Wafer Scale Fabrication of Nano Probes for Atomic Force Microscopy

Qi Laura Ye*1,2, Hongbing Liu2, Alan M. Cassell1,2, Kuo-Jen Chao3, and Jie Han1,2

1 Center For Nanotechnology, NASA Ames Research Center, Moffett Field, California 94035, USA
2 Integrated Nanosystems, Inc., NASA Research Park, Moffett Field, California 94035, USA
3 Charles Evans & Associates, 810 Kifer Road, Sunnyvale, CA 94086, USA

* Corresponding author: Phone: (650) 604-0497, Fax: (650) 604-0987, E-mail: yqe@mail.arc.nasa.gov

ABSTRACT

We have developed an innovative wafer scale fabrication method for making carbon nanotube (CNT) probes for atomic force microscopy imaging. Our method combines nanopatterning and nanomaterials synthesis with traditional silicon micromachining technologies. Our fabrication process has produced 244 CNT nano probes per 4-inch wafer with control over the CNT location, diameter, length, orientation, and crystalline morphology. CNT nano probes with diameters of 40-80 nm and lengths of 2-6 µm are found to be functional nano probes with no need for shortening. This reliable and true bottom-up wafer scale integration and fabrication process provides a new class of high performance nanoprobes. AFM imaging results show that the CNT probes are strong, wear-resistant, and capable of high resolution AFM imaging.

Keywords: wafer scale fabration, carbon nanotube AFM probes, nanopatterning, nanomaterials synthesis

1 INTRODUCTION

Carbon nanotubes (CNTs) possess remarkable electrical, mechanical, and thermal properties [1]. The idea of using carbon nanotubes as nano probes in scanning probe microscopy was first introduced by Dai et al. in 1996 [2]. The intrinsic nanometer scale diameter, high aspect ratio, and strong mechanical robustness of CNTs make them ideal for high lateral resolution imaging [3,4] and deep trench/via critical dimension imaging [5] in semiconductor in-line processing applications. CNT probes are also highly desired in biological and chemical applications [6-8] where gentle probe-sample interactions are required. When CNT probes approach the sample surface during AFM tapping mode imaging, the CNT buckles elastically which restricts the maximum force that can be applied to soft samples. CNT probes can also be functionalized at the tube open ends [9,10]. They can be made into multi-purpose nano probes by imaging and sensing at the same time, and probing and manipulating materials at the same time. Therefore, CNT probes may be the ultimate probing tips for AFM.

The unique advantages of CNT probes have attracted many efforts to fabricate CNT based imaging probes. Most reported work so far has relied on a "pick and stick" approach to manually attach multi-wall CNTs on silicon pyramid tips under an optical microscope [2-8]. To improve this approach, an electric field has been applied to move multi-wall CNTs on a conducting film to a silicon pyramid tip [11]. However, these approaches are tedious hit-or-miss manual assembly processes, and can only fabricate CNT probes one at a time. Advances have been made by direct catalytic growth of CNTs on silicon pyramid tips using thermal chemical vapor deposition (CVD) methods, either through coating catalysts all over the silicon pyramids or through creating nanopores on top of the flattened silicon pyramid tips [12-14]. Wafer scale production of CNT probes have also been attempted [15,16]. These approaches have scaled up the CNT probe fabrication processes and increased the fabrication throughput. However, thermal CVD growth has little control over the CNT location, density, length, and orientation. It is extremely difficult to obtain individual free standing and well-oriented multi-wall CNTs using thermal CVD. Readily usable probe yields are very low. In addition, these processes all rely on commercially available silicon probes or prefabricated commercial silicon probe wafers. At the end of the fabrication, these processes still require one at a time manipulation approach to remove extra CNTs and/or to shorten the remaining CNTs for probe use. In order to solve the problems that exist with current CNT probe technologies, we have developed an innovative bottom-up wafer scale fabrication method for the reliable mass fabrication of CNT probes through integration of nanopatterning and nanomaterials synthesis with traditional silicon cantilever microfabrication technology.

2 EXPERIMENTS

Our method consists of six major steps: (1) wafer-scale nanopatterning and registration; (2) catalyst deposition and protection; (3) silicon microfabrication of cantilevers; (4) protection scheme release; (5) directional growth of CNTs from silicon cantilevers using PECVD method; and (6) CNT probe characterization, performance evaluation, and testing.

