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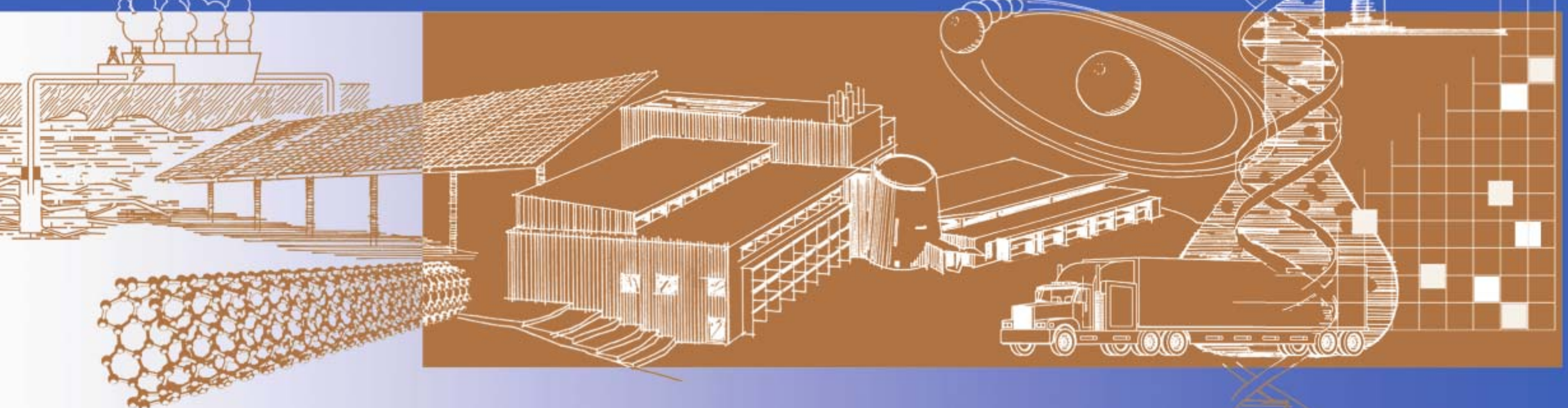

Scanning Tunneling Luminescence of Grain Boundaries in $Cu(In,Ga)Se_2$

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ABSTRACT

At the Laboratory, photon emission in semiconductors has been mapped in the nanoscale using scanning tunneling microscopy (STM). In this Solar Program Review Meeting, we report on the latest results obtained in $Cu(In,Ga)Se_2$ (CIGS) thin films by this adapted STM. Scanning tunneling luminescence (STL) spectroscopy suggests that photons are emitted near the surface of CIGS. STL is excited either by (i) diffusion of tunneling electrons and subsequent recombination with available holes in CIGS or (ii) impact ionization by hot electrons. Which process becomes predominant depends on the voltage applied to the STM tip. Photon mapping shows electronically active, extended defects near the surface of CIGS thin films.

1. Objectives

We are developing an advanced photon emission spectroscopy with nanometer resolution based in STM. Nanostructures might be successfully applied in next-generation photovoltaics, and STL will contribute decisively to our understanding of electron transport and recombination in the nanoscale. As proof of principle, we have observed STL from individual quantum dots.

In this contribution grain boundaries intersecting the surface of $CuInSe_2$ (CIS) are investigated by STL. This issue is attracting considerable attention in our community because such grain boundaries are believed to contribute effectively to photoconversion efficiency [1].

2. Technical Approach

We have adapted an STM to be operated in conjunction with cathodoluminescence (CL). One of the advantages of this approach is that the STM tip can be accurately positioned into the focus of the parabolic mirror of the CL detection system, improving dramatically the photosensitivity in STL. Emission spectra are acquired either by a Roper Scientific Silicon EEV 1340 400 CCD or an InGaAs 512 1 multichannel detector, depending on the spectral range of interest. In the case of photon mapping, a GaAs photomultiplier or a Ge detector are available.

STM observations were performed in constant current mode on the CIGS thin films that produced recent record solar efficiencies at the Laboratory. We chose electrochemically etched PtIr tips, provided by Molecular Imaging, for these measurements.

3. Results and Accomplishments

Figure 1 shows the bias dependence of the photon intensity in STL. The STM tip scans the CIS surface in constant current mode with the tunneling current set to I_t = 50 nA. We clearly identify a threshold voltage at about 5 to 6 volts. Below this threshold, STL is excited by tunneling of *electrons* and subsequent recombination with available *holes* in CIS. Excitation is thus *unipolar*. Therefore, the photon intensity should be essentially proportional to the density of majority carriers seen by the tip in the semiconductor. Above the threshold, secondary electrons and holes are generated by impact ionization of hot electrons. In this case, STL becomes fundamentally similar to cathodoluminescence (or photoluminescence) because excitation is *bipolar*.

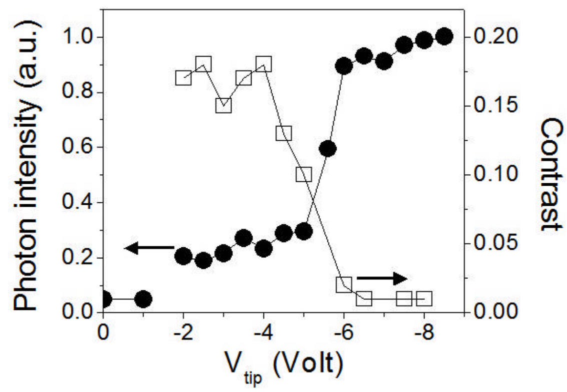

Fig. 1. Bias dependence of the photon intensity and contrast of grain boundaries and dislocations in CIS thin films, measured under the excitation provided by tunneling electrons in STM. I_t = 50 nA. T = 120 K. The contrast is defined as the difference in photon intensity between the grain boundaries and grain interiors, normalized to the second.

