



US 20070015350A1

(19) **United States**

(12) **Patent Application Publication**
Crowley

(10) **Pub. No.: US 2007/0015350 A1**

(43) **Pub. Date: Jan. 18, 2007**

(54) **METHODS OF MANUFACTURING CARBON NANOTUBES**

division of application No. 08/988,801, filed on Dec. 11, 1997, now Pat. No. 6,038,060.

(76) Inventor: **Robert Joseph Crowley**, Sudbury, MA (US)

(60) Provisional application No. 60/036,085, filed on Jan. 16, 1997.

Correspondence Address:
Donald N. Halgren
35 Central St.
Manchester, MA 01944 (US)

Publication Classification

(51) **Int. Cl.**
H01L 21/20 (2006.01)
(52) **U.S. Cl.** **438/584; 977/742**

(21) Appl. No.: **11/509,833**

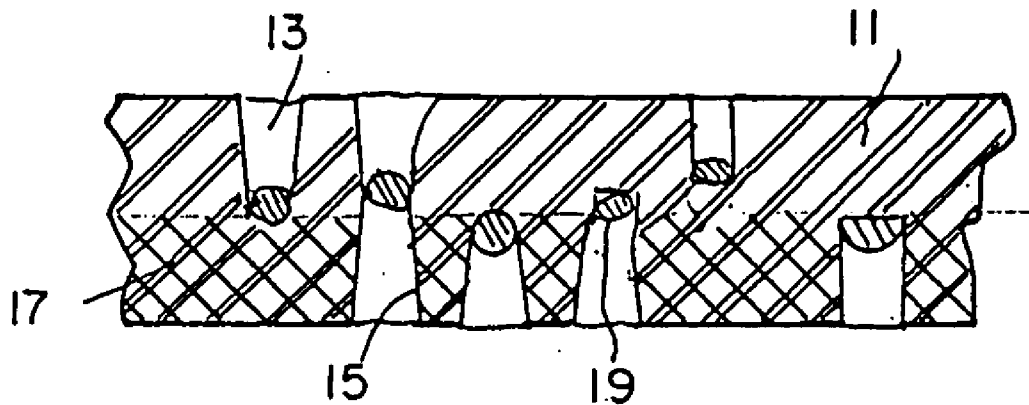
(22) Filed: **Aug. 24, 2006**

(57) **ABSTRACT**

Related U.S. Application Data

(62) Division of application No. 10/789,390, filed on Feb. 27, 2004, now Pat. No. 7,099,071, which is a division of application No. 10/646,945, filed on Aug. 22, 2003, which is a division of application No. 09/901,309, filed on Jul. 9, 2001, now Pat. No. 6,700,550, which is a division of application No. 09/523,626, filed on Mar. 13, 2000, now Pat. No. 6,258,401, which is a

An optical antenna collects, modifies and emits energy at light wavelengths. Linear conductors sized to correspond to the light wavelengths are used. Nonlinear junctions of small dimension are used to rectify an alternating waveform induced upon the conductors by the lightwave electromagnetic energy. The optical antenna and junctions are effective to produce harmonic energy at light wavelengths. The linear conductors may be comprised of carbon nanotubes that are attached to a substrate material, which may then be connected to an electrical port.



