Positioning Pd catalyst particles for carbon nanotube growth using charge patterns created with a scanning electron microscope

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Positioning of charged nanoparticles with the help of charge patterns in an insulator substrate is a known method. However, the creation of charge patterns with a scanning electron microscope for this is relatively new. Here a scanning electron microscope is used for the creation of localized charge patterns in an insulator, while a glowing wire generator is used as the nanoparticle source. The deposited palladium nanoparticles are used as catalysts for the localized growth of carbon nanotubes in a chemical vapor deposition oven. The authors show first the results on local carbon nanotube growth using this procedure. © *2009 American Vacuum Society.*
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I. INTRODUCTION

Nanoparticles can be used in a wide range of applications, such as for therapeutic drugs, optoelectronic devices, fuel cells, lab on a chip, catalysts, medical devices, permanent magnets, and quantum dots.[1] Some of these applications need nanoparticles in predefined patterns. While a variety of techniques are available for the fabrication of nanoparticles, it is less straightforward to position these particles in predefined patterns. A method of positioning nanoparticles invented by Krinke *et al.*[2] is to use charged nanoparticles, suspend them in a carrier gas, and direct them to charge patterns created in the insulator. Krinke and co-workers[2,3] created these patterns by contact charging with a sharp metal tip or by using metal coated polydimethylsiloxane (PDMS) stamps with a voltage applied between the insulating substrate and the tip or stamp. With this method they achieved patterns of nanoparticles on the insulator with a resolution of about 100 nm. The limiting factors of this technique are the writing speed (in the case of the sharp tip) or the lifetime of the PMDS stamp.

Another method to create charge patterns on an insulator is to write a pattern with a finely focused electron beam.[4,5] In previous work, we have shown that a resolution of 100 nm can be obtained for deposited lines of charged nanoparticles on an insulator.[4] In that work, the charged nanoparticles were created with a glowing wire generator (GWG) and size selected with a differential mobility analyzer (DMA). In this article, we report the use of this technique for the growth of carbon nanotubes from palladium catalyst particles[6] on an electrically insulating surface.[7] We shall first discuss the basic principle of defining charge patterns in an insulator with a finely focused electron beam, the basic working of the glowing wire generator and the deposition of charged nanoparticles, and finally the results of carbon nanotube growth on predefined positions.

II. THEORY

The charging of an insulator with a finely focused e-beam is dominated by complex physical phenomena. The result from the scattering of the incident primary electrons (PEs) in the solid is a spectrum of elastically backscattered electrons (BSEs) and secondary electrons (SEs) that are emitted from the sample. In an uncharged substrate the relative numbers of BSEs and SEs depend (among others) on the kinetic energy of the primary electrons. In a charged substrate they are almost impossible to predict because they mutually influence each other.[8]

In general, the balance between the number of incoming PEs and the number of outgoing BSEs and SEs determines whether an insulator is positively or negatively charged.[9] This, however, does not tell how the charge is spatially stored in the insulating substrate. The charge distribution is responsible for the electrostatic field distribution, which determines the achievable spatial resolution of the deposition process of charged nanoparticles. So the challenge is not so much to focus the electron beam down to a small spot size but to keep the charge storage localized. Studies on the physics of charging with a focused electron beam and the induced charge distribution have been done, e.g., by Renoud *et al.*,[10] Fitting *et al.*,[8] and Cazaux *et al.*[11] Renoud *et al.*[10] showed using a Monte Carlo simulation that it is possible to create a highly localized positive charge distribution that should allow for a spatial resolution better than 50 nm for the deposition of charged nanoparticles. Nevertheless, negative charging occurs at higher primary electron energy, which leads to a larger charge storage volume. In our studies so far we have only used negative charging, which is much more easy than positive charging.[8]

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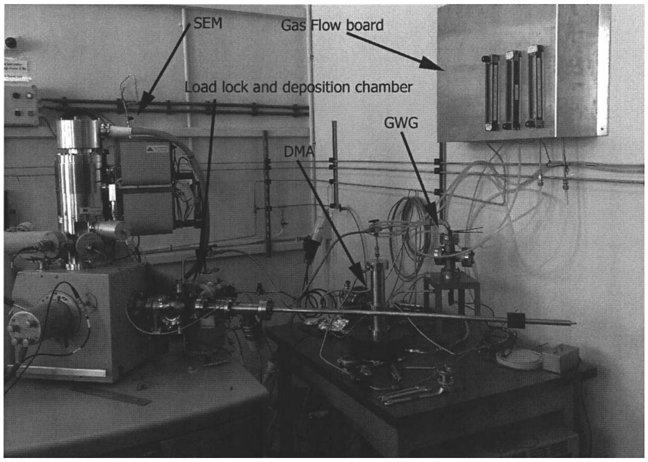

FIG. 1. Experimental setup.

