Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2899255 A1 2017/01/31

(21) 2 899 255

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(22) Date de dépôt/Filing Date: 2015/07/31

(41) Mise à la disp. pub./Open to Public Insp.: 2017/01/31

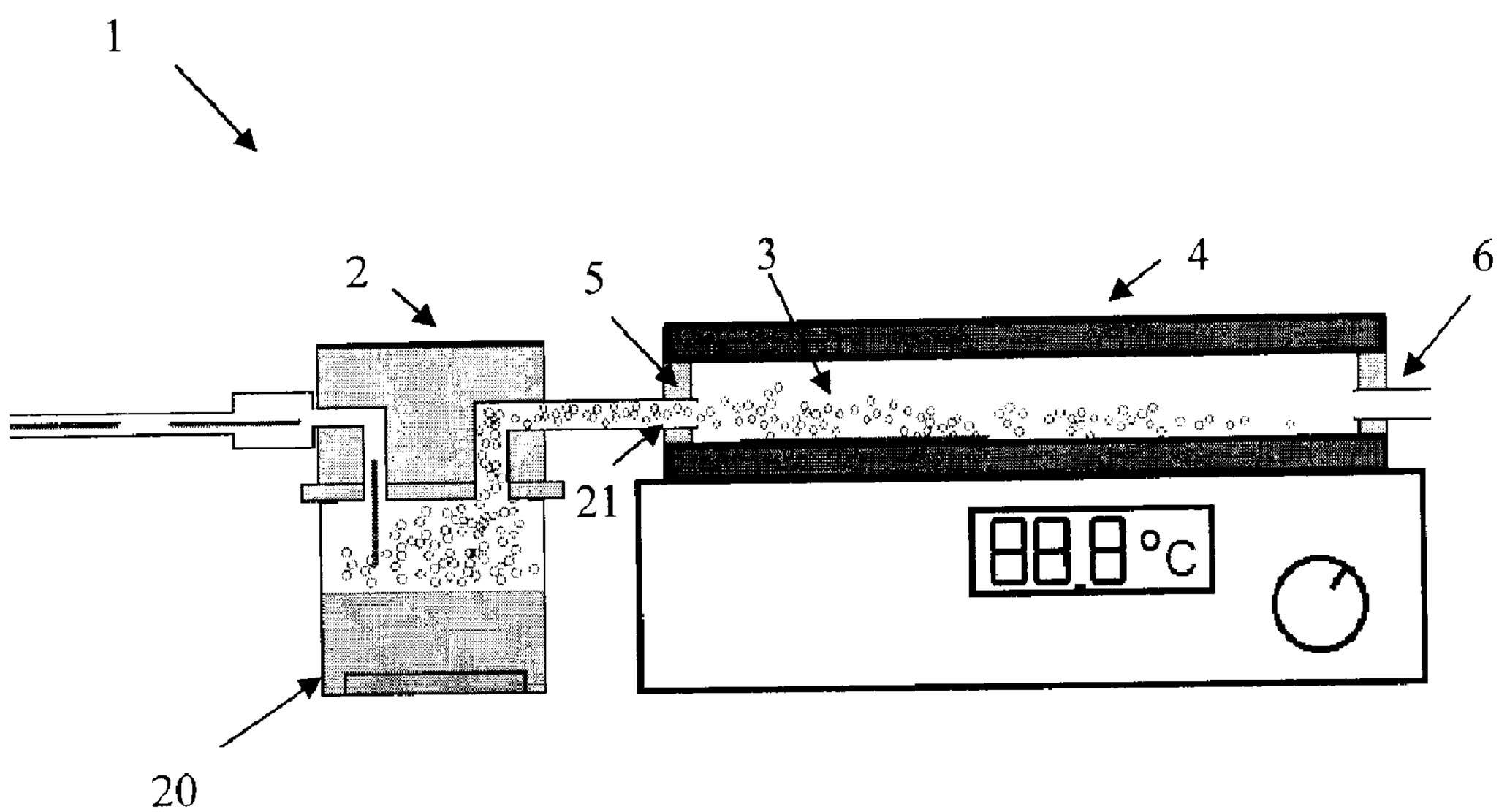
(51) Cl.Int./Int.Cl. *C08J 7/06* (2006.01),
B05B 1/10 (2006.01), *B05D 1/02* (2006.01),
B82Y 30/00 (2011.01)

(71) Demandeur/Applicant:
NATIONAL RESEARCH COUNCIL OF CANADA, CA

(72) Inventeurs/Inventors:
LEFEBVRE, JACQUES, CA;
MALENFANT, PATRICK, CA

(74) Agent: LEMAY, CATHERINE

(54) Titre : APPAREIL ET METHODE DE DEPOT PAR AEROSOL DE NANOPARTICULES SUR UN SUBSTRAT
(54) Title: APPARATUS AND METHOD FOR AEROSOL DEPOSITION OF NANOPARTICLES ON A SUBSTRATE



(57) Abrégé/Abstract:
Provided is an apparatus for aerosol deposition of nanoparticles on a substrate. The apparatus includes: an aerosol generator for generating an aerosol of micron-sized droplets, each droplet having a limited number of nanoparticles; and a deposition chamber for receiving the aerosol from the aerosol generator. The deposition chamber having an electrostatic field for attracting droplets in the aerosol to the substrate. The electrostatic field being substantially perpendicular to the substrate. The apparatus allows for films/networks of nanoparticles to be patterned on the substrate to sub-millimetre feature sizes, which allows the fabrication of transistor devices for printable electronics applications. Also provided are methods for depositing nanoparticles on a substrate and materials having networks of such nanoparticles.

ABSTRACT

Provided is an apparatus for aerosol deposition of nanoparticles on a substrate. The apparatus includes: an aerosol generator for generating an aerosol of micron-sized droplets, each droplet having a limited number of nanoparticles; and a deposition chamber for receiving the aerosol from the aerosol generator. The deposition chamber having an electrostatic field for attracting droplets in the aerosol to the substrate. The electrostatic field being substantially perpendicular to the substrate. The apparatus allows for films/networks of nanoparticles to be patterned on the substrate to sub-millimetre feature sizes, which allows the fabrication of transistor devices for printable electronics applications. Also provided are methods for depositing nanoparticles on a substrate and materials having networks of such nanoparticles.

APPARATUS AND METHOD FOR AEROSOL DEPOSITION OF NANOPARTICLES ON A SUBSTRATE

FIELD OF INVENTION

[0001] The invention is generally directed to printable electronics. More specifically, the invention is directed to an apparatus and method for aerosol deposition of nanoparticles on a substrate.

BACKGROUND OF INVENTION

[0002] The low cost and flexibility of being able to use conventional printing methods and equipment to print electrical circuits on various surfaces including plastic rolls has expanded the potential environments where electronics are used.

[0003] Similar to traditional printing methods, printable electronics require depositing inks on a surface in a defined pattern. The inks used in printable electronics include functional electronic or optical materials, such as inks having carbon nanotubes, the material acting as a macroscopic transistor channel when printed to form a network.

[0004] Carbon nanotubes have outstanding electrical properties with semiconducting single-walled carbon nanotubes (SWCNTs) performing as semiconducting channels in high mobility transistors in printable electronics applications. In such applications, thousands of carbon nanotubes are laid down on a surface and form a network of electrically connected wires. These networks form readily upon soaking a substrate in a carbon nanotube containing solution (or ink). For several applications where the network should not cover an entire surface but be patterned to sub-millimetre feature sizes, a printing apparatus is required. Several technologies exist for the deposition of ink materials and they fall into essentially two categories: 1) serial, such as inkjet or aerosol jet; and 2) parallel, such as screen, gravure and flexo-printing. However, the majority of these systems are not adapted to ultrathin films (i.e. films that have a thickness of <10 nm) such as those used in the carbon nanotube network transistors.

[0005] Furthermore, the present systems require specific ink formulations, which are engineered to have physical parameters within a set window. However, additives introduced into such formulations can severely degrade electrical performance of transistor devices. In addition,

deposited films are generally much thicker than needed for transistor operation. Therefore, there is a need for a deposition system that can be used to assemble carbon nanotubes and other types of nanoparticles into networks of thin film transistors.

SUMMARY OF INVENTION

[0006] According to an aspect of the present invention, there is provided an apparatus for aerosol deposition of nanoparticles on a substrate. The apparatus includes: an aerosol generator for generating an aerosol of micron-sized droplets, each droplet comprising a limited number of nanoparticles; and a deposition chamber for receiving the aerosol from the aerosol generator. The deposition chamber having an electrostatic field for attracting individual droplets in the aerosol to a substrate. The electrostatic field is substantially perpendicular to the substrate.

[0007] In an embodiment, the apparatus also includes an injector nozzle with one to several openings either parallel or perpendicular to the deposition substrate.

[0008] In one embodiment, the deposition chamber further includes a stencil mask positioned between the flow of the aerosol and the substrate.

[0009] In a further embodiment, the electrostatic field is provided by interspaced charged plates and the substrate is positioned on the grounded plate.

[0010] In yet a further embodiment, the charged plates are electrostatically charged insulators or voltage biased conductors.

[0011] In a still further embodiment, the charged plates are patterned to spatially modulate the electric field and promote nanoparticle deposition at specific locations on the substrate.

[0012] In another embodiment, the aerosol flows in a laminar fashion and is spatially engineered to afford nanoparticle deposition at specific locations on the substrate.

[0013] According to another aspect of the invention, there is provided the use of the apparatus described above in the production of a thin film of nanoparticles.

[0014] In one embodiment, the apparatus is used in the production of a thin film transistor.

[0015] In another embodiment, the apparatus is used in the production of a conductive electrode, a diode, a photovoltaic cell, a physical sensor or chemical sensor. The conductive electrode being either a transparent or non-transparent electrode.

[0016] According to another aspect of the invention, there is provided a method for depositing nanoparticles on a substrate. The method comprising the steps of: generating an aerosol of micron-sized droplets, each droplet comprising a limited number of carbon nanoparticles; and subjecting the aerosol to an electrostatic field that causes the micron-sized droplets to be deposited on a substrate.

[0017] In an embodiment, the method further comprises a step of passing the micron-sized droplets through a mask prior to being deposited on the substrate.