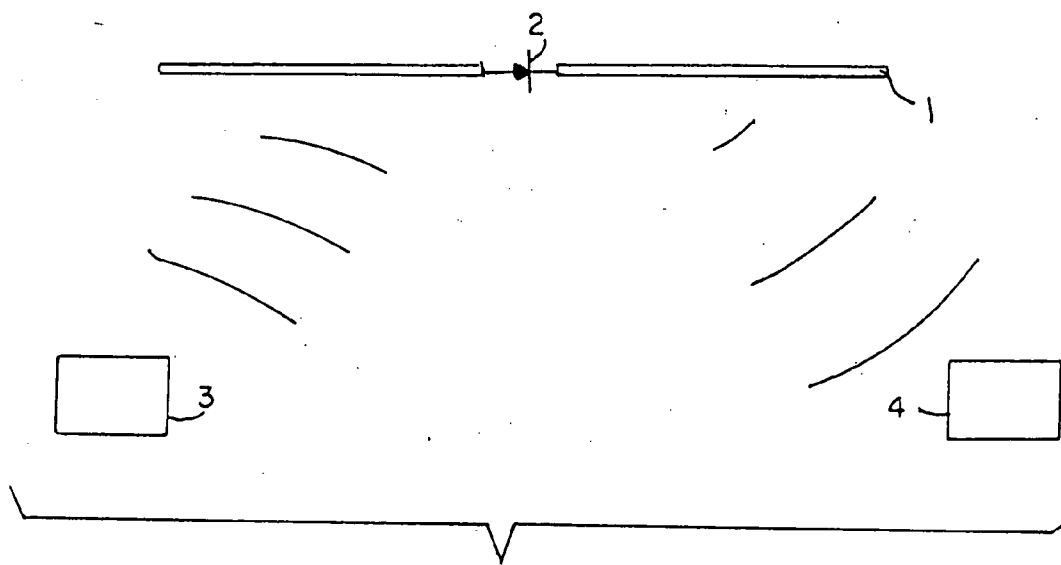


FIG. 1
(PRIOR ART)

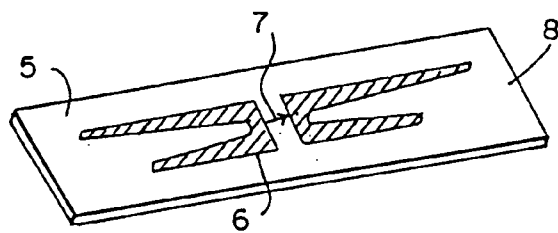


FIG. 1a
(PRIOR ART)