III. EXPERIMENT

The charge patterns are created with an FEI Quanta 200 FEG environmental scanning electron microscope (SEM). An in-house developed software package is used to enable automated patterning. On the SEM a loadlock is mounted such that the charged sample can be transferred in vacuum to a dedicated deposition chamber where the nanoparticles are deposited onto the substrate. After transferring the substrate to the deposition chamber, this chamber is vented with the same inert gas that is later used as a carrier gas of the nanoparticles. This minimizes the loss of quality of the charge pattern in the insulating substrate (venting with humid air may discharge the substrate). Figure 1 shows the experimental setup.

The nanoparticles are created with a GWG. In a GWG a purified metal wire (99.99% pure Pd) is being evaporated by passing a high current through it while it is suspended in an inert gas (argon in our experiments). A supersaturated vapor is formed, which condenses into nanoparticles.[12,13] The nanoparticles have a range of diameters and some of the particles can be singly charged, with both polarities possible. This process is sketched in Fig. 2(a), and in Fig. 2(b) GWG in operation is shown.

The choice of materials that can be used for the generation of the nanoparticles depends on the evaporation rate which is related to the metal vapor pressure. Experimental results have shown that the partial pressure of the metal at the melting temperature $[Ps(T_m)]$ must be higher than 5×10^{-3} Pa for a material to be usable in a GWG.[13]

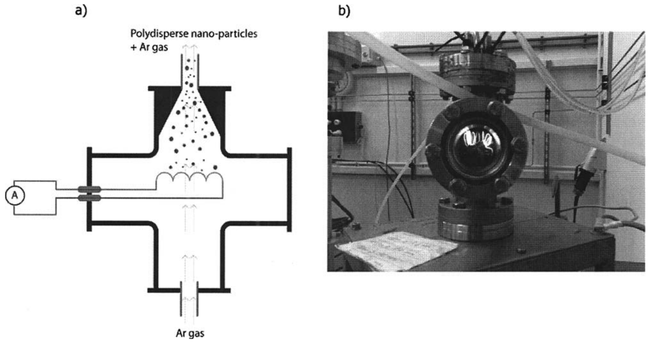

FIG. 2. (a) In the reaction chamber, argon gas flows around a glowing wire. (b) A glowing wire generator in operation.

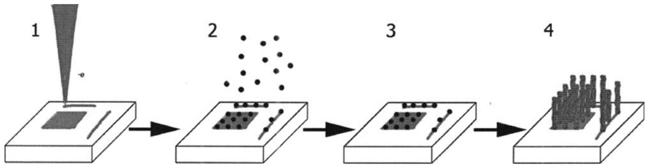

FIG. 3. (1) Creation of charge patterns in an insulator with a fine focused e-beam. (2) Deposition of charged nanoparticles onto the patterns in an argon atmosphere. (3) Catalyst particles on an insulator in a chemical vapor deposition oven. (4) Growing of multiwalled carbon nanotubes.

Following the fabrication of the nanoparticles, they need to be selected by diameter and polarity. The selection is done with a DMA, which is a device that separates the charged nanoparticles based on their electrical mobility that is related to the diameter of the nanoparticle and charge state.[14]

After having been selected for size and polarity, the particles are dragged along with the inert gas toward the sample mounted in the deposition chamber, where they are deposited on the charge patterns. In the next step, the sample is transferred to a chemical vapor deposition (CVD) chamber for the carbon nanotube growth. Here, the Pd nanoparticles act as catalyst for carbon nanotube growth.[6,7] In Fig. 3 the total experimental procedure is schematically shown.

IV. RESULTS

Figure 4 shows an array of positively charged Pd nanoparticles deposited on a negatively charge pattern. This charge pattern was created with a defocused electron beam of approximately 500 nm in diameter, a beam energy of 7 keV, a probe current of 1.7 nA, a beam step size of 4 μm, and a dwell time per dot of 21 μs. The substrate is a 6 μm thick layer of Si_3N_4 (created by plasma enhanced-CVD) on a

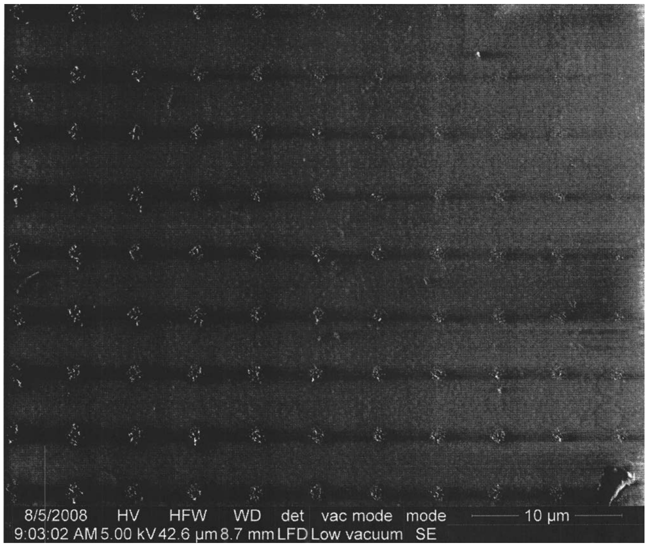

FIG. 4. Array of the deposited Pd nanoparticles on a Si_3N_4 substrate.

