Nanowire Placement with Ink Jet Heads

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Abstract

We have shown that thermal ink jet print heads can be used to place GaN nanowires on patterned substrates. The semiconductor nanowires had diameters ranging from 70 to 300 nm and lengths from 5 µm to 20 µm. They were dispersed in alcohol-water solutions for loading into ink reservoirs. To avoid clogging, the thermal ink jet heads were chosen with drop weights from 72 to 165 ng. The thermal ink jet method was successfully used to place nanowires across narrow gaps in metal patterns. When using a low-power optical microscope to align the nozzle with substrate pattern features, the placement accuracy is much higher than with micropipette placement. For unknown reasons, nanowires would not pass through piezoelectric ink jet heads. These experiments demonstrate that ink jet technology holds promise for low-cost, rapid, massively parallel placement and processing of nanowires for optoelectronic, electronic, and sensor applications.

Introduction

Semiconductor nanostructures provide opportunities for novel device architectures and improved performance and yield, but handling of these materials efficiently will require new manufacturing technologies. In this paper we describe placement of GaN nanowires on patterned Si substrates to within 35 µm by use of thermal ink jet technology. We have previously shown that nanowires can be dispersed in solvent solutions onto patterned planar surfaces and partially directed with applied electric fields through a dielectrophoretic mechanism [1]. The adhesion between a dispersed nanowire and its substrate is sufficient to survive subsequent conventional photolithographic processing, thus enabling the deposition of electrical contact pads. For example, bridge structures such as the one illustrated in Fig. 1 have been made in this way. The yield offered by this method is limited, however, by the ~5 µL drop size produced by a metered pipette. This volume is equivalent to a spherical drop 2 mm in diameter that disperses over a substrate area on the order of 1 cm^2. Although pipettes with metered volumes down to 200 nL are commercially available, this still reduces the drop volume by only a factor of 40. In contrast, ink jet drop volumes around 150 pL can readily be achieved, allowing confinement of the nanowires in a solvent sphere of 70 µm diameter. Although placement yield varies significantly with geometrical parameters such as the number and area of acceptable sites and the density of nanowires in the solvent, we expect to improve device yields from below ~10 % afforded by the dielectrophoresis process to greater than 90 % with the ink-jet techniques.

By addressing the efficient coupling of the nanoscale semiconductor device to the macro world, ink jet dispersal could demonstrate a path for full utilization of semiconductor nanostructures in a manufacturing process. GaN and related compounds are particularly attractive for nanostructure growth because conventional bulk and epitaxial growth methods produce material with high defect density and therefore low yields. Native substrates for the nitride semiconductors are only now becoming available in small diameters (1 to 8 cm) and at high cost. GaN nanowires with diameters on the order of 200 nm and lengths of 10 µm contain sufficient material to sustain operation as diode lasers, light emitting diodes, detectors, or field effect transistors [2,3,4]. The superior optical and crystalline quality [5,6] that we have demonstrated for nanowires relative to epitaxial material makes them valuable from a performance standpoint alone, and avoiding expensive native substrates also lowers manufacturing costs. Alloys of GaN with InN and AlN span a large range of the optical spectrum, from 0.7 eV to 6.2 eV, thus making them suitable for applications from ultraviolet medical and sterilization systems to solar cells and telecommunications.

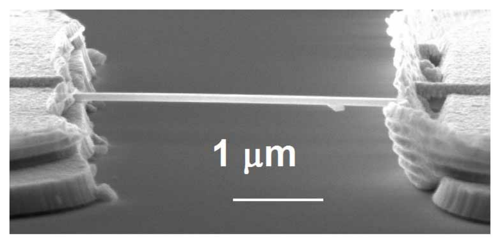

***Figure 1**. GaN nanowire placed on metal pads with dielectrophoresis guiding followed by processing with conventional photolithography to add electrical contact pads.*

Experiment Description

Nanowire dispersals were attempted with two different ink jet systems, one based on thermal ink jet (TIJ) technology and the other on piezoelectric ink jet (PIJ). The TIJ head is a prototype instrument named Thermal Ink jet Picojet System (TIPS®) obtained from Hewlett Packard Corporation,** for which iTi Corporation is a "beta test site" for new applications. The instrument is programmable for use of up to 16 nozzles and 1 to 2000 drops per dispersal cycle. A number of exchangeable nozzles were available with reservoirs holding 1to 2 ml of fluid. For these experiments, we used heads in which only 1 or 2 nozzles were activated and with larger apertures, for which the drop weight ranged from 41 to 165 ng. Because the specific gravity of the dispersal solutions was close to 1.0, the corresponding drop

** Manufacturers of certain instrumentation are identified in this manuscript for technical clarity only. Inclusion in this paper implies neither endorsement by NIST nor that similar instrumentation by other manufacturers would not perform equally well for the application described.

volumes are from 40 to 165 pL. The TIPS unit was attached to optical mounts that held it about 40 ° off normal to allow use of a low power stereo microscope for aligning the nozzles with the substrate features. A solution of 10 % by volume of isopropanol in water was used for dispersals.