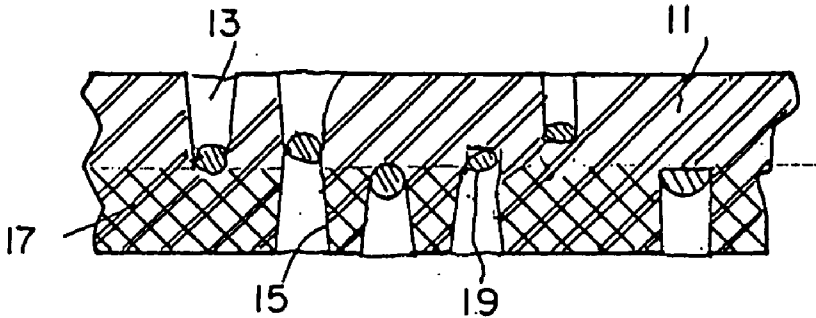


FIG. 2

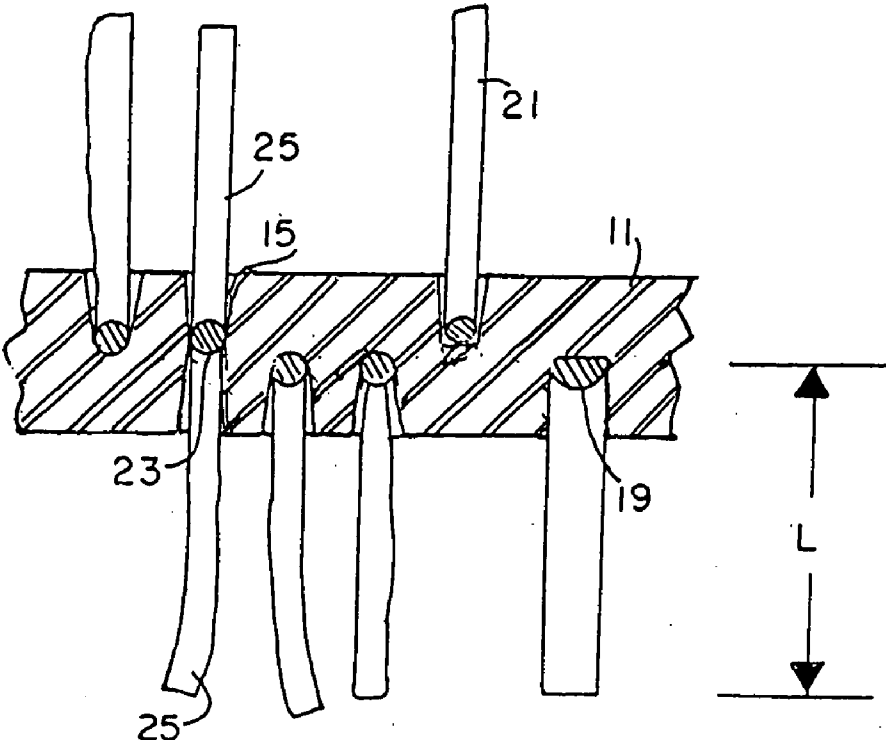


FIG. 3

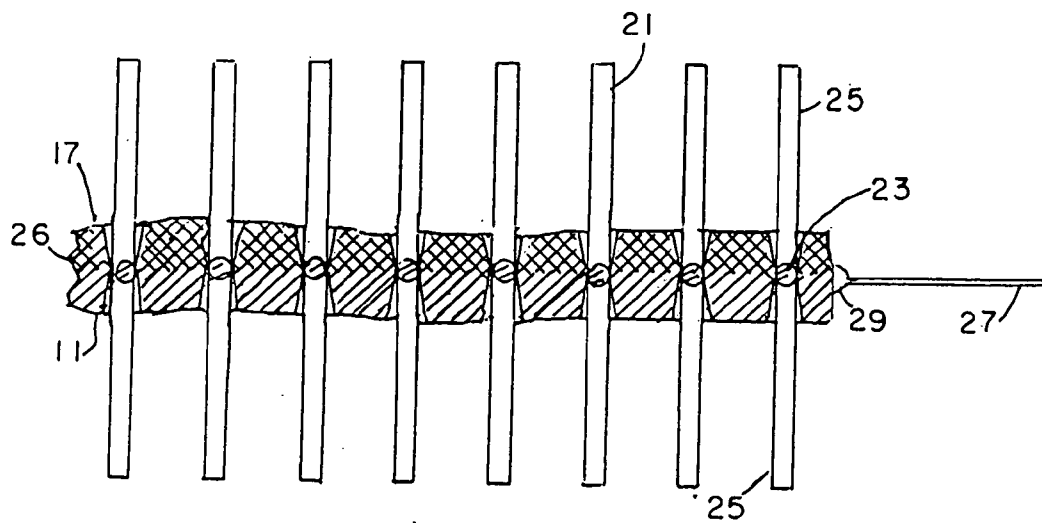


FIG. 4

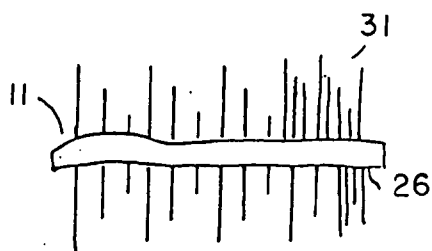


FIG. 4a

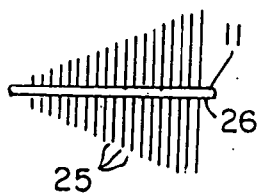
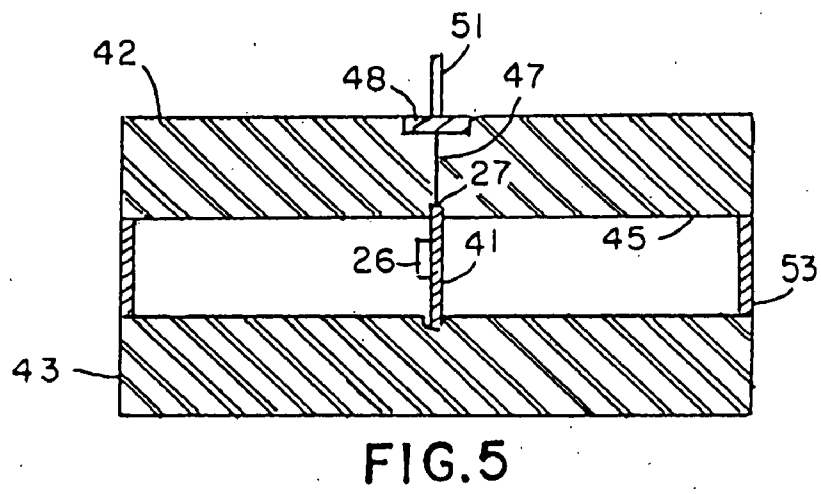
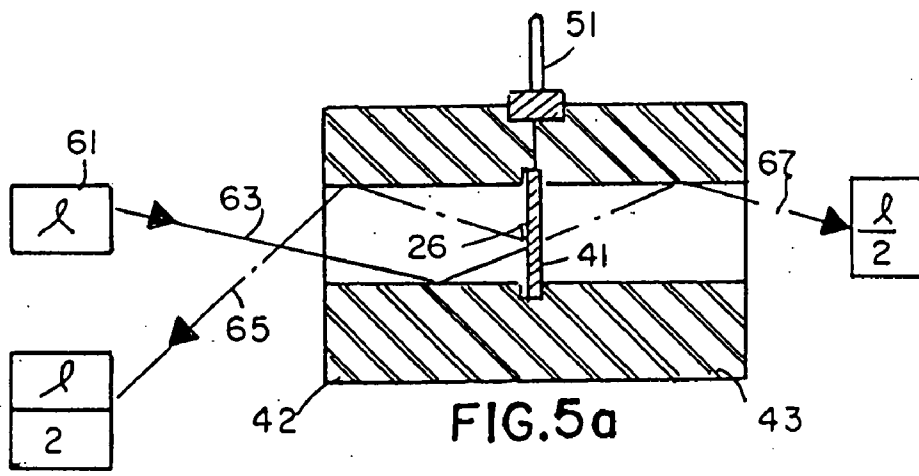


FIG. 4b



METHODS OF MANUFACTURING CARBON NANOTUBES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This is based on U.S. provisional patent application by Robert J. Crowley, Ser. No. 60/036,085, filed on Jan. 16, 1997.

