Windows of Opportunity: A New Platform to Understand Structure-Property Relationships in Nanotechnology

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ABSTRACT

Excitement about nanotechnology derives from unique size/structure dependent properties of nanoscale materials. Methods to prepare a wide range of materials and structures are now available, but a limited fundamental understanding of structure-function relationships remains a significant challenge for the design of useful new nanoscale materials, assemblies, and devices. In order to address this challenge, improved characterization platforms that can provide much richer information in terms of direct correlation of these relationships are required. In this paper we present a revolutionary new window of opportunity for nanostructure visualization and characterization in the form of advanced TEM grids that accommodate a wide range of characterization methods on the *same* sample.

Keywords: transmission electron microscopy, surface science, characterization, nanoscale materials.

I. INTRODUCTION

Imagine if one could directly observe the correlation in electronic response and the nanoscale structure for single electron transistors, or if one could directly observe the effects of surface chemistry on adsorption and organization of nanoparticle arrays or even atomic arrays onto functionalized surfaces, or if one can observe the nucleation and self-assembly of 2-D arrays of quantum dots during molecular beam epitaxy and to correlate the structure of these arrays with their performance in quantum computing and quantum cryptography, or if one could watch the effects of temperature and deposition parameters on nanostructure evolution in real-time for advanced coatings, or if one can directly image antibody/antigen interactions for antibodies anchored to a surface. All of these examples represent new opportunities for enhancing our fundamental understanding of how structure influences behavior at the nanoscale. This paper presents a new, enabling characterization platform based on an improved version of transmission electron microscopy (TEM) grids that can bring all of these examples and many more to reality.

Transmission electron microscopy (TEM) is one of the most direct and widely used methods of "seeing" structures at the nanoscale. TEM has been extensively used by materials scientists and biologists for many years to visualize structures based on electron density in the samples. The imaging capabilities of TEMs have dramatically improved over the past 10-15 years due to enhancements in electron optics, detection hardware, and image processing capabilities, allowing researchers unprecedented abilities to resolve sub-Ångström structural features in samples. While these remarkable capabilities open a wide range of opportunities for structural characterization of materials, existing sample preparation methods and TEM grids have become the limiting factor. These methods still require either time-intensive destructive sample preparation which can actually change the sample or the use of surrogate samples for analysis. There is a strong need for new approaches that minimize these current limitations and improve the quality of information provided by TEM analysis. Moreover, as researchers address the myriad challenges of commercializing nanotechnology, there is an even more pressing need for enabling platforms that allow one to not only characterize both the structural and compositional characteristics afforded by TEM, but also to understand how these characteristics influence the optical, electronic, chemical, and/or biological properties of materials and assemblies *all in the SAME sample*. The availability of new platforms with these capabilities will open the window of opportunity for materials scientists, nanoscientists, and biologists as well as for researchers that do not commonly use TEM including chemists, surface scientists, biotechnologists, and engineers to harness the powers of TEM in ways previously not possible.

Recently, researchers at the University of Oregon reported the development of a new type of analysis platform for TEM to characterize nanoparticle arrays.[1] These patent pending TEM grids which employ thermal SiO_2 grid windows were developed to address limitations in existing grids that prevented the processing of grid surfaces to meaningfully represent surfaces on which these arrays would be deposited. In particular, the deposition of nanoparticles arrays onto planar surfaces is highly dependent upon the interaction of those particles with the surface chemistry. Hence, there was a need to be able to control the surface chemistry of the grids to optimize deposition conditions

while still allowing for structural imaging of the resulting arrays to provide feedback. The resulting grids provide an unprecedented new capability for sample processing, TEM analysis, and the opportunity for utilizing a wide range of other surface analytical methods. Figure 1 shows a schematic cross-section of these grids along with scanning electron microscope images of actual grids.
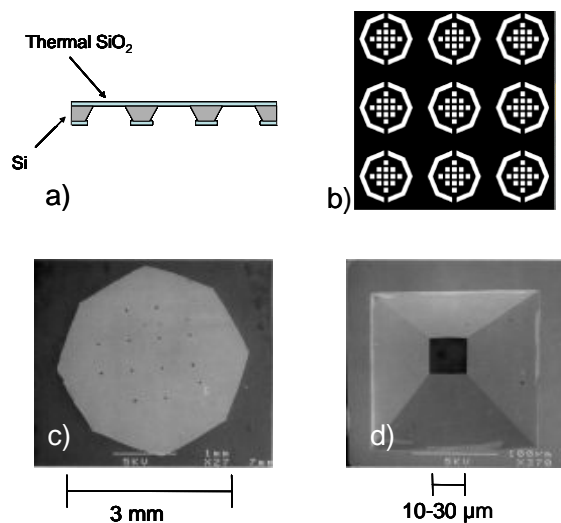

