Extended Abstracts of the 1991 International Conference on Solid State Devices and Materials, Yokohama, 1991, pp. 675-677

D-5-1

Invited

Atomic Imaging, Atomic Processing and Nanocharacterization of Semiconductor Surfaces

Lawrence L. KAZMERSKI and Helio R. MOUTINHO

Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401 U.S.A.

Scanning proximal probe techniques are used to provide integrated imaging, processing and electrical characterization on the nanoscale level for the same regions in $CuInSe_2$. The high-resolution conditions of the instrument are used for specific atom imaging and nanoprocessing by passivation of defects using oxygen. The same areas are analyzed for minority-carrier losses by a nanoscale electron-beam induced current (NEBIC) technique. A specially-designed catheter-based STM probe having two isolated tips is introduced to process specific defect areas on the $CuInSe_2$ (220) surface. The control of single atoms at defects, including the removal of single atoms and placement of single extrinsic atoms. The effects on the local electronic properties are demonstrated by comparing conventional EBIC measurements with NEBIC on the same regions.

1. INTRODUCTION

The introduction of the scanning tunneling microscope (STM) has not only provided for the direct imaging of electronic and atomic structure on the nanometer level, but has opened possibilities for the processing and engineering of materials on these same scales. The ability to provide spectroscopic and specific-atom information on the surface under investigation is a key element in providing the precision required to perform processing on selected regions down to the single-atom level. In this paper, the ability of the instrument to perform nanoscale processing is reported with the results correlated with the spectroscopic STM information. These investigations are performed on the chalcopyrite semiconductor, $CuInSe_2$[1]. This material is currently an important semiconductor for thin-film photovoltaics, with efficiencies exceeding 12% for research cells and with among the best module stabilities for solar cell technologies. $CuInSe_2$ also has properties (two distinct cleavage planes, no discernible surface reconstruction, relatively non-reactive to contaminants in ambient conditions) that make it an excellent material for nanoprobe investigations [2]. The spatial resolution provided by the electron probe of the STM is used to evaluate the *minority-carrier current and conductivity* variations of the identical regions examined and processed by the same instrument, providing integrated observation, processing and electrical characterization of a semiconductor within a single instrument on a nanoscale level. Initial experiments leading toward the direct atomic engineering of semiconductor surfaces are described. These involve the placing of small number of extrinsic atoms at or near preselected locations on the semiconductor surface using a specially-designed STM probe that allows imaging, detection, confined atomic-species introduction and smart processing. Finally, the control of single atoms at defects in $CuInSe_2$ is demonstrated, including the removal of single lattice atoms and the placement of single extrinsic atoms. The effective control on the local electro-optical properties is shown by comparing NEBIC with conventional EBIC measurements on the same regions.

2. NANOPROCESSING AND CHARACTERIZATION

The same probe that is used to provide STM images with nanometer resolution has been used to generate patterns using lithography as well as to etch and to change the structure of surfaces [3,4]. Because the STM probe provides relatively-high electric fields during it operation, the potential exists for the direct *"writing"* of atomic patterns onto desired regions of a surface from ambient reactive gases. This is especially useful in the case of $CuInSe_2$, which has been shown to be sensitive to oxygen physisorption during exposure to high energy density electron beams during SEM and AES analysis [2,5]. The sensitivity $CuInSe_2$ solar cells to the low-temperature (200-250°C) treatment in oxygen has been established. The resolution of the STM provides the capability for not only precision pattern writing, but also the potential for changing the local atomic structure/chemistry of a surface and the eventual atomic engineering of materials.

Figure 1a presents a spectroscopic image of a common Σ9 medium-angle coherent grain boundary on the (112) metallic plane. It has been proposed that the oxygen used in the processing of the cells is bonded at the grain boundary regions, eliminating them as recombination sites for the minority carriers. It would be advantageous to write oxygen directly on the grain boundary imaged by the STM in order to determine such an effect. Under low-voltage and close tip-surface proximity, the oxidation process was unsuccessful. However, by increasing the tunneling distance to about twice that used for atomic imaging and increasing the voltage to the 30-60 volt range, a recognizable topographic image of the defect feature can be obtained and the desired oxygen