TECHNICAL FIELD

[0002] This invention relates to small aligned conductors and junctions configured to efficiently admit, modify and emit electromagnetic radiation around light wavelengths.

BACKGROUND INFORMATION

[0003] Optical materials employing microstructures that exhibit the property of birefringence are commonly used to generate harmonic energy around light wavelengths. These materials are useful for frequency doubling, tripling or multiplying one or more fundamental inputs. Layered crystal structures are known to exhibit practical nonlinear transmission of light energy that usually result in harmonic generation with efficiencies that are generally low. Attempts have been made to optimize the harmonic generating efficiency of various materials by orienting molecules sandwiched between substrate materials. In U.S. Pat. No. 5,589,235, an applied magnetic field is used to pre-align molecules, and then a source of radiation is used to cross-link the molecules so that they maintain their position after the magnetic field is removed. In another attempt to fabricate a device that exhibits high harmonic generating efficiency, U.S. Pat. No. 5,380,410 describes a method by which periodic electrodes may be fabricated to provide inversion regions that improve the efficiency of a ferroelectric material which exhibits an intrinsic nonlinear optical property. The fabrication of a nonlinear optical region or layer on a material that generally has inherently linear characteristics is disclosed in U.S. Pat. No. 5,157,674 which teaches a process by which a charge transfer dopant is introduced to produce a semiconducting region on a bulk glass or microcrystalline substrate.

[0004] One apparent drawback to these approaches is wavelength-dependent attenuation. This attenuation occurs when lightwave energy propagates through lossy materials, resulting in attenuation. In general, both polymer and glass substrate materials exhibit high attenuation through absorption in the near UV and UV regions. Microcrystalline materials that utilize birefringence generally must have sufficient light path propagation length to produce sufficient phase changes for significant harmonic generation. Longer path lengths usually result in even greater attenuation.

[0005] Researchers have had to resort to modification of bulk materials or orientation of molecules in a solution or matrix to produce structures that exhibit optical nonlinearity, and usable harmonic generation. These researchers have not been able to successfully utilize practices that are now common in the electromagnetic radio electronics fields, even though light waves are merely electromagnetic waves of short wavelengths, primarily because techniques and materials for the fabrication of practical electromagnetically responsive elements in the small sizes necessary for efficient use at light wavelengths in the ranges of 10,000 nanometers

and shorter are not available. Optical crystal materials and composite materials, due to their structure, make it difficult to optimize the orientation of individual electromagnetically responsive elements.

[0006] An important aspect of successful fabrication and use of radio frequency nonlinear harmonic generating materials is the ability to control the orientation and sizes of those elements with respect to various electromagnetic fields. This is possible since radio frequency waves, and even microwaves, are relatively long. Developers of nonlinear, harmonic-producing devices for radio wave applications have been able to successfully fabricate numerous circuits, cavities, transmission lines, junctions and other structures scaled to radio wavelengths. This practice has been extended over time to include VHF, UHF, microwave and so-called millimeter wave regimes, and has included discrete components, transmission lines and antenna systems that have been scaled down to operate optimally at ever-higher frequencies.

[0007] Designers have also been able to fabricate nonlinear junctions that are small with respect to the wavelengths involved. These junctions are capable of rectification, mixing, detection and amplification over a portion of the full cycle of the alternating current, electromagnetic wave energy, and include conventional diodes, Schottky diodes, tunnel diodes, transistors, field effect transistors, bipolar transistors including discrete components and mass array fabricated devices such as integrated circuits and linear and two-dimensional arrays. Harmonic energy near light wavelengths is described comprising the steps of exposing a conductor to an infrared, visible or ultraviolet electromagnetic light energy having an alternating waveform, inducing a current with electromagnetic energy in the conductor to cause an electrical charge to cross a junction, and emitting at least a portion of the energy at a harmonic multiple of the light energy.