Figure 1. New TEM grids for advanced characterization of nanomaterials and devices. Grids are produced using thermal SiO$_2$ grown onto Si wafers (a). The grids can be produced in a wafer format (b) that allows for popping-out the grids for imaging but also enhanced processing and handling. (c) SEM image of 3 mm TEM grid with 12 windows. (d) Underside SEM view of thermal SiO$_2$ windows and etch pit. The SiO$_2$ windows provide for enhanced processing capabilities and control over interfacial chemistry.

The present paper highlights some of the unique attributes of these new TEM grids and provides examples of some of the additional capabilities and applications that can be realized using these grids.

II. DESCRIPTION

The new TEM grids presented in this paper (and shown in Fig. 1) are produced via photolithography and wet-chemical etching of thermally oxidized thin Si wafers. The grid and window dimensions and usage form factor can be controlled through the photolithography and processing conditions. Standard TEM grids are 3 mm octagons with 12 or 16 10-30 µm square windows, but it is also possible to produce other window shapes, e.g. slit that are 10-30 µm wide by 2 mm long, with built-in indexing capabilities. It is also possible to create wafers of "pop-out" grids (Fig 1b) that allow for enhanced wafer level handling and processing including such steps as cleaning, spin coating, and patterning

of electrodes for example. The grids are rigid due to their Si frame and will not deform during handling.

The window thickness can be controlled by the thermal oxidation conditions as well as by post-fabrication etching. Typical grids have windows that are 30-100 nm in thickness. The oxide film is grown at 1100 °C which allows for viscous flow of the oxide to relieve compressive stress introduced during growth.[2] This stress-relief prevents the windows from buckling or breaking when the supporting silicon is etched away. The windows do not appear to be bowed, as there is no evidence of a change in focal plane. While SiO$_2$ glass is known to be a fragile material, particularly at extremely thin dimensions, the geometry of the windows in combination with the oxide growth process results in windows that are surprisingly robust and can withstand multiple processing steps.

The use of thermally-grown SiO$_2$ windows in these grids provides for numerous advantages over other types of TEM grids. First, Si and SiO$_2$ are chemically and thermally stable materials. They are the two most commonly found materials in semiconductor processing and will withstand a wide range of aggressive cleaning procedures including UV/ozone, oxygen plasma treatment, pirhana, and RCA cleaning. This allows one to ensure any adsorbed organic or metallic impurities are removed prior to sample preparation. Moreover, it allows one to use acidic solutions for deposition or processing of samples on the grids. The grids can be heated to >1000°C with little or no change in structure. This temperature stability allows for direct monitoring of changes in structure as a function of temperature for process optimization. Existing TEM grids cannot provide this level of chemical nor thermal stability.

A second advantage is that growth of thermal oxide windows results in ultra-low surface roughness that is imparted by the Si wafer; the background scattering of these TEM grids is significantly lower than many other grids with thinner windows. Hence, it is possible to use thicker windows for equal or better imaging resolution than other grids to enhance the mechanical properties of the windows.

A third advantage is that thermal SiO$_2$ is representative of one of the most widely functionalized surfaces in analytical chemistry. Unlike other TEM grids, the well-defined surface of thermal SiO$_2$ allows for a wide range of surface modification and chemical functionalization to promote specific and non-specific interaction of the sample with the grid. It is possible to control the relative hydrophobicity and hydrophilicity of the grids by surface modification to enable deposition of a wide range of materials from both aqueous and organic solutions. For example, as-grown carbon nanotubes are hydrophobic which forces them to agglomerate when deposited on hydrophilic surfaces. By modifying the surface of the grids to be hydrophobic, it is possible to preserve their isolated structure

for imaging as well as for understanding and possibly optimizing how they deposit on planar surfaces.

In addition to modification of the surface for non-specific interactions, it is possible to modify the surface of the grids to promote the specific interaction and/or covalent attachment of a wide range of chemical and biological molecules to the surface. This will allow for observation of interactions with bound species on planar surfaces. As an example, it is possible to covalently attach an antibody to the surface of the grid. This grid could then be immersed in a solution of antigens to observe binding events when the antigen is appropriately labeled.