The diffusion length of hot *tunneling electrons* in CIS determines the spatial resolution of STL. To answer this very common question, Fig. 2 shows the emission spectrum measured simultaneously by STM and CL. Cathodoluminescence is primarily excited in grain interiors and, as reported before [2], the spectrum is dramatically sensitive to the external excitation (represented by the electron-beam current, I_b), with an absolute shift in photon energy of +30 meV. Above saturation, which is observed at approximately I_b = 1 nA, the photon energy of the CL spectrum becomes constant. The photon energy of the STL spectrum, in contrast, is not affected by V_{tip} and I_t settings used for STM observations. This suggests that STL is excited under saturation; that is, the density of minority carriers induced by tunneling electrons becomes comparable to majority carriers. In addition, the emission observed in STM is considerably higher in energy when compared to CL. Because there is considerable evidence of an unusually increased bandgap at the surface of CIS thin films, and absolutely no correspondence between CL and STL, we believe that the STM emission is confined to the surface layer, which is tenths of nanometers in depth and more deficient in Cu than grain interiors, as revealed by secondary-ion mass spectrometry (SIMS) measurements.

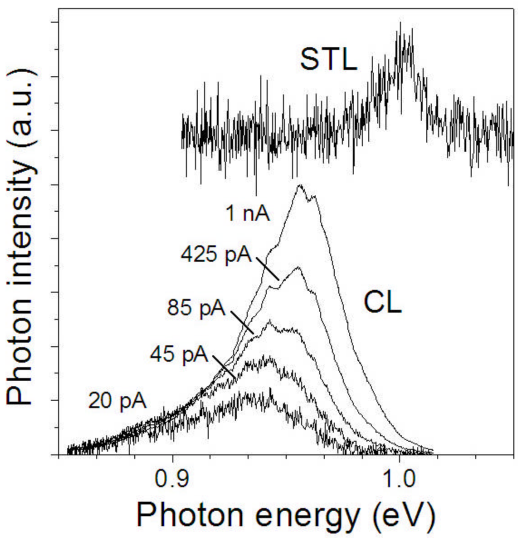

Fig. 2. STL emission spectrum from CIS thin films at V_{tip} = -8 V, I_t = 25 nA, and T = 120 K. Acquisition time = 100 s. The effect of excitation density (electron-beam current, I_b) on the CL spectrum is shown for comparison. Because the spectra are not shown to scale, the readout noise of the detector can be used for estimating the relative intensities.

Photon mapping is performed in constant current mode, with the synchronization of the Ge detector (which offers high photosensitivity in the infrared) with the STM tip while scanning the CIS surface. Figure 3 shows the STM and corresponding STL images, acquired simultaneously, at V_{tip} = -3 V and I_t = 50 nA. Extended linear defects (grain boundaries and dislocations) are revealed by their reduced emission in STM (Fig. 4b). Grain boundaries do not necessarily follow the topography, mainly because we are actually seeing a {112} reconstructed surface. Therefore, we can only partially correlate surface morphology with the location of these defects.

These images were acquired below the threshold voltage and, therefore, the excitation is unipolar, as discussed above. In that case, reduced STM emission at grain boundaries and dislocations can be explained by either a reduced density of holes or increased density of electron traps. We attempt to solve the puzzle by investigating how the voltage applied to the STM tip affects the contrast of these defects in STL. As seen in Fig. 1, the contrast is practically nullified above the threshold voltage, and no grain boundaries or dislocations are seen by STL: they just disappear. Above the threshold, the STL excitation is bipolar. STM provides excellent resolution, and it is most probable that electrons and holes can be generated within an individual grain boundary without interfering with its surroundings. In this case, the STL emission should be proportional to V_{tip} I_t, which is constant. Assuming that the trap density is similar for grain boundaries and grain interiors, those cannot be resolved, in agreement with our observations. This suggests that a reduced density of holes, instead of increased density of electron traps, is responsible for the reduced STM emission.

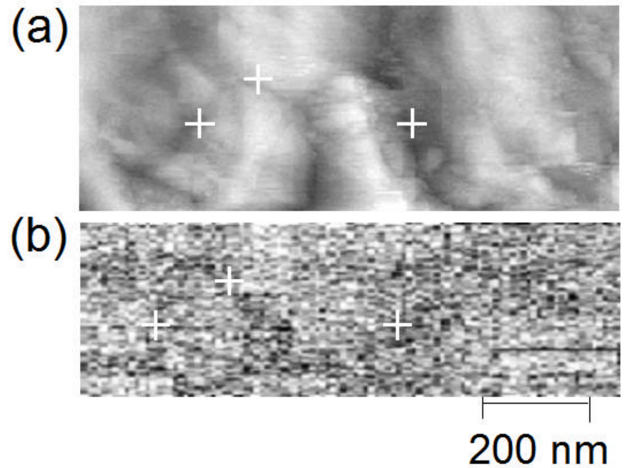

Fig. 3. (a) A constant current mode STM image and (b) corresponding photon map (raw data), which are acquired simultaneously while the tip is scanning the CIS surface. V_{tip} = -3 V, I_t = 50 nA, T = 120 K. Time/line = 2.5 s. P-gain = 9, I-gain = 10.

4. Conclusions

We reported on the observation of photon emission in CIS thin films by STM. When STL is excited by recombination of *tunneling electrons* with available *holes* (majority carriers in CIS), grain boundaries and dislocations near the CIS surface are revealed by their reduced emission. We have investigated how the voltage applied to the STM tip affects the photon emission, and concluded that a reduced density of holes is responsible for the observed behavior.

ACKNOWLEDGEMENTS

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