[0008] In one aspect, the invention relates to the use of a substrate material to support carbon nanotubes which are used as frequency selective electrical conductors. In one embodiment, the conductors are polarized with respect to the substrate. In another embodiment, a foraminous substrate is used to influence and support the orientation of the electrical conductors. In another embodiment, the foraminous substrate supports a nanoparticle which creates at least a portion of a nonlinear electrical junction. In another aspect, the invention relates to a conductive element with a nonlinear charge transfer region that is small with respect to that element.

[0009] In one aspect, the invention relates to an antenna structure that admits and radiates at light wavelengths. In another aspect, a lightwave electromagnetic antenna having a linear conductor is attached to a substrate material, with the linear conductor having an electrical length sized to respond to an electromagnetic light wavelength. In another aspect, the invention relates to antennas with conducting elements of less than 2000 nanometers in length that operate near light wavelengths. In one embodiment, the conductors form a traveling wave structure. In another embodiment, the conductors are arranged to form a log periodic structure.

[0010] In another aspect, the invention relates to a conductive element with an electrical length about a multiple of $\frac{1}{4}$ wavelength of a light wavelength. In one embodiment, the electrical length of the conductor inclusive of a junction may

be about 600 nanometers corresponding to $\frac{1}{2}$ wavelength of infrared light. Impinging infrared light energy is collected, rectified and reradiated at a multiple of the infrared light frequency with high efficiency. In another embodiment, the electrical lengths of the conductor may be in a range from about 20 nanometers to about 2000 nanometers corresponding to ultraviolet, visible and infrared light. In one embodiment, the lengths of the conductors may be staggered to form a broadband structure. In one embodiment, the conductors are arranged in a generally parallel relationship.

[0011] In another aspect, the invention relates to an array of conductive elements with electrical lengths around a multiple of $\frac{1}{4}$ wavelength of light, arranged so that at least one optical port and at least one electrical port, are held in communication via a nonlinear junction. In one embodiment, the electrical port is a terminal on a optical device which modifies a charge transfer characteristic of a junction. In one embodiment, a device for rectifying an alternating waveform occurring around light wavelengths is comprised of a short conductor of less than 10,000 nanometers in length and a nonlinear region with an electrical length less than the light wavelength. In another embodiment, the nonlinear junction region consists of a nanoparticle. In another embodiment, the junction is a polarized, doped region with an electrical length shorter than $\frac{1}{2}$ of the light wavelength.

[0012] In another aspect, the invention relates to the process by which the growth of lightwave antenna elements upon a substrate may be controlled by observation of an optical property. In one embodiment, various lengths of nanotubes are grown in a controlled manner upon the substrate.

[0013] The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following description and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis being placed upon illustrating the principles of the invention.

[0015] FIG. 1 is a side view of a prior art radio frequency dipole antenna with a center diode junction shown in relation to a signal generator and a signal receiver located in space around the antenna.

[0016] FIG. 1a is a perspective view of a prior art radio frequency theft control tag.

[0017] FIG. 2 is a cross-section of a foraminous substrate material structure with nanoparticles.

[0018] FIG. 3 is a partial cross-section of a foraminous substrate material with nanoparticles and linear elements disposed at right angles to the substrate.

[0019] FIG. 4 is a partial cross-section of a light modifying device with arranged linear elements of approximately equal lengths joined at a substrate and a terminal attached to the substrate.

[0020] FIG. 4a is a partial cross-section of a light modifying device in which linear elements are of various lengths along the length of a substrate material.

[0021] FIG. 4b is a partial cross-section of a light modifying device in which linear element lengths are tapered with respect to each other and a substrate material.

[0022] FIG. 5 is a cross-section of a light modifying device in which the substrate with linear elements are disposed with respect to an electrical terminal and two optical windows to form a 3 port system.

[0023] FIG. 5a is a schematic diagram of the light modifying device of FIG 5 in which lightwave energy is admitted and transmitted after undergoing frequency conversion, mixing or amplification.