It is also possible to modify the surface chemistry of the grid from SiO_2 to other metal oxides including TiO_2, Al_2O_3, ZrO_2, Ta_2O_5 or metal nitrides such as AlN or TiN through atomic layer deposition (ALD) to emulate other materials. These grids can then be used to directly investigate synergistic surface interactions that are observed in catalysis for example. Figure 2 shows an image of commercial ZnO nanopowder (Aldrich) deposited onto an Al_2O_3-coated (5 nm) SiO_2 grid. The presence of the 5 nm coating of Al_2O_3 on the SiO_2 grid has been verified by XRD. The window shows excellent electron transparency.
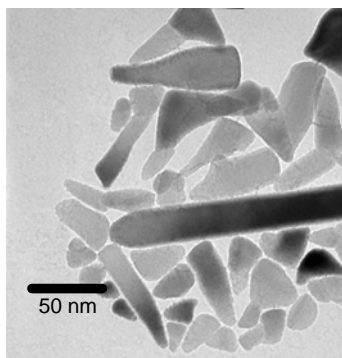

Figure 2. Zinc oxide nanocrystals deposited onto Al_2O_3-modified SiO_2 TEM grids.

These combined features of the SiO_2 windows would enable a new opportunity for process development in coating technologies in which one could monitor nucleation, growth, and organization of monolayers and multilayers. One could observe conditions favorable for defect formation including dislocations, pinholes, grain boundary effects. One could utilize TEM as a part of the process optimization for a range of deposition methods including evaporation, atomic layer deposition (ALD), sputtering, spin-on coatings, chemical vapor deposition (CVD), plasma-assisted CVD, and physical vapor deposition (PVD) among others. Step-by step analysis could be used to understand structural evolution in these thin films which serve as seed layers for thicker films. Moreover, one could monitor the effects of surface modification on adhesion of the thin films.

When comparing these SiO_2 TEM grids to commercially available grids, there are two types of grids worth mentioning, silicon monoxide (SiO_x) and silicon nitride (Si_3N_4). Commercially available SiO_x TEM grids are often used as approximations for SiO_2 surfaces; however, these substrates are not rigid, the surfaces are rough, and SiO_x has an ambiguous chemical structure that is a mixture of SiO and $SiO_{2.6}$. This surface does not have the same well-defined chemical reactivity nor stability as native or thermally grown SiO_2 on silicon. Due to the reactivity of the polymer-coated metal grid that typically supports the SiO_x film, these grids cannot withstand even the mildest environments that are used for cleaning and processing SiO_2/Si.

Recently, silicon nitride has emerged as a new type of TEM grid that is commercially available from selected vendors. It has been shown that the surfaces of silicon nitride grids can be oxidized through O_2 plasma treatment,[3] but the chemical nature and reactivity of the surface has not been determined. It has also been shown that the chemical composition of oxidized silicon nitride surface depends strongly on the method of oxidation, ranging from an oxynitride composition at lower levels of oxidation toward a "silicon oxide-rich" layer after more extensive oxidation.[4] The reactivity of the "native oxide" on silicon nitride has been shown to depend on the method of sample preparation.[5] Given the marked dependence of the surface reactivity of silicon dioxide and oxidized silicon nitride on the method of preparation and given the lack of reliable information regarding the ability to reproducibly functionalize the oxidized Si_3N_4 surface, the best approach to reliably image nanostructures on chemically modified surfaces is to use a surface that is prepared in the same manner as will be used for bulk measurements.

III. ADVANCED APPLICATIONS

The rich surface chemistry of the SiO_2 TEM grids combined with their chemical, thermal and physical stability, creates a unique opportunity to not only improve sample preparation and imaging resolution in TEM, but also to utilize these grids as platforms in a number of advanced applications that will actually accelerate research. As an example, the ability to utilize multiple analytical methods to characterize the samples is unique for these grids and will allow for unprecedented understanding of structure-property relationships. It is possible to combine structural/chemical evaluation of samples deposited on the grids with a wide range of surface analytical techniques including atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), surface-enhanced Raman spectroscopy (SERS), secondary ion mass spectroscopy (SIMS), surface plasmon resonance (SPR), scanning tunneling microscopy (STM), electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM),

ellipsometry, and fourier transform infrared (FTIR) among others.