[0018] In a further embodiment, the electrostatic field is provided by interspaced charged plates and the substrate is positioned on the grounded charged plate. The charged plates being electrostatically charged insulators or voltage biased conductors. The charged plates can be patterned to spatially modulate the electric field and promote carbon nanotube deposition at specific locations on the substrate.

[0019] In a still further embodiment, the aerosol flows in a laminar fashion and is spatially engineered to afford nanoparticle deposition at specific locations on the substrate. The substrate can have a conductive surface or a dielectric surface.

[0020] According to another aspect of the invention, there is provided a material that has a hydrophobic surface and at least one nanoparticle adhered on the surface.

[0021] In one embodiment, a plurality of nanoparticles is provided in a network. The nanoparticles can act as transistors.

[0022] In a further embodiment, the surface has a water contact angle greater than 80^{o} such as poly(vinylphenol) based dielectric or a polytetrafluoroethylene based dielectric, for

example Xerox™ Dielectric xdi-d1.2 or Teflon®-AF, or a fluoropolymer, such as the amorphous (non-crystalline) fluoropolymer CyTOP ®.

[0023] In a still further embodiment, the material is provided as a semiconductor in a thin film transistor. In other embodiments, the material can be a conductive electrode, a diode, a photovoltaic cell, a physical sensor or chemical sensor. The conductive electrode being either a transparent or non-transparent electrode.

[0024] In the inventions described above, the substrate is a conductive surface or a dielectric surface. The surface being a hydrophilic or hydrophobic surface, in some embodiments.

[0025] In other embodiments, the substrate has a surface or polymer with water contact angle greater than 80°, for example between 85° and 120°, about 90° or between 117-120°. Example surfaces, or polymers, include, but are not limited to: polyvinylidene chloride and fluorides; polyhexamethylene adipamide (Nylon 66); Nylon 7; poly(dodecano-12-lactam)(Nylon 12); polyamide; cellulose acetate; polysulfone; polymethyl methacrylate; polyvinyl acetate; polycarbonate; polystyrene; polypropylene; polyimide; epoxy; polyethylene terephthalate; silicones; olefins (alkenes); cellulose nitrate; ultra-high-molecular-weight polyethylene; polychloroprene; polyvinyl chloride; latex; butyl rubber; and polytetrafluoroethylene. In some embodiments, the hydrophobic surface is a poly(vinylphenol) based dielectric or a polytetrafluoroethylene based dielectric.

[0026] In addition, in the inventions described above, each micron-sized droplet can comprise less than 5 nanoparticles per droplet. For example, one nanoparticle per droplet.

[0027] Moreover, in the inventions described above, the nanoparticle can be boron nitride, molybdenum disulfide, tungsten disulfide, a carbon- or phosphorus-based nanoparticle. In another embodiment, the nanoparticle can be a combination of the above materials. In each case, the nanoparticle can take on various crystalline forms, such as single-walled or multi-walled nanotubes, nanorods, nanospheres, nanoflakes or nanoribbons. In one embodiment, the nanoparticle is a single-walled carbon nanotube.

[0028] According to another aspect of the present invention, the apparatus described hereinabove can form part of a roll-to-roll printing system.

[0029] According to another aspect of the present invention, there is provided a material comprising polymers having carbon nanotube networks deposited thereon by the apparatus described above for use as gate dielectrics in a bottom gate transistor or as an encapsulation layer.

[0030] According to a further aspect of the present invention, there is provided a material comprising polymers having carbon nanotube networks deposited thereon by the apparatus described above for use as gate dielectrics in an air exposed transistor without an encapsulation layer.

[0031] In one embodiment, the material has transfer characteristics with hysteresis from 0-1 MV/m.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] These and other features, aspects and advantages of the present invention will become better understood with regard to the following description and accompanying drawings wherein:

[0033] FIG. 1 is a schematic of an apparatus according to an embodiment of the present invention;

[0034] FIG. 2 is a scanning electron microscopy image of a network of single-walled carbon nanotubes assembled using the apparatus of the present invention;

[0035] FIG. 3 is a schematic of the deposition chamber according to an embodiment of the present invention;

[0036] FIG. 4 is an optical (top) and scanning electron microscopy (bottom) image showing patterned nanotube networks obtained combining a shadow mask with the apparatus of the present invention;

[0037] FIG. 5 is an optical image of a series of depositions performed under different electric field intensities, (a) and (b) being the same image taken under different illumination conditions;

[0038] FIG. 6 is a graphical representation of carbon nanotube transistors on polymer dielectrics. Transfer characteristics are shown on linear and logarithmic scales for forward and reverse sweep directions. a) Xerox Dielectric xdi-d1.2. Sweep rate is 0.22 V/s. b) Teflon-AF. Sweep rate .55 V/s;

[0039] FIG. 7 is a graphical representation of a gate dielectric stress test. a) Transfer characteristics for Xerox Dielectric xdi-d1.2 taken at different sweep ranges from ±10 V to ±60 V. The sweep frequency is 110 mHz. Inset shows extracted threshold voltages (Vt) for forward (F) and reverse (R) sweep directions. b) Time evolution of the transistor conductance (red trace) for Xerox Dielectric xdi-d1.2 under a sequence of gate voltages (blue trace). c) Transfer characteristics for Teflon-AF dielectric taken at different sweep ranges from ±15 V to ±75 V. The sweep frequency is 110 mHz. Inset shows extracted threshold voltages (Vt) for forward (F) and reverse (R) sweep directions. d) Time evolution of transistor conductance (red trace) for Teflon-AF dielectric under a sequence of gate voltages (blue trace); and

[0040] FIG. 8 is a graphical representation of transfer characteristics of encapsulated, bottom gate SWCNT network transistor using Xerox Dielectric xdi-d1.2 both dielectric and encapsulation layers.

DESCRIPTION OF THE INVENTION

[0041] The following description is of illustrative embodiments by way of example only and without limitation to the combination of features necessary for carrying the invention into effect.

[0042] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. It must also be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise.

[0043] As shown in FIG. 1, the apparatus (1) for deposition of carbon nanotubes on a substrate includes: an aerosol generator (2) for generating an aerosol of micron-sized droplets (3) and a deposition chamber (4) for receiving the droplets from the generator (2). The deposition chamber (4) has an electrostatic field (5) for attracting droplets (3) in the aerosol to a substrate. The electrostatic field (5) being substantially perpendicular to the substrate. In other words, the electrostatic field is more or less 90 degrees to the substrate. The apparatus (1) described herein can form part of a roll-to-roll printing system.

[0044] In most cases, the aerosol generator (2) is a separate unit within the apparatus (1). However, the aerosol generator (2) can be integrally connected to the deposition chamber (4). In either case, the aerosol generator (2) is responsible for generating an aerosol of micron-sized droplets (3). The aerosol generator (2) will typically include a mist generating chamber (20) and a nozzle (21). However, it is possible to generate an aerosol by linking a container containing a solution directly to an atomizer nozzle. For example, in order to produce the micron-sized droplets, a high frequency ultrasonic atomizer, is typically used although other types of atomizers, in the form of nozzles, can create atomization from a variety of mechanical means, such as, but not limited to, electrostatic processes and centrifugal forces, may be used. Moreover, aerosol can be generated using a pneumatic aerosol generator or electrospray processes. In one embodiment, each droplet (3) contains a limited number of nanoparticles, for example, five or less nanoparticles. However, droplets containing a nanoparticle, such as a single-walled carbon nanotube, are particularly useful in forming electrical networks (FIG. 2).

[0045] The aerosol of micron-sized droplets (3) is fed into a deposition chamber (4) through an inlet (5) connected to the nozzle (21) or through a conduit (6) connecting the nozzle (21) to the deposition chamber (4). The aerosol travels through the deposition chamber (4), and if not deposited on the substrate, exits the chamber (4) through an outlet (7). As shown in FIG.

23, the droplets (3) are attracted or drawn to the substrate (8) by an electrostatic field created by a charged top plate (9) and grounded bottom plate (10), such as, but not limited to, electrostatically charged insulators or voltage biased conductors. The substrate (8) is positioned on the bottom plate (10) to receive the individual droplets (3) from the aerosol.

[0046] In one embodiment, one or more injector nozzles (11) are provided in conjunction with the charged top plate (9) to introduce the droplets (3) to the electrostatic field created between the charged top plate (9) and the grounded bottom plate (10). In this embodiment, the droplets (3) are propelled through openings in the charged top plate and attracted or drawn to the substrate (8) through the electrostatic field. Optionally a stencil mask can be provided between the flow of the aerosol and the substrate (8). As shown in FIG. 4, use of a stencil mask allows for the deposition of droplets (3) to be patterned on the substrate (8) in a predefined manner.

[0047] In another embodiment, the charged top (9) and/or bottom plates (10) are patterned to spatially modulate the electrostatic field in order to promote carbon nanotube deposition at specific locations on the substrate (8). Similarly, the aerosol can flow in a laminar fashion through the deposition chamber (4) and be spatially engineered to afford carbon nanotube deposition at specific locations on the substrate (8).

[0048] The precipitation of carbon nanotube particles on the substrate (8) can also be controlled or patterned by adjusting the deposition parameters of the starting solution of the material being deposited or adhered onto the substrate; the aerosol flow rate; the electrostatic field; the nozzle temperature, the substrate temperature and atmospheric content of the deposition chamber; and/or the composition of the carrier gas that flows through the deposition chamber.

[0049] The apparatus (1) described herein allows for nanoparticle films/networks, for example, to be patterned on the substrate to sub-millimetre feature sizes. Nanoparticles containing droplets that either carry a net charge or are charge neutral but have strong electrical polarizability, are particularly useful in the apparatus (1). Charged/polarizable droplets will interact with the electrostatic field in the deposition chamber (4), causing the nanoparticles to be adhered to the substrate (8). The intensity of the interaction with the electrostatic field can be adjusted in two ways: externally, using Corona discharge or UV exposure, for example, to

change the charge on the droplet; or intrinsically, by modifying the solution's chemical characteristics.

[0050] Examples of nanoparticles that can be used in the apparatus (1) include, but are not limited to, boron nitride, molybdenum disulfide, tungsten disulfide, and phosphorus- or carbon-based nanoparticles. Depending on the application, any one of the crystalline forms of these compounds could be used. For example, carbon-based nanoparticles could include carbon nanotubes, nanorods, nanospheres, nanoflakes and nanoribbons. Single-walled carbon nanotubes are particularly useful for high performance printed transistors. Further examples of nanoparticles, can include polymers having a molecular weight between about 1,000 and 1,000,000 g/mol. Other examples of nanoparticles that can be used in the apparatus (1) can be a combination of the above materials.