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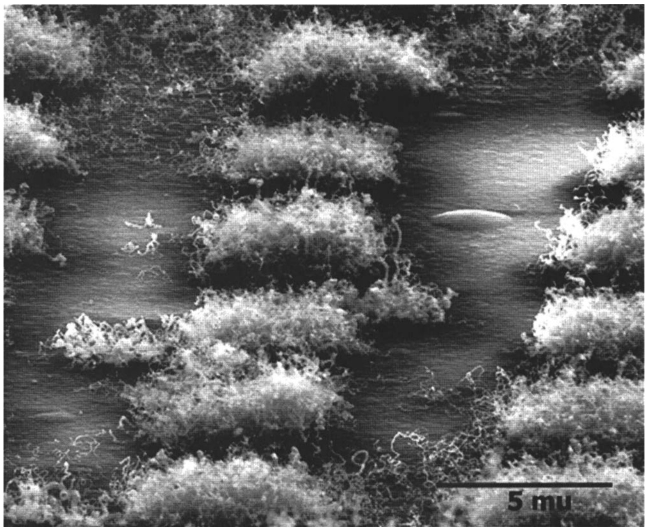

FIG. 5. Carbon nanotubes grown in a dot array with Pd nanoparticles as catalyst.

Si substrate. The total deposition time of the charged nanoparticles (with a diameter of 50–70 nm) onto the sample was approximately 45 min.

Figure 5 shows an array of dots containing many deposited Pd nanoparticles from which carbon nanotubes have grown using the CVD process. The distance between the dots was 10 μm, the nanoparticles had an average diameter of 20.4 nm, and the particle deposition time was approximately 20 min. The carbon nanotubes were grown in a gas mixture of $C_2H_4:CH_4:H_2$ with a ratio of 0.7:1.5:0.5 at a temperature of 600 °C and a pressure of 500 mbar. The grown carbon nanotubes had an average diameter of 24.0 nm as measured from high resolution SEM images. Growth times varied per experiment but were typically about 10 min.

Figure 6 shows a line of carbon nanotubes that have been grown from nanoparticles. The charge pattern was written with a beam energy of 7 keV, a beam diameter of approximately 100 nm, a probe current of 1.7 nA, and a dwell time per pixel of 21 μs. The substrate, the deposition time, the diameter of the selected nanoparticles, and the nanotube growth recipe are similar as for the dot array.

This demonstrates that it is possible to create predefined patterns of nanoparticles with good control over the particle diameter and the particle position. Furthermore, these particles can serve as catalyst particles for carbon nanotube growth. This result opens the possibility of creating arbitrary patterns with catalyst nanoparticles with a simple and straightforward technique. Further work concentrates on the following issues. First, we aim to decrease the size of nanoparticle lines. We expect that a resolution of 50 nm is feasible. Second, we are investigating the relationship between the diameter of the grown carbon nanotube and the nanoparticle diameter, the reactivity of the nanoparticle as catalyst, and the vertical alignment of the carbon nanotubes. Finally, we plan to create functional devices with nanoparticles of other materials than Pd to further explore this fabrication technique.

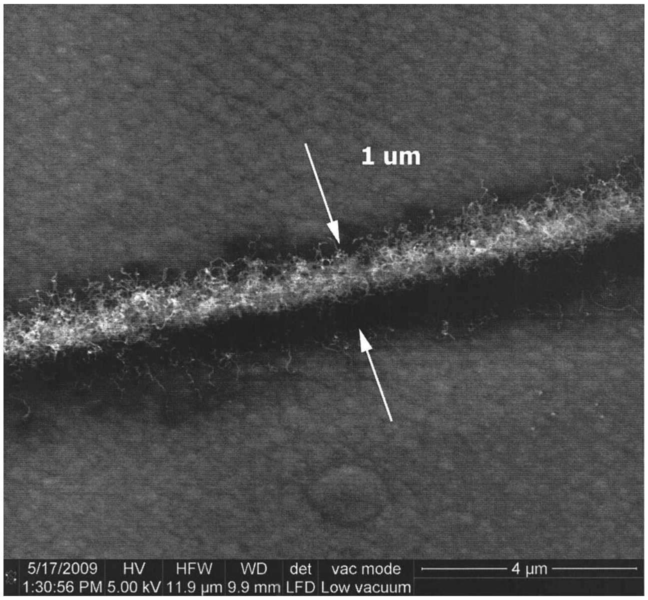

FIG. 6. Line of carbon nanotubes created with line of Pd catalyst nanoparticles.

V. CONCLUSIONS AND OUTLOOK

We have demonstrated that it is possible to position positively charged palladium nanoparticles onto negatively charge patterns created with a SEM, and that these particles can be used as a catalyst for subsequent carbon nanotube growth using a CVD process. This shows that high spatial accuracies can be obtained for nano- and microfabrication techniques to create functional devices where the diameter and position control of the nanoparticles are important.

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