Multimodal Optical Nanoprobe For Advanced In-Situ Electron Microscopy

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Introduction

In-situ electron microscopy has gained considerable attention in recent years. It provides a "live" view of a material or device under study at various length scales [1–4]. For example, by heating or cooling a sample one can study structural change at the atomic scale to understand the driving forces and mechanisms of phase transitions. By applying electric and magnetic fields on a ferroelectric or magnetic architecture in operation, one can directly observe how electric and magnetic domains switch, how anions and cations shift their positions, and how spins change their configuration across a domain wall, aiding the development of better electromagnetic devices. In the study of photovoltaic devices and junctions, a major challenge is to directly correlate light-induced electric currents with local structural inhomogeneities and dynamics. Such a capability would allow us to evaluate the performance of individual p-n junctions and to improve optoelectronic efficiency.

In collaboration with Nanofactory Instruments AB in Sweden, we have developed a multimodal optical nanoprobe (MON): a scanning/transmission electron microscope (S/TEM) sample stage integrated with optical excitation and transportmeasurement capabilities, compatible with various commercial electron microscopy systems. This in-situ specimen holder enables the simultaneous measurement of optical, electrical, and mechanical properties of samples inside any S/TEM without compromising the microscope's performance. To our knowledge it provides the only means currently available for the simultaneous in-situ correlation of optical, spectroscopic, electronic, and structural properties of complex materials and devices at length scales ranging from hundreds of micrometers to fractions of a nanometer. Examples of mutually compatible measurements include atomic imaging, nanoprobe electron diffraction to identify local phase inhomogeneity, and spectroscopy using electroninduced characteristic X-ray and electron energy-loss signals to identify local chemical composition and bonding states. Of particular technological importance is the ability to investigate the siteor location-specific properties of engineered material interfaces such as the p-n junctions of photovoltaic structures. In this article we describe the design [5–7] and the functioning of the component parts of the system, as well as its possible applications.

Building Blocks and Components

MON body and optical interface. Inside a transmission electron microscope (TEM), a high-energy electron beam travels through vacuum in the center of the microscope column. The most common way of introducing the sample into the S/TEM column is through a side-entry goniometer stage. The goniometer stage provides high-precision sample movement (XYZ positioning and .... tilt) and a seal between the vacuum inside the column and the outside world. The MON is composed of 3 modules: body, external optics, and sample. The MON body module serves as a connection between the external optical components of the system and the sample module where the sample is held for examination (Figure 1).

The MON body has within it two channels that pass all the way to the sample module from the external optics module. These channels are used as optical pathways, each several mm in diameter. Each channel can pass light either as a narrow, free space laser beam or via an optical fiber threaded through. Depending on the choice, the part of the body external to the vacuum can be terminated with either an optical window for free laser beams or with a polytetrafluoroethylene (PTFE) vacuum feed-through for the optical fiber.

In addition to mechanical interfaces for external optics, there are several electrical connectors built into this part of the body external to the TEM column (Figure 2). There are a total of 6 electrical connectors available; two are reserved for a scanning tunneling microscope (STM)/nanoprobe (one for the STM tip and one for the sample) and the remaining four connectors are available for additional in-situ electrical measurements of the sample.

Sample module. The sample module is where the sample is affixed. It is the part of the MON that enters into the narrow space between the objective lens polepieces. The maximum thickness of the tip is limited by the gap between the objective lens polepieces. The gap between polepieces in an ultra-highresolution microscope is about 2–3 mm, whereas a more standard-resolution microscope has a gap of about 4–5 mm.

The frame of the sample module has two optical channels, one on each side of the sample, that extend the optical channels from the MON body (Figure 3). At the end of each channel, a tiny 90º mirror is mounted on a rod. Using four tiny screws, each of these mirrors can be adjusted (ex situ) so that the incoming light is reflected precisely onto the sample. If desired, light scattering from or passing through a sample can be collected from the opposite mirror and reflected back through the other optical channel for analysis. In addition, to provide a focusing and recollimating capability, light optical lenses can be affixed between mirrors and the sample, or alternatively the flat turning mirrors can be replaced with curved mirrors, such as off-axis parabaloids.

The MON system also contains a nanomanipulator/STM tip operated by a compact, three-dimensional inertial sliding mechanism consisting of a sapphire ball attached rigidly to a piezoelectric tube and a movable part with six springs that embraces the sapphire ball developed by Nanofactory Instruments AB (Figure 2, right panel) [8]. This mechanism enables fine and coarse motion of either the sample or the nanoprobe tip, as well as the rastering of the tip. When the piezo tube in the body of the MON is energized, small expansions and contractions provide mechanical pulses to the balanced sapphire ball, imparting a gliding motion to the legs of the 3D manipulator. The 3D manipulator moves in the X, Y, and Z directions in response to electrical pulses in the piezo tube. This system is capable of fine movements as small as 0.3 nm along any of these directions. This fine movement capability is of critical importance when probing samples to determine their surface structural and electronic characteristics. A coarse motion (up to the maximum TEM sample size) is achieved by applying a voltage pulse of either sawtooth or cycloid shape to the piezo tube. This robust design ensures vibration isolation and a low mechanical noise level, as well as minimizing the need for external vibration damping [8].