E-beam lithography is used to define the nano-sized catalyst spots on whole wafers. We used a high-speed electron beam writer Hitachi HL-700F e-beam system to pattern catalyst features on a 4-inch Silicon-On-Insulator (SOI) wafer (10 µm Si device layer, 1 µm oxide layer, and 380 µm Si handle layer). To investigate the optimal catalyst feature sizes for achieving single isolated CNT growth per catalyst site, we patterned catalyst dot sizes ranging from 50 nm to 300 nm in diameter with an interval of 50 nm. On a 4-inch SOI wafer, 244 dots were e-beam patterned for 244 cantilever tip locations at the end of the cantilever diving boards. As a control, we also patterned eight 1 µm catalyst sites at certain spots on the wafer. During the same e-beam lithography step, micron scale global and local alignment marks were also patterned.
over the whole wafer to register these nanometer sized dot arrays. A highly sensitive resist layer composed of poly(methylmethacrylate) (PMMA) (100 nm PMMA layer thickness) was applied to the 4-inch SOI wafer and then exposed at an e-beam dosage of 900 μC/cm². The nanometer dot arrays along with the global and local alignment marks could be written in less than 20 minutes. The stitching error across a 4-inch wafer was found to be only 0.5 μm. By writing the alignment marks in the same e-beam lithography step that defined the nano-catalyst spots, we successfully integrated the nano and microfabrication processes.

After nanopatterning and e-beam resist layer developing (1:3 methyl isobutyl ketone : isopropyl alcohol), a short O₂ plasma descum was performed (150W, 250 mTorr, 10 sec) to clean the wafer prior to metallization. 20 nm Cr or Ti was evaporated on the wafer as barrier layer. 20 nm Ni was deposited on top as CNT growth catalysts by electron beam evaporation. The e-beam resist layers was lifted-off in acetone, leaving the catalyst dots deposited at the defined spots on the wafer. The whole wafer was then thoroughly cleaned, rinsed, and dried for microfabrication.

In order for the catalyst seeds that define the CNT locations to survive harsh dry and wet etch chemicals used in microfabrication, we developed catalyst protection schemes before commencing the conventional microfabrication of silicon cantilevers. PECVD-grown Si₃N₄ protection layer with a thickness of 200 nm was deposited on the front-side for protecting deep reactive ion etching (DRIE). ProTEK chemical series (ProTEK EXP02103-18 etch protectant) from Brewer Science, Inc., was coated on the backside for protecting backside KOH wet etching. 500 Å ProTEK protectant survived 33% KOH etching at 80°C for more than 6 hours.

The cantilevers were fabricated from SOI wafers through a simple two-mask fabrication process. The front-side mask defined the outline of the cantilevers (cantilever body, cantilever beam, and the tabs that held the cantilevers to the silicon wafer frame). The backside mask shaped the body of the cantilevers. Each fabrication step was aligned to the global alignment marks that were initially patterned by e-beam lithography. This insured that the catalyst sites and the final CNTs were located at the exact locations on the cantilever diving boards where they were designed. The process overall layer-by-layer alignment accuracies were found to be within ±1 μm.

We used a home-made 4-inch hot filament direct current PECVD reactor for CNT growth which permitted vast flexibility in process parameter control and monitoring. In addition to normal process variables such as pressure, plasma power, and gas mixture flow and composition, it was possible to also control the electrode gap, electrode geometry (for angled CNT growth), substrate temperature, and gas filament heating. We conducted detailed CNT growth studies using high throughput combinatorial methodologies [17,18] to achieve individual isolated CNT growth at pre-defined locations on silicon cantilevers. The CNT probes possessed the desired properties for diameter, length, orientation, and crystallinity.

3 RESULTS

Figure 1 shows SEM image of an individual CNT grown from a 200 nm catalyst site on a cantilever beam. Only one isolated individual CNT has been grown from the catalyst site. The individual CNT is found to be 60 nm in probe diameter and 5 μm in length. The tube axis is tilted 13° towards the front of the diving board end with respect to the cantilever beam surface normal. This 13° angle is required because most commercial AFMs are equipped with tip mounting holders that tilt the cantilevers at 13° relative to the image surface and AFM scanning head. This controlled angle growth is only possible in PECVD where an electric field is present in the plasma discharge to direct the nanotubes to grow and align parallel to the electric field.