Figures 3 and 4 show examples of surface analytical techniques applied to 1-D and 2-D arrays of Au nanoparticles deposited on the TEM grid surfaces. In both cases, the grids have been carried through multiple processing steps to achieve the desired structure. Figure 3 shows an AFM image (tapping mode – amplitude) and the corresponding TEM image of an array of DNA stretched across the surface of the TEM grid. The grids were cleaned using RCA SC-1 methods to promote an increased concentration of surface hydroxyl groups. Subsequently, the surface was exposed to octyl-trichlorosilane to create a hydrophobic surface. The grid was then soaked in a solution of DNA and pulled from solution to molecularly comb it into a linear array across the surface. The bundling and clumping of the DNA present in Figure 3 is due to the presence of $MgCl_2$ in the DNA solution. The grid was then soaked in a solution of Au NPs with a positively-charged surface functionality which specifically interacts with the negatively charged phosphate groups in the DNA backbone. These Au particles then provide contrast during imaging for the DNA.
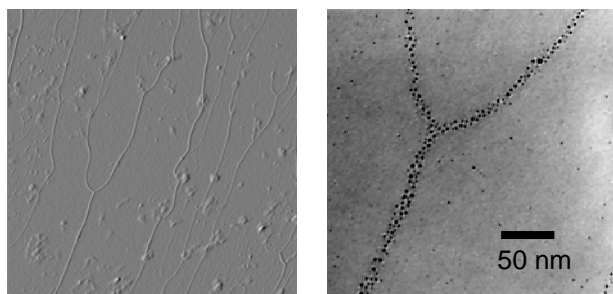

Figure 3. Array of DNA on TEM grid surface. AFM image on left was recorded using tapping mode AFM in the amplitude setting. TEM image on right shows Au NPs selectively sticking to branched DNA.

Figure 4 shows an XPS plot of a TEM grid that has been modified with HfO_2 to promote the specific interaction of AuNPs with the grid surface. In this case, the grids were cleaned using oxygen plasma and RCA SC1 treatments followed by functionalization with $HfOCl_2$ to forma monolayer of HfO_2. Finally, the grids were soaked in a solution of Au NPs to promote the self-assembly of the phophonate-functionalized AuNPs on the HfO_2 surface. The XPS data in Figure 4 was taken prior to deposition of the AuNPs to determine the relative coverage of the HfO_2 monolayer on the surface of the grid. The O 1s, Si 2p, and Hf 4f peaks are all enlarged in this image. The TEM image on the right shows the structure of the 2-D array of AuNPs that have self-assembled onto the grid surface.
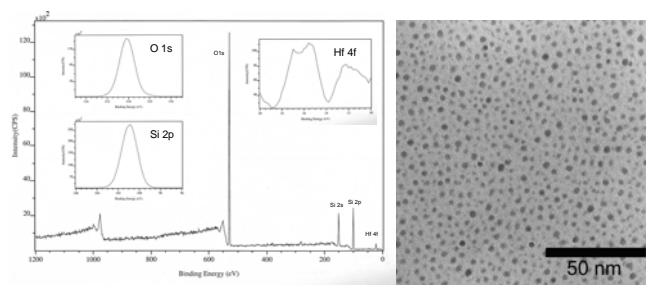

Figure 4. XPS spectra (left) of HfO_2-functionalized SiO_2 TEM grid. TEM image (right) of AuNP array assembled on HfO_2 monolayer.

In addition to employing surface analytical methods, it is possible to pattern the grids with electrodes to enable electrical measurements of nanostructures (such as the ones in Figure 3 and 4) or even single particles including IV curves, impedance spectroscopy, and electrochemical analysis. One can also employ a number of other optical characterization methods including optical microscopy, fluorescence and confocal microscopy, and near-field scanning optical microscopy.

IV. CONCLUSIONS

The new TEM grid that is presented in this paper represents an opportunity to expand the range of useful information than can obtained be through TEM and other analytical methods by directly correlating structure-property relationships in nanomaterials and systems. The nature of the thermal SiO_2 windows in the grids allows for enhanced processing and surface modification when compared to existing grids. This unique capability allows for step-by-step processing analysis for bottom-up processing of nanosystems, and allows one to tailor the surface of the grid for specific applications. When combined with the rich amount of information that can be obtained using other analytical methods, these grids are must-have development tools for the nanotechnologist.

V. REFERENCES

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