External optics module. The purpose of the optics module is to couple light sources and/or photonic analytical equipment to the sample module with an eye toward extending the versatility of the optical system beyond fiber optics if needed. If the laser source is sufficiently light and compact, it can be mounted directly on the sample holder using the external alignment setup (Figure 4), or a fiber may be conntected to the end of the MON to provide free space light from a remote source. Using a 6D (3 translation and 3 rotation) manipulation stage, free laser light can be aligned through the optical channels in the body. Omitting the external alignment setup, conventional optical components (mirrors, lenses, etc.) can be used to direct laser light though the transparent window at the back of the MON body. As the light traverses the body, it arrives in the channel on the side of the sample area and is directed onto the sample by the miniature steering mirrors.

Laser spectroscopy module. This is a general-purpose spectroscopy module optimized for use in high-resolution and analytical microscopy experiments. The platform is currently built around a “white-light,” or supercontinuum, laser source and is optimized for energy and optoelectronic applications where correlation of structural and optoelectronic properties are required. Of particular interest is the ability to simulate solar radiation using the supercontinuum laser for photovoltaics research. The overall layout of the spectroscopy module is diagrammed in Figure 5.

We employ original equipment manufacturer (OEM) versions of these broadband lasers, which can simultaneously provide spectral coverage across all the relevant solar wavelengths in the ultraviolet, visible, and near infrared (typically 370 nm–2400 nm). In addition to providing a coherent (and thus highly focusable) beam of white light, the high average power of these sources means that they can act as a continuously tunable source of monochromatic radiation using appropriate filtering procedures. Resonant electronic excitation can be achieved through automated filtering of the laser supercontinuum into select components. Narrow band excitation can be achieved using a monochromator or an acousto-optical filter. More specialized applications might require the use of different lasers, such as Ti:Sapphire lasers, that can be supplied by a user and can be easily integrated into the spectroscopy suite (Figure 6).

Additionally, the pulsed nature of the “white-light” supercontinuum allows it to be used for time-resolved microscopy experiments. Laser sources exist that are suitable for both ultrafast (<10 ps pulse width) or nanosecond timing experiments. For example, it could be synchronized to a pulsed photocathode for optical pump–electron probe experiments.

The spectroscopy module is highly configurable and can be optimized for the most common optical experiments that are applied to light harvesting materials: (a) Electroluminescence/Fluorescence Mode, where the excitation beam is filtered to deliver high-energy photons to the material and induce luminescence in the material under investigation that can be collected through the second channel. (b) Photovoltaic (PV) Mode, where the full spectrum of the light is used in conjunction with the local electrical probe of the MON system to measure I-V curves in the light and dark. (c) Band/Tunable Excitation Mode, where filtered excitation light is substituted for the full spectrum and the resulting photocurrent is useful for probing a material's external quantum efficiency (EQE). A pulse picker can also be inserted to control the number of light pulses per second reaching a sample. Light entering the module at (A) is collimated and filtered for the desired intensity and spectral region (Figure 6). Filtered light is focused onto another fiber, (H) , by the lens (G). The second fiber runs to the MON.

Applications

It is expected that the materials of greatest interest for examination with this device are optically active samples such as quantum dots, cathodoluminescent and electroluminescent materials, nanowires, photovoltaics, complex oxides, and other optoelectronic systems in which structural, electronic, optical, and mechanical properties are intertwined. Examples include optoelectronic behavior of photovoltaic junctions, failure analysis of semiconductor devices, strain effects on optoelectronic properties, and near-field scanning optical microscopy (NSOM). It is also an ideal system for timeresolved microscopy and spectroscopies, using a synchronized pulsed laser to excite the sample in TEM. Currently, the optical pump part of the pump-probe setup in an ultrafast TEM is introduced through the column of the microscope [9, 10], which is rather difficult and challenging. With our MON, the pump-laser can be introduced through the sample holder without any modification of the microscope.

An example of photovoltaic applications of our system is illustrated in Figure 7. Here, a commercial light emitting diode (LED) was used as a test sample to measure photovoltaic properties in the PV mode. Note that the size of device is a few hundred microns, not a typical dimension for thin TEM samples. The TEM image in Figure 7 shows the electrical contact made using movable W probe electrode. Currentvoltage curves inside a TEM show the photovoltaic effects when the device is illuminated with laser light of wavelength 454 nm. The inset shows that short-circuit current (Isc) decreases and open-circuit voltage (Voc) increases with the power density of laser. For the 1.91 mW/mm2 laser illumination, Isc and Voc were measured up to ..76 ± 1 nA and 1.14 ± 0.05 V, respectively. A dark current of 40 nA was measured, which is attributed to a ground loop formed between the TEM and measurement electronics. This issue will be addressed in order to obtain more reliable and accurate property measurements with our optical holder. Currently, a noise filtering technique using a lock-in amplifier is being tested on TEM samples prepared by ion-beam milling.

Conclusion

The optical activity of thin films, device structures, material interfaces, and nanomaterials is currently a driving force in the field of applied and basic research in condensed matter systems and in energy-related materials in particular. The MON offers several new capabilities in a single "plug-and-play" package and is, in principle, compatible with any existing electron microscope. It opens the door to in-situ simultaneous electrical, optical, mechanical, and structural measurements and manipulations of samples in a S/TEM. It should be particularly useful in the investigation of optically active materials and devices: photovoltaic cells, quantum dots, photo resistors, nanomaterials, and new materials and devices yet to be discovered. In addition, it should provide better spatial resolution for wavelength-specific imaging of labeled biological tissue.

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