Low-Z, Chemically Resistant, Microfabricated Carbon Composite Transmission Electron Microscope Grids

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ABSTRACT

An issue that often impacts analysis of microscopy samples is the presence of high-Z atoms in the sample support structure. For example, TEM support grids are typically copper and introduce copper counts in energy dispersive x-ray spectroscopy (EDXS) analysis. In many cases, it is also desirable that the chosen support materials be resistant to chemicals and various processing methods. We present an improved transmission electron microscope (TEM) grid made by carbon-infiltrated carbon nanotube templated microfabrication (CNT-M). Several membranes were suspended on these grids including amorphous carbon, silicon dioxide, alumina, and boron carbide. These grids provide a significant advantage in analytical TEM applications due to improved chemical resistivity and an absence of high-Z atoms which allow for a wider range of sample preparation and processing techniques.

Keywords: TEM grid, CNT-M

1 INTRODUCTION

Samples that are prepared for observation and characterization in a transmission electron microscope (TEM) must be electron transparent but still able to be handled and manipulated. Significant efforts are spent preparing specimens, thinning, or devising support mechanisms for specimens. One common method is the use of metal grids with thin support films bridging the grid gaps. Samples are then deposited on the thin support film for TEM observation. Many varieties of grid materials are avalable but the most common is copper. Subsequent analysis on the common grids by means of energy dispersive x-ray spectroscopy (EDXS) will be sensitive to the high-Z atoms used in the support grid and show unwanted and confusing counts from the support structure. This is especially problematic when analyzing samples that contain either the same elements as the support grid or that have overlap in the EDXS spectra with elements in the support grid.

Metal atoms are also undesirable for applications and sample preperations involving exposure to chemicals or biological agents, where metals can react with the sample or the materials used in preparing the sample. To address this problem, TEM grids from less reactive metals or low-Z elements are also available. However, grids of materials such as beryllium or diamond can be both expensive and/or toxic.

Carbon is a low-Z atom which can be fabricated into three dimensional geometries. Previous attempts to incorporate carbon as a material in TEM grids include: casting carbon fibers in a polyester mold [1], and coating metals in a carbon nanotube film [2]. The former have limited chemical resistance, and the latter do not avoid the use of high-Z atoms. The two methods which currently exist for fabricating high-aspect ratio, all-carbon devices are: carbonization of SU-8 photo-resist [3], and carbon nanotube templated microfabrication (CNT-M)[4]. The carbonization process for SU-8 structures results in shrinkage of up to 80% of the original dimensions of a structure. This does not allow for accurate dimensional control, an important element in the construction of TEM grids which must fit into a 3.05 mm diameter slot in the TEM stage. CNT-M is a process whereby three dimensional carbon nanotube structures can be grown from a patterned two dimensional catalyst layer. Here we use CNT-M to fabricate TEM grids of controlled geometry which are chemically resistant and devoid of high-Z and metal atom contaminants.

We present here the fabrication of all carbon TEM grids with several thin support membranes attached. The grids are lithographically patterned and use the CNT-M process to create a carbon nanotube composite structure. The infiltration material is carbon. A versitile process to cover these grids with a wide variety of support membranes is presented. Support membrane examples include amorphous carbon, slicon dioxide, alumina, and boron carbide.

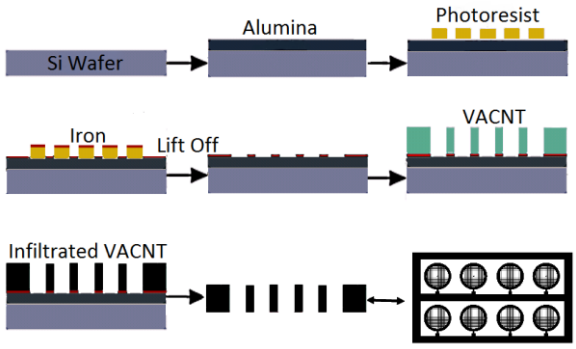

Figure 1: Overview of the CNT-M process. A Si wafer is coated in a barrier layer of alumina, and then patterned with an iron catalyst layer. CNTs are grown and infiltrated with carbon by a CVD process.

2 MATERIALS AND METHODS

2.1 CNT-M (Carbon Nanotube Templated – Microfabrication)

The CNT-M process (illustrated in figure 1) creates a 3 dimensional structure by using carbon nanotube forest growth to convert a two dimensional lithographically formed pattern of catalyst into the third vertical dimension. Infiltration of the 3-d forest pattern with another material creates the 3-d solid (or porous) structure.