![SEM image of CNT AFM cantilever probe with an individual CNT grown from a 200 nm catalyst site on a cantilever beam. Side view with ×3500 magnification. One single isolated CNT of 60 nm in probe diameter and 5 μm in length is grown per site from 200 nm catalyst spot size. The CNT is oriented at a 13° angle with respect to the cantilever beam surface normal.](image)

Among the varied catalyst dot sizes, individual CNTs were obtained only from 50 nm to 200 nm catalyst sizes. 250 nm and 300 nm catalyst sizes gave multiple CNTs. Using the optimized catalyst formulation (20 nm Cr/Ti and 20 nm Ni) and growth conditions, the best CNT growth occurred at a gas mixture of 80 sccm NH₃ and 22.5 sccm C₂H₂ at a chamber pressure of 4 Torr, following a hot filament pretreatment (without plasma) with 80 sccm NH₃ for 10 min. Growth of well-aligned individual CNTs occurred at a bias voltage of -550 V (360 W, 690 mA, 800 Ω). In order to achieve a 3 to 5 μm length of CNT which we found best for AFM imaging, 10 minutes growth time was needed using the above process conditions. CNT growth rate was found to be ~550 nm/min, after 1 min induction/nucleation time.

To assess the crystalline quality of the individual CNTs on cantilevers after growth, high-resolution transmission electron microscopy (TEM) analysis was performed. Figure 2 shows the TEM images of individual CNT with a well aligned and non-entangled multi-wall carbon nanofiber bamboo morphology. The individual CNT probe diameter of 60 nm is confirmed in these TEM images. We can clearly see the multi-wall CNT wall
structures and the defected crossover parts. This bamboo morphology is normally achieved in tip growth mechanism at high bias in PECVD. Because of this unique bamboo morphology, our CNT probes are typically much stiffer than pure multi-wall CNTs of the same diameter and length. The clear TEM images in Figure 2 indicate that there was no electron beam induced thermal vibration observed with this 5 µm long CNT. Ni catalyst is wrapped with thin graphite layers at the very end. There is no need to etch away this Ni particle before the CNT probe can be used for AFM imaging.

![Cross-sectional TEM images](image)

Figure 2. Cross-sectional TEM images of an individual CNT with bamboo morphology. (a) CNT probe body part with x100K magnification. Multi-wall CNT wall structures with defected crossover parts clearly visible. (b) CNT tip end with x100K magnification. Ni catalyst is wrapped with thin graphite layers at the very end. The clear TEM images here indicate that there is no electron beam induced thermal vibration observed with this 5 µm long CNT.

The CNT probe evaluation and testing were conducted on commercial AFMs (Digital Instruments Multimode AFM with a Nanoscope IIIA controller and Digital Instruments Dimension 5000 system). Figure 3 shows AFM images of a photoresist patterned 1 µm trench using CNT AFM probe made from this work. Figure 3(a) shows the interaction curve derived from tapping mode imaging (amplitude and deflection signals). It exhibits well-defined amplitude-dampening event resulted from the CNT AFM probe tip pushed towards and extracted from the sample surface. The fluctuation in the amplitude vs. distance signal indicates the presence of a CNT [2]. Figure 3(b) and 3(c) show 2D and 3D AFM images of this photoresist patterned 1 µm trench using a CNT probe that is 60 nm in tip diameter and 5 µm in length. As seen in Figure 3(b) and 3(c), the CNT probe is able to fully resolve the sidewalls and the bottom of this 1 µm trench that is 450 nm deep. The bottom of the trench is clearly visible. The trench slope angles were measured to be 80 and 69 degrees through the line cut section analysis, very well matched with the resist etching profile characterized by cross-sectional SEM.

![AFM images](image)

Figure 3. AFM images of a 1 µm trench using CNT AFM probe made from this work. (a) The force vs. distance curve. (b) 2D AFM image of 1 µm trench. (c) 3D image of 1 µm trench. The CNT probe is 60 nm in tip diameter and 5 µm in length. It is able to fully resolve the sidewalls and the bottom of this 1 µm trench that is 450 nm deep. The bottom of this 1 µm trench is clearly visible.