[0051] The substrate (8) used in the apparatus is chosen based on the product being manufactured. In most cases, the substrate will be an electrically insulating material, such as, a hydrophilic or hydrophobic dielectric surface, that when coated with a network of single-walled carbon nanotubes can function as a thin (or ultra thin) film transistors. However, other applications may require the use of a conductive substrate, such as metal, having nanoparticles adhered thereto. The substrate will often be patterned with multiple materials typical of printed devices, for example dry/cured conductive, insulating and dielectric inks. The manufactured product can be a diode, a conductive electrode (transparent or non-transparent), a photovoltaic cell, a physical sensor, a chemical sensor or all possible combinations of such devices.

[0052] In one particularly interesting embodiment, the substrate is a surface or polymer with water contact angle greater than 80°. Such primarily hydrophobic surfaces typically have water contact angles between 85-120°, with particularly useful surfaces having contact angles around 90°+/- 5° or between 117-120°. Examples of such surfaces, or polymers, include, but are not limited to: polyvinylidene chloride and fluorides; polyhexamethylene adipamide (Nylon 66); Nylon 7; poly(dodecano-12-lactam)(Nylon 12); polyamide; cellulose acetate; polysulfone; polymethyl methacrylate; polyvinyl acetate; polycarbonate; polystyrene; polypropylene; polyimide; epoxy; polyethylene terephthalate; silicones; olefins (alkenes); cellulose nitrate; ultra-high-molecular-weight polyethylene; polychloroprene; polyvinyl chloride; latex; butyl rubber;

and polytetrafluoroethylene. In some embodiments, the hydrophobic surface is a poly(vinylphenol) based dielectric or a polytetrafluoroethylene based dielectric. A non-limiting example of a poly(vinylphenol) based dielectric would be Xerox™ Dielectric xdi-d1.2 (supplied by the Xerox Research Centre of Canada), whereas an example of polytetrafluoroethylene based dielectric includes: Teflon®-AF. In other embodiments, the hydrophobic surface is a fluoropolymer, such as the amorphous (non-crystalline) fluoropolymer CyTOP®. Such polymers having carbon nanotube networks deposited thereon by the apparatus described above, can be used as gate dielectrics in a bottom gate transistor or as an encapsulation layer. In air exposed transistors without an encapsulation layer, the transfer characteristics of the material indicate little to no hysteresis (i.e. from 0-1 MV/m, which corresponds to 0-1V for a 500nm dielectric with a dielectric constant of 2). These examples demonstrate the value of electrostatically assisted aerosol deposition to overcome the fabrication challenges present especially in hydrophobic polymer dielectrics. Results indicate that such transistors printed on these substrates are very robust and can meet some of the performance metrics required for the fabrication of commercial products.

EXAMPLES:

[0053] The effect of modifying the intensity of the electric field in the deposition chamber on the deposition of carbon nanotubes on the substrate was examined. As shown in FIG. 5, seven injector nozzles were used to deposit single-walled carbon nanotubes on a silicon substrate. The seven injector nozzles gave rise to the seven horizontal deposition patterns shown in the top section of FIG. 5a. From right to left, the applied voltage varied from +2400V to -2400V in steps of 200V, which corresponds to 25 different conditions. Between each voltage, the sample was translated 600 μm in the horizontal direction. At the highest fields, isolated dark stripes were clearly visible, with lateral dimensions below 100 x 600 μm^2. As the field weakens, the deposition pattern spreads until the laminar flow from neighboring nozzles prevents further spreading. This is clearer in FIG. 5b which was taken under different illumination conditions. It should be noted that when the field is absent (vertical middle section), little material is deposited.

[0054] Aerosol deposition appears to be much less sensitive to surface energy where poor carbon nanotube adherence is found using other deposition methods. For Xerox Dielectric xdi-

d1.2 (supplied by the Xerox Research Centre of Canada), networks formed readily on polymer layers obtained from spin coating, without surface treatment. The Xerox Dielectric comprises a dielectric material and a low surface tension additive (see US Patent No. 8,821,962, the contents of which is herein incorporated by reference). The low surface tension additive enables the formation of a thin, smooth dielectric layer with fewer pinholes and enhanced device yield. The dielectric material comprises a high-k dielectric, Poly(4-vinylphenol) (PVP) and a low-k dielectric, Poly(methyl silsesquioxane) (pMSSQ). Direct comparisons were made with networks on SiO_2 and, except for the hysteresis being larger on SiO_2, electrical data were similar in many respects (nominal mobility and current *On/Off* ratio). In the case of Teflon-AF, a 15 minute UV-Ozone exposure (conditions were not optimized) was used to promote carbon nanotube adhesion. The treatment led to minimal change of the water contact angle from 120^o to 117^o (a direct measure of hydrophobicity). For both Xerox Dielectric xdi-d1.2 and Teflon-AF, carbon nanotube adhesion was sufficiently strong for the rinsing steps required to remove excess dispersant in the nanotube ink formulation.

[0055] Table 1: Polymer dielectric physical parameters

	MATERIAL	DIELECTRIC CONSTANT	CONTACT ANGLE	THICKNESS (NM)
XEROX DIELECTRIC xdi-d1.2	POLY(VINYLPHENOL)/POLY (METHYL SILSESQUIOXANE) BLEND	4.0	89^o	530
TEFLON® AF 2400 X SOL	POLY(PERFLUORODIOXOLE -CO- TETRAFLUOROETHYLENE	1.9	120^o (117^o)	480

[0056] Table 2: Transistor performance parameters from Fig.7.

	MOBILITY (CM^2/VS)	THRESHOLD VOLTAGE (V)	HYSTERESIS (V)
XEROX DIELECTRIC xdi-d1.2	6.5	4.15	0.004±0.030
TEFLON-AF	4.1	10.5	0.45±0.02

[0057] Transistors fabricated with Xerox Dielectric xdi-d1.2 and Teflon-AF dielectrics were found to have good performance metrics in terms of hole mobility, *On*-current and *Off*-current. Transistor transfer characteristics (source-drain conductance versus gate voltage) are shown in FIG.6 and Table 2 summarizes performance numbers obtained from data analysis. In striking contrast with devices on SiO_2/Si surfaces under similar measurement conditions (and dielectric thicknesses), the magnitude of the hysteresis between forward and reverse gate sweeps are small for both dielectrics. In the case of Xerox Dielectric xdi-d1.2 (Fig. 6a), the hysteresis is essentially absent (0.004±0.030 V) with forward and reverse sweeps tracking perfectly on both linear and logarithmic scales. For Teflon-AF (Fig. 6b), the hysteresis is also very small with a value of 0.45±0.02 V.

[0058] In order to further assess the dielectric quality of the polymers, two sets of "*stress test*" measurements were performed. When transistor devices are stressed, large voltages are applied to the gate or source-drain electrode, and electrical data is acquired dynamically. Those results are shown in FIG. 7. In Fig. 7 a) and c), transfer curves are obtained at progressively greater gate voltage sweep ranges. In both cases, a hysteresis eventually develops together with a shift of threshold voltage (V_t). The inset in FIG. 7 a) and c) displays V_t for forward (F) and reverse (R) sweep direction. For Xerox Dielectric xdi-d1.2, a 1V hysteresis is found for V_G = ±20 V range and grows to >30 V for V_G = ±60 V. The opening of the hysteresis is asymmetric, growing first on the forward sweep (turn off) while the reverse sweep starts opening significantly only beyond V_G = -35 V. These results indicate both donor and acceptor trap charges are contributing to the hysteresis. The linear dependence of V_t *vs* $\pm V_G$ suggests a simple energy distribution of charge traps. PVP based dielectrics have yielded good electrical performance in organic TFTs, and crosslinking chemistry has been shown to dramatically impact TFT

performance, yet the use of PVP in SWCNT TFTs is scarcely reported, with no mention on the magnitude of hysteresis. Inadequately cross-linked PVP contains a significant number of hydroxyl groups which exacerbates the redox reaction for devices exposed to air ambient, thus leading to large hysteresis (similar to SiO_2). In fact, it has been noted that PVP is inherently hygroscopic and in the context of SWCNT based devices, and the redox chemistry that can occur, a hydrophobic formulation as described herein is clearly advantageous. The large contact angle measured on Xerox xdi-d1.2 is attributed to the migration of Poly(methyl silsesquioxane) to the surface of the PVP dielectric. Pure poly(vinyl phenol), with a large number of hydroxyl groups at the surface would show strong hydrophilicity.

[0059] Similar to Xerox Dielectric xdi-d1.2, increase in the gate voltage range in Teflon-AF devices (Fig. 7c) leads to a gradual appearance of a hysteresis. The magnitude however is smaller and is only 5V for the $V_G = \pm 75$ V sweep range (Teflon-AF has a low dielectric constant, $\kappa = 1.9$, and direct comparison with Xerox Dielectric xdi-d1.2 can be made using electric polarization field $P=V/\kappa d$, where d is the film thickness). A gradual shift of V_t to more positive V_G, from $V_t = 7V$ to 20V was noted. The asymmetry found between F and R sweep directions in the case of Xerox Dielectric xdi-d1.2 is not seen for Teflon-AF. Teflon-AF is an amorphous fluoropolymer having highly electronegative fluorine atoms. This attribute results in efficient electron withdrawing from the carbon nanotube and easy electron trapping at the Teflon surface. For holes however, a deep HOMO level would prevent significant bias stress for negative gate voltages.

[0060] The second "stress test" consisted of measuring the time evolution of conductance while the transistor is being subsequently switched between its "*On*" and "*Off*" state. For Xerox Dielectric xdi-d1.2, V_G within the ±20 V range was looked at where the hysteresis remained quite small. The time evolution in FIG. 7b displays six consecutive switch-*Off*s where V_G takes different values from 0 to 20 V, corresponding to various degrees of stress in the *Off* state. Here, the effect of $V_G > 0$ was studied since that's where the hysteresis growth is most pronounced (asymmetry in FIG. 4a and inset). In all cases, when the transistor is switched-*On* at $V_G = -20V$, a transient is seen in the conductance on the timescale of seconds. The magnitude of the overshoot is larger for larger *Off*-state gate voltage, which is consistent with a bigger applied

stress. The conductance recovers within 10% of the average value of 4.3 μA/V demonstrating good dielectric robustness.