Carbon nanotubes were synthesized by thermal chemical vapor deposition (CVD), where carbon nanotubes were grown on prepared silicon wafers by the decomposition of a carbon-containing gas. The prepared wafers were patterned with 30 nm of Al_2O_3 and 7 nm of Fe using standard photolithography techniques and lift off. (blanket layers of alumina as in figure 1 can also be used) CNT growth and infiltration was done in a 1″ tube furnace. After a heating time of 10 minutes in hydrogen (200 sccm), CNTs were grown at 750 ºC with ethylene (150 sccm) and hydrogen (400 sccm) gases. CNT forests were infiltrated with carbon at 900 ºC in 100 sccm ethylene and 200 sccm argon or hydrogen. Flowing hydrogen during carbon infiltration leaves CNT structures attached to substrate, while flowing argon causes spontaneous release upon cooling. Cooling was done in 250 sccm argon for 15 minutes, at which time the furnace was opened with argon continuing to flow through the sealed tube until the furnace temperature dropped to 300 ºC. The tube was then opened and the samples removed.

The infiltration process deposits on the nanotubes locking them together to make a solid structure. This final structure can be porous or dense depending upon the degree and quality of the infiltration. The deposition also coats non-nanotube regions creatign a "floor layer". Samples were etched in a 300 W oxygen plasma at 100 mTorr for 5 minutes to remove the floor layer.

We used a lithography mask where each 4" silicon wafer contained 250 individual TEM grids. The grids are attached together in sets of 8 as seen in figure 1. Figure 2 shows an SEM image of the fabricated grids. Grid height was a function of CNT growth time with 3 minutes of growth produced forests approximately 50 µm tall.

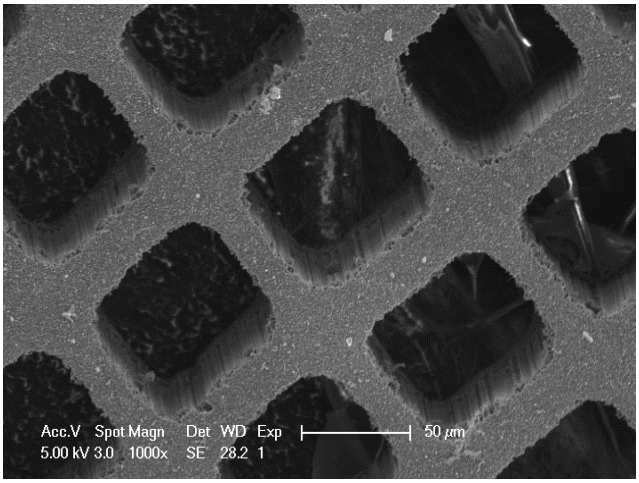

Figure 2: SEM image of a CNT-M TEM grid. Sample tilted to 15 degrees to emphasize vertical sidewall growth.

2.2 Thin Films

To attach the thin support membranes we used a process that would allow direct application of the film to many grid supports at the same time. In this process, a thick sacrificial layer is deposited on the structures while they are still attached to the flat silicon substrate. This covers both the grids and within the grid holes. Removal of the grids and sacrifical layer gives a flat surface on the wafer side of the structure. Deposition of the thin membrane is on that flat surface. The sacrifical layer is then removed.

The sacrifical layer is a 0.5 % solution of Formvar powder prepared in 1,2-Dichloroethane. Formvar was sprayed onto TEM grids, still attached to the silicon substrate, by an ultrasonic sprayer. Samples were placed in 49% HF for 10 minutes, rinsed in DI water for 10 minutes, and removed from substrate. Thin films were then directly deposited onto the substrate-defined side of Formvar coated grids.

Carbon films were sputtered in a Kurt Lesker PVD-75 system. Silicon dioxide and aluminum oxide films were deposited by a Denton E-Beam Evaporator. Boron Carbide films were deposited by magnetron sputtering. Grids were annealed in argon at 400 C for 15 minutes.

Chemical testing was performed by placing grids in KOH, HCl, or HF solutions for several hours. Grids were then rinsed in deionized water for 10 minutes. TEM characterization, along with collection of EDX and EELS data, were done in a Tecnai F20 TEM. Thin films were deposited on glass slides and thickness confirmed by characterization on a Veeco Dimension 5 AFM.