4 DISCUSSION

Our wafer scale growth optimization centered on controlling the CNT parameters from the nanometer sized catalyst spots over 4-inch wafer scale. Based on SEM and TEM analysis, an assessment of the wafer scale CNT probe yield and variations in diameter, length, orientation, and crystallinity has been recorded. Using the optimized catalyst formulation and growth conditions, for released CNT AFM cantilever probes, we have achieved an individual CNT growth yield of 85-90% from 100 to 200 nm catalyst sites. In a typical growth run, the base diameter of an individual CNT probe varies from 60 nm to 80 nm, while the tip diameter varies from 40 to 60 nm. The CNT lengths show a distribution of ±20%. The orientation of individual CNTs on cantilevers varies from 10° to 20° with respect to the cantilever beam surface normal. Our PECVD growth provides mostly bamboo structure CNTs with their crystalline morphologies very similar to the ones demonstrated in Figure 2(a) and 2(b). Across the wafer, CNT probes maintain reasonably consistent diameter, length, orientation, and bamboo morphology. Careful inspection of cantilevers from different areas of the 4-inch wafer has allowed us to analyze statistics for quality control and assurance. We are currently working on further improvement of our process control and yield.

Before we finalized our fabrication process, we investigated various other approaches for obtaining the desired CNT probes on cantilevers. We found that growing CNTs prior to cantilever microfabrication posed many processing challenges due to the inherent mechanical instability of individual CNTs exposed to liquid based processing agents or to CNT protection and stripping chemicals. Preliminary tests showed that upon exposing the as-
grown CNTs to photoresist coating and removal or to nitride layer protection and stripping, the CNTs would be heavily damaged or totally removed from the silicon substrate. Since vertical CNT orientation was a prerequisite for obtaining usable probes, growing the CNTs at the end of the fabrication process proved to be a better approach with a reasonable yield of usable CNT probes per wafer. We also found that our wafer scale catalyst deposition and liftoff steps could not follow cantilever microfabrication. Resist layers must be extremely consistent in this process to yield uniform spot sizes for catalyst deposition, something impossible to achieve on a post-fabricated cantilever wafer. Therefore, we had opted to deposit and protect the catalyst ahead of cantilever fabrication, in predefined diameter and placement on final cantilever beam. This approach seems to be the best option.

It is known that a carbon nanotube probe is able to fully trace the bottom of the trenches without producing image artifacts [2,3,5]. CNT probes can also dramatically improve the imaging resolution and lifetime [2-5]. The image obtained by the conventional silicon probe is limited by its geometry. The micromachined silicon pyramid is physically unable to accurately trace the topographic variations of the surface, especially in critical dimension measurements. Probes fabricated from silicon tend to have limited lifetime due to the inherent chemical/mechanical instability of silicon. The silicon probe is brittle, and as such, even when an ultra sharp silicon probe is used for high aspect ratio feature imaging, the probe could easily become worn out or rendered unusable due to mechanical breaking or tip wear. By contrast, the remarkable flexibility of the hexagonal graphitic network allows the CNTs to sustain large distortions via axial compression, such as those encountered with tapping mode imaging [19,20]. Published experimental work has demonstrated that axial deformations are elastic with no atomic defects forming in the hexagonal lattice [21,22].

While most pure multi-wall CNTs with lengths greater than 3 μm require shortening for AFM imaging [2-5], we are able to collect satisfactory AFM images using our fabricated CNT probes with lengths as long as 6 μm. Therefore, we can eliminate the shortening step in our process. Furthermore, our as-grown CNT probes with length between 2 to 6 μm are found to be imageable. This reduces the CNT length uniformity requirement for wafer scale individual CNT growth. Our process yield is therefore greatly improved.

5 CONCLUSION

We demonstrate here an example of integrating CNTs with silicon cantilevers for reliable fabrication of CNT based probes at wafer scale for AFM imaging applications. In our case, the nano-micro integration is achieved through catalyst nanopatterning and registration at wafer scale and through effective nano-catalyst protection and release before and after microfabrication. Our wafer scale fabrication method provides CNT probes that are directly grown from the silicon cantilevers at wafer scale. CNT probe locations and diameters are defined by e-beam lithography. CNT length, orientation, and crystalline quality are controlled by plasma enhanced chemical vapor deposition (PECVD) method. PECVD method enables us to grow well-aligned single carbon nanotubes on individual catalyst sites on silicon cantilevers with control over CNT location, diameter, length, and crystallinity. Due to the crystalline morphology of our PECVD-grown CNTs, there is no need in our process to conduct post fabrication treatment to remove and/or to shorten the CNT probes. With effective catalyst protection schemes, this fabrication process is very similar to conventional approach for fabricating wafer scale silicon AFM probes. Process control is therefore feasible and the overall yield is greatly improved. The probes made from this method display good image acquisition characteristics. No shortening or post-fabrication treatment is necessary. AFM scanning tests show imaging capabilities of these probes in critical dimension measurements. This is a truly bottom up wafer scale CNT AFM probe fabrication method.

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