A second set of experiments was conducted with a piezoelectric jet head. These heads had Dimatix S-Class 128 nozzles with aperture size 52 to 54 μm. Higher viscosity solutions are required for this print head; therefore, solutions of 60 % (by weight, roughly 57 % by volume) ethylene glycol in water were prepared for nanowire dispersal.

Nanowires were grown by molecular beam epitaxy on silicon substrates (Fig. 2). Details of the growth method have been previously published [7,8]. Briefly, the wires formed spontaneously on Si (111) substrates under growth conditions of high temperature (near 820 °C) and high nitrogen flux. The wire growth rates were from 0.1 to 0.2 μm/h, and lengths up to 25 μm have been achieved. Unless wires coalesced during growth, they typically formed with hexagonal cross-section and diameters ranging from 50 to 400 nm (Fig. 2). An irregularly pitted layer called a matrix layer generally formed between the wires during growth, along with larger features including coalesced wires. Because these larger pieces can also detach into the dispersal solution and increase clogging, the growth run used in this experiment was chosen for its relatively thin matrix layer and low degree of wire coalescence. Dispersal solutions were generated by cleaving a section of wafer covered with nanowires into small pieces roughly 3 mm x 4 mm, and placing two such pieces in a small vial. Approximately 1.5 ml of solvent was added to the vial, and the mixture was then placed in an ultrasonic bath for 35 s. Dispersal solutions were shaken briefly by hand prior to transfer into ink jet reservoirs.

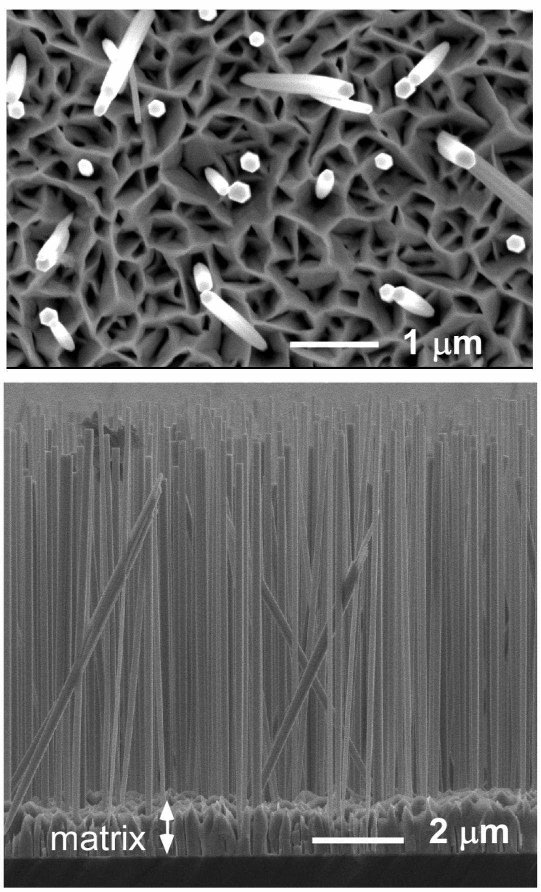

***Figure 2**. Field emission scanning electron micrographs of GaN nanowires used in this experiment taken with nanowires still on the silicon substrate. Upper photo: Top view. Lower photo: Side view.*

Thermal Ink Jet Results

The TIJ experiments demonstrated that we could successfully jet nanowires from nozzles that had a drop mass of at least 72 ng. The drop outline on the dispersal substrate was defined in some cases by residual ink contamination in the reservoir tip, as illustrated in Fig. 3. The nanowire solutions contained on the order of ten nanowires per drop. After attaching the sample and TIPS head to precision mounts, we were able to align the nozzle using a low power optical microscope to place nanowires relative to predefined metal features on the substrate surface. This microscope had sufficient magnification to see the pattern features and the drops, but not individual nanowires. (Figs. 3 and 4 were obtained from inspection with a separate, higher magnification microscope with polarization contrast.) The geometry of the TIPS nozzle prevented us from focusing clearly on the nozzle heads, but the placement of the drops on the surface was sufficiently reproducible that, with some practice, we could predict drop location relative to the out-of-focus head image to within about 30 μm. The nanowires appeared to clog nozzles with drop mass of 41 ng, that is, no ejected liquid could be observed with these nozzles.

