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Nanoprobes for Future Generations of Photovoltaics

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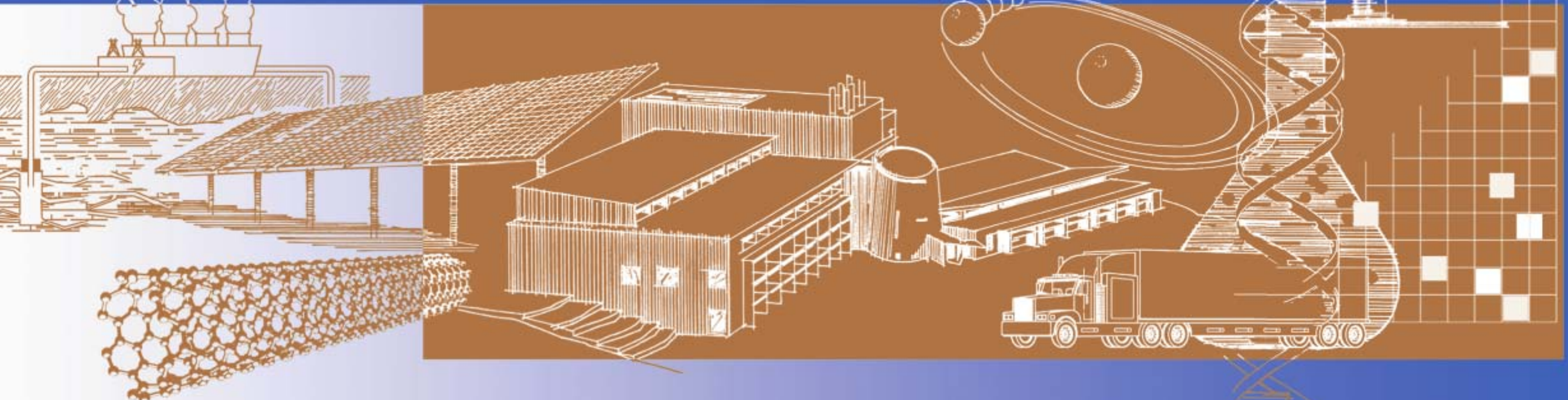

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Nanoprobes for Future Generations of Photovoltaics

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ABSTRACT

In this Solar Program Review Meeting, we report on our most recent progress in scanning probe microscopy (SPM) and its application to photovoltaics. We have developed an SPM to be operated in combination with a scanning electron microscope (SEM) JEOL5800. The SPM platform is compatible with a helium closed-circuit cryostat and fully accessible to the optics of the cathodoluminescence (CL) detectors with which the JEOL5800 is equipped.

Among the innovative modes of operation that the combination—and synergy—of SPM and electron microscopy provides, we describe (i) measurements of the lateral electron transport based on scanning tunneling microscopy (STM) and atomic force microscopy (AFM); (ii) scanning tunneling luminescence (STL); (iii) electroluminescence mapping; and (iv) near-field cathodoluminescence.

1. Objectives

SPM is becoming such important instrument in research because the scanning ultrasharp tip represents indeed a *nanoprobe* that can be adapted to measure multiple properties of the surface—electrostatic potential, thermal and electrical conductivities or capacitance, to name a few—in different modes of operation. Among them, scanning Kelvin probe microscopy (SKPM), conductive AFM (C-AFM), and scanning capacitance microscopy (SCM), are routinely used in our laboratory. On the other hand, there remain opportunities for not yet anticipated applications.

In this sense, we have combined SPM with electron microscopy as an approach to meet the ever-increasing demands in resolution imposed by the successive generation of photovoltaics. This manuscript features recent developments in the field.

2. Technical Approach

Figure 1 depicts a schematic representation of the SEM/SPM integration platform. The SPM is based on an XY-nanopositioning system attached to the stage of the JEOL5800 electron microscope. Height control in the Z direction is given by a 2×2-quadrant piezotube, which supplies a displacement of 50 nm/V while maintaining the low profile needed to accommodate the mirror of the cathodoluminescence optics when required by the measurements. An assembly of high thermal conductivity copper braids coupled to a low-vibration closed-circuit cryostat provides variable temperature (50 K-300 K).

The conventional AFM scanning head, which includes multiple components (piezoscanner, laser, alignment optics, split photodiode), makes it extremely difficult to project an AFM integrated inside an SEM and compatible with the cathodoluminescence and electron optics. Instead, we are using self-sensing and actuating piezoelectric tuning forks. The force sensor consists of a commercial micro-fabricated cantilever with an integrated ultrasharp tip attached to the tuning fork. Sensors are designed for operation in non-contact and tapping modes.