[0061] In FIG. 7d, a similar test on transistors was performed made with Teflon-AF. A sequence of ten *Off*-states is presented with both *On* and *Off* values of the gate voltages being varied. In the first five cycles, a constant *Off*-state V_G = 30V is applied with different *On*-state V_G. The *On*-state shows a conductance overshoot with a few percent decay for the largest stress applied (V_G = -75 V). The transient occurs on a timescale of seconds. In the sequence that follows, a constant *On*-state V_G = -60 V with different degrees of *Off*-State bias stresses (similar to FIG. 7b) are applied. A short transient was also found here with the largest magnitude seen for the larger bias stress. In all cases, the conductance settles to within 2% of the average conductance of 6 μA/V.

[0062] Two performance requirements for applications in electronics are met when SWCNT networks are assembled on top of hydrophobic polymer dielectrics: the absence of hysteresis and time stability, particularly in the device's *On*-state. The absence of hysteresis and the robustness to *stress tests* indicate first that the polymers, the major component of the formulation, perform well as dielectrics, with a low level of dynamic charge traps. This is expected considering they are formulated for use as dielectrics in electronics applications, but it should be noted that many publications using PVP as a dielectric do not provide the same performance attributes that were observed with the Xerox Dielectric xdi-d1.2 formulation. The crosslinking chemistry and the layering property of the polymer blend have a significant effect on device performance and is a good match with semiconducting-SWCNT as the semiconducting channel. These results should serve as a guide to obtain robust bottom gate devices using normal processing in air ambient and Xerox Dielectric xdi-d1.2 represents a practical route to using established printing techniques and simple processes (conventional solvents).

[0063] Encapsulation of transistors with Xerox Dielectric xdi-d1.2 produces the desired shift in threshold voltage. FIG. 8 shows a transfer characteristic with V_t near 0V. Although the *On/Off* ratio measured at 0 V is poor (<4) for un-encapsulated devices in air ambient, it improves to 10^2 after encapsulation.

[0064] It will be understood that numerous modifications thereto will appear to those skilled in the art. Accordingly, the above description and accompanying drawings should be taken as illustrative of the invention and not in a limiting sense. It will further be understood that it is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features herein before set forth, and as follows in the scope of the appended claims.

WE CLAIM:

1. An apparatus for deposition of nanoparticles on a substrate, said apparatus comprising:

an aerosol generator for generating an aerosol of micron-sized droplets, each droplet comprising a limited number of nanoparticles; and

a deposition chamber for receiving the micron-sized droplets from the aerosol generator, said deposition chamber comprising:

an electrostatic field for attracting droplets in the aerosol to the substrate, wherein the electrostatic field is substantially perpendicular to the substrate.

2. The apparatus of claim 1, further comprising an injector nozzle with one to several openings either parallel or perpendicular to the deposition substrate.

3. The apparatus of claim 1 or 2, wherein the deposition chamber further comprises a stencil mask positioned between the flow of the aerosol and the substrate.

4. The apparatus of any one of claims 1 to 3, wherein each micron-sized droplet comprises less than 5 nanoparticles per droplet.

5. The apparatus of claim 4, wherein each micron-sized droplet comprises one nanoparticle per droplet.

6. The apparatus of any one of claims 1 to 5, wherein the electrostatic field is provided by interspaced charged plates and the substrate is positioned on the grounded plate.

7. The apparatus of claim 6, wherein the charged plates are electrostatically charged insulators or voltage biased conductors.

8. The apparatus of claim 6, wherein the charged plates are patterned to spatially modulate the electric field and promote nanoparticle deposition at specific locations on the substrate.

9. The apparatus of claim 1, wherein the aerosol flows in a laminar fashion and is spatially engineered to afford nanoparticle deposition at specific locations on the substrate.

10. The apparatus of any one of claims 1 to 9, wherein the substrate has an at least partially conductive surface.

11. The apparatus of any one of claims 1 to 9, wherein the substrate has an at least partially dielectric surface.

12. The apparatus of claim 10 or 11, wherein the substrate has a hydrophilic or hydrophobic surface.

13. The apparatus of claim 10 or 11, wherein the substrate has a surface with water contact angle greater than or equal to 80^{o}.

14. The apparatus of claim 13, wherein the water contact angle is between 85^{o}-120^{o}.

15. The apparatus of claim 14, wherein the water contact angle is about 90^{o}.

16. The apparatus of claim 14, wherein the water contact angle is between 117^{o} to 120^{o}.

17. The apparatus of claim 13, wherein the surface is selected from the group consisting of: polyvinylidene chloride and fluorides; polyhexamethylene adipamide (Nylon 66); Nylon 7; poly(dodecano-12-lactam)(Nylon 12); polyamide; cellulose acetate; polysulfone; polymethyl methacrylate; polyvinyl acetate; polycarbonate; polystyrene; polypropylene; polyimide; epoxy; polyethylene terephthalate; silicones; olefins (alkenes); cellulose nitrate; ultra-high-molecular-weight polyethylene; polychloroprene; polyvinyl chloride; latex; butyl rubber; and polytetrafluoroethylene.

18. The apparatus of claim 13, wherein the surface is a poly(4-vinylphenol) based dielectric or a polytetrafluoroethylene based dielectric.

19. The apparatus of any one of claims 1 to 18, wherein the nanoparticle is boron nitride, molybdenum disulfide, tungsten disulfide, a carbon- or phosphorus-based nanoparticle.

20. The apparatus of claim 19, wherein the carbon-based nanoparticle is a nanotube, nanorod, nanosphere, nanoflake or nanoribbon.

21. The apparatus of any one of claims 1 to 18, wherein the nanoparticle is a single-walled

carbon nanotube.

22. Use of the apparatus of any one of claims 1 to 21 in the production of a thin film of nanoparticles.

23. The use of claim 22, wherein a thin film transistor is produced.

24. Use of the apparatus of any one of claims 1 to 21 in the production of a diode, a conductive electrode, photovoltaic cell, a physical sensor or a chemical sensor.

25. The use of claim 24, wherein the conductive electrode is a transparent or non-transparent electrode.

26. A method for depositing nanoparticles on a substrate, the method comprising the steps of:

generating an aerosol of micron-sized droplets, each droplet comprising a limited number of nanoparticles; and

subjecting the aerosol to an electrostatic field that causes the micron-sized droplets to be deposited on a substrate.

27. The method of claim 26, further comprising the step of passing the micron-sized droplets through a mask prior to being deposited on the substrate.

28. The method of claim 26 or 27, wherein each micron-sized droplet comprises less than 5 nanoparticles per droplet.

29. The method of claim 28, wherein each micron-sized liquid droplet comprises a single nanoparticle.

30. The method of any one of claims 26 to 29, wherein the electrostatic field is provided by interspaced charged plates and the substrate is positioned on the grounded charged plate.

31. The method of claim 30, wherein the charged plates are electrostatically charged insulators or voltage biased conductors.

32. The method of claim 30, wherein the charged plates are patterned to spatially modulate

the electric field and promote nanoparticle deposition at specific locations on the substrate.

33. The method of claim 26, wherein the aerosol flows in a laminar fashion and is spatially engineered to afford nanoparticle deposition at specific locations on the substrate.

34. The method of any one of claims 26 to 33, wherein the substrate has an at least partially conductive surface.

35. The method of any one of claims 26 to 33, wherein the substrate has an at least partially dielectric surface.

36. The method of claim 34 or 35, wherein the substrate has a hydrophilic or hydrophobic surface.

37. The method of claim 36, wherein the substrate has a surface with water contact angle greater than or equal to 80^{o}.

38. The method of claim 37, wherein the water contact angle is between 85^{o}-120^{o}.

39. The method of claim 38, wherein the water contact angle is about 90^{o}.

40. The method of claim 38, wherein the water contact angle is between 117^{o} to 120^{o}.

41. The method of claim 37, wherein the surface is selected from the group consisting of: polyvinylidene chloride and fluorides; polyhexamethylene adipamide (Nylon 66); Nylon 7; poly(dodecano-12-lactam)(Nylon 12); polyamide; cellulose acetate; polysulfone; polymethyl methacrylate; polyvinyl acetate; polycarbonate; polystyrene; polypropylene; polyimide; epoxy; polyethylene terephthalate; silicones; olefins (alkenes); cellulose nitrate; ultra-high-molecular-weight polyethylene; polychloroprene; polyvinyl chloride; latex; butyl rubber; and polytetrafluoroethylene.

42. The method of claim 37, wherein the hydrophobic surface is a poly(4-vinylphenol) based dielectric or a polytetrafluoroethylene based dielectric.

43. The method of any one of claims 26 to 42, wherein the nanoparticle is boron nitride, molybdenum disulfide, tungsten disulfide, a carbon- or phosphorus-based nanoparticle.

44. The method of claim 43, wherein the carbon-based nanoparticle is a nanotube, nanorod, nanosphere, nanoflake, or nanoribbon.

45. The method of any one of claims 26 to 42, wherein the nanoparticle is a single-walled carbon nanotube.

46. A material comprising a surface with a water contact angle of greater than or equal to 80^{o} and at least one nanoparticle adhered onto the surface.

47. The material of claim 46, wherein the water contact angle is between 85^{o}-120^{o}.

48. The material of claim 47, wherein the water contact angle is about 90^{o}.

49. The material of claim 47, wherein the water contact angle is between 117^{o} to 120^{o}.

50. The material of any one of claims 46 to 49, wherein the nanoparticle is boron nitride, molybdenum disulfide, tungsten disulfide, a carbon- or phosphorus-based nanoparticle.

51. The material of claim 43, wherein the carbon-based nanoparticle is a nanotube, nanorod, nanosphere, nanoflake, or nanoribbon.