DESCRIPTION

[0024] Referring to FIG. 1, a prior art radio frequency dipole antenna 1 is shown as it is used in many forms of radio communications and shown particularly in this case for illustrating one common use and technique for harmonic generation and reradiation. Such antennas ordinarily comprise two $\frac{1}{4}$ wave sections joined at or near the center and may include a nonlinear diode junction 2 connected therebetween. It is known that a $\frac{1}{2}$ wave antenna has desirable properties that efficiently pick up and radiates radio frequency energy, and therefore the so-called dipole antenna is considered to be a basic building block in the antenna art. This desirable antenna property is generally known as resonance, and it should be understood that there are other lengths of conductors that exhibit resonant effects as a function of frequency and length. An alarm system for theft control purposes may be constructed with such an antenna and a transmitter 3 operating at frequency n, and a receiver 4, tuned to listen for signal(s) at frequency 2n. When transmitted signal n impinges upon the antenna 1, a changing electrical field induces a current which travels through the length of that antenna. Ordinarily that field would reverse in the case of linear operation (no diode) of the antenna elements, but in this case the presence of the nonlinear diode junction 2 partway through the element creates a conductance change part way through the conduction cycle which limits and distorts the ordinarily linear current flow and converts it into a nonlinear, non-sinusoidal waveform. Nonlinear waveforms contain harmonic energy and may be described by transform equations which are based on Fourier's Theory of Trigonometric Series which among other things show that all components of a given waveform are comprised of at least one or more sinusoidal waveforms that are mathematically related. Some of the harmonic energy is reradiated into space and may be picked up by nearby receiver 4, which may then sound an alarm. A typical transmitted signal may be 1000 MHz. In this case, the electrical length of the dipole antenna may be one-half of the wave length of 1000 MHz, which in free space is approximately 30 centimeters, resulting in a corresponding half-wave dipole structure of about 15 centimeters long.

[0025] Referring now to FIG. 1A, a prior art radio frequency theft control tag of which tag 5 is comprised of a thin conductor 6 and a small diode 7 mounted within a flat plastic housing or substrate 8. The thin conductor 6 may be a foil shaped to form one or more dipole antenna lengths in parallel which may be harmonically related as a function of electrical length, therefore the dipole antenna 1 previously shown in FIG. 1 may be modified so that it reradiates even more efficiently at double the input frequency. A typical theft control tag system may operate at about 5000 MHz,

[0026] The substrate itself should be thin. The thinnest substrates may be in a range of 200 nanometers or less and may be produced by tapering the edge of a thin section of substrate material down to a near molecular edge by acid etching, drawing; or other ablative process. Alternatively, thin sections may be produced in thicker areas by ablative methods such as spark erosion or laser ablation, the advantage being that a stronger surrounding support structure may be formed around a very thin active area of the substrate.

[0027] It is important to point out that oxides of metals such-as iron are commonly known to have semiconducting properties and therefore may form part of a semiconducting junction. The small size of these particular nanoparticles makes them suitable for junctions that are electrically short enough to operate effectively at very high frequencies, including light frequencies since they are small relative to light wavelengths. A typical red light wavelength may be around 600 nanometers, and an iron nanoparticle may be less than 100 nanometers and typically may be in the range of 10 to 30 nanometers average diameter.

[0028] Referring to FIG. 3, a prepared substrate **11** with embedded nanoparticles **19** may be supplied with acetylenefed carbon nanotubes **21** extending from depressions **13** or apertures **15**. The mechanism of nanotube generation and growth in a prepared foraminous substance appears to involve a process in which particles act like seeds for the initiation of nanotube growth, and that the orientation and direction of the initiated nanotube growth is then influenced by the orientations of the depressions and apertures, which may simply serve as guides at the early stage of growth. Other forces and influences such as a static electric field, a magnetic field, or the application of various electromagnetic fields such as radio wave energy and lightwave energy, may also influence the orientation and growth process. In particular, the application of a static electric field to the substrate and subsequent charging of the growing nanotubes may improve separation and aid in the regularity and evenness of the separation of individual strands through the mutual repulsion force resulting from an adjacent like charge. The apparatus to grow nanotubes consists of a chamber (not shown) into which acetylene is introduced and burned incompletely which creates soot. The soot is comprised of regularly shaped carbon atoms which have been observed to self assemble into the nanotube configuration.

[0029] Still referring to FIG. 3, the length L of the nanotube may be controlled by regulating the time allowed for growth. The average length of the nanotube or nanotubes may be monitored by measuring the light absorption characteristics during the growth process which change as the tube grows. Generally, as the tube lengthens it admits longer wavelengths according to a relationship known in electromagnetic theory in which the propagation time of the electric charge across a body determines its electrical length and its admittance or ability to preferentially absorb and/or radiate at a specific wavelength. For a $\frac{1}{2}$ wavelength dipole arrangement each side of the substrate may have an approximately $\frac{1}{4}$ wavelength long conductor, and is most responsive to a wavefront that propagates in a direction that is perpendicular to the broad side of the conductors. Conductor lengths L that correspond to $\frac{1}{4}$ wavelength from ultraviolet, through the visible and to infrared light may have a range from about 60 nanometers to about 10000 nanometers may be accomplished using current techniques. The axial rela-