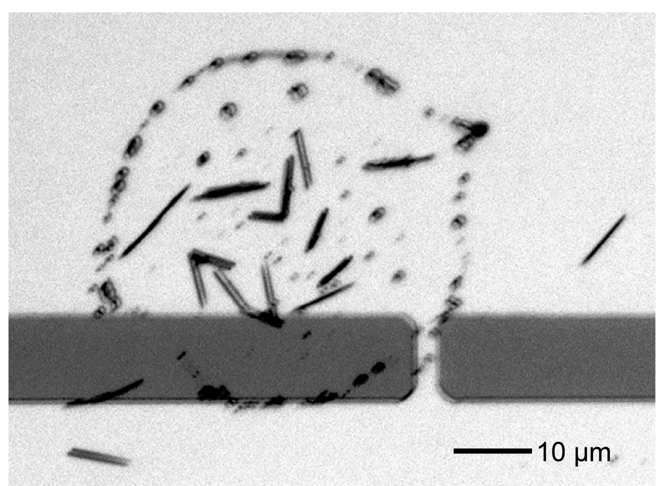

***Figure 3**.Optical micrograph of GaN nanowires showing dispersed drop diameter of approximately 50 μm when using 165 ng nozzle of thermal ink jet head. The dark rectangles are metal lines deposited by photolithography prior to the nanowire dispersal.*

In a second round of experiments, we combined dielectrophoresis guiding with TIJ nanowire placement. The target substrate was patterned with bus bars that allowed simultaneous application of voltage across more than 100 bridge gaps. An AC sine wave voltage of 20 V (peak-to-peak) at 75 kHz was applied across the gaps. By moving the substrate with an x-y stage and actuating the TIJ head, several bridges were dosed using the smaller nozzle size for 72 ng drop weight. The drops could be observed through the microscope, and they dried in about 1 to 2 s. This procedure produced a number of devices in which two nanowires bridged the gap, as shown in Fig. 4. There were also several drops where wires were dispensed but did not bridge the gap, which might indicate insufficient time for the electric field to guide wires. The larger nozzle and drop sizes also appeared to reduce nanowire clustering. We note that the yield for single-nanowire bridges would have been higher with a more dilute solution. A higher power microscope would have permitted by repeatedly dosing in the same spot until a nanowire was observed in the gap. Finally, it is clear that periodic solution agitation and cleaner solutions (no residual ink) would increase the placement uniformity.

Piezoelectric Ink Jet Results

The PIJ head was a commercial print head designed for regular printing use, and therefore available only in smaller drop sizes. We attempted to observe nanowire ejection from the print head using a drop visualization tool [9]. For unknown reasons, the nanowires used in the TIJ experiments did not pass through the PIJ nozzles. Glycol solutions containing nanowires purged quickly but would not jet when the nozzles were operated in normal print mode. The print head contained an internal filter with rated particle filter size of 20 µm, and it is possible that this filter removed the nanowires even though their length is around half the target particle size. It is also possible that the voltages used in the piezoelectric valves impacted the ability of nanowires to flow smoothly. Although this first experiment was unsuccessful, the underlying problems might be easily addressed with simple design modifications to the print head.

Conclusions

We have demonstrated that TIJ printing can be used to place semiconductor nanowires with dimensions of approximately 0.2 µm in diameter and 10 µm in length. Nanowires were jetted without noticeable damage through nozzles with drop weight down to 72 ng. The method was compatible with dielectrophoresis guiding across metal gaps. The yield of successful placement could be improved by combining solutions of lower density with immediate sensing of nanowire placement in order to continue dosing until a single nanowire is detected. Successful printing using commercial PIJ heads was not achieved, either because of smaller orifice size, internal filters, or other unknown obstacles.

Acknowledgment

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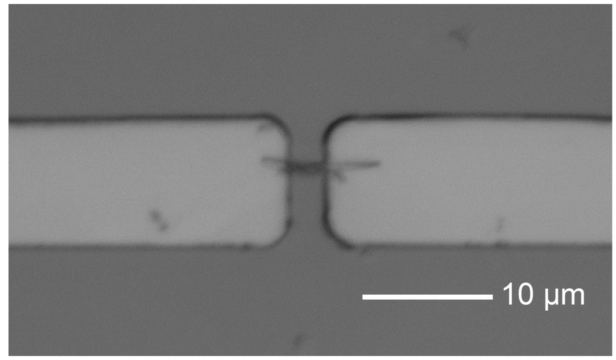

***Figure 4**.Optical micrograph showing two nanowires placed on a bridge structure with the TIJ head while voltage was applied across the center gap.*

References

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Author Biography

Kris A. Bertness received her Ph.D. in physics from Stanford University (1987) and her B.A. in physics from Oberlin College (1981). Prior to joining NIST in 1995, she was at Varian Research Center and the National Renewable Energy Laboratory. Her primary areas of research are semiconductor crystal growth, esp. nanostructures and GaN nanowires, and optoelectronic device design and characterization. Bertness is a senior member of IEEE.