52. The material of any one of claims 46 to 49, wherein the nanoparticle is a single-walled carbon nanotube.

53. The material of claim 43, wherein a plurality of carbon nanotubes are provided in a network.

54. The material of claim 53, wherein the carbon nanotube network is the channel of a transistor.

55. The material of claim 53 or 54, wherein the carbon nanotubes are single-walled carbon nanotubes.

56. The material of claim 46, wherein the surface is selected from the group consisting of: polyvinylidene chloride and fluorides; polyhexamethylene adipamide (Nylon 66); Nylon 7; poly(dodecano-12-lactam)(Nylon 12); polyamide; cellulose acetate; polysulfone; polymethyl

methacrylate; polyvinyl acetate; polycarbonate; polystyrene; polypropylene; polyimide; epoxy; polyethylene terephthalate; silicones; olefins (alkenes); cellulose nitrate; ultra-high-molecular-weight polyethylene; polychloroprene; polyvinyl chloride; latex; butyl rubber; and polytetrafluoroethylene.

57. The material of any one of claims 46 to 55, wherein the surface is a poly(4-vinylphenol) based dielectric or a polytetrafluoroethylene based dielectric.

58. The material of claim 57, wherein the poly(4-vinylphenol) based dielectric is Xerox™ Dielectric xdi-d1.2.

59. The material of claim 57, wherein the polytetrafluoroethylene based dielectric is Teflon®-AF

60. The material of any one of claims 46 to 55, wherein the surface is a fluoropolymer.

61. The material of claim 60, wherein the fluoropolymer is the amorphous (non-crystalline) fluoropolymer CyTOP.

62. The material of any one of claims 46 to 61 for use in a thin film of nanotubes.

63. The material of claim 62, wherein the thin film of nanotubes is a semiconductor channel in a thin film transistor.

64. The material of any one of claims 46 to 63 for use in a diode, a conductive electrode, photovoltaic cell, a physical sensor or a chemical sensor.

65. The material of claim 64, wherein the conductive electrode is a transparent or non-transparent electrode.

66. A roll-to-roll printing system comprising the apparatus of any one of claims 1 to 21.

67. A material comprising polymers having carbon nanotubes deposited thereon by the apparatus of any one of claims 1 to 21 for use as gate dielectrics in a bottom gate transistor.

68. A material comprising polymers and carbon nanotubes, wherein the polymers and

carbon nanotubes are deposited on a substrate by the apparatus of any one of claims 1 to 21, and wherein the carbon nanotubes are positioned on the polymers for use as a dielectric in a bottom gate transistor.

69. The material of claim 68, wherein the polymers are positioned on the carbon nanotubes for use as a dielectric in a top gate transistor or as an encapsulation layer.

70. The material of any one of claims 67 to 69, wherein the polymers and carbon nanotube networks are simultaneously deposited on the substrate by the apparatus of any one of claims 1 to 21.

71. A material comprising polymers having carbon nanotube networks deposited thereon by the apparatus of any one of claims 1 to 21 for use as gate dielectrics in an air exposed transistor without an encapsulation layer.