tionship of the two $\frac{1}{4}$ wavelength conductor set **25** and their more-or-less perpendicular disposition relative to the substrate make this array polarization sensitive to lightwave energy. In general, a higher current and lower voltage may be observed near the center of a resonant dipole arrangement in accordance with the conventional antenna art. It may be desirable to raise the voltage near the junction which may be accomplished either by adjusting the length of the antenna element or by placing the junction off center. It is known that $\frac{1}{2}$ wavelength resonant antennas exhibit current minima and voltage maxima at the ends of the conductors, therefore, it may be desirable to approach lengths of $\frac{1}{2}$ wavelength on each side of the substrate thereby producing a resonant structure about at about one full wavelength.

[0030] The thickness of the substrate and the thickness of the conductor may result in a longer charge transport pathway that tends to shorten the overall length of the dipole antenna somewhat. This shortening effect is well known in the radio art as it relates to thick antenna elements, but is less appreciated as it relates to the intersection of antenna elements since the delay times associated with radio frequency connections and intervening junctions are usually small with respect to the wavelength involved. In lightwave regimes these delays are more significant. To reduce internal charge transport or propagation of charge delay in the invention, a paired junction **23** may be constructed by growing two opposing nanotubes from one iron particle with the advantage of better electrical length control and less dependence upon substrate thickness to define the length of the structure.

[0031] It should be pointed out that the exact role and semiconductive properties of reduced metals within a substrate and their operation when connected to at least one end of a carbon nanotube has not been studied in sufficient detail, and it is possible that any discontinuity represented by any interruption of the nanotube itself, including termination, distortion etc., may be found to have inherent nonlinear properties which could additionally benefit the efficiency of the present invention. Due to the small size of these junctions and the high frequencies involved, tunneling effects, in addition to band gap effects, may be produced at or near the junctions or physical discontinuities of the structures as generally described.

[0032] Referring now to FIG. 4, an optical antenna array **26** has paired junctions **23** and conductor sets **25** of approximately equal lengths joined at substrate **11**. Electrical terminal **27** is bonded to the substrate **11** by bond **29** which may be in electrical communication with either doped or undoped regions of the substrate. Application of a current to terminal **27** is effective to bias the electrical transport properties of the assembly. Application of an alternating waveform is effective to modulate the transport properties across the optical antenna array **26** in a periodic manner which causes it to act in a way that is similar to a diode switch or mixer arrangement as commonly encountered in the electrical and radio art. Since the inherent transport properties across the optical antenna array **26** are nonlinear, mixing and superimposition of the modulating electrical waveform with the light waveform is produced. Conversely, variations in the amplitude or phase of the light waveform are effective to influence the electrical port. These may produce sum and difference signals through the various processes known as heterodyn-

ing and modulating, and may result in an amplification or increase of the total power realized.

[0033] Referring to FIG. 4a, the optical antenna array 26 is supplied with staggered conductor sets 31 disposed upon substrate 11. As in the prior art radio frequency tag 5 shown in FIG 1a, the lengths of the antenna or conductor elements are effective to enhance reradiation at certain wavelengths of operation. Referring once again to the light modifying device assembly of FIG. 4a, two, three or more wavelengths may be selectively admitted and radiated depending upon the mix and distribution of element lengths. Best efficiency is obtained when the radiated energy is harmonically related to admitted energy. Practical devices with bandwidths broad enough to admit and radiate over a wide range of wavelengths are accommodated with this construction. To produce elements of varying lengths on the substrate, the process of particle deposition and nanotube growth may be repeated multiple times on a single substrate since the material C₆₀ can withstand considerable thermal cycling without damage.

[0034] Referring to FIG. 4b, an optical antenna array 26 is patterned after a commonly known antenna type known as a log-periodic dipole array. Tapered length conductor sets 25 are effective to operate over a wide range of wavelengths, and coupling of the electromagnetic fields between adjacent elements is effective to selectively reinforce wave propagation so that a directional preference of the optical antenna array 26 is obtained. The log-periodic dipole array is merely exemplary; other antenna types include, but are not limited to, dipole, Yagi-Uda, collinear, phased array, rhombic or other structures that are known to radiate and admit electromagnetic energy in accordance with the antenna art, and conductors that are scaled and positioned with regard to the wavelengths of electromagnetic energy involved which may include transmission line structures comprised of more or less linear conductors.