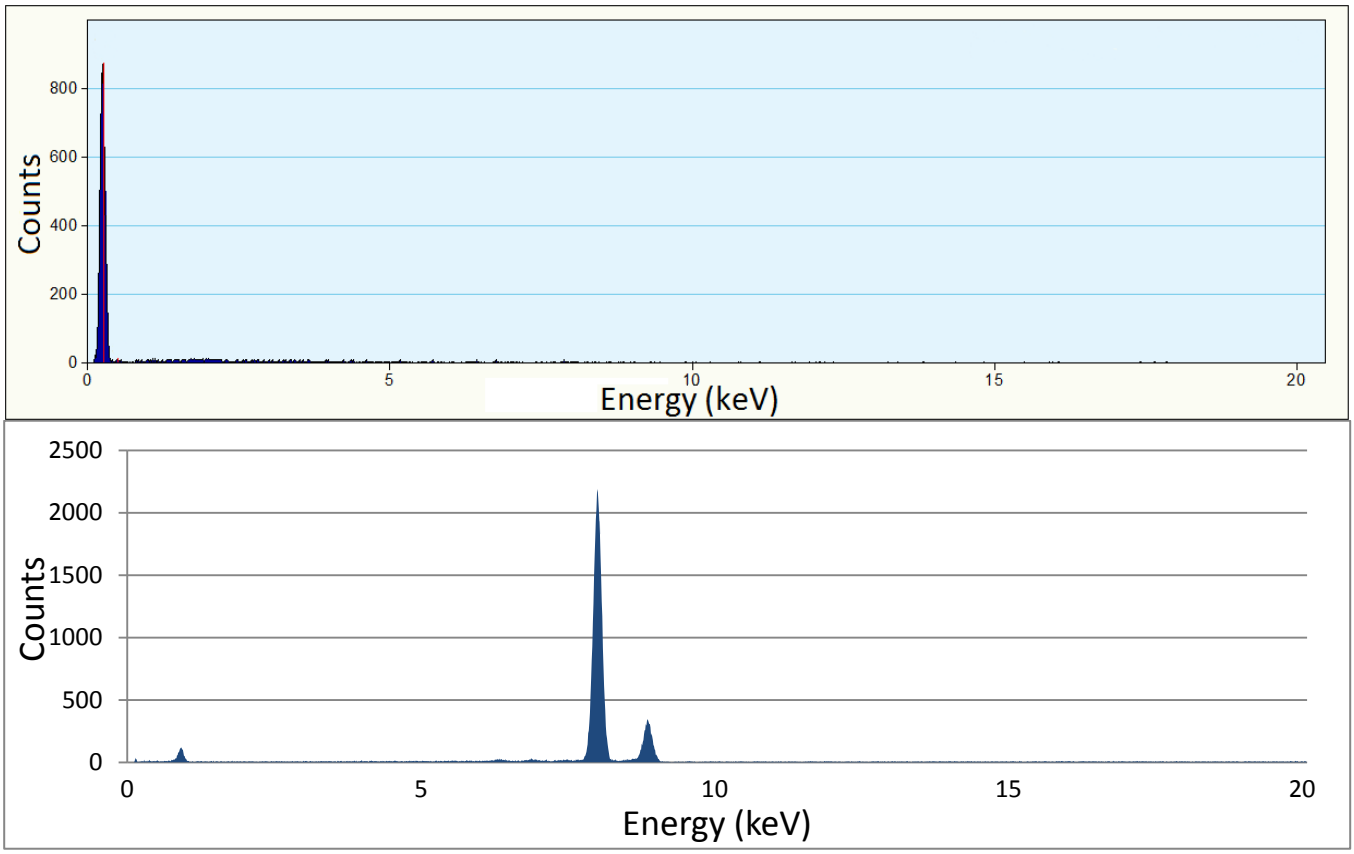

Figure 3: 100 s of XRD data collected from all-carbon TEM grid (top), and a commercial copper grid (bottom).

3 RESULTS

EDX analysis of grids showed carbon peaks with no other atomic signatures (See figure 3). This indicated the absence of the Fe growth catalyst and Al_20_3 diffusion barrier used during the growth process. Chemically tested grids showed no measurable deformation or change in mechanical properties of the grid. EDX detected no non-carbon signature after chemical tests.

Force testing has been conducted to determine the materials properties of CNT-M structures[5]. This testing has confirmed a yield tensile strength of 110 MPa and a Young's modulus of 6 GPa. Bulk copper is known to have a yield tensile strength of 70 MPa and a Young's modulus of 117 GPa.

