

(19) World Intellectual Property Organization
International Bureau



PCT



(43) International Publication Date
8 May 2008 (08.05.2008)

(10) International Publication Number
WO 2008/054549 A2

- (51) **International Patent Classification:**
B05D 5/02 (2006.01)

(21) **International Application Number:**
PCT/US2007/013012

(22) **International Filing Date:** 31 May 2007 (31.05.2007)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
11/444,165 31 May 2006 (31.05.2006) US

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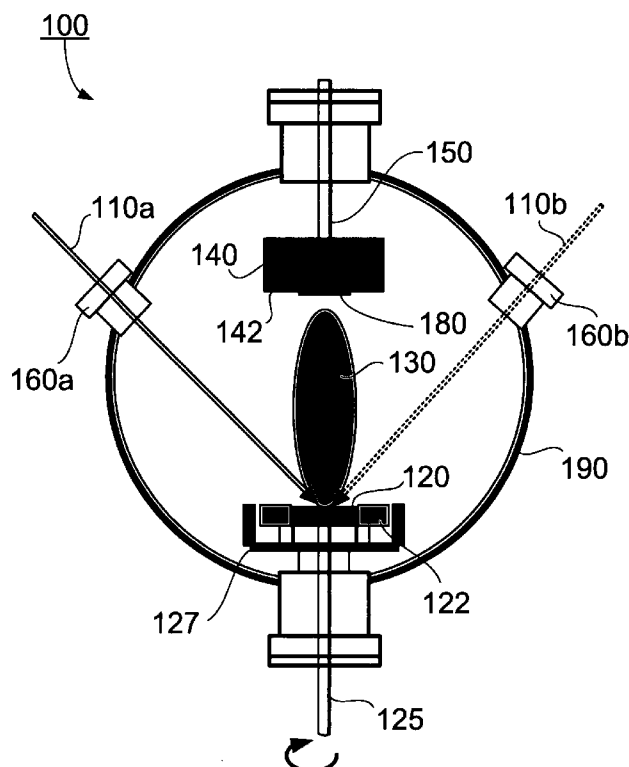
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(81) **Designated States (unless otherwise indicated, for every
kind of national protection available):** AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG,
ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL,
IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK,
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MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL,
PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA,
ZM, ZW.

(84) **Designated States (unless otherwise indicated, for every
kind of regional protection available):** ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL,

[Continued on next page]

- (54) Title:** SOLVENT-ENHANCED WAVELENGTH-SELECTIVE INFRARED LASER VAPOR DEPOSITION OF POLYMERS AND APPLICATIONS OF SAME



(57) Abstract: A method for depositing a conductive polymeric material that has a charge/hole-transport property onto a substrate. In one embodiment, the method comprises the steps of providing a solution having the conductive polymeric material, a first solvent element with a vibrational mode and a second solvent element with a vibrational mode; freezing the solution to form a target; directing light of a wavelength in the infrared region which is resonant with one of the vibrational mode of the first solvent element and the vibrational mode of the second solvent element to vaporize the target; vaporizing the conductive polymeric material in the target with the light without substantially changing the charge/hole-transport property of the conductive polymeric material; and depositing the vaporized conductive polymeric material on the substrate to form a film of the conductive polymeric material..



PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished
upon receipt of that report*

**SOLVENT-ENHANCED WAVELENGTH-SELECTIVE INFRARED LASER
VAPOR DEPOSITION OF POLYMERS AND APPLICATIONS OF SAME**

5 This application is being filed as PCT International Patent application in the name of Vanderbilt University, a U.S. national corporation, Applicant for all countries except the U.S., and **Hee K. Park, Stephen L. Johnson, and Richard F. Haglund, Jr.** each a U.S. resident, Applicants for the designation of the U.S. only, on 31 May 2007.

10 **STATEMENT OF FEDERALLY-SPONSORED RESEARCH**

 The present invention was made with Government support awarded by the Department of Defense Medical Free-Electron Laser Program under Contract No. F49620-01-1-0429. The United States Government may have certain rights to this invention pursuant to this grant.

15

CROSS-REFERENCE TO RELATED PATENT APPLICATION

 This application claims the benefit, pursuant to 35 U.S.C. §119(a), of U.S. patent application Serial No. 11/444,165, filed May 31, 2006, entitled "SOLVENT-
ENHANCED WAVELENGTH-SELECTIVE INFRARED LASER VAPOR
20 DEPOSITION OF POLYMERS AND APPLICATIONS OF SAME," by Hee K. Park, Stephen L. Johnson, and Richard F. Haglund, Jr., which is incorporated herein by reference in its entirety.

 The U.S. patent application Serial No. 11/444,165 is related to a copending U.S. patent application Serial No. 11/337,301, filed January 23, 2006, entitled "Methods and
25 Apparatus for Transferring a Material onto a Substrate Using A Resonant Infrared Pulsed Laser," by Richard Haglund, Jr., Nicole L. Dygert and Kenneth E. Schriver, which is a continuation-in-part of U.S. patent application Serial No. 10/059,978, filed January 29, 2002, now issued as U.S. Patent No. 6,998,156, entitled "Deposition of Thin Films Using an Infrared Laser," by Daniel Bubb, James Horwitz, John Callahan, Richard Haglund, Jr.

and Michael Papantonakis, and which itself claims the benefit, pursuant to 35 U.S.C. §119(e), of U.S. provisional patent application Serial No. 60/714,819, filed September 7, 2005, entitled "A Resonant Infrared Pulsed Laser System for Transferring a Material Onto a Substrate and Applications of Same," by Richard F. Haglund, Jr., Nicole L.

5 Dygert, and Kenneth E. Schriver, the contents of which are incorporated herein in their entireties by reference, respectively. The above-identified copending application has the same assignee as the present invention and at least one common inventor with the present invention.

Some references, which may include patents, patent applications and various
10 publications, are cited and discussed in the description of this invention. The citation and/or discussion of such references is provided merely to clarify the description of the present invention and is not an admission that any such reference is "prior art" to the invention described herein. All references cited and discussed in this specification are incorporated herein by reference in their entireties and to the same extent as if each
15 reference was individually incorporated by reference. In terms of notation, hereinafter, "[n]" represents the nth reference cited in the reference list. For example, [10] represents the 10th reference cited in the reference list, namely, R. F. Haglund, Jr., D. M. Bubb, D. R. Ermer, J. S. Horwitz, E. J. Houser, G. K. Hubler, B. Ivanov, M. R. Papantonakis, B. R. Ringeisen and K. E. Schriver, "Resonant Infrared Laser Materials Processing at High
20 Vibrational Excitation Density: Applications and Mechanisms," in Laser Precision Micro-manufacturing 2003, eds. A. Ostendorf, H. Helvajian, K. Sugioka, Proc. SPIE 5063, 13-23, 2003.

FIELD OF THE INVENTION

25 The present invention generally relates to a laser vaporization deposition and in particular to methods and apparatus of deposition of thin films of one or more materials which utilize one or more solvents and selective laser excitation of a vibrational mode of one or more solvents.

BACKGROUND OF THE INVENTION

Infrared pulsed laser deposition (hereinafter "PLD") was first reported in 1960's but did not emerge as a thin film coating technology at that time for a number of reasons. These include the slow repetition rate of the available lasers, and the lack of
5 commercially available high power lasers. At that time, infrared PLD used infrared laser light of 1.06 μm that was not resonant with any single photon absorption band of the material being deposited. Although PLD developed through the years it was not until late 1980's that ultraviolet PLD became popular with the discovery of complex
superconducting ceramics and the commercial availability of high energy, high repetition
10 rate lasers. Ultraviolet PLD is now a common laboratory technique used for the production of a broad range of thin film materials.

Ultraviolet PLD has been an extremely successful technique for the deposition of thin films of a large variety of complex, multi-component inorganic materials. Ultraviolet PLD has also been applied to the growth of thin polymeric and organic films,
15 with varying degrees of success. It has been shown that polymethyl methacrylate, polytetrafluoroethylene and polyalphanaphthyl styrene undergo rapid depolymerization during ultraviolet laser ablation, with the monomer of each strongly present in the ablation plume. The photochemical modification occurs because the energy of the ultraviolet laser causes the irradiated material to be electronically excited. The geometry
20 of the excited electronic state can be very different from the ground electronic state. Relaxation of the excited state can be to either the ground state of the starting material, or the ground state of a geometrically different material. Deposited films are therefore photochemically modified from the starting material, showing a dramatic reduction in the number average molecular weight. For these polymers, depositing the film at an elevated
25 substrate temperature can increase the molecular weight distribution of the deposited thin film material. On arrival, monomeric material repolymerizes on the heated substrate surface, with degree of repolymerization being determined by the thermal activity of the surface. Therefore, even in some of the most successful cases of ultraviolet PLD, the intense interaction between the target material and laser leads to chemical modification of

the polymer.

An alternative approach to PLD of polymeric materials with ultraviolet lasers is matrix-assisted pulsed laser evaporation (hereinafter "MAPLE"), disclosed in U.S. Pat. No. 6,025,036 and other references, where roughly 0.1-1% of a polymer material to be deposited is dissolved in an appropriate solvent and frozen to form an ablation target. The ultraviolet laser light interacts mostly with the solvent and the guest material is evaporated much more gently than in conventional PLD. While this technique can produce smooth and uniform polymer films, it requires that the polymer of interest be soluble in a non-interacting solvent. Finding a suitable solvent system that is also non-photochemically active is a significant challenge and limits the usefulness of the technique. There are examples where electronic excitation of the solvent/polymer system has been observed to produce undesirable photochemical modification of the polymer, such as reduction in the average weight average molecular weight. An additional disadvantage of the matrix-assisted pulsed laser evaporation is that the deposition rate is about an order of magnitude lower than conventional PLD, which can render matrix-assisted pulsed laser evaporation ineffective for applications that require thick, i.e., greater than about 1 μm , coatings.

Recent published reports show that it is possible to transfer a number of organic and polymeric materials from a bulk sample into a thin film by the way of infrared laser ablation from a target [3-5]. In infrared laser vaporization (IR-LVD), the target contains the material to be deposited in a suitable carrier. Infrared laser radiation, tuned to a weak vibrational resonance of the target, is then focused onto the target under vacuum. The incident radiation is absorbed by the matrix, generating a plume of ablated material that subsequently condenses onto a nearby substrate. IR-LVD differs from the MAPLE process using ultraviolet excimer lasers [6] in two fundamental ways: (1) it does not rely on the use of a strong electronic excitation to initiate the phase change and vaporization of the matrix, and hence does not require the use of volatile organic matrix material; and (2) the IR-LVD process does not produce significant electronic excitation because vaporization is induced by vibrational excitation. Thus IR-LVD avoids the principal

vaporization mechanisms capable of inducing photochemical damage to the target material. Also, because of the greater penetration depth of the IR laser in the matrix material, vaporization and deposition rates are substantially higher than those characteristic of UV-MAPLE.

5 The ability to deposit polymeric materials in the form of a thin film is important for a wide range of uses including electronics, chemical sensors, photonics, analytical chemistry and biological sciences and technologies. An important biomedical application of polymer thin films is for biocompatible polymer thin films on drug particles. The coating serves to both delay and regulate the release of the drug in the body. Two
10 techniques that have been demonstrated in the coating of drug particles include wet chemical technique and a vapor deposition technique. In the wet chemical technique, the coated particle can be more than 50% coating on weight bases. A coating that minimizes the coating to drug weight ratio is desired for obvious reasons. It is also important to control the thickness of the deposited film since control of the dissolution rate governs
15 the rate of drug delivery. While UVPLD has been used to deposit much thinner (on the order of a few hundred Å) coatings on drug particles, the deposition process introduces significant and undesirable chemical modification in the coating material as a consequence of the ultraviolet excitation.

 Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (hereafter
20 “PEDOT:PSS”) is a novel, widely used material in the fabrication of organic light emitting devices (OLEDs) [1, 2]. Its high conductivity and near transparency in thin film form make it a perfect candidate for an anode or hole-transport layer (HTP) in an OLED. The inherent difficulty in its processing, however, has proven to be an obstacle to efficiently manufacturable and reliable devices. An all-vacuum process, which is
25 desirable in the fabrication of any high performance electronic device, is not presently possible due to the current processing methods of PEDOT:PSS, which is usually deposited via a spin-coat technique. It is clear that an alternative deposition process that does not require the exposure of the device to atmosphere during fabrication is highly desirable.

Therefore, a heretofore unaddressed need still exists in the art to address the aforementioned deficiencies and inadequacies.

SUMMARY OF THE INVENTION

5 Among other unique features, the present invention provides, for the first time, a method for depositing PEDOT:PSS onto a substrate other than the spin-coat technique. Furthermore, the present invention provides a method for depositing a conductive polymeric material such as PEDOT:PSS onto a substrate using a solvent having two or more components in connection with laser vaporization.

10 More specifically, the present invention, in one aspect, relates to a method for depositing PEDOT:PSS onto a substrate. In one embodiment, the method includes the steps of providing PEDOT:PSS in water; mixing PEDOT:PSS in water and N-Methyl-2-pyrrolidinone to form a solution; freezing the solution to form a target; directing light of a wavelength in the infrared region which is resonant with a vibrational mode of water or
15 N-Methyl-2-pyrrolidinone to vaporize the target; vaporizing PEDOT:PSS in the target with the light without decomposing the PEDOT:PSS; and depositing the vaporized PEDOT:PSS on the substrate to form a film of PEDOT:PSS thereon in solid form.

 The method further includes the steps of subjecting the target and the substrate to an environment selected from the group consisting of sub-atmospheric, atmospheric and
20 above atmospheric pressure and locating the target and the substrate in the vicinity of each other so that the vaporized PEDOT:PSS from the target can be deposited on the substrate by a movement of the vaporized PEDOT:PSS caused by the vaporizing step, where the temperature of the substrate is such that the vaporized PEDOT:PSS deposited on the substrate becomes solid. The environment is sub-atmospheric pressure and the
25 sub-atmospheric pressure is in the range of about 1×10^{-0} Torr to 1×10^{-6} Torr. The distance between the target and the substrate is in the range of about 1 to 20 cm.

 In one embodiment, the mixing step comprises the step of mixing PEDOT:PSS in water and N-Methyl-2-pyrrolidinone in a container, and the freezing step comprises the step of placing the container with the solution in liquid nitrogen. The step of vaporizing

PEDOT:PSS in the target with the light without decomposing the PEDOT:PSS comprises the step of regulating the light so that the average irradiance or fluence of the light is between a first threshold and a second threshold that is greater than the first threshold. In one embodiment, the first threshold for the average irradiance of the light is about 1 W/cm², and the first threshold for the average fluence of the light is about 1 mJ/cm². The second threshold for the average irradiance of the light is about 100 GW/cm², and the second threshold for the average fluence of the light is about 100 J/cm².

In one embodiment, the solvent has a concentration of N-Methyl-2-pyrrolidinone in the range of about 0.01% to 90% by volume. The PEDOT:PSS in the solution is in the range of about 0.1% to 20% by weight. The thickness of the film of PEDOT:PSS deposited on the substrate is in the range of about 10 Å to 500 microns. The light, in one embodiment, is provided by a tunable pulsed laser in one or more pulses and deposition rate of PEDOT:PSS on the substrate is in the range of about 0.001 to 300 ng/cm²/pulse. In another embodiment, the light is provided by a laser source delivering a stream of pulses of 100 fs to 5 ms duration at a pulse repetition frequency in the range of about 1 Hz to 3 GHz, where the laser is operating in a continuous wave mode.

The vibrational mode is in the infrared region of 1-15 microns, preferably, in the infrared region of 2-10 microns. In one embodiment, the light is resonant with a vibrational mode of water in liquid form or in solid form, and the vibrational mode of water in liquid form is about 3.0 microns and the vibrational mode of water in solid form is about 2.94 microns. In another embodiment, the light is resonant with a vibrational mode of N-Methyl-2-pyrrolidinone, and the vibrational mode of N-Methyl-2-pyrrolidinone is about 3.45 microns.

In another aspect, the present invention relates to a film of PEDOT:PSS made according to the above method, where the film is conductive.

In yet another aspect, the present invention relates to a method for depositing a conductive polymeric material that has a charge/hole-transport property onto a substrate. In one embodiment, the method includes the following steps: at step (a), a solution having the conductive polymeric material, a first solvent element with a vibrational mode

and a second solvent element with a vibrational mode is provided. The conductive polymeric material in one embodiment comprises PEDOT:PSS. The PEDOT:PSS in the solution is in the range of about 0.1% to 20% by weight. The first solvent element has a concentration in the range of about 5% to 95% by volume in the solution, the second solvent element has a concentration in the range of about 1% to 90% by volume in the solution, and the conductive polymeric material is in the range of about 0.1% to 90% by weight in the solution. In one embodiment, the first solvent element comprises a chemically stable solvent, where the chemically stable solvent comprises water. The second solvent element has a solvent that is at least partially soluble in the first solvent element. In one embodiment, the second solvent element includes N-Methyl-2-pyrrolidinone. At step (b), the solution is cooled to form a target. In one embodiment, the providing step comprises the step of mixing the conductive polymeric material, a first solvent element having a vibrational mode and a second solvent element having a vibrational mode in a container, and the cooling step comprises the step of placing the container with the solution in a coolant.

At step (c), light of a wavelength in the infrared region which is resonant with one of the vibrational mode of the first solvent element and the vibrational mode of the second solvent element is directed at the target to vaporize the target. The vibrational mode is in the infrared region of 1-15 microns, preferably, in the infrared region of 2-10 microns. In one embodiment, the light is resonant with a vibrational mode of water in liquid form or in solid form. In another embodiment, the light is resonant with a vibrational mode of N-Methyl-2-pyrrolidinone, and the vibrational mode of N-Methyl-2-pyrrolidinone is about 3.45 microns.

At step (d), the conductive polymeric material in the target is vaporized with the light without substantially changing the charge/hole-transport property of the conductive polymeric material. The vaporizing step includes the step of regulating the light so that the average irradiance or fluence of the light is between a first threshold and a second threshold that is greater than the first threshold. In one embodiment, the first threshold for the average irradiance of the light is about 1 W/cm^2 , and the first threshold for the

average fluence of the light is about 1 mJ/cm^2 . The second threshold for the average irradiance of the light is about 100 GW/cm^2 , and the second threshold for the average fluence of the light is about 100 J/cm^2 . In one embodiment, the light is provided by a tunable pulsed laser in one or more pulses and deposition rate of the conductive

5 polymeric material on the substrate is in the range of about 0.001 to $300 \text{ ng/cm}^2/\text{pulse}$. In another embodiment, the light is provided by a laser source delivering a stream of pulses of 100 fs to 5 ms duration at a pulse repetition frequency in the range of about 1 Hz to 3 GHz . In one embodiment, the laser is operating in a continuous wave mode.

At step (e) the vaporized conductive polymeric material is deposited on the
10 substrate to form a film of the conductive polymeric material, where the thickness of the film of the conductive polymeric material deposited on the substrate is in the range of about $10 \text{ \AA}$ to 500 microns .

Furthermore, the method includes the steps of subjecting the target and the substrate to an environment selected from the group consisting of sub-atmospheric,
15 atmospheric and above atmospheric pressure and locating the target and the substrate in the vicinity of each other so that the vaporized conductive polymeric material from the target can be deposited on the substrate by a movement of the vaporized conductive polymeric material caused by the vaporizing step, wherein the temperature of the substrate is such that the vaporized conductive polymeric material deposited on the
20 substrate becomes solid, where the environment is sub-atmospheric pressure and the sub-atmospheric pressure is in the range of about $1 \times 10^{-0} \text{ Torr}$ to $1 \times 10^{-6} \text{ Torr}$, and the distance between the target and the substrate is in the range of about 1 to 20 cm .

In a further aspect, the present invention relates to a conductive polymeric film made according to steps (a)-(e) of the method as disclosed above.

25 In yet a further aspect, the present invention relates to a method for depositing a conductive polymeric material onto a substrate. In one embodiment, the method comprises the steps of (i) providing a solution having the conductive polymeric material and a plurality of solvent elements, wherein at least a first solvent element has a vibrational mode and at least a second solvent element has a vibrational mode; (ii)

forming a target with the solution; (iii) directing light of a wavelength in the infrared region to vaporize the target; and (iv) depositing the vaporized conductive polymeric material on the substrate to form a film of the conductive polymeric material, where the thickness of the film of the conductive polymeric material deposited on the substrate is in the range of about 10 Å to 500 microns.

The method may further comprise the steps of subjecting the target and the substrate to an environment selected from the group consisting of sub-atmospheric, atmospheric and above atmospheric pressure and locating the target and the substrate in the vicinity of each other so that the vaporized conductive polymeric material from the target can be deposited on the substrate by a movement of the vaporized conductive polymeric material, wherein the temperature of the substrate is such that the vaporized conductive polymeric material deposited on the substrate becomes solid, wherein the environment is sub-atmospheric pressure and the sub-atmospheric pressure is in the range of about 1×10^{-0} Torr to 1×10^{-6} Torr, and the distance between the target and the substrate is in the range of about 1 to 20 cm.

In one embodiment, the conductive polymeric material comprises Poly(3,4-ethylenedioxythiophene) ("PEDOT") or PEDOT:PSS. The first solvent element comprises a material that facilitates the vaporization of the target. In one embodiment, the first solvent element comprises a chemically stable solvent, wherein the chemically stable solvent as an example may comprise water. The second solvent element comprises a photochemical catalyst. In one embodiment, the second solvent element comprises a solvent that is at least partially soluble in the first solvent element, wherein the second solvent element as an example may comprise N-Methyl-2-pyrrolidinone. In one embodiment, the first solvent element has a concentration in the range of about 5% to 95% by volume in the solution, the second solvent element has a concentration in the range of about 1% to 90% by volume in the solution, and the conductive polymeric material is in the range of about 0.1% to 90% by weight in the solution. The PEDOT or PEDOT:PSS in the solution is in the range of about 0.1% to 20% by weight.

The light is resonant with one of the vibrational modes of the plurality of the solvent elements, wherein the vibrational mode is in the infrared region of 1 to 100 microns. In one embodiment, the light is resonant with a vibrational mode of water in liquid form or in solid form. In another embodiment, the light is resonant with a vibrational mode of N-Methyl-2-pyrrolidinone, and the vibrational mode of N-Methyl-2-pyrrolidinone is about 3.45 microns. The light in one embodiment is provided by a tunable pulsed laser in one or more pulses and deposition rate of the conductive polymeric material on the substrate is in the range of about 0.001 to 300 ng/cm²/pulse. In another embodiment, the light is provided by a laser source delivering a stream of pulses of 100 fs to 5 ms duration at a pulse repetition frequency ranging from 1 Hz to 3 GHz. The laser may be operating in a continuous wave mode.

In one aspect, the present invention relates to a conductive polymeric film made according to steps (i)-(iv) of the method as disclosed above.

In another aspect, the present invention relates to an apparatus for depositing a conductive polymeric material onto a substrate, wherein a target is formed with the conductive polymeric material, a first solvent element having a vibrational or electronic absorption mode and a second solvent element having a vibrational or electronic absorption mode.

In one embodiment, the apparatus has a first coherent light source of a wavelength resonant with a vibrational or electronic absorption mode of the first solvent element and the second solvent element. In one embodiment, the coherent light source comprises an infrared laser. The infrared laser is capable of emitting pulses of coherent light with a fluency in a range of about 0.01 to 100 J/cm², where the pulses of coherent light have a pulse duration in a range of about 100 fs to 5 ms at a pulse repetition frequency in a range of about 1 Hz to 3 GHz. The infrared laser is configured such that the pulses of coherent light are delivered in the form of a pulse train in a burst of a micropulse mode lasting microseconds to milliseconds or in the form of a pulse train on a continuous basis. In another embodiment, the infrared laser is capable of emitting coherent light of a continuous wave mode. In one embodiment, the infrared laser comprises a free electron

laser, a CO₂ laser, a tunable Optical Parametric Oscillator (“OPO”) laser system, a tunable Optical Parametric Amplifier (“OPA”) laser system, an N₂ laser, an excimer laser, a Holmium-doped:Yttrium Aluminum Garnet (Ho:YAG) laser, or an Erbium doped: Yttrium Aluminum Garnet (“Er:YAG”) laser.

5 The apparatus further has a second light source of a wavelength resonant with the other vibrational or electronic absorption mode of the first solvent element and a second solvent element. The second light source comprises a laser or a broadband source.

 The apparatus also includes means for directing the first coherent light and the second light at the target to vaporize the target and/or induce a photochemical interaction
10 between the conductive polymeric material and at least one of the first solvent element and the second solvent element so that the vaporized material can be deposited on the substrate.

 These and other aspects of the present invention will become apparent from the following description of the preferred embodiment taken in conjunction with the
15 following drawings, although variations and modifications therein may be affected without departing from the spirit and scope of the novel concepts of the disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

 The patent or application file contains at least one drawing executed in color.
20 Copies of this patent or patent application publication with color drawing(s) will be provided by the Patent and Trademark Office upon request and payment of the necessary fee.

 Fig. 1 shows schematically an apparatus for depositing a conductive polymeric material onto a substrate according to one embodiment of the present invention.

25 Fig. 2 shows schematically an FEL pulse structure that can be used to practice the present invention.

 Fig. 3 shows Fourier-transform infrared (FTIR) spectra for a spin-coated PEDOT:PSS film and a PEDOT: PSS film deposited by infrared laser vaporization according to one embodiment of the present invention.

Fig. 4 shows FTIR spectra for a frozen PEDOT:PSS target and an infrared laser vaporization deposited PEDOT:PSS film according to one embodiment of the present invention.

Fig. 5 shows FTIR spectra for infrared laser vaporization deposited PEDOT:PSS
5 films with different solvents according to embodiments of the present invention.

Fig. 6 shows FTIR spectra for a spin-coated MEH-PPV film and infrared laser vaporization deposited MEH-PPV films with different solvent concentrations according to embodiments of the present invention.

Fig. 7 shows a visible micrograph of a PEDOT:PSS film deposited by IR laser
10 vaporization on a glass substrate according to one embodiment of the present invention.

Fig. 8 shows a scanning electron micrograph of the surface of PEDOT:PSS film deposited by IR laser vaporization on a glass substrate according to one embodiment of the present invention.

Fig. 9 shows scanning electron micrographs of the surface of PEDOT:PSS film
15 deposited by IR laser vaporization with different laser power according to one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is more particularly described in the following examples
20 that are intended as illustrative only since numerous modifications and variations therein will be apparent to those skilled in the art. Various embodiments of the invention are now described in detail. Referring to the drawings, like numbers indicate like parts throughout the views. As used in the description herein and throughout the claims that follow, the meaning of “a,” “an,” and “the” includes plural reference unless the context
25 clearly dictates otherwise. Also, as used in the description herein and throughout the claims that follow, the meaning of “in” includes “in” and “on” unless the context clearly dictates otherwise. Additionally, certain theories are proposed and disclosed herein; however, in no way they, whether they are right or wrong, should limit the scope of the invention. Furthermore, titles or subtitles may be used in the specification for the

convenience of a reader, which shall have no influence on the scope of the present invention.

The description will be made as to the embodiments of the present invention in conjunction with the accompanying drawings of Figs. 1-9. In accordance with the purposes of this invention, as embodied and broadly described herein, this invention, in one aspect, relates to a method of deposition of thin films of materials which utilizes one or more solvents and selective laser excitation of a vibrational mode for producing a vapor of the materials in a vacuum-compatible process that leads to the deposition of smooth films with desired electronic, optical, thermal, physical or chemical properties. The film as formed is suitable for use, for example, in a multi-layer organic or polymer electronic device.

In one embodiment, the method comprises the steps of providing a solution having a conductive polymeric material and a plurality of solvent elements; forming a target with the solution; directing light of a wavelength in the infrared region to vaporize the target; and depositing the vaporized conductive polymeric material on the substrate to form a film of the conductive polymeric material. The film is conductive. The thickness of the film of the conductive polymeric material deposited on the substrate in one embodiment is in the range of about 10 Å to 500 microns.

The conductive polymeric material, in one embodiment, includes Poly(3,4-ethylenedioxythiophene) ("PEDOT") or PEDOT:PSS. PEDOT or PEDOT-PSS is a hole-transport material widely used in organic light-emitting diodes (hereinafter "OLEDs"). Other types of electro-active and optically active polymeric materials can also be utilized to practice the present invention.

The plurality of solvent elements have at least a first solvent element having a vibrational mode and at least a second solvent element having a vibrational mode. The first solvent element includes a material that facilitates the vaporization of the target. In one embodiment, the first solvent element comprises a chemically stable solvent. The chemically stable solvent can be water. The second solvent element comprises a photochemical catalyst. The second solvent element includes a solvent that is at least

partially soluble in the first solvent element. In one embodiment, the second solvent element comprises N-Methyl-2-pyrrolidinone (hereinafter "NMP").

In one embodiment, the first solvent element has a concentration in the range of about 5% to 95% by volume in the solution, the second solvent element has a
5 concentration in the range of about 1% to 90% by volume in the solution, and the conductive polymeric material is in the range of about 0.1% to 90% by weight in the solution.

In one embodiment, the providing step includes the steps of providing PEDOT:PSS in water, and mixing PEDOT:PSS in water and N-Methyl-2-pyrrolidinone
10 to form a solution, which is contained in a container. The PEDOT:PSS in the solution is in the range of about 0.1% to 90% by weight, preferably, in the range of about 0.1% to 20% by weight. Then the container with the solution is placed in liquid nitrogen to form the target in a frozen solid state.

The light is resonant with one of the vibrational modes of the plurality of the
15 solvent elements, where the vibrational mode is in the infrared region of 1 to 100 microns. In one embodiment, the light is resonant with a vibrational mode of water in liquid form or in solid form, and the vibrational mode of water in liquid form is about 3.0 microns and the vibrational mode of water in solid form is about 2.94 microns. In another embodiment, the light is resonant with a vibrational mode of N-Methyl-2-
20 pyrrolidinone, and the vibrational mode of N-Methyl-2-pyrrolidinone is about 3.45 microns.

In one embodiment, the step of directing light of a wavelength in the infrared region to vaporize the target includes the step of regulating the light so that the average irradiance or fluence of the light is between a first threshold and a second threshold that is
25 greater than the first threshold so as to vaporize the conductive polymeric material such as PEDOT or PEDOT:PSS in the target with the light without decomposing the conductive polymeric material. In one embodiment, the first threshold for the average irradiance of the light is about 1 W/cm^2 , and the first threshold for the average fluence of the light is about 1 mJ/cm^2 . The second threshold for the average irradiance of the light

is about 100 GW/cm^2 , and the second threshold for the average fluence of the light is about 100 J/cm^2 .

The light in one embodiment is provided by a tunable pulsed laser in one or more pulses and deposition rate of the conductive polymeric material on the substrate is in the
5 range of about 0.001 to $300 \text{ ng/cm}^2/\text{pulse}$. In another embodiment, the light is provided by a laser source delivering a stream of pulses of 100 fs to 5 ms duration at a pulse repetition frequency ranging from 1 Hz to 3 GHz . The laser may be operating in a continuous wave mode.

The method may further comprise the steps of subjecting the target and the
10 substrate to an environment selected from the group consisting of sub-atmospheric, atmospheric and above atmospheric pressure and locating the target and the substrate in the vicinity of each other so that the vaporized conductive polymeric material from the target can be deposited on the substrate by a movement of the vaporized conductive polymeric material. The temperature of the substrate is such that the vaporized
15 conductive polymeric material deposited on the substrate becomes solid. The environment in one embodiment is sub-atmospheric pressure and the sub-atmospheric pressure is in the range of about $1 \times 10^{-0} \text{ Torr}$ to $1 \times 10^{-6} \text{ Torr}$. The distance between the target and the substrate is in the range of about 1 to 20 cm .

Some of the advantages of the inventive methods over the conventional
20 technologies for organic and polymer film deposition include: (1) the use of one or multiple solvents makes possible separate optimization of the ablation process and the film deposition mechanism; (2) the selectivity in choosing the optimum ablation wavelength opens up flexibility in the choice of the vaporization laser; (3) the LVD process renders unnecessary a separate liquid-phase processing facility that necessarily
25 involves a separate materials and stream; (4) the LVD process is extremely efficient in the use of expensive raw materials, thus reducing the cost of processing; (5) the process is applicable to many different polymers, thus enabling changes or substitutions of materials without expensive process development; and (5) this multiple solvent LVD process makes possible the fabrication of entire electronic, photonic or electro-optic devices —

such as OLED structures or thin-film transistors — in vacuum, thus eliminating a major source of contamination in the manufacture of organic devices and ultimately enhancing product yield.

This technique can be used for a wide range of materials including electro-active
5 and optically active polymeric materials for application ranging from electronics to biological sciences. The technique is general and can be extended to all organic, organometallic, inorganic, and biological materials or combinations of materials, particularly in the form of thin films, and to any material which can be transferred to a substrate by vaporizing a target material by resonantly exciting a vibrational mode of one
10 of the multiple solvents whereby a vapor plume is formed which is deposited typically in the form of a solid thin film on a substrate.

Referring now to Fig. 1, an apparatus 100 for depositing a conductive polymeric material that has a charge/hole-transport property onto a substrate is shown according to one embodiment of the present invention. The apparatus 100 has an infrared laser source
15 (not shown) capable of emitting an infrared laser beam 110a with a wavelength resonant with a vibrational mode of one or more solvents in a target 120. The infrared laser beam 110a tuned to the vibrational mode of one or more solvents is directed at the target 120 through a focusing means 160a to vaporize the target 120 into a laser plume 130. The target 120 is placed in a target well 122 received by a target carousel 127 that is engaged
20 with a rotatable platform 125. The substrate 140 is positioned on a heatable sample stage 150 and has a surface 142 facing opposite to the target 120 such that the laser plume 130 of the vaporized target material is capable of reaching the surface 142 of the substrate 140 by a movement away from the target well 122 and towards the substrate surface 142 which is caused by the vaporization and being deposited thereon. Once the target
25 material or some of the target material is deposited on the surface 142 of the substrate 140 by means of the laser plume 130, it can be thermally cured to form a film 180 of the target material. Curing can be done by the laser beam 110a, in which case the relative position and orientation of the sample stage 150 and the focus means 160a is adjustable so that the laser beam 110 is reachable to the deposited material on the substrate 140.

Curing can also be done by an optional, second light source (not shown), in which case the second light source is positioned such that the light beam 110b from the second light source through a focus means 160b is reachable to the deposited material on the substrate 140. Curing can also be done by heating or by other means such as electrical current
5 heating, in which case one or more electrical resistors are associated with the stage for heating the deposited material. The stage itself can be conductive to function as an electrical heater. The one or more resistors can be placed according to a predetermined pattern to selectively heat the target material deposited on the substrate. The light beam 110b from the optional second light source can be a laser or a broadband light source,
10 which can be in resonant with a vibrational or electronic mode of other solvent(s) in the target to facilitate the vaporization and/or deposition process.

The substrate 140 can be of any solid material that can be vaporized by resonant infrared excitation, including organic, especially polymeric materials, inorganic materials, and biological materials. The substrate 140 can be any material that will
15 accept the vapor as a deposited coating and can include planar or non-planar surfaces as well as particles.

In the embodiment shown in Fig. 1, the apparatus 100 operates in a vacuum chamber 190, where the atmospheric pressure can be adjusted in the range of about 1 Torr to 1×10^{-6} Torr.

20 The apparatus 100 shown in Fig. 1 can be used to deposit a film of a polymeric material, or any other material that can be vaporized by application of infrared energy to the target material. The film as formed is essentially chemically the same as the original target material without having undergone any essential chemical and/or structural modification.

25 A suitable laser light source for resonant infrared pulsed laser deposition is an FEL that is continuously tunable in the mid-infrared range of 2-10 μm or 5,000 to 1,000 cm^{-1} . The present data was collected using an FEL at Vanderbilt University in Nashville, Tennessee. The Vanderbilt FEL laser produces an approximately 4 μs wide macropulse at a repetition rate of 30 Hz, as shown in Fig. 2. The macropulse is made up of

approximately 20,000 1-ps micropulses separated by 350 ps. The energy in each macropulse is on the order of 10 mJ so that the peak unfocused power in each micropulse is very high. The average power of the FEL laser is on the order of 2-3 W. For thin films deposited on a substrate by resonant infrared pulsed laser deposition, as described herein, the fluence is typically between 2 and 3 J/cm² and typical deposition rate is 100 ng/cm²/macropulse although it is in the range of 1 to 300 ng/cm²/pulse. The picosecond pulse structure of the FEL may play a unique and critical role in making possible IR-LVD with low pulse energy but high intensity [10]. Fortunately, it appears that there may be a solution to this problem in the form of tunable, all-solid-state IR laser systems built from commercial components.

Other laser sources, for example, a CO₂ laser, a tunable OPO laser system, a tunable OPA laser system, an N₂ laser, an excimer laser, an Er:YAG laser, an HO:YAG laser, or the like, can also be employed to practice the current invention.

EXAMPLES OF THE INVENTION

Without intent to limit the scope of the invention, additional exemplary methods and their related results according to the embodiments of the present invention are given below. Note that titles or subtitles may be used in the examples for convenience of a reader, which in no way should limit the scope of the invention. Moreover, certain theories are proposed and disclosed herein; however, in no way they, whether they are right or wrong, should limit the scope of the invention so long as data are processed, sampled, converted, or the like according to the invention without regard for any particular theory or scheme of action.

As examples of the process of the present invention, among other things, a one solvent and a two-solvent laser vaporization deposition for the hole-transport polymer PEDOT:PSS were performed. In addition, a luminescent polymer poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) was also successfully deposited according the present invention. The laser vaporization deposition involves dissolving the polymer of interest in one or more solvents, and irradiating the sample with the FEL

tuned to a vibrational band of the one or more solvents to generate a vapor plume. The laser-generated vapor plume impinges on a growth surface, which may be a silicon wafer, glass microscope slide, sodium-chloride plate, transparent conducting electrode, or other suitable substrate. The substrate may be maintained at any desirable temperature, including room temperature (may be desirable for flexible substrates). The samples produced in this way are studied by visible and electron microscopy, spectroscopic ellipsometry, and relevant electrical probes; the properties measured by all these means so far are consistent with transfer of the intact polymers without significant alteration of its electronic properties.

10 *Experimental Procedure:* Referring back to Figs. 1 and 2, a solution having PEDOT:PSS suspended in water (H.C. Stark Co., Berlin,. Germany) was pipetted into an aluminum target well 120 having a diameter of about 4 cm and a depth of about 1 cm and frozen by immersion in liquid nitrogen to form a target 120. The target 120 was then placed in a vacuum chamber 190, oriented vertically as shown in Fig. 1. The target 120 was vaporized by a laser beam 110a through focusing means 160a, wherein the laser beam 110a is from a picosecond, continuously tunable infrared free-electron laser (FEL) operating in the wavelength range of about 2-10 μm [7]. The FEL produces a macropulse 4 μs in duration at a 30 Hz repetition rate; the macropulse comprises some 20,000 1-ps micropulses spaced 350 ps apart, which was shown in Fig. 2. In operation, the laser beam 110a was tuned to a weak vibrational resonance of the target material 120. In the exemplary experiment, the FEL was tuned to a wavelength of about 3 μm , corresponding to the O-H stretching vibration of water/ice. The beam 110a was focused through an IR-transparent BaF₂ window onto the target 120 by a 200-mm focal-length CaF₂ lens. The focal-spot size on the target 120 was approximately 1.5 mm in diameter, and the threshold macropulse energy for observable vaporization and material transfer was 4 mJ. For most of the experimental data reported here, FEL macropulse energies were on the order of 10 mJ, for an average power of 300 mW. The target 120 was rotated as the laser was scanned across its surface to ensure that a fresh spot was addressed with each laser pulse.

For each deposition, the frozen PEDOT:PSS target was exposed for about 3-5 minutes to FEL radiation (5400-9000 macropulses). A collector substrate was positioned parallel to the target surface at a distance of approximately 8 cm in order to collect the vaporized material. The vaporized material reaches the substrate by a movement caused by the radiation and vaporization, which is away from the target surface. The distance is adjustable. For optical and scanning electron microscopy (hereinafter "SEM"), glass collection substrates were used to collect the deposited PEDOT:PSS, while NaCl flats were used as substrates for Fourier transform infrared (hereinafter "FTIR") spectroscopy.

Similar procedures were performed using a solution formed with PEDOT:PSS suspended in water and NMP, which was then frozen to form a target.

FTIR Spectroscopy: Fig. 3 shows FTIR spectra 310 and 320 of a bulk spin-cast PEDOT:PSS film and a laser vaporization deposited PEDOT:PSS film, respectively. Both films were made on NaCl sample plates for subsequent FTIR analysis. The overall shape and individual features (doublet or triplet peak structures, for example) of the two spectra 310 and 320 are very similar, which implies that the local electronic structure of the PEDOT:PSS was preserved during the laser vaporization deposition. Referring to Fig. 4, FTIR spectra 410 and 420 for a frozen PEDOT:PSS target and an infrared laser vaporization deposited (IR-LVD) PEDOT:PSS film are respectively shown. For the IR-LVD PEDOT:PSS film, the laser beam is tuned to a wavelength of about 2.94 μm . FTIR spectra 410 and 420 of the frozen PEDOT:PSS target and the IR-LVD PEDOT:PSS film are essentially identical to each other, which is also virtually identical to p-doped PEDOT:PSS spectra in the literature (not shown).

Referring to Fig. 5, FTIR spectra 510, 520 and 530 were for IR-LVD PEDOT:PSS films produced with a single solvent of water, two solvents of water and ISP in a ratio of 1:1, and two solvents of water and NMP in a ratio of 1:1, respectively. Again, the similarity of the FTIR spectra 510, 520 and 530 was shown among the three IR-LVD PEDOT:PSS films. However, the IR-LVD PEDOT:PSS film produced with the two solvents of water and NMP is conductive, and the other two IR-LVD PEDOT:PSS film is almost non-conductive.

The similarity of the FTIR spectra is a necessary, though not sufficient, indicator that the local structure and bonding of the transferred material is preserved during the IR-LVD process.

Referring to Fig. 6, FTIR spectrum 530 was for a spin-coated MEH-PPV film, FTIR spectrum 520 was an infrared laser vaporization deposited MEH-PPV film with NMP solvent have a concentration of 20% by weight and a laser excitation of a wavelength of about 7.75 μm and energy of 10 mJ, and FTIR spectrum 510 was an infrared laser vaporization deposited MEH-PPV film with NMP solvent have a concentration of 10% by weight and a laser excitation of a wavelength of about 8.25 μm and energy of 5 mJ, respectively.

Table 1: Vibrational Bands of PEDOT:PSS [8]

Vibrational Mode	Wave Number (cm^{-1})	Neat Target
Doping-induced	1303	—
C=C stretch of thiophene ring	1186	Present
Alkylene dioxy-group vibration	1080	—
Doping-induced	1039	Present
Doping-induced	1011	Present
Doping-induced	972	—
C-S stretch of thiophene ring	873	—
C-S stretch of thiophene ring	827	Weak

One indicator of the critical role of sample preparation and the choice of vibrational excitation mode comes from experiments in which the Baytron P solution was placed on a hot plate at 50 C to evaporate waters of hydration, and the dehydrated material was ground into a black powder and pressed into a flat target. Laser vaporization of the neat residual film was attempted at two wavelengths corresponding to the anharmonic stretching modes at 7.63 and 8.43 μm . The macropulse-energy threshold for laser vaporization of this neat target was found to be 12 mJ, a factor of three higher than for the deposition of PEDOT:PSS from the water-ice film. Moreover, at 7.63 μm , the film deposition was spotty and inefficient. There was also evidence of

strong electronic excitation due to vibrational bond-breaking: the vaporized material in the plume luminesced strongly. For the deposition carried out at an FEL wavelength of 8.43 μm , film deposition was ineffective and the morphology of the deposited material was powdery rather than stringy. FTIR spectra of the films deposited from the neat target showed that most of the IR vibrational modes were not present in the deposited material, as listed in Table 1, indicating a loss of local integrity in the electronic structure of the deposited material.

Film Morphology: Both optical and scanning electron micrographs (SEM) were also taken of the IR-LVD PEDOT:PSS films in order to examine morphology and film continuity. Fig. 7 shows an IR-LVD PEDOT:PSS film under 40X magnification in an optical microscope. The wide lines through the center were made by passing a razorblade over the surface in order to demonstrate the continuity of the film. The thickness was not monitored in this experiment, but the deposition rate from similar experiments suggests that for this deposition time, a film of a few hundred nm thick would be a reasonable expectation; experiments are in progress to determine this by spectroscopic ellipsometry and Rutherford backscattering spectrometry. The clear areas were scratches made by a razor blade to demonstrate the density of the deposited film.

Fig. 8 shows an SEM image of a IR-LVD PEDOT:PSS film, where the film seems smooth, but also exhibits signs of larger clusters or particulates of PEDOT:PSS on top of a continuous background. These clusters are believed to be due to the existence of forward directed droplets that are generated in the ablation plume, and which can probably be filtered out by blocking the central portion of the plume of laser vaporized material, a technique that has been used by a number of investigators to mitigate the effects of particulates in laser ablation plumes. The scale bar, 375 nm, indicates that the particulates or clusters have diameters on the scale of tens of nanometers.

Fig. 9 shows SEM images of the surface of PEDOT:PSS film deposited by IR laser vaporization with different laser power: (a) high laser power, (b) medium laser power, and (c) just above threshold.

The present invention, among other things, discloses a novel thin-film deposition process of multi-solvent laser vapor deposition using selective infrared laser excitation, which can be used to deposit thin films of organic and polymeric charge injection, charge-transport and luminescent materials on inorganic and flexible substrates. This technique thus has the potential to eliminate the spin-coating step in current OLED fabrication processes. Moreover, given the fact that MEH-PPV can also be deposited by IR-LVD [9], the present invention allows a cleaner, simpler OLED fabrication process that takes place from start to finish in vacuum. Thus this invention opens the door to a vacuum-phase fabrication process applicable to optical, electronic and electro-optical devices, whereas at present many of these devices are manufactured in a multistep process that involves a combination of liquid-phase and vacuum-phase processing. Since process optimization of all the various layers in all such devices is a key element of the cost, as well as a determining factor in the lifetime and reliability of these devices, the multi-solvent LVD technique has the potential to achieve significant cost reductions and process simplification.

In summary of experiments performed according to the present invention, films of PEDOT:PSS were first successfully formed by resonant infrared laser vapor deposition (LVD) of a target formed by freezing PEDOT:PSS suspended (1-5% by weight) in water in a vacuum environment of about 5 Torr due to a weak pumping system and the high vapor pressure of the frozen PEDOT:PSS target. The morphologies of the films as seen by direct observation and confirmed by SEM were however rough and with large particulates. The Fourier-transform infrared (FTIR) spectra demonstrated that the local bonding structure of the material was preserved.

Additional PEDOT:PSS films grown by LVD were done of a target formed by freezing PEDOT:PSS suspended (1-5% by weight) in water in a vacuum environment of about 3×10^{-3} Torr, approximately three orders of magnitude lower than the previous experiments. One result of this change in pressure was that the frozen target remained frozen longer (lower convection losses). Another was that the deposited films appeared smoother than before as seen by direct observation. And, the FTIR spectra demonstrated

that the resulting material was chemically the same as spin cast PEDOT:PSS.

Spectrometric ellipsometry (SE) was performed on both spin coated PEDOT:PSS films, and the FEL deposited films according to the present invention and gave an indication that the FEL deposited films were not conductive. The modeling used to fit the SE data

5 of the spin cast films assumed film parameters that were metallic in nature, and this same method of fitting would not work at all for the FEL deposited films. The resistivities of the films were measured, and it was found that the spin coated films had little to no conductivity at all.

Further PEDOT:PSS films grown by LVD were done of a target formed by
10 freezing PEDOT:PSS suspended (1-5% by weight) in water with an additional solvent element or a first co-matrix element, namely NMP, mixed at a concentration of 50% by volume. The vacuum pressure during the deposition was again about 3×10^{-3} Torr. The deposited films at about wavelength $3.0 \mu\text{m}$ (water O-H vibrational resonance) appeared very smooth with no surface particulates. Moreover, the films were electrically
15 conductive with resistivities well within acceptable limits. Other depositions with NMP concentrations as low as 5% by volume were also used, and the resulting films were also conductive.

Depositions were also carried out at a wavelength of $3.45 \mu\text{m}$ (NMP resonance) to see if the excitation of the co-matrix component gave the same results, and the
20 experiments suggest that it does. The films also appeared very smooth with no large particulates and were conductive.

Further experiments were done with isopropanol (ISP) as a co-matrix component. Concentrations of the ISP varied from 5-50% by volume. The morphology was again better than films grown using no co-matrix, the conductivity of these films was however
25 poor, suggesting that the mechanism for conductivity in the NMP case might not be due simply to morphology.

Thus, it is understood that in the successful deposition of the conducting polymer PEDOT:PSS by laser vaporization, obtaining smoother films (which reduced the possibility of conduction-reducing grain boundaries) was by itself insufficient. The fact

that the co-matrix NMP or an equivalent seems to be essential regardless of whether the laser excites the O-H water vibration or the C-H NMP vibration indicates that the NMP makes it possible to maintain the essential charge-transport properties of the PEDOT:PSS, even when it is present in only very small concentration. This makes the
5 NMP sound like a catalyst, and it may well be.

At this point, however, it is not clear what the effect of the NMP, or a like material is. It could be chemical, thermal or electrical, or a combination of all of those effects, or even a combination of one or more of these with the direct interaction of the IR laser light. But at least it is a material that is at least partially soluble in the other co-
10 matrix component such as water.

Thus, in the case of a single (possibly tunable) laser to drive the vaporization process, the present invention may be practiced by use of one element of a co-matrix (or a multi-components matrix) to elicit a secondary property through interaction with the solute, while using the other component(s) to optimize the ablation yield. For examples,
15 co-matrix component A acts as a photochemical catalyst to induce a change in the solute while co-matrix component B helps to optimize the ablation process by preventing the formation of condensates in the ablation plume. Alternatively, co-matrix component A undergoes a chemical reaction with the solvent to exchange one chemical functionality for another that is needed in the electronic properties of the deposited film; again, co-
20 matrix component B may be chosen to optimize the laser vaporization characteristics. Additionally, if the solute for reasons either of manufacturing or storage convenience is dissolved in co-matrix component A, the component A is not desirable in the final thin film, then one may use co-matrix component B to interact with component A during the ablation process to render it more volatile so that it is pumped away before the solute
25 arrives at the growth surface.

Moreover, in the case of a tunable ablation laser in conjunction with a second light source (laser or broadband lamp source), the present invention may be practiced by inducing a photochemical interaction between co-matrix component A and the solute while using co-matrix component B to facilitate the ablation process. For example, if it is

desired to have a solute bound to a functional group A in the final thin-film product, but the solute must be processed in another solvent B. The co-matrix component B is then targeted by the vaporization process, while component A reacts with the solute to produce the desired final product.

5 These and other embodiments that can be developed, are based on a theory that the ablation plume as a spatially and temporally delimited reaction volume, which if properly controlled by the use of two or more components in the solvent *and* by the proper choice of laser vaporization protocol, can be used to produce a vapor of some desired material that is then deposited on the substrate.

10 The foregoing description of the exemplary embodiments of the invention has been presented only for the purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise forms disclosed. Many modifications and variations are possible in light of the above teaching.

 The embodiments were chosen and described in order to explain the principles of
15 the invention and their practical application so as to enable others skilled in the art to utilize the invention and various embodiments and with various modifications as are suited to the particular use contemplated. Alternative embodiments will become apparent to those skilled in the art to which the present invention pertains without departing from its spirit and scope. Accordingly, the scope of the present invention is defined by the
20 appended claims rather than the foregoing description and the exemplary embodiments described therein.

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CLAIMS

What is claimed is:

1. A method for depositing Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) ("PEDOT:PSS") onto a substrate, comprising the steps of:
 - a. providing PEDOT:PSS in water;
 - b. mixing PEDOT:PSS in water and N-Methyl-2-pyrrolidinone to form a solution;
 - c. freezing the solution to form a target;
 - d. directing light of a wavelength in the infrared region which is resonant with a vibrational mode of water or N-Methyl-2-pyrrolidinone to vaporize the target;
 - e. vaporizing PEDOT:PSS in the target with the light without decomposing the PEDOT:PSS; and
 - f. depositing the vaporized PEDOT:PSS on the substrate to form a film of PEDOT:PSS thereon in solid form.
2. The method of claim 1, wherein the solvent has a concentration of N-Methyl-2-pyrrolidinone in the range of about 0.01% to 90% by volume.
3. The method of claim 1, wherein the PEDOT:PSS in the solution is in the range of about 0.1% to 20% by weight.
4. The method of claim 1, wherein the mixing step comprises the step of mixing PEDOT:PSS in water and N-Methyl-2-pyrrolidinone in a container, and the freezing step comprises the step of placing the container with the solution in liquid nitrogen.

5. The method of claim 1, wherein the vibrational mode is in the infrared region of 1-15 microns.
6. The method of claim 1, wherein the vibrational mode is in the infrared region of 2-10 microns.
7. The method of claim 1, wherein the light is resonant with a vibrational mode of water in liquid form or in solid form, and the vibrational mode of water in liquid form is about 3 microns and the vibrational mode of water in solid form is about 3.1 microns.
8. The method of claim 1, wherein the light is resonant with a vibrational mode of N-Methyl-2-pyrrolidinone, and the vibrational mode of N-Methyl-2-pyrrolidinone is about 3.45 microns.
9. The method of claim 1, further comprising the steps of subjecting the target and the substrate to an environment selected from the group consisting of sub-atmospheric, atmospheric and above atmospheric pressure and locating the target and the substrate in the vicinity of each other so that the vaporized PEDOT:PSS from the target can be deposited on the substrate by a movement of the vaporized PEDOT:PSS caused by the vaporizing step, wherein the temperature of the substrate is such that the vaporized PEDOT:PSS deposited on the substrate becomes solid.
10. The method of claim 9, wherein the environment is sub-atmospheric pressure and the sub-atmospheric pressure is in the range of about 1×10^{-0} Torr to 1×10^{-6} Torr.
11. The method of claim 9, wherein the distance between the target and the substrate is in the range of about 1 to 20 cm.

12. The method of claim 1, wherein the thickness of the film of PEDOT:PSS deposited on the substrate is in the range of about 10 Å to 500 microns.
13. The method of claim 1, wherein the light is provided by a tunable pulsed laser in one or more pulses and deposition rate of PEDOT:PSS on the substrate is in the range of about 0.001 to 300 ng/cm²/pulse.
14. The method of claim 1, wherein the light is provided by a laser source delivering a stream of pulses of 100 fs to 5 ms duration at a pulse repetition frequency in the range of about 1 Hz to 3 GHz.
15. The method of claim 14, wherein the laser is operating in a continuous wave mode.
16. The method of claim 1, wherein the step of vaporizing PEDOT:PSS in the target with the light without decomposing the PEDOT:PSS comprises the step of regulating the light so that the average irradiance or fluence of the light is between a first threshold and a second threshold that is greater than the first threshold.
17. The method of claim 16, wherein the first threshold for the average irradiance of the light is about 1 W/cm², and the first threshold for the average fluence of the light is about 1 mJ/cm².
18. The method of claim 16, wherein the second threshold for the average irradiance of the light is about 100 GW/cm², and the second threshold for the average fluence of the light is about 100 J/cm².
19. A film made according to the method of claim 1.

20. The film of claim 19 being conductive.
21. A method for depositing a conductive polymeric material that has a charge/hole-transport property onto a substrate, comprising the steps of:
 - a. providing a solution having the conductive polymeric material, a first solvent element with a vibrational mode and a second solvent element with a vibrational mode;
 - b. cooling the solution to form a target;
 - c. directing light of a wavelength in the infrared region which is resonant with one of the vibrational mode of the first solvent element and the vibrational mode of the second solvent element to vaporize the target;
 - d. vaporizing the conductive polymeric material in the target with the light without substantially changing the charge/hole-transport property of the conductive polymeric material; and
 - e. depositing the vaporized conductive polymeric material on the substrate to form a film of the conductive polymeric material.
22. The method of claim 21, wherein the first solvent element comprises a chemically stable solvent.
23. The method of claim 22, wherein the chemically stable solvent comprises water.
24. The method of claim 23, wherein the light is resonant with a vibrational mode of water in liquid form or in solid form.
25. The method of claim 21, wherein the second solvent element comprises a solvent that is at least partially soluble in the first solvent element and has a vibrational mode that may be different from that of the first solvent element.

26. The method of claim 25, wherein the second solvent element comprises N-Methyl-2-pyrrolidinone.
27. The method of claim 26, wherein the light is resonant with a vibrational mode of N-Methyl-2-pyrrolidinone, and the vibrational mode of N-Methyl-2-pyrrolidinone is about 3.45 microns.
28. The method of claim 21, wherein the first solvent element has a concentration in the range of about 5% to 95% by volume in the solution, the second solvent element has a concentration in the range of about 1% to 90% by volume in the solution, and the conductive polymeric material is in the range of about 0.1% to 90% by weight in the solution.
29. The method of claim 28, wherein the conductive polymeric material comprises Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) ("PEDOT:PSS").
30. The method of claim 29, wherein the PEDOT:PSS in the solution is in the range of about 0.1% to 20% by weight.
31. The method of claim 21, wherein the providing step comprises the step of mixing the conductive polymeric material, a first solvent element with a vibrational mode and a second solvent element with a vibrational mode in a container, and the cooling step comprises the step of placing the container with the solution in a coolant.
32. The method of claim 21, wherein the vibrational mode is in the infrared region of 1-15 microns.

33. The method of claim 21, wherein the vibrational mode is in the infrared region of 2-10 microns.
34. The method of claim 21, further comprising the steps of subjecting the target and the substrate to an environment selected from the group consisting of sub-atmospheric, atmospheric and above atmospheric pressure and locating the target and the substrate in the vicinity of each other so that the vaporized conductive polymeric material from the target can be deposited on the substrate by a movement of the vaporized conductive polymeric material caused by the vaporizing step, wherein the temperature of the substrate is such that the vaporized conductive polymeric material deposited on the substrate becomes solid.
35. The method of claim 34, wherein the environment is sub-atmospheric pressure and the sub-atmospheric pressure is in the range of about 1×10^{-0} Torr to 1×10^{-6} Torr.
36. The method of claim 34, wherein the distance between the target and the substrate is in the range of about 1 to 20 cm.
37. The method of claim 21, wherein the thickness of the film of the conductive polymeric material deposited on the substrate is in the range of about 10 Å to 500 microns.
38. The method of claim 21, wherein the light is provided by a tunable pulsed laser in one or more pulses and deposition rate of the conductive polymeric material on the substrate is in the range of about 0.001 to 300 ng/cm²/pulse.

39. The method of claim 21, wherein the light is provided by a laser source delivering a stream of pulses of 100 fs to 5 ms duration at a pulse repetition frequency in the range of about 1 Hz to 3 GHz.
40. The method of claim 39, wherein the laser is operating in a continuous wave mode.
41. The method of claim 21, wherein the step of vaporizing the conductive polymeric material in the target with the light comprises the step of regulating the light so that the average irradiance or fluence of the light is between a first threshold and a second threshold that is greater than the first threshold.
42. The method of claim 41, wherein the first threshold for the average irradiance of the light is about 1 W/cm^2 , and the first threshold for the average fluence of the light is about 1 mJ/cm^2 .
43. The method of claim 41, wherein the second threshold for the average irradiance of the light is about 100 GW/cm^2 , and the second threshold for the average fluence of the light is about 100 J/cm^2 .
44. A conductive polymeric film made according to the method of claim 21.
45. A method for depositing a conductive polymeric material onto a substrate, comprising the steps of:
 - a. providing a solution having the conductive polymeric material and a plurality of solvent elements, wherein at least a first solvent element has a vibrational mode and at least a second solvent element has a vibrational mode;
 - b. forming a target with the solution;

- c. directing light of a wavelength in the infrared region to vaporize the target;
and
 - d. depositing the vaporized conductive polymeric material on the substrate to form a film of the conductive polymeric material.
46. The method of claim 45, wherein the first solvent element comprises a chemically stable solvent.
47. The method of claim 46, wherein the chemically stable solvent comprises water.
48. The method of claim 47, wherein the light is resonant with a vibrational mode of water in liquid form or in solid form.
49. The method of claim 45, wherein the second solvent element comprises a solvent that is at least partially soluble in the first solvent element and has a vibrational mode that may be different from that of the first solvent element.
50. The method of claim 49, wherein the second solvent element comprises N-Methyl-2-pyrrolidinone.
51. The method of claim 50, wherein the light is resonant with a vibrational mode of N-Methyl-2-pyrrolidinone, and the vibrational mode of N-Methyl-2-pyrrolidinone is about 3.45 microns.
52. The method of claim 45, wherein the first solvent element has a concentration in the range of about 5% to 95% by volume in the solution, the second solvent element has a concentration in the range of about 1% to 90% by volume in the solution, and the conductive polymeric material is in the range of about 0.1% to 90% by weight in the solution.

53. The method of claim 52, wherein the first solvent element comprises a material that facilitates the vaporization of the target.
54. The method of claim 52, wherein the second solvent element comprises a photochemical catalyst.
55. The method of claim 52, wherein the conductive polymeric material comprises Poly(3,4-ethylenedioxythiophene) ("PEDOT") or Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) ("PEDOT:PSS").
56. The method of claim 53, wherein the PEDOT:PSS in the solution is in the range of about 0.1% to 20% by weight.
57. The method of claim 45, wherein the light is resonant with one of the vibrational modes of the plurality of the solvent elements.
58. The method of claim 57, wherein the vibrational mode is in the infrared region of 1 to 100 microns.
59. The method of claim 45, further comprising the steps of subjecting the target and the substrate to an environment selected from the group consisting of sub-atmospheric, atmospheric and above atmospheric pressure and locating the target and the substrate in the vicinity of each other so that the vaporized conductive polymeric material from the target can be deposited on the substrate by a movement of the vaporized conductive polymeric material, wherein the temperature of the substrate is such that the vaporized conductive polymeric material deposited on the substrate becomes solid.

60. The method of claim 59, wherein the environment is sub-atmospheric pressure and the sub-atmospheric pressure is in the range of about 1×10^{-0} Torr to 1×10^{-6} Torr.
61. The method of claim 59, wherein the distance between the target and the substrate is in the range of about 1 to 20 cm.
62. The method of claim 45, wherein the thickness of the film of the conductive polymeric material deposited on the substrate is in the range of about 10 Å to 500 microns.
63. The method of claim 45, wherein the light is provided by a tunable pulsed laser in one or more pulses and deposition rate of the conductive polymeric material on the substrate is in the range of about 0.001 to 300 ng/cm²/pulse.
64. The method of claim 45, wherein the light is provided by a laser source delivering a stream of pulses of 100 fs to 5 ms duration at a pulse repetition frequency ranging from 1 Hz to 3 GHz.
65. The method of claim 64, wherein the laser is operating in a continuous wave mode.
66. A conductive polymeric film made according to the method of claim 45.
67. An apparatus for depositing a conductive polymeric material onto a substrate, wherein a target is formed with the conductive polymeric material, a first solvent element having a vibrational or electronic absorption mode and a second solvent element having a vibrational or electronic absorption mode, comprising:

- a. a first coherent light source of a wavelength resonant with a vibrational or electronic absorption mode of the first solvent element and a second solvent element;
 - b. a second light source of a wavelength resonant with the other vibrational or electronic absorption mode of the first solvent element and a second solvent element; and
 - c. means for directing the first coherent light and the second light at the target to vaporize the target and/or induce a photochemical interaction between the conductive polymeric material and at least one of the first solvent element and the second solvent element so that the vaporized material can be deposited on the substrate.
68. The apparatus of claim 67, wherein the coherent light source comprises an infrared laser.
69. The apparatus of claim 68, wherein the infrared laser is capable of emitting pulses of coherent light with a fluency in a range of about 0.01 to 100 J/cm².
70. The apparatus of claim 69, wherein the pulses of coherent light have a pulse duration in a range of about 100 fs to 5 ms at a pulse repetition frequency in a range of about 1 Hz to 3 GHz.
71. The apparatus of claim 70, wherein the infrared laser is configured such that the pulses of coherent light are delivered in the form of a pulse train in a burst of a micropulse mode lasting microseconds to milliseconds.
72. The apparatus of claim 71, wherein the infrared laser is configured such that the pulses of coherent light are delivered in the form of a pulse train on a continuous basis.

73. The apparatus of claim 70, where the infrared laser is capable of emitting coherent light of a continuous wave mode.
74. The apparatus of claim 70, where the infrared laser comprises a free electron laser, a CO₂ laser, a tunable Optical Parametric Oscillator (“OPO”) laser system, a tunable Optical Parametric Amplifier (“OPA”) laser system, an N₂ laser, an excimer laser, a Holmium-doped:Yttrium Aluminum Garnet (Ho:YAG) laser, or an Erbium doped: Yttrium Aluminum Garnet (“Er:YAG”) laser.
75. The apparatus of claim 68, wherein the second light source comprises a laser or a broadband source.

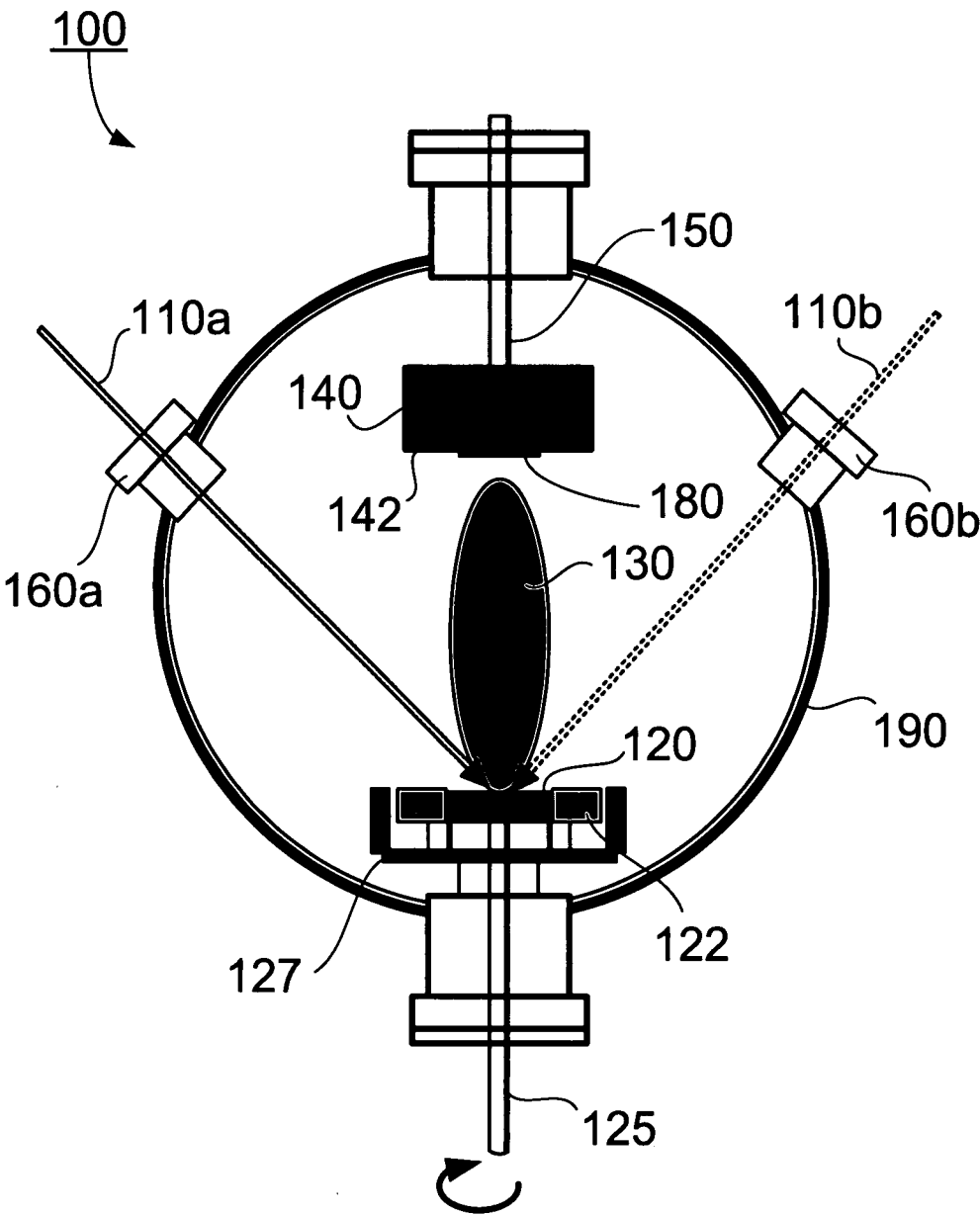


Fig. 1

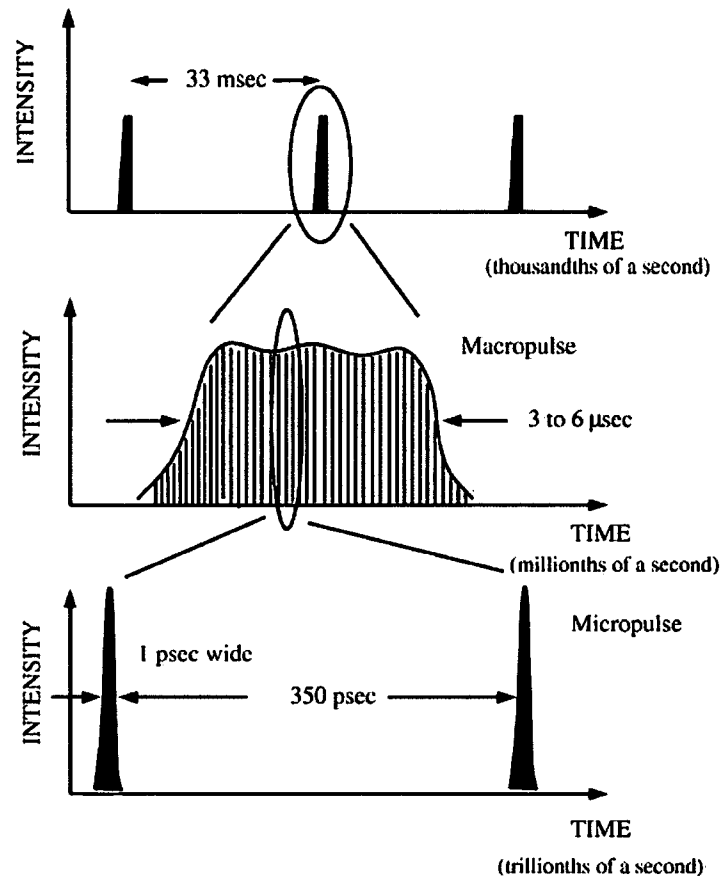


Fig. 2

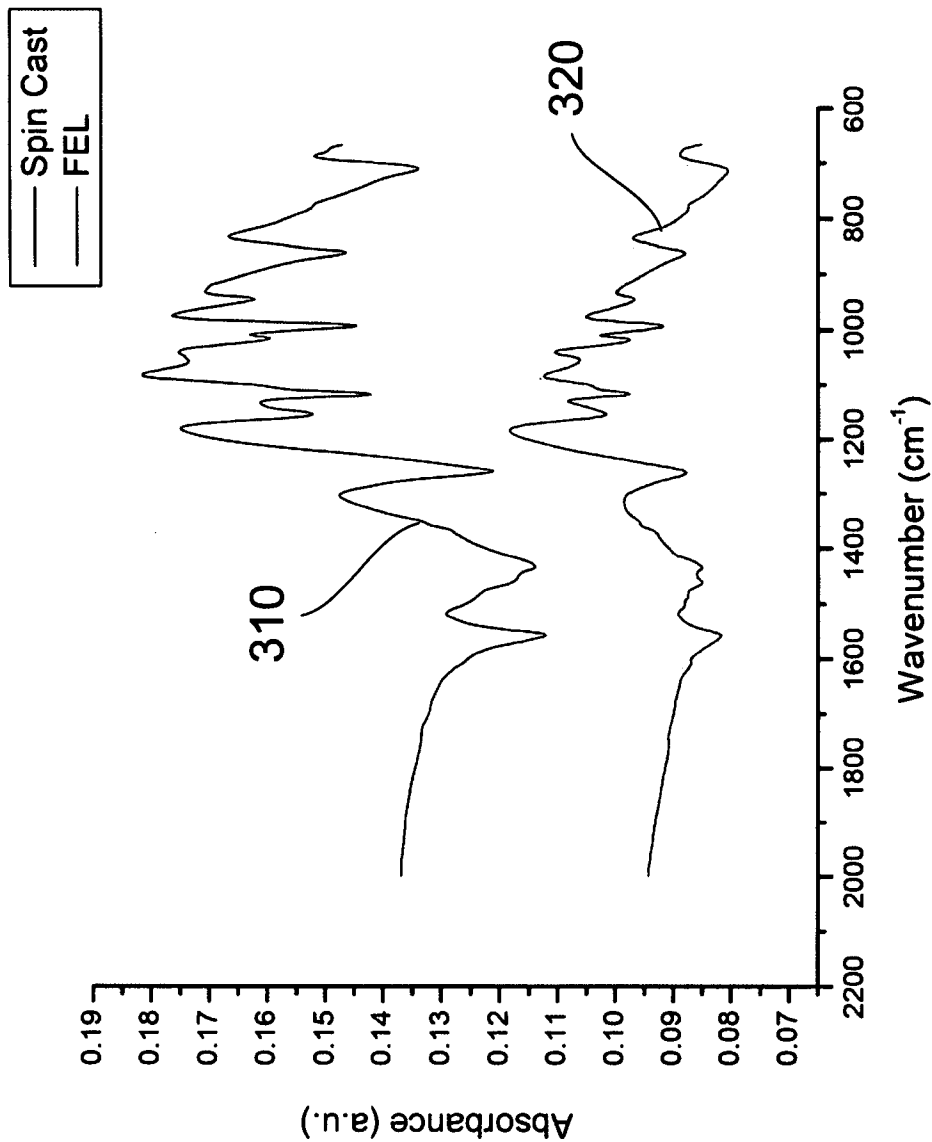


Fig. 3

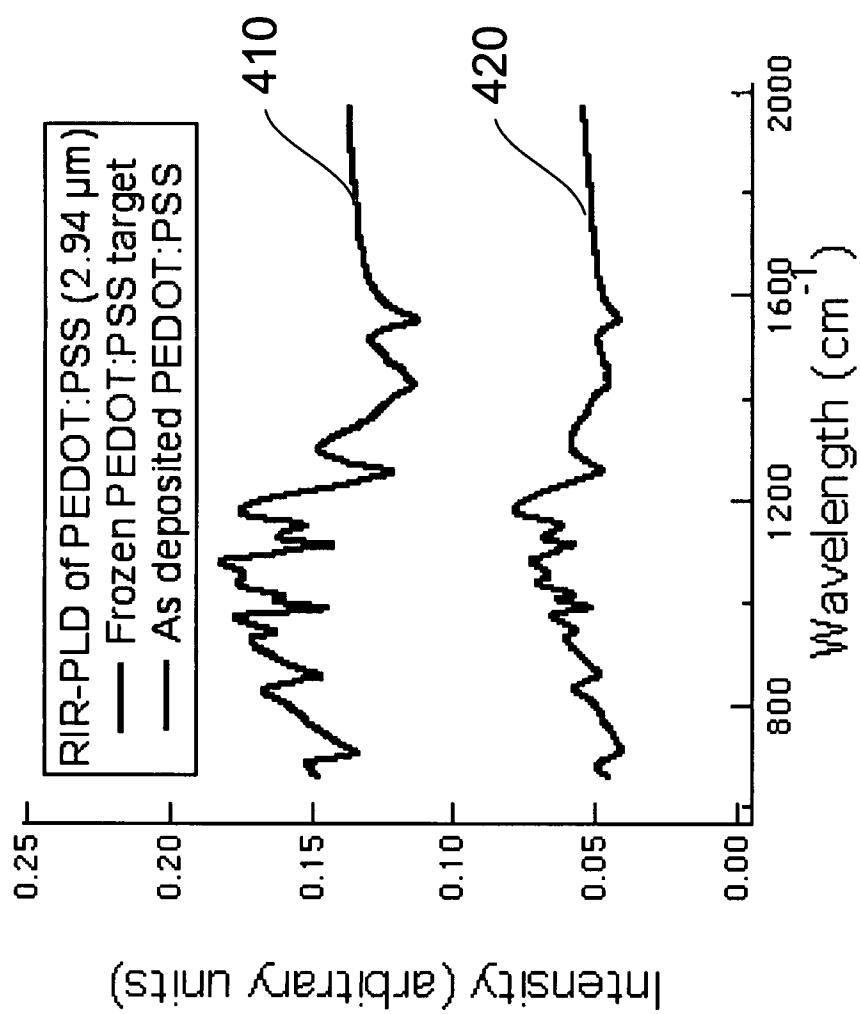


Fig. 4

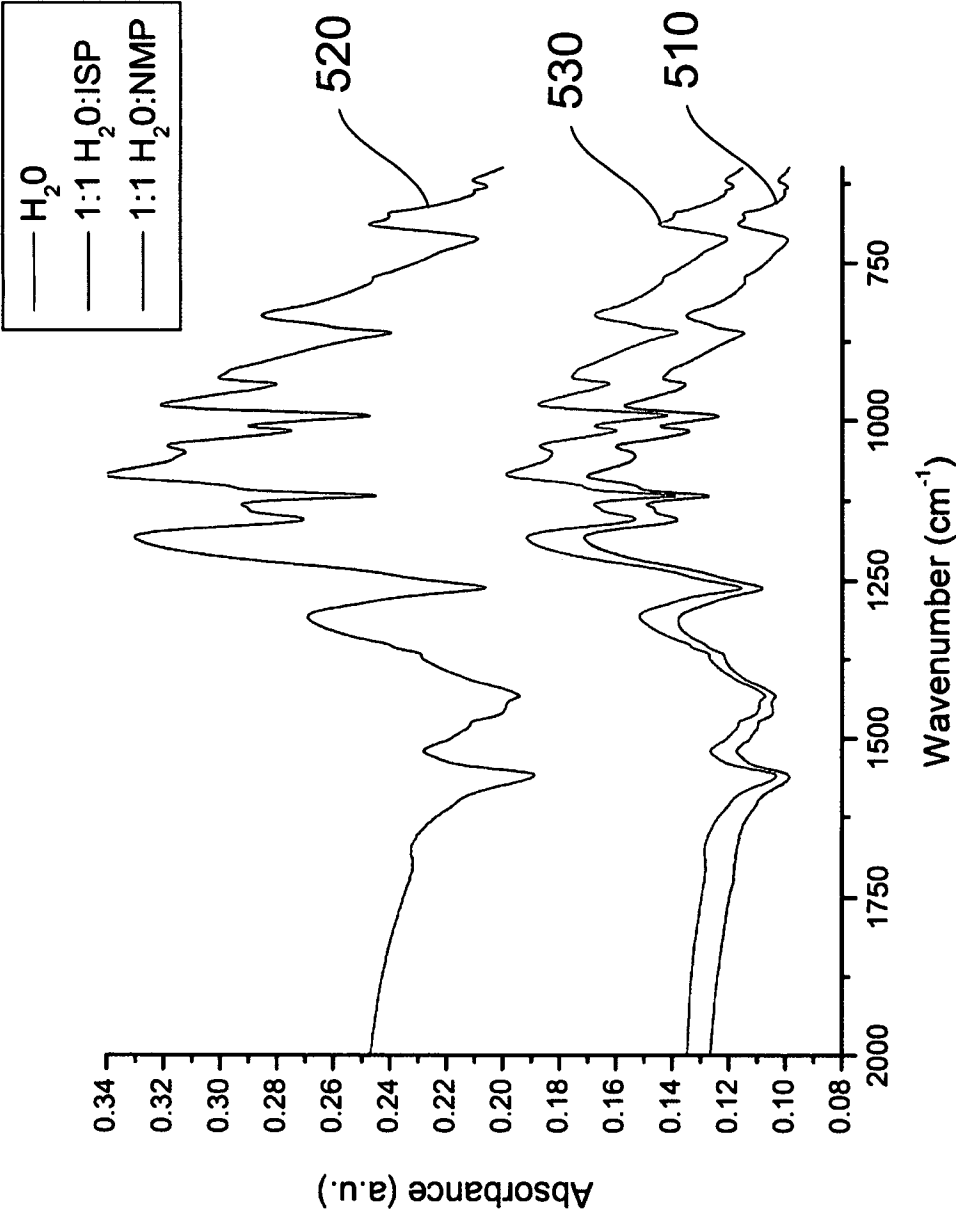


Fig. 5

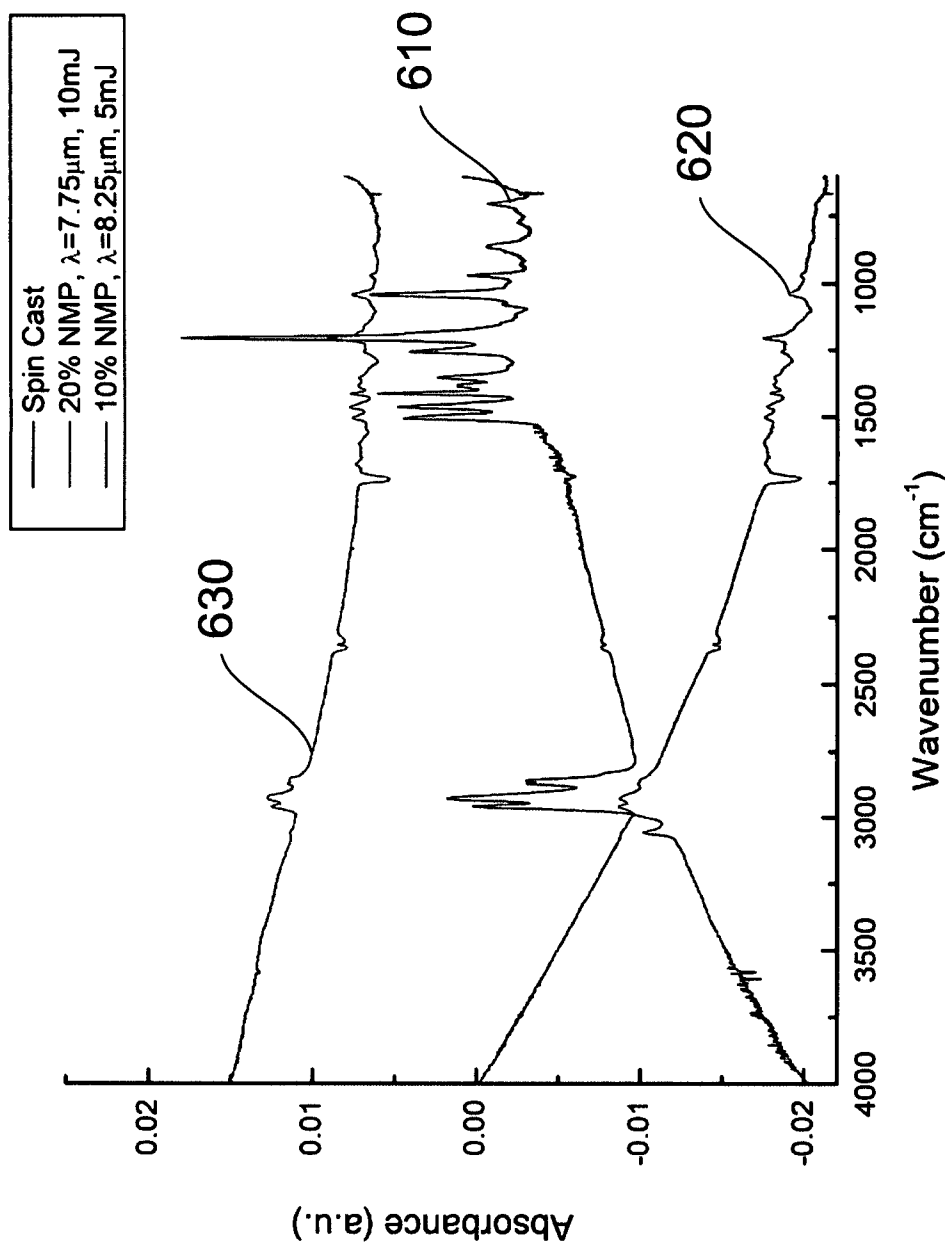


Fig. 6

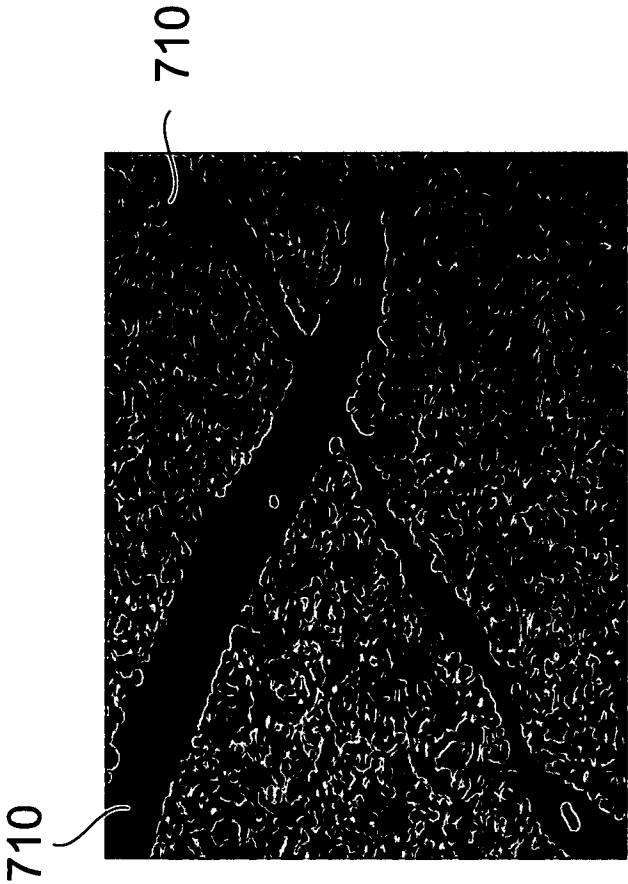


Fig. 7

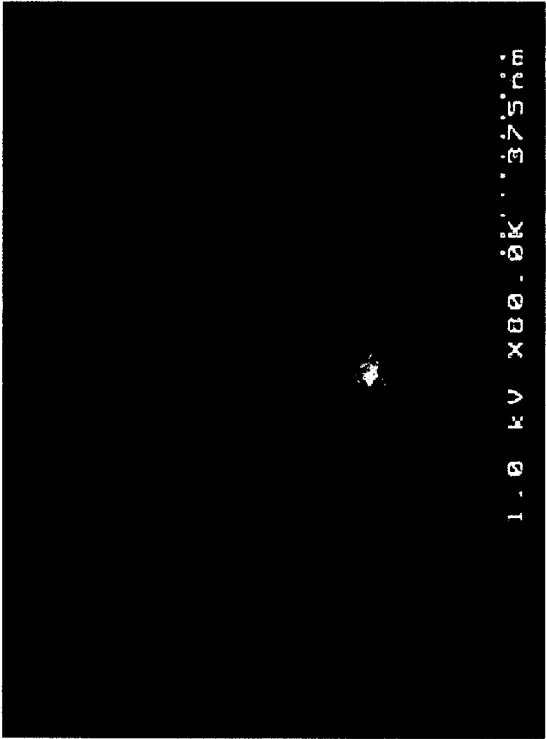


Fig. 8

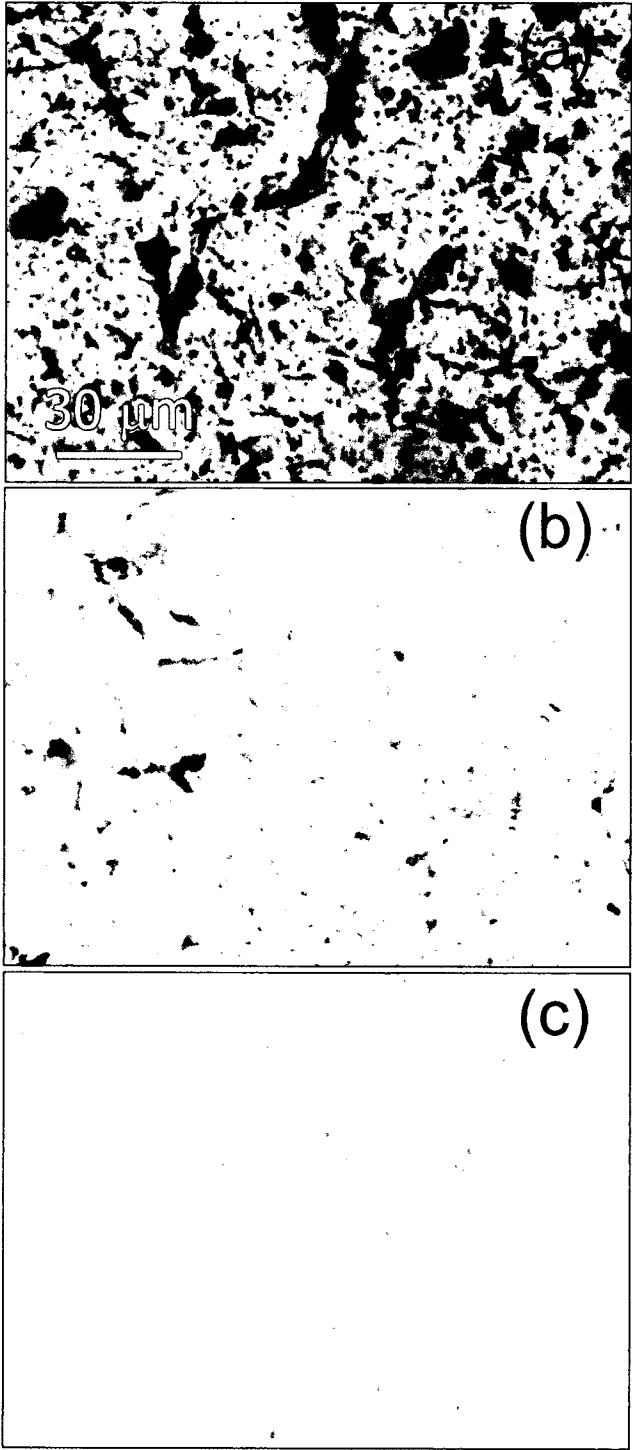


Fig. 9