[0035] Referring now to FIG. 5, an optical antenna array device 42 encloses the optical antenna array 26 which is mounted in a tubular holder 43 by means of a mounting plate 41. The holder may be made from machined aluminum which may have an outside diameter of about 1mm and an inside diameter of about 0.25mm or less. Larger or smaller structures may be constructed within the scope of the invention. A coating of aluminum 45 is deposited in center bore of holder 43 by a vacuum metalization process. The coating acts like a mirror which helps direct light from window 53 to and from the optical antenna array 26. Electrical wire 47 is brought out through insulator 49 to terminal 51 for the purpose of attaching and electronic device such as art oscillator, a receiver, a spectrum analyzer, a pulse generator, an amplifier, a power supply or the like to electrical terminal 27.

[0036] Referring to FIG. 5a, the operation of the optical antenna array device 42 is shown in block diagram form. Light source 61 (λ) shines light beam 63 into holder 43 and onto mounting plate 41 carrying the optical antenna array 26. The glancing angle of the light beam against the inside of the holder helps avoid a condition where all the light energy wave front is entirely perpendicular to the plane of the substrates. Mounting plate 41 may alternatively be positioned diagonally in holder 43 so that light energy propagates in a direction that is generally broadside to the long

axes of the carbon nanotubes 21, as shown in FIG. 4, which are aligned with a generally perpendicular orientation with respect to the substrate material 11.

[0037] Returning once again to FIG. 5a, light beam 63 may interact with optical antenna array 26 which may produce reflected beam 65 ($\lambda/2$) at least a portion of which contains high levels of second, third or higher order harmonic energy. Simultaneously, transmitted beam 67 ($\lambda/2$) may interact with optical antenna array 26 which generates significant harmonic energy and propagates in a direction generally opposite light beam 63. Some isolation is afforded by the light loss that occurs at the optical antenna array 26 so that a plurality of light beams of different wavelengths may be introduced simultaneously, and their products may be detected at terminal 51. Polarization and isolation may be enhanced by the use of polarizing filters (not shown) and magnetic rings (also not shown) attached to one or more ends of holder 43.

[0038] What has been described is a practical harmonic generating device that can operate over a wide range of light wavelengths utilizing an optical antenna array system that is optimized for lightwave operation. The use of an array of elements that are produced at dimensions and oriented in a repeatable manner create optimal conditions for efficient collection, conversion and radiation of electromagnetic lightwave energy. This high efficiency is due to the ordered arrangement of conductive elements optimally dimensioned for electromagnetic radiation as previously practiced in the radio and antenna art which may now be practically applied to optical wavelengths. Further, attenuation effects are minimized through the use of optical elements which may operate in free space being attached at only one end, rather than in bulk, disordered form or in a solution. The invention allows the fabrication and practical use of linear conductors as antennas with lengths that correspond to light wavelengths and therefore allows the application of radiowave antenna, transmission and radiation practices, including harmonic generation and mixing, detection and frequency multiplication, to the lightwave regime.

[0039] Variations, modifications, and other implementations of what is described herein will occur to those of ordinary skill in the art without departing from the spirit and scope of the invention as claimed. Accordingly, the invention is to be defined not by the preceding illustrative description but instead by the spirit and scope of the following claims.

1-18. (canceled)

19. A method of controlling the manufacture of carbon nanotubes on a substrate, comprising:

providing a substrate with a plurality of growth locations thereon;

heating said substrate in a chamber;

introducing a carbon bearing gas to said chamber to create carbon nanotubes on said growth locations on said substrate;

applying an external controlling field to said chamber during said heating of said substrate; and

controlling growth of said carbon nanotubes on said substrate.

20. The method of controlling the manufacture of carbon nanotubes on a substrate as recited in claim 19, wherein said external controlling field comprises a static electric field.

21. The method of controlling the manufacture of carbon nanotubes on a substrate as recited in claim 19, wherein said external controlling field comprises a magnetic field.

22. The method of controlling the manufacture of carbon nanotubes on a substrate as recited in claim 19, wherein said external controlling field comprises an electromagnetic field.

23. The method of controlling the manufacture of carbon nanotubes on a substrate as recited in claim 19, comprising:

influencing a separation of nanotubes by adjacent repulsion.

24. A method of controlling growth of a nanotube on a substrate comprising:

growing a plurality of nanotubes on a substrate;

applying an external field to said nanotubes during said growth of said nanotubes;

influencing the direction of said growing of said nanotubes by orientation of said external field relative to said nanotubes.

25. The method of controlling growth of a nanotube on a substrate as recited in claim 24, wherein said external field is a static electric field.

26. The method of controlling growth of a nanotube on a substrate as recited in claim 24, wherein said external field is an electromagnetic field.

* * * * *