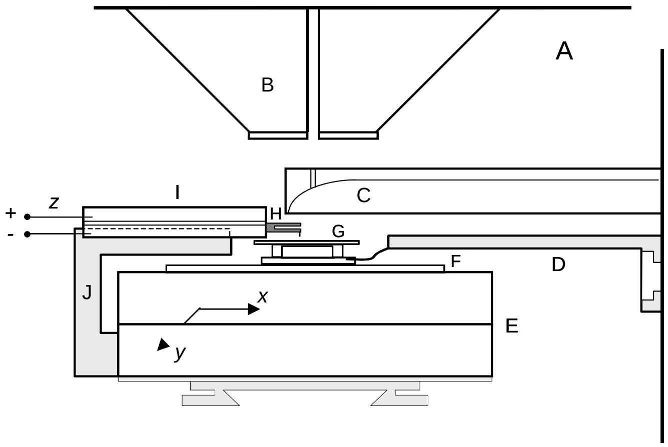

Fig. 1. Schematic representation of the SEM/SPM platform. Vacuum chamber (A) and objective lens (B) of the electron microscope. (C) CL optics. (D) Cryostat assembly. (E) XY piezostage. (F) Thermal insulation plate. (G) Stage. (H) Tuning fork sensor. (I) Z piezotube. (J) Piezowalker.

3. Results and Accomplishments

3.1. Lateral Transport Measurements

We have pioneered a method to investigate the lateral transport in semiconductors based on the combination of STM or AFM with the excitation provided by the electron beam in SEM. This method represents a *two-probe* microscopy because the scanning of both the electron beam and the tip are performed simultaneously and independently. Using this approach, we have investigated the transport across individual grain boundaries in $Cu(In,Ga)Se_2$ (CIGS) and silicon thin films. Basically, additional carriers are excited locally by the electron beam (second probe) and their effect on the tunneling current (STM) or current (C-AFM) is measured by the tip (primary probe).

How effective the lateral transport is across a single grain boundary can be observed by maintaining the tip over one grain and measuring the difference in current when electrons are excited within the grain interior and across the grain boundary. Using this method, we have found evidence for a significant barrier for electron transport across grain boundaries in $CuGaSe_2$ (CGS), which is not present in $CuInSe_2$ (CIS). In silicon thin films, we have mapped the current flow between adjacent grains.

3.2. Scanning Tunneling Luminescence (STL)

STL is the photon emission stimulated by the tunneling current. Photon maps with unprecedented resolution have been obtained when synchronizing the scanning of the STM tip with the detection of the luminescence. As a proof of principle, we have resolved the spectrum of individual quantum dots.

In semiconductors, STL is excited by either (1) recombination of *tunneling electrons* with available *holes* (or vice versa) or (2) electron-hole recombination excited by impact ionization due to hot tunneling electrons (holes). Which of the two processes becomes dominant depends on the voltage applied to the STM tip.

At NREL, we have applied this method to investigate grain boundaries in CIS. When STL is excited by recombination of tunneling electrons with available holes in CIS ($V = -3V$), the photon intensity decreases at grain boundaries when compared to grain interiors. When STL is excited by impact ionization due to hot tunneling electrons ($V = -8V$), the photon intensity is similar at both grain boundaries and grain interiors. These observations suggest that (i) the density of holes is relatively low at grain boundaries intersecting the surface of CIS and (ii) there are no additional recombination centers at such grain boundaries.[1]

3.3. Electroluminescence (EL) Mapping

During intermittent contact in AFM, we have observed individually injected current pulses when a bias is applied to the conducting tip. The current pulses can thus stimulate EL when an electrostatic junction is under forward bias. Therefore, this AFM is capable of mapping topography, current density, and EL.

Tapping-mode conductive AFM represents a very attractive approach to the electrical characterization of nanostructures such as those based on carbon nanotubes, which are damaged easily under the force sustained by the tip in contact mode.

We are applying this method to map the electroluminescence of CIGS and CdTe solar cells.[2] Because of the local injection of current, the results are very sensitive to the local properties of the contact between the tip and the surface.

There is a second approach for mapping the EL based on near-field scanning optical microscopy (NSOM). In this case, EL is stimulated by a forward bias applied to the terminal contacts of the diode and detected by the optical fiber tip. The tuning fork controls the distance from the end of the fiber to the surface under examination – about 20 to 30 nm for operation in the near field.

NSOM-based EL mapping can be applied to solar cells without further requirements and it avoids the artifacts of the local contact. On the other hand, the lateral resolution is not better than ~100 nm.

3.4 Near-Field Cathodoluminescence (NFCL)

Cathodoluminescence can be detected in the near field with the NSOM tip. In this case, the observed CL is confined to the surface: the near-field detection excludes the luminescence emitted deeper in the semiconductor. In this sense, NFCL is a surface sensitive CL.

4. Conclusions

We have described the development of an SPM platform integrated inside an SEM. STM, AFM, and NSOM are now available in combination with an array of beam injection methods. This unique capability is providing access to local optoelectronic properties not probed before.

ACKNOWLEDGEMENTS

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[1] M. J. Romero, C.-S. Jiang, R. Noufi, and M. M. Al-Jassim, Appl. Phys. Lett. **86**, 143115 (2005).
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