72. The material of claim 68, wherein the material has transfer characteristics with hysteresis from 0-1 MV/m.

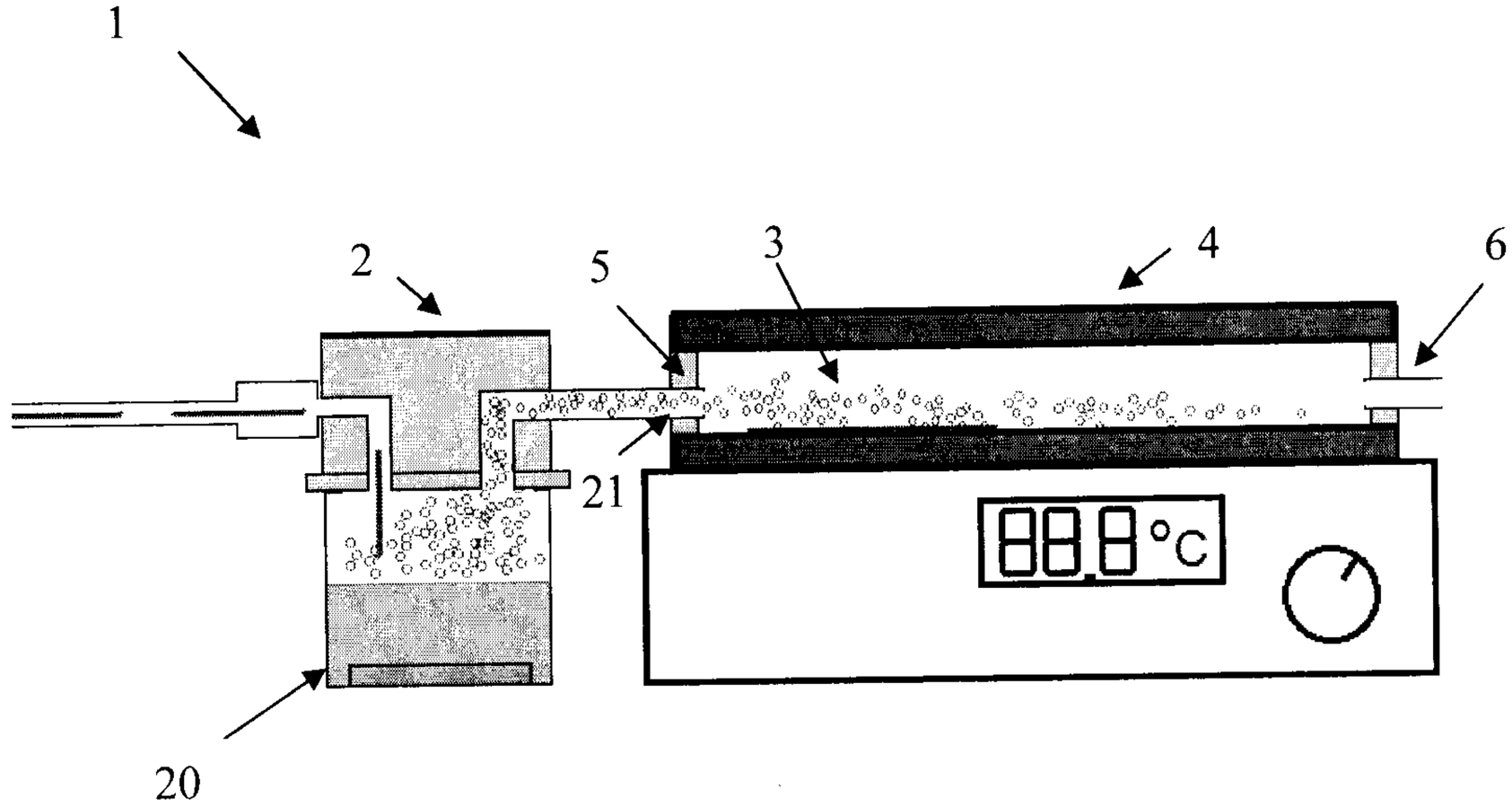


FIG. 1

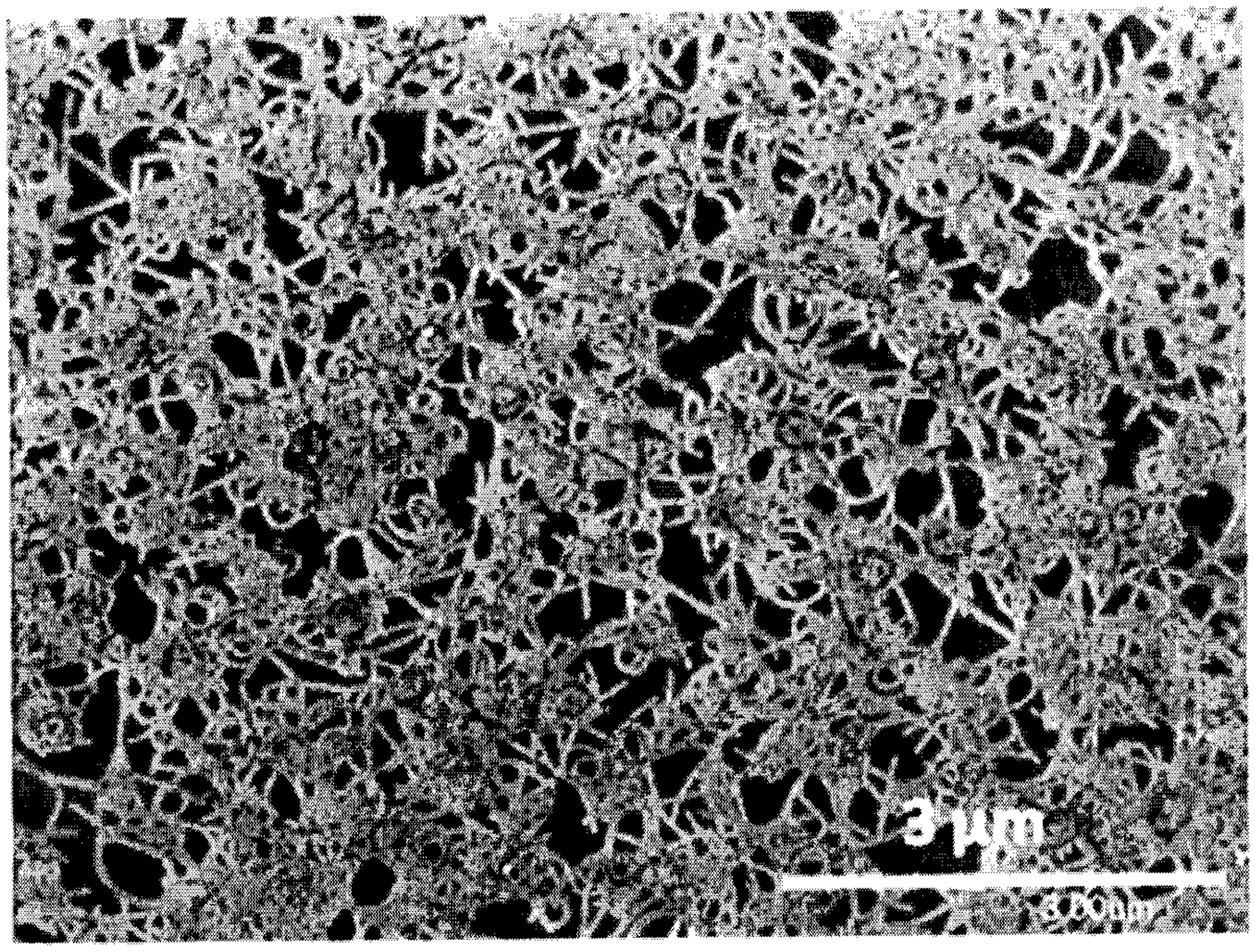


FIG. 2

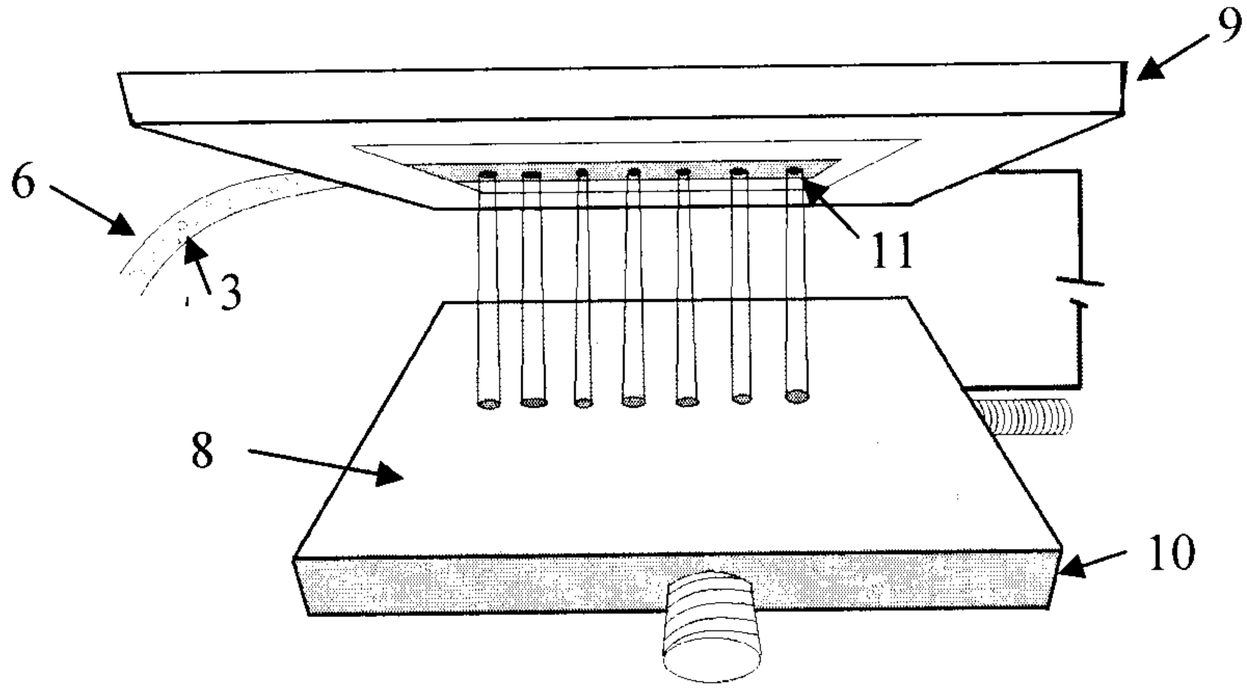
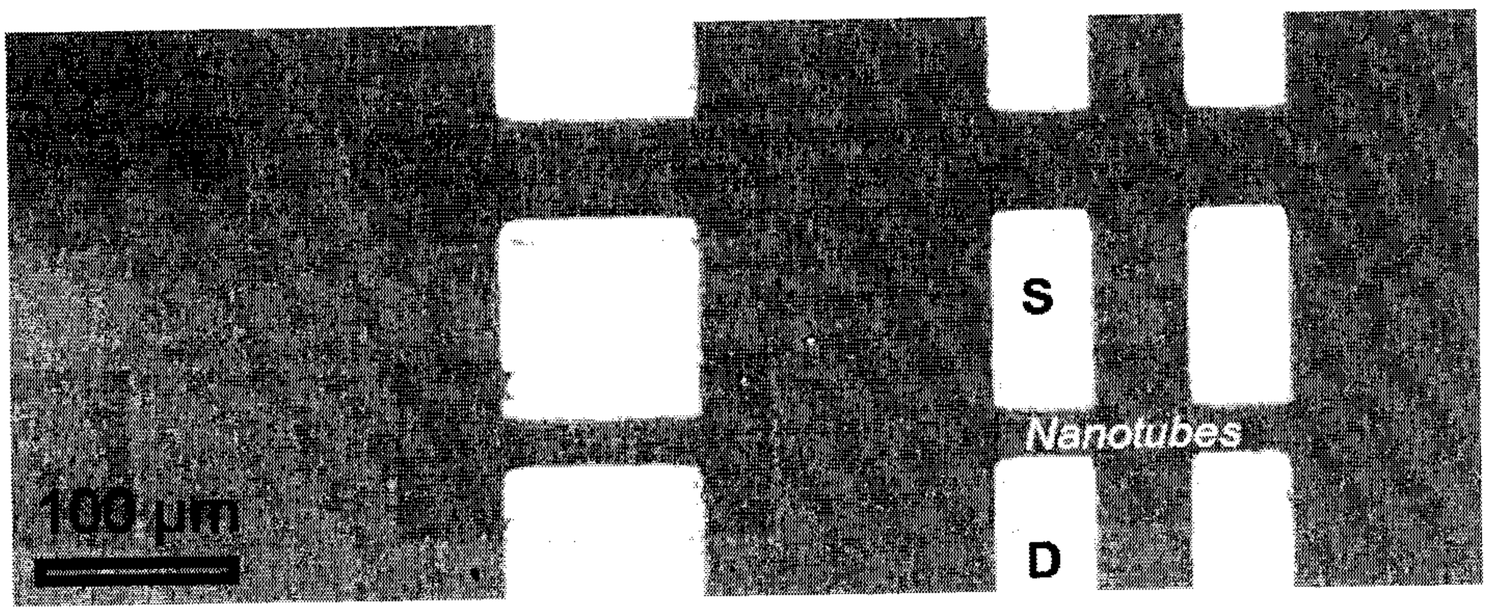


FIG. 3



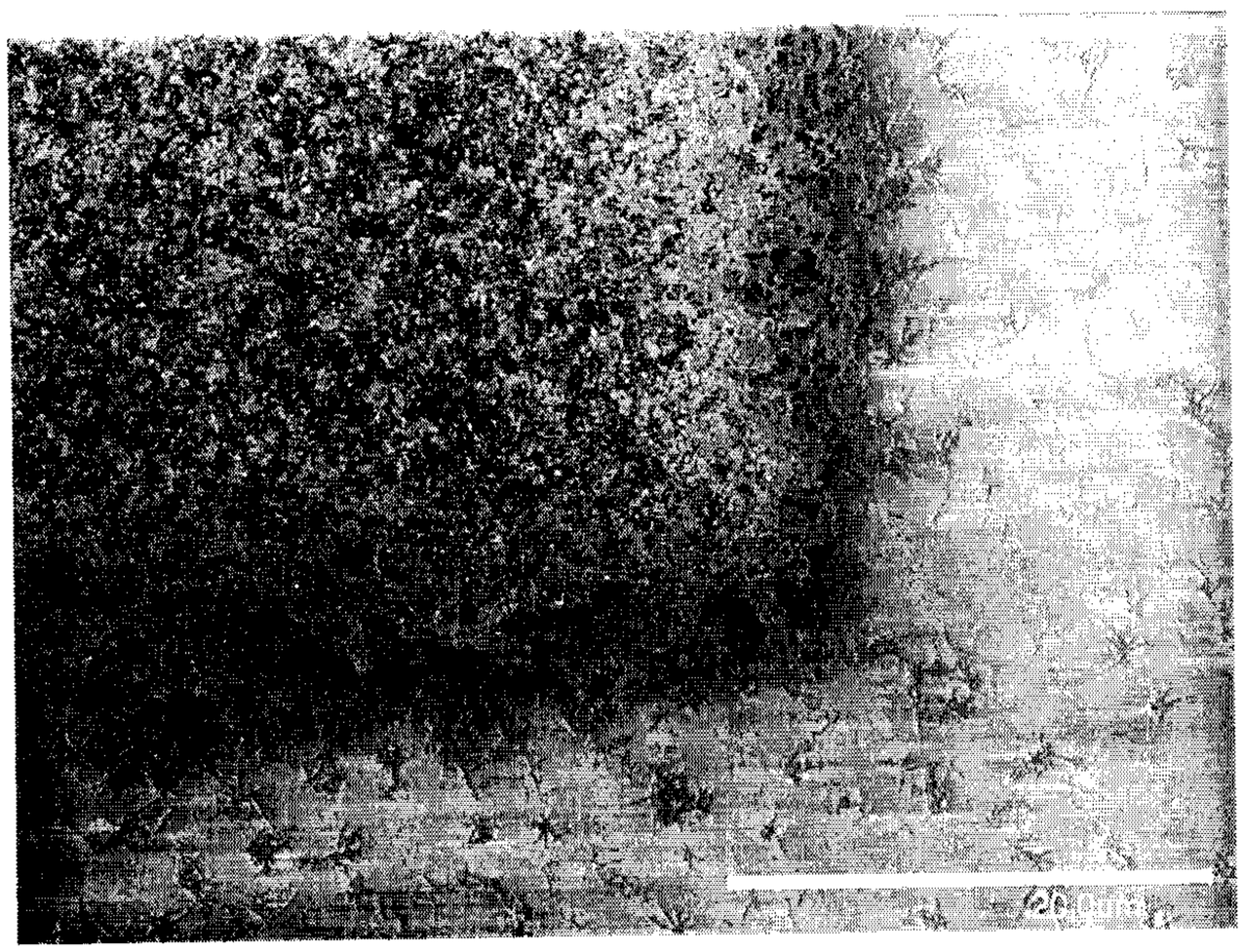
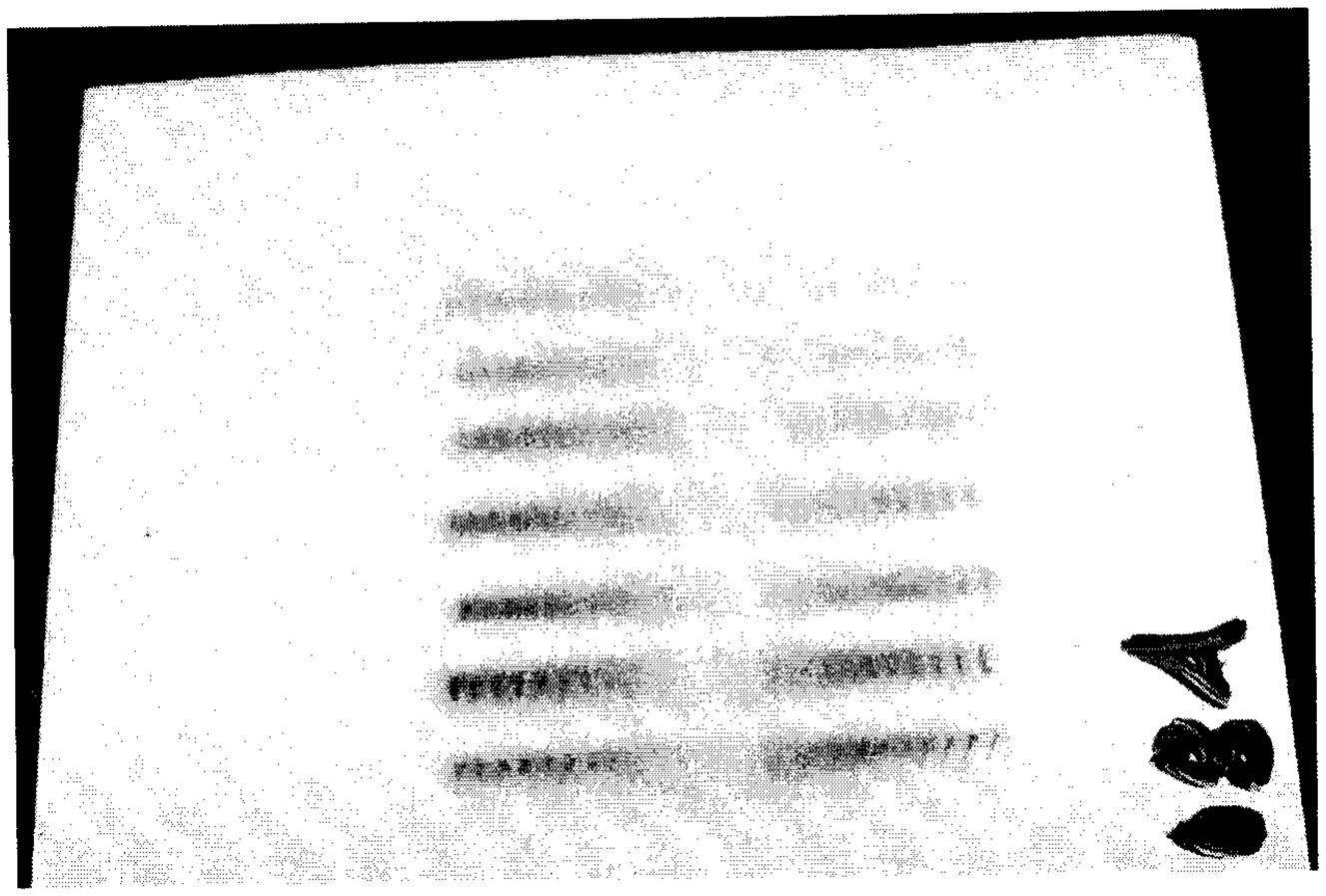