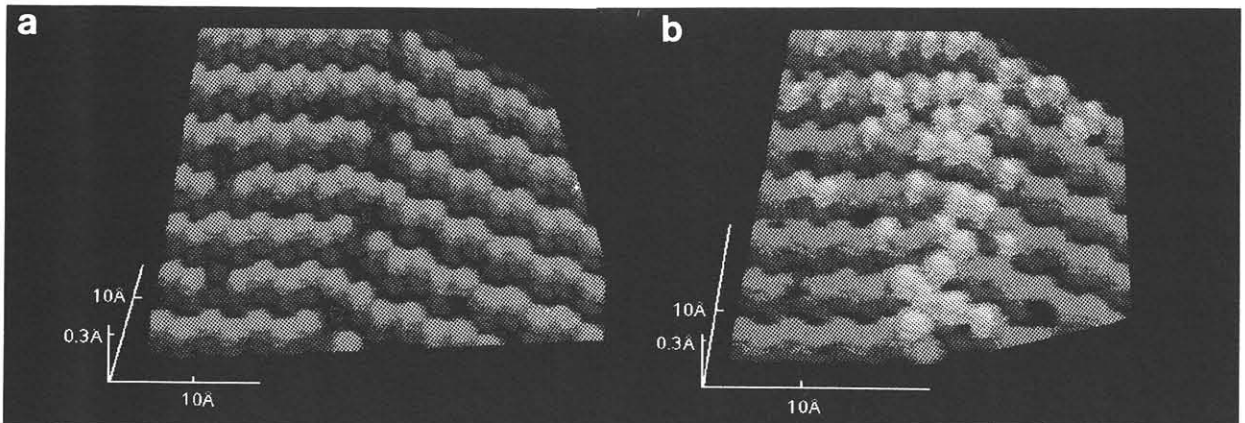

Fig. 1 (a) Spectroscopic STM image of Σ9 grain boundary defect on $CuInSe_2$ (112)-metallic surface having Cu and In; (b) Image of same region as (a), after nanoprocessing with oxygen (light).

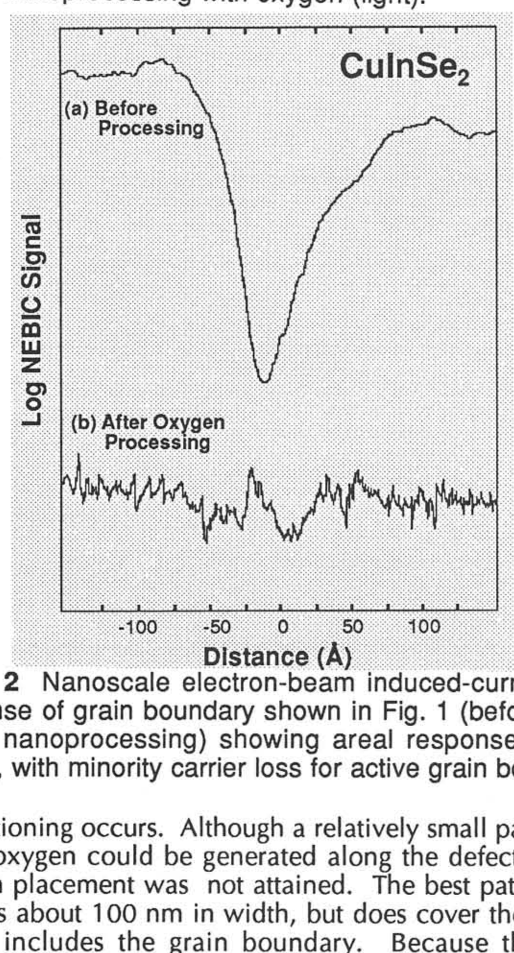

Fig. 2 Nanoscale electron-beam induced-current response of grain boundary shown in Fig. 1 (before oxygen nanoprocessing) showing areal response of region, with minority carrier loss for active grain boundary

positioning occurs. Although a relatively small pattern of the oxygen could be generated along the defect, single atom placement was not attained. The best pattern extends about 100 nm in width, but does cover the region that includes the grain boundary. Because the field generated between the tip and the surface is spatially non-uniform and decreasing radially from the defect under these conditions, the pattern generated is not a dense oxygen coverage. The result can provide an oxygen coverage on the defect that can be imaged on the atomic scale. Figure 1b shows approximