## Continuous nanoparticle generation and assembly by atmospheric pressure arc discharge

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This letter describes a nanoparticle generation and deposition system which combines aspects of high temperature plasmas with room temperature aerosols. The process works at atmospheric pressure and produces nanoparticles of Au or ZnO through cathode erosion inside a dc arc discharge plasma. The particles are positively charged by the arc and form a room temperature aerosol. From the aerosol, nanoparticles assemble on conductive sample surfaces through openings in patterned resist with resolution enhanced by electrodynamic nanolenses. We report that continued operation of the system results in funneled deposition of nanoparticles into well positioned three dimensional nanostructures. © 2009 American Institute of Physics. [doi:10.1063/1.3197646]

The synthesis and the integration of inorganic nanomaterials continues to attract considerable growth as it provides a potential solution to the manufacture of low cost printable electronics, optoelectronics, and solar cells with higher performance than their organic counterpart. There are a number of different methods to the synthesis and integration: wet chemical synthetic routes combined with inkjet printing compete against gas phase synthesis and deposition methods. Solution based processes require the formulation of stable printable inks using organic ligands,<sup>1,2</sup> which are often orthogonal to what is desired from an electronic point of view. Gas phase methods eliminate this requirement providing a larger selection of materials including Si, Ge, GaN, and GaAs. Considering gas phase processes the use of plasmas remains the dominant method in the synthesis, etching, and deposition of thin films and nanomaterials.<sup>3</sup> Typically, a distinction is made between low and atmospheric pressure plasmas. Low pressure plasmas provide high uniformity in coatings or etching applications but suffer from low mass flow, deposition, or etch rate. Atmospheric pressure plasmas on the other hand provide a high mass flow, deposition, or etching rates,<sup>4</sup> but typically suffer from lower uniformity. Such atmospheric pressure plasma systems consist of two distinctly different regions. The first region is the visible plasma region which contains high energy electrons and ions at temperatures up to 22000 K with electron  $n_e$  and ion densities  $n_i$  ranging from 10<sup>8</sup> to 10<sup>15</sup> cm<sup>-3</sup> used to evaporate, sputter, or dissociate precursor materials.<sup>5,6</sup> High temperature plasmas in the form of dc arc discharges led to the discovery and industrial production of fullerenes and carbon nanotubes<sup>7-10</sup> through erosion of graphite electrodes and have since then emerged to form other technologically relevant nanomaterials including GaN,<sup>11</sup> Pd,<sup>12</sup> and Si (Ref. 13) to name a few. The second "cold" region surrounding the visible plasma can be described as low energy room temperature gas with ions, electrons, and neutral or charged nanoparticles and is governed by aerosol science. The fact that these aerosols contain charged nanomaterials at low temperature makes these systems ideally suited for charge directed printing of electronically functional inorganic materials. In other words,

it is conceivable that plasma systems can be utilized to produce functional charged nanoparticles that feed into nanoxerographic<sup>14–18</sup> type processes to print nanoparticles as opposed to micrometer-sized toner particles. Existing nanoxerographic printers provide sub-100 nm lateral resolution by depositing charged nanoparticles onto oppositely charged surface areas. Yet these xerographic methods were limited to initial charge concentrations in the dielectric layer that were insufficient to form patterned nanoparticle films with thicknesses exceeding a single or few monolayers.<sup>14–18</sup> Localized deposition of patterned films with any desired thickness has remained a challenge.

This letter describes a deposition system which combines an atmospheric pressure plasma with an electrodynamic deposition process to form nanostructures from sub-20 nm metallic or semiconducting nanoparticles. More specifically, the apparatus uses a dc arc discharge between two consumable Au or Zn electrodes to continuously generate nanoparticles and a third sample electrode placed nearby for nanoparticle collection. The resist becomes highly charged resulting in the formation of localized electrodynamic nanolenses which focus nanoparticle deposition. The deposition process does not deplete the underlying charge pattern enabling the deposition of tall nanostructures (more than 100 ML). While the present paper is limited to two materials, we anticipate that the process can be extended to any nanomaterial type that has been formed using high temperature plasma.

Figure 1(a) illustrates the basic elements and dimensions of the apparatus. The apparatus was enclosed in Fig. 1(b), a modified polypropylene desiccator sealed to prevent nanoparticle inhalation. A 10 kV, 100 mA controlled current power supply (Gamma High Voltage Research Inc., RR5– 120R/CPC/M994) was used to ignite and maintain a 10 W dc arc discharge between two identical consumable electrodes. For consumable electrodes we used Au and Zn in wire form (2–5 mm diameter). The materials were clamped into slits in copper rods allowing adjustment of the separation. The anode [top electrodes in Figs. 1(a) and 1(b)] was given a high positive potential and the cathode [bottom in Figs. 1(a) and 1(b)] was grounded. Photographs of the arc [Fig. 1(b) inset] displayed the expected arc luminescence for atmospheric

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FIG. 1. (Color) Schematic and photograph of the basic elements. (a) An atmospheric pressure dc arc discharge is established between two consumable electrodes that are separated by 2 mm. (b and inset) The photograph shows the typical appearance of the arc between Au electrodes. Produced positively charged nanoparticles are collected on a grounded substrate outside the plasma region. Flux and deposition of charged particles is monitored using a Keithley (6517A) electrometer.

pressure air conditions (20.95% O<sub>2</sub> by mole). Spectroscopy of blue-white O<sub>2</sub> discharges shows peaks at 419 nm (Ref. 19) due to positive ionization of  $O_2$  into  $O_2^+$ , where these ions present in the arc may play a role in nanoparticle charging and formation. The process of nanoparticle formation using atmospheric pressure arcs is established and we refer to Smirnov<sup>20</sup> for an introduction. In brief, high mobility electrons generated by the arc are accelerated by the applied electric field to the anode, producing gas ions as they travel. Incident positive gas ions are brought to the cathode where they impact the cathode tip surface. Erosion is observed only at the cathode because the heavy positive gas ions release more kinetic energy than the electrons when impacting the electrode surface. The eroded material is collected at the sample. During collection, an electrometer can be used to measure a positive current,  $I_{sub} \sim 1$  nA, indicating that the deposited nanoparticles are positively charged. The erosion process increases with the arc current. To prevent rapid evaporation of the cathodes all experiments were performed at 10 W with controlled arc currents <100 mA which is quite similar to what is used in atmospheric pressure arc discharge lamps.<sup>6</sup>

Figure 2 depicts scanning electron micrographs of gold nanoparticles deposited onto a silicon substrate electrode that was partially shielded using patterned poly(methyl methacrylate) (PMMA). After patterning the samples were exposed to 49% HF for 30 s before deposition to remove the native SiO<sub>2</sub> layer. Deposition into openings is achieved down to 200 nm [Fig. 2(a)] where electrodynamic focusing allows resolution below 100 nm with deposit geometries that depend on resist feature size and time. Initially, nanoparticles are focused into clusters at the center of the resist opening [Fig. 2(b)] then



FIG. 2. Gold nanoparticle collection in submicron features in 80 nm thin PMMA e-beam resist. Continuous charge-based nanoparticle deposition results in three-dimensional deposition into arrays with 200 nm diameter openings (a) to 500 nm openings [(b) and (c)]. Au nanoparticles are initially (b) focused into the center of the openings then (c) broaden as nanoparticles continue to deposit over 15 min. Scale bars: 1  $\mu$ m in (b) and (c).



FIG. 3. (Color) Representative images of Au and ZnO nanoparticle deposits in S1805 photoresist as a function of deposition time increasing from (a) and (d) 2 to (b) and (e) 15 to (c) and (f) 30 min at constant 10 W arc discharge power. Morphology differences [(c) and (f) insets] are attributed to differences in charge-based deposition behavior of the nanomaterials. Scale bars: 1  $\mu$ m for (a), (c), and (f).

after 15 min of deposition [Fig. 2(c)] the deposits broaden. Throughout the lengthy deposition process it can be seen that particles are absent from the resist, suggesting that nanoparticles are repelled from deposition there.

This is quite remarkable and holds for even micronscale features as shown in Fig. 3. Whether depositing metallic Au [Figs. 3(a)-3(c)] over time or semiconducting ZnO [Figs. 3(d)-3(f)], the insulating surfaces appear to self-equilibrate to a sufficiently high potential for the nanoparticle flux to be directed to the grounded regions. The focusing effect and small standard deviation in location of the deposits become apparent using Au nanoparticles and 1  $\mu$ m circular openings [Fig. 3(a) inset]. Here the Au particles initially deposit into an area that is approximately seven times smaller in area than the opening but spread out over time yielding towerlike structures that can be several micrometers tall [Fig. 3(b)]. Continued deposition causes the tops of towers to broaden [Fig. 3(c)]. These towers contain several hundred layers of 10–20 nm particles. Thin <1  $\mu$ m deposits [Figs. 3(a) and 3(b) are very uniform over large areas while thick >2  $\mu$ m deposits [Fig. 3(c)] begin to show some level of variations over mm sized areas. For the case of ZnO, we observe the more resistive nanomaterial to cause deposit broadening at smaller deposit heights, ultimately resulting in different deposit morphology and porosity [Figs. 3(c) and 3(f) insets].

The process is understood to work in the following way: material deposition does not occur on insulators without a conductive substrate, suggesting field directed assembly to be the dominant mechanism. The arc produces a gas medium of high mobility bipolar gas ions and orders of magnitude lower mobility/heavier charged nanoparticles. After introduction of uncharged resist, we expect adsorption of these charged species to be controlled by drift and diffusion favoring high mobility gas ions initially, until a steady state is reached where the resist surface is charged. The system equilibrates and establishes whatever necessary fringing field to funnel material to conducting surfaces where they become neutralized. The process is fundamentally different from known xerographic methods, where deposition occurs onto the insulating surface instead of the conductor. It is an elec-

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trodynamic instead of electrostatic process which means that films of any desired thickness can be formed without depleting the charge differentials that direct the deposition process.

In summary, the reported gas-phase nanomaterial production process was shown to produce nanoparticles of Au and ZnO. Collection of positively charged nanoparticles in predetermined areas is demonstrated over extended periods of time without depleting the Coulomb forces that direct the deposition process. The process works in the gas phase at atmospheric pressure and does not require vacuum equipment. The process eliminates the need to remove particles from the reactor walls to formulate stable suspensions/ electronic inks otherwise required if serial inkjet type methods were to be used to print the materials. Methods of selfaligned integration of nanoparticles are important to a number of fields including printable electronics, sensors, or catalysis. The process improves deposition efficiency through the focusing effect; no lift-off is required and material is conserved which is attractive considering material cost. At present, we have only varied a few process parameters. Questions of ultimate uniformity, extension to large area deposition using multiple spatially separated discharge regions will require further research.

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- <sup>1</sup>H. Fan, K. Yang, D. M. Boye, T. Sigmon, K. J. Malloy, H. Xu, G. P. Lopez, and C. J. Brinker, Science 304, 567 (2004).
- <sup>2</sup>L.-C. Ma, R. Subramanian, H.-W. Huang, V. Ray, C.-U. Kim, and S. J. Koh, Nano Lett. 7, 439 (2007).
- <sup>3</sup>A. Schutze, J. Y. Jeong, S. E. Babayan, J. Park, G. S. Selwyn, and R. F. Hicks, IEEE Trans. Plasma Sci. 26, 1685 (1998).
- <sup>4</sup>J. S. Chang, P. A. Lawless, and T. Yamamoto, IEEE Trans. Plasma Sci. **19**, 1152 (1991).
- <sup>5</sup>C. Tendero, C. Tixier, P. Tristant, J. Desmaison, and P. Leprince, Spectrochim. Acta, Part B 61, 2 (2006).
- <sup>6</sup>M. Redwitz, O. Langenscheidt, and J. Mentel, J. Phys. D: Appl. Phys. 38, 3143 (2005).
- <sup>7</sup>W. Kraetschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) 347, 354 (1990).
- <sup>8</sup>S. Iijima, Nature (London) 354, 56 (1991).
- <sup>9</sup>T. W. Ebbesen and P. M. Ajayan, Nature (London) 358, 220 (1992).
- <sup>10</sup>C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapells, S. Lefrant, P. Deniard, R. Lee, and J. E. Fischer, Nature (London) 388, 756 (1997).
- <sup>11</sup>W. Han, P. Redlich, F. Ernst, and M. Ruhle, Appl. Phys. Lett. 76, 652 (2000).
- <sup>12</sup>D. Bera, S. C. Kuiry, M. McCutchen, A. Kruize, H. Heinrich, M. Meyyap-
- pan, and S. Seal, Chem. Phys. Lett. **386**, 364 (2004). <sup>13</sup>S.-M. Liu, M. Kobayashi, S. Sato, and K. Kimura, Chem. Commun. (Cambridge) 2005, 4690.
- <sup>14</sup>T. J. Krinke, H. Fissan, K. Deppert, M. H. Magnusson, and L. Samuelson, Appl. Phys. Lett. 78, 3708 (2001).
- <sup>15</sup>H. O. Jacobs and G. M. Whitesides, Science **291**, 1763 (2001).
- <sup>16</sup>C. R. Barry, J. Gu, and H. O. Jacobs, Nano Lett. 5, 2078 (2005).
- <sup>17</sup>I. W. Lenggoro, H. M. Lee, and K. Okuyama, J. Colloid Interface Sci. 303, 124 (2006).
- <sup>18</sup>N. Naujoks and A. Stemmer, J. Nanosci. Nanotechnol. 6, 2445 (2006).
- <sup>19</sup>J. Peters, J. Heberlein, and J. Lindsay, J. Phys. D 40, 3960 (2007).
- <sup>20</sup>B. M. Smirnov, *Physics of Ionized Gases* (Wiley, New York, 2001).