Meeting, Banff, Canada, May 19-22, 2000

J.M. Xu, "Nano and Molecular Electronics", Institute of Fiber Optics, Shanghai, China, June 11-14, 2000.

J.M. Xu, "Carbon Nanotube Arrays as an Emerging IR Base Material", QWIP-2000, July 27-29, 2000, Dana Point, CA.

J.M. Xu, "Next Generation Nanotubes – Structure, Fabrication and Electro-Opto-Mechano responses, MIT Quantum Electronics Seminar, MIT, MA, USA Oct. 18, 2000.

J.M. Xu, "Nanotube Electronics – Potential, Reality, Critique", the 3<sup>rd</sup> Advanced Workshop on Future Trends in Microelectronics, Bendor, France, June 24-29, 2001

J.M. Xu, "Exploration of Carbon Nanotube Arrays for IR Detection", Progress in Semiconductor Detector Conference, June 4-5, Williamsburg, USA.

J.M. Xu, "Nanotube Electronics – Potential, Reality, Critique", National Nano Device Laboratories, Taiwan, July 17, 2001

J.M. Xu, "Nanotube Electronics – Potential, Reality, Critique", Industrial Technologies Research Institute, Taiwan, July 18, 2001

J.M. Xu, "Self-Organized High-Ordered NanoPore Array – an Epitaxy Perspective and a New Growth Platform", 13th American Conf. On Crystal Growth & Epitaxy, Burlington, Vermont, Aug 12-16, 2001.

J.M. Xu, "A big world of tiny things" (part 2), "Voyage of Discovery" Faculty Forum Series of Brown President Inauguration, Oct. 13, 2001

J.M. Xu, "Highly ordered nanotube arrays for IR sensing & Extensions to UV-Vis with Organic-Nanotube Composite Matrix, Air Force Materials Directorate Review, Nov 7, 2001.

J.M. Xu, "Next Generation Nanotubes", Centennial Meeting of the Electrochemistry Society, May, 2002, Philadelphia

J.M. Xu, "Nanoelectronics – Dreaming large, thinking small", Canadian Institute for Advanced Research 20th Anniversary All-Program Meeting, June 15-17, 2002

J.M. Xu, "Nanotube Electronics – Potential, Reality, and Critique", Colloquium, Intel R&D, Portland, Oregon. July 12, 2002

J.M. Xu, "Carbon Nanotubes for IR Sensing", SPIE 2002, Seattle, July 2002.

J.M. Xu, "Nanoelectronics – evolution from CMOS to Nanotubes and DNAs", Univ of Florida, Gainesville, Feb 21, 2003

J.M. Xu, "Highly Ordered Carbon Nanotube Array, Electro-Optic Properties and Applications", MIT Lincoln Lab, March 12, 2003

J.M. Xu, "Nanoelectronics – evolution from CMOS to Nanotubes and DNAs", Argonne National Lab, Illinois, March 20, 2003

J.M. Xu, "Nanoelectronics, Nano-Bio-Optics, and Future IT", JDSU, HQ, Office of Technology Planning, March 28, 2003

J.M. Xu, "Highly Ordered Carbon Nanotube Array, Electronic and IR Properties, and Applications", U of Texas – Arlington, Dallas, April 1, 2003

J.M. Xu, "Nanoelectronics, Nano-Bio-Optics, and Future IT", Nortel Optical System Technology Planning Forum, April 2, 2003

J.M. Xu, "Electronics Evolution from CMOS to Nanotubes, DNAs and Proteins", A.J. Drexel Institute of Basic and Applied Protein Sciences, Inaugural Seminar, Drexel University, Philadelphia, May 12, 2003.

J.M. Xu, "Nanotechnology and Biotechnology Fusion", Plenary Speech, Special Forum on Growth Engines of Korea, Korea Ministry of Commerce, Industry, and Energy, LG HQ, Seoul, July 24, 2003

J.M. Xu, "Nanoelectronics – evolution from CMOS to Nanotube, DNA, and Protein", Korea Institute of Advanced Study, Seoul, July 31, 2003.

J.M. Xu, "Nanoelectronics – evolution from CMOS to Nanotube, DNA and Protein", Seoul National University, Seoul, August 1, 2003.

J.M. Xu, "Nanoelectronics – evolution from CMOS to Nanotube, Molecular Electronics and Molecular Magnetics", Chungnam National University, Daejeon, August 7, 2003.

J.M. Xu, "Nanoelectronics – evolution from CMOS to Nanotube, DNA and Protein", Kyungpook National University, Dae-Gu, August 12, 2003.

J.M. Xu, "Nanoelectronics – evolution from CMOS to Nanotubes and DNAs", Plenary Speech, 11th Canadian Semiconductor Technology Conference, Ottawa, August 18, 2003.

J.M. Xu, "Nanoelectronics and BioMed Engineering", BioMed Engineering Program, Seminar Series, Brown Sept. 25, 2003

J.M. Xu, "Carbon Nanotube as Sensor Materials", 2004 Symposium of Nanomaterials for Defense Applications, Maui, Hawaii, Feb 18-24, 2004

J.M. Xu, "Nanoelectronics – Evolution from CMOS, to Nanotube, DNA, Protein", Keynote, Nagoya University 1ST Symposium on Micro, Nano, Electro-Mechanical Systems, Nagoya, Japan, March 9, 2004

J.M. Xu, "Carbon Nanotube Quantum Electro-Mechanical Couplings", Boston College Workshop on Meso and Nano Materials, March 19-20, 2004

J.M. Xu, "Carbon Nanotube Sensory", The 3rd US-Korea Workshop on Nanostructured Materials and Nanomanufacturing, Seoul, May 10-11, 2004

J.M. Xu, "Nanoelectronics – Evolution from CMOS to Nanotube, DNA and Protein", The 1st US-Korea Workshop on Nanoelectronics, Seoul, May 10-11, 2004

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