FIG. 4

(a)



(b)

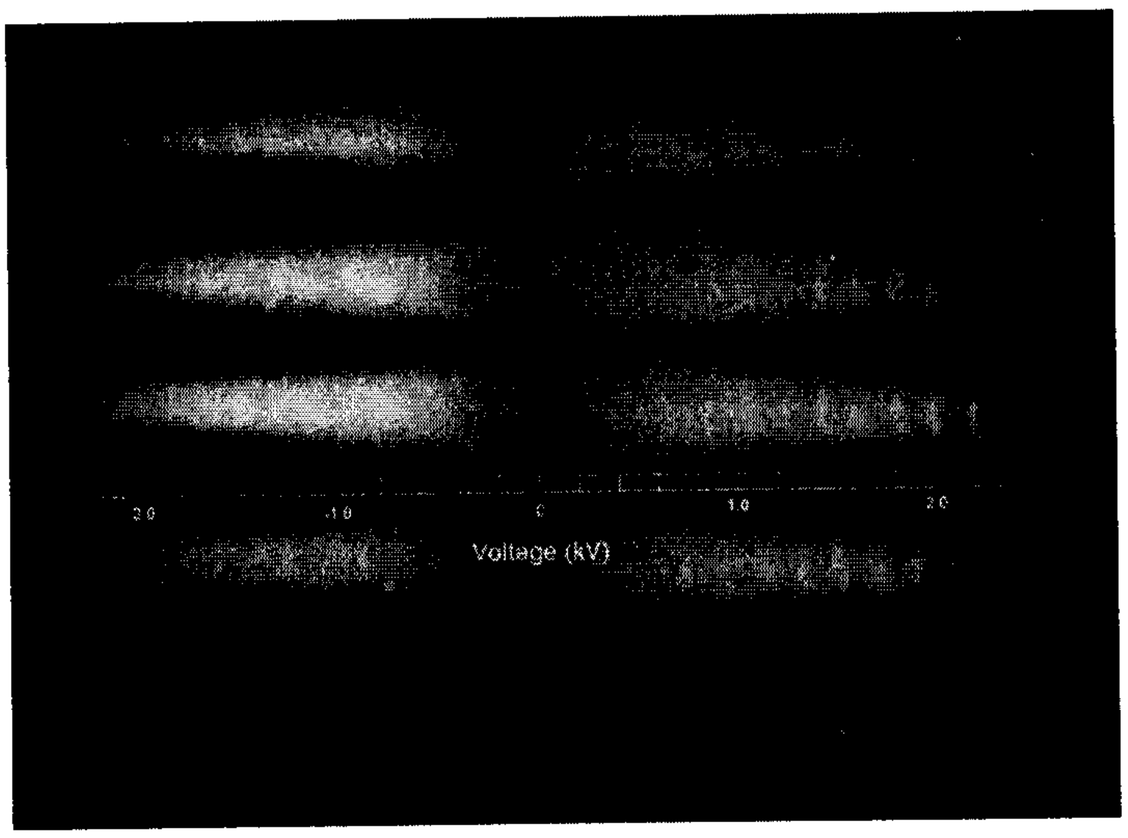


FIG. 5

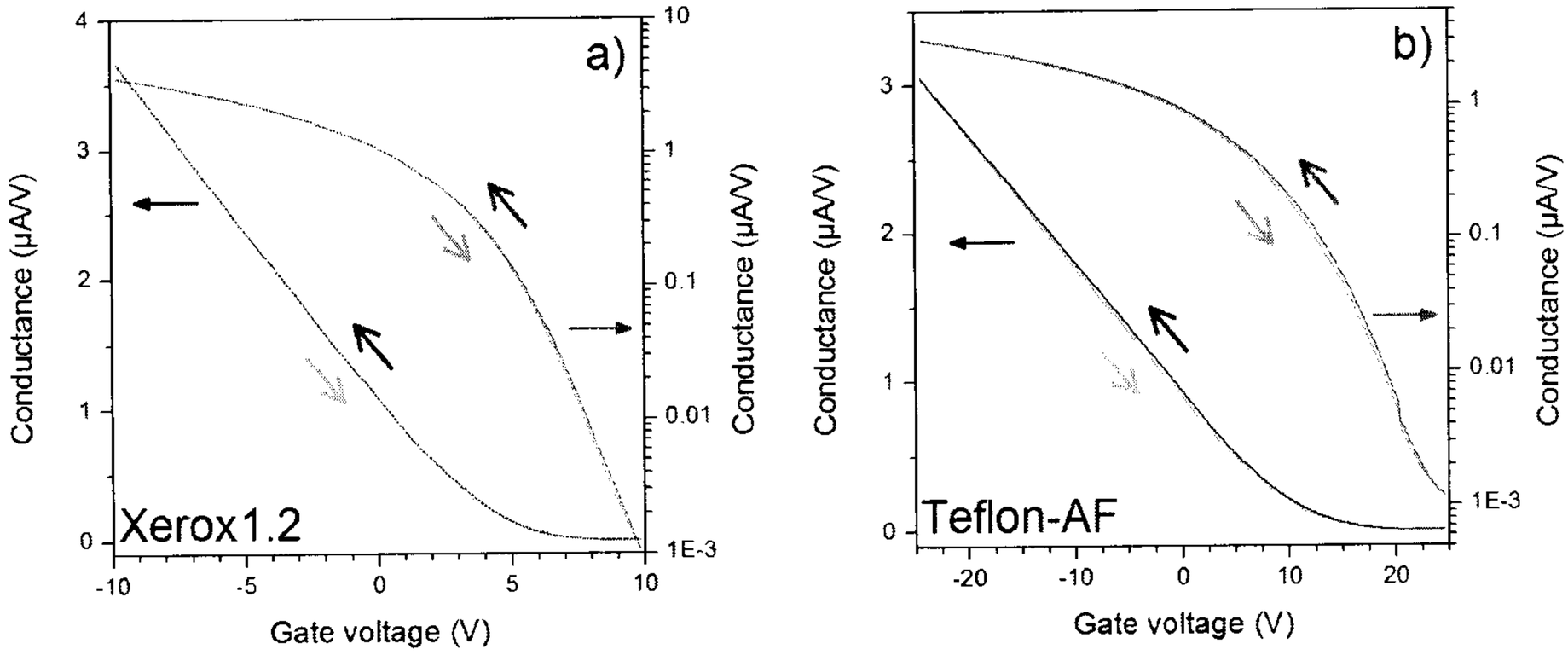

a)
Xerox1.2
Conductance (μA/V)
Conductance (μA/V)
Gate voltage (V)
4
3
2
1
0
10
1
0.1
0.01
1E-3
-10
-5
0
5
10
b)
Teflon-AF
Conductance (μA/V)
Conductance (μA/V)
Gate voltage (V)
3
2
1
0
1
0.1
0.01
1E-3
-20
-10
0
10
20