AFM measurement of thin films on glass slides confirm deposition of 25 nm thick carbon films (see figure 4). The thickness of the sputtered carbon films increases as a function of exposure time. 15 minutes produced a 10 nm film, and 20 minutes produced a 25 nm film. Other films were deposited in systems equipped with crystal deposition monitors, and AFM measurements confirmed the accuracy of the deposition monitors. TEM analysis of thin films shows amorphous structures with good electron transmission (see figure 5).

4 DISCUSSION

Carbon grids are more resistant to bending than metal grids. However, carbon grids will break under the same applied force that would cause metal grids to bend or crease. Carbon grids are more chemically resistant than metal grids, and contain no detectable high-z atoms. The microfabrication process used to make the grids allows reliable control over the dimensions of the grid. The microfabrication process also allows control over the number of grids that are locked together during growth and processing.

Our thin film deposition method requires very little handling, and allows for processing large batches of grids. This method has been succesfully shown to produce thin, suspended films with thicknesses from 10-25 nm. This method may be preferable to the current method for depositing thin films on TEM grids, as it poses less risk of damaging grids due to handling.

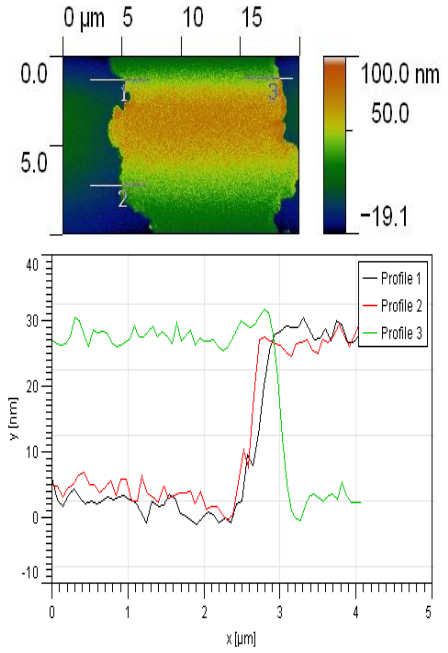

Figure 4: AFM image of alumina film deposited on a glass slide. Three measurements show good agreement for a thickness of 25 nm.

5 CONCLUSION

We have made TEM grids that are composed entirely of carbon. These grids are more resistant to bending than commercially available grids, have a greater tensile strength, and can be made and processed in batches. We have coated batches of grids in amorphous carbon, alumina, silicon dioxide, and boron carbide thin films.

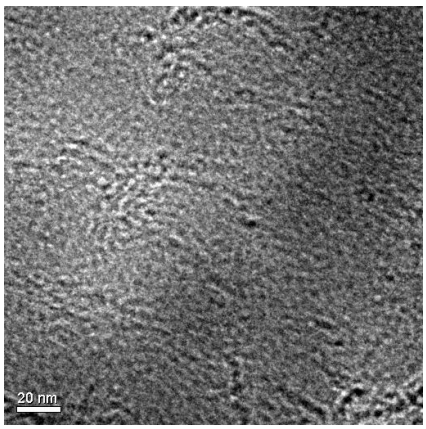

Figure 5: HRTEM image of a 25 nm thick boron carbide film, showing a lack of crystalline structure. Image taken at 200keV.

6 ACKNOWLEDGEMENTS

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REFERENCES

[1] Warren, J.B. & Kundrath, M.R. US Patents 4,163,900 and 4,250,127, 1979.

[2] Zhang et al., "Superaligned Carbon Nanotube Grid for High Resolution Transmission Electron Microscopy of Nanomaterials," Nano Lett., 8 (8), 2564–2569, 2008.

[3] Park, B.Y., Taherabadi, L., Wang, C., Zoval, J. & Madou, M.J., "Electrical Properties and Shrinkage of Carbonized Photoresist Films and the Implications for Carbon Microelectromechanical Systems Devices in Conductive Media," J. Electrochem. Soc., 152, J136–J143, 2005.

[4] Hutchinson, DN et al., "Carbon Nanotubes as a Framework for High-Aspect-Ratio MEMS Fabrication," JMEMS, 19, 75, 2010

[5] Fazio, W et al. "Material Properties of Carbon-Infiltrated Carbon Nanotube-Templated Structures for Microfabrication of Compliant Mechanisms," ASME Proc., 2011