FIG. 6

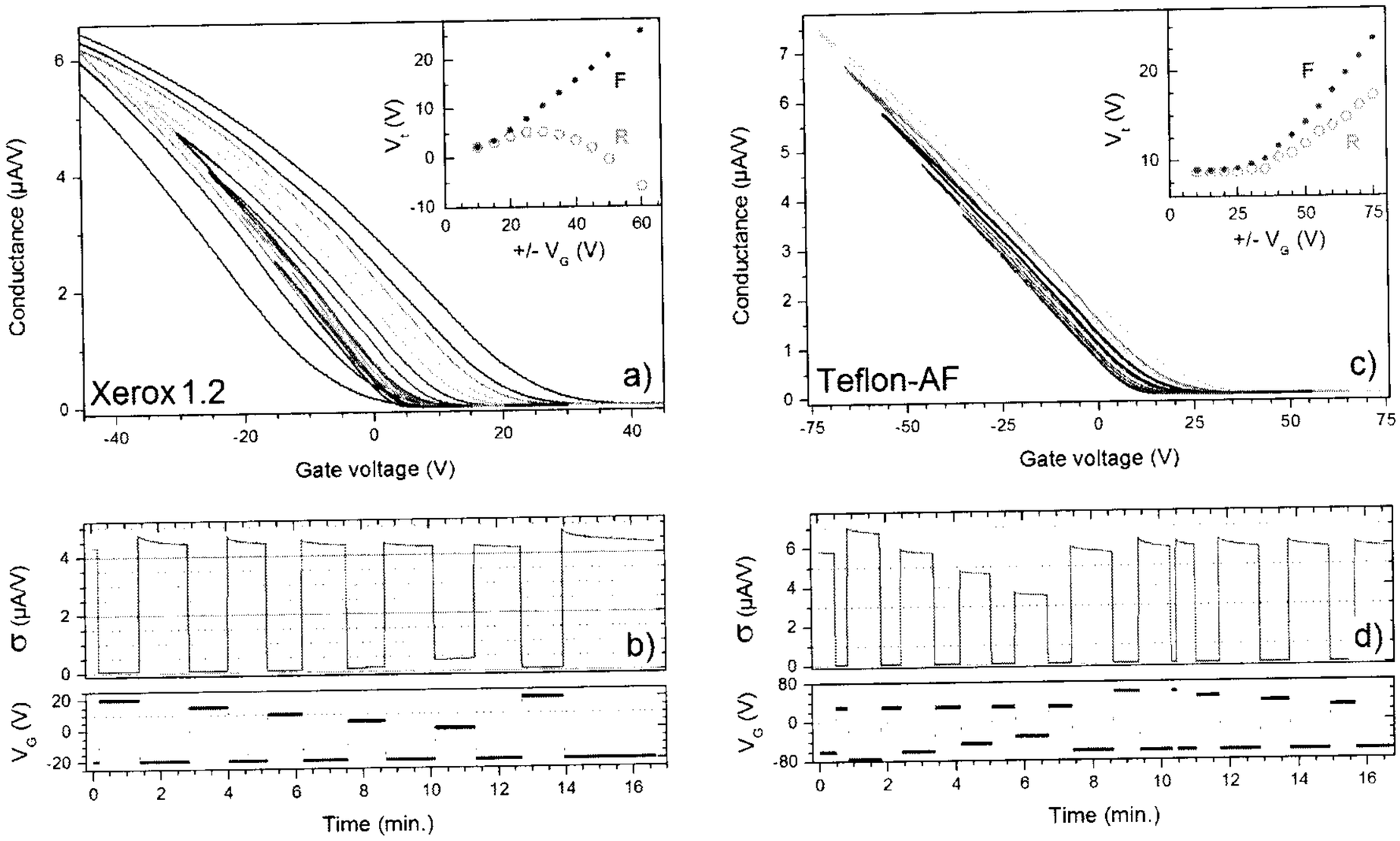

Conductance (μA/V)
Xerox 1.2
a)
V_t (V)
F
R
+/- V_G (V)
Gate voltage (V)
Teflon-AF
c)
σ (μA/V)
b)
d)
V_G (V)
Time (min.)

FIG. 7

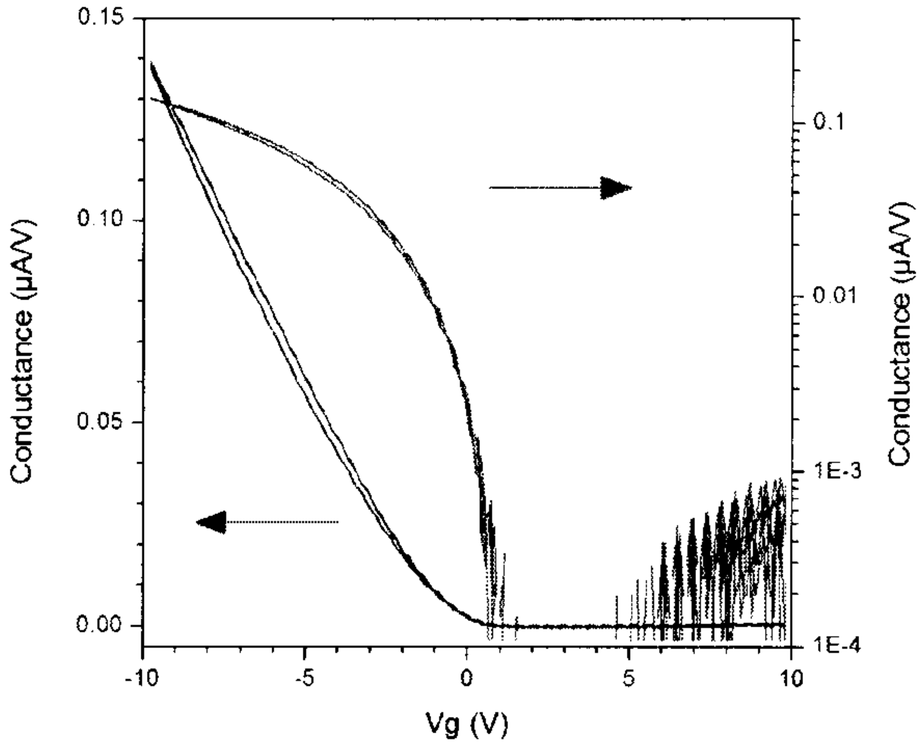
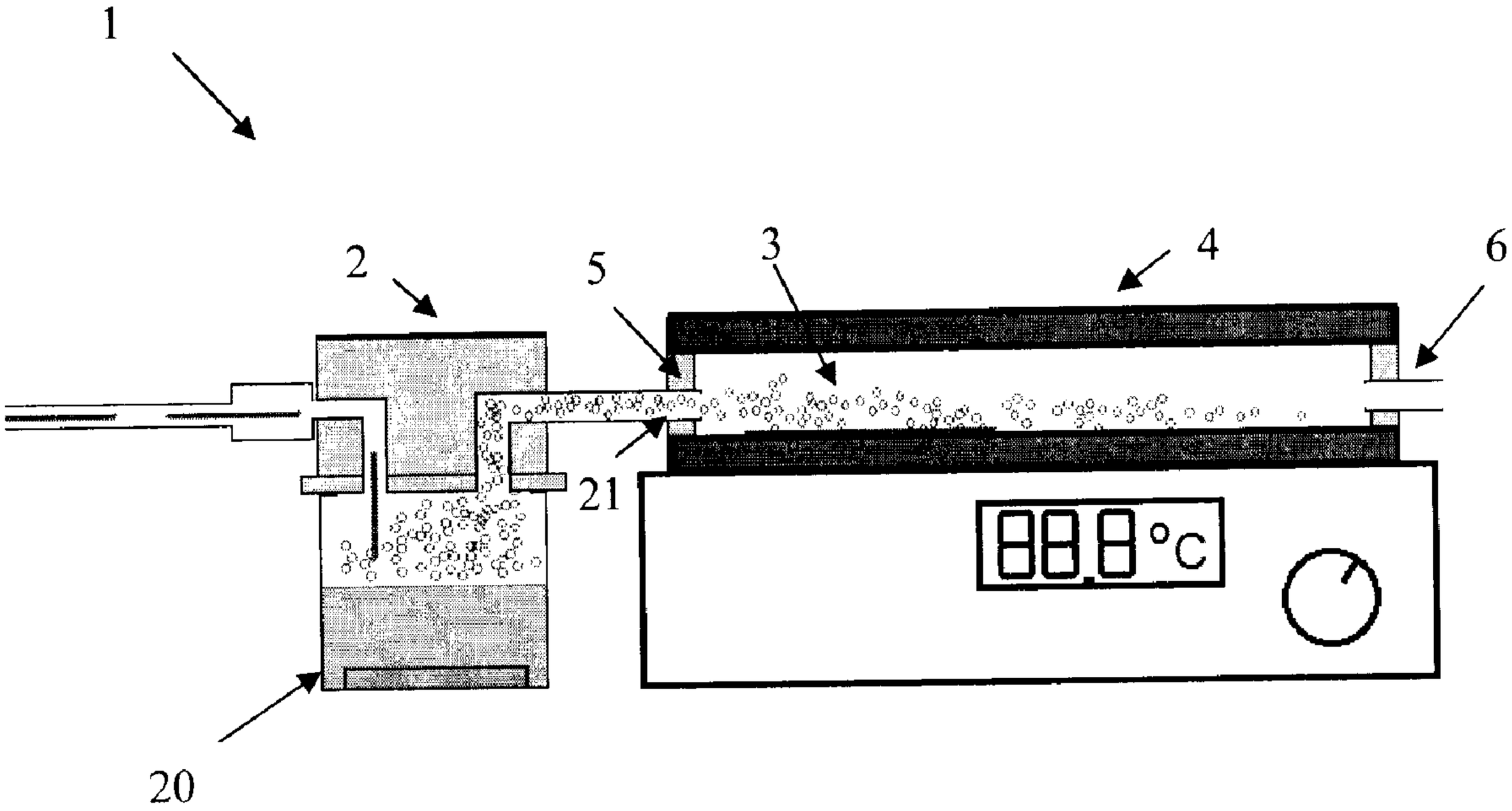

0.15
0.10
0.05
0.00
Conductance (μA/V)
0.1
0.01
1E-3
1E-4
Conductance (μA/V)
-10
-5
0
5
10
Vg (V)

FIG. 8


1
2
3
4
5
6
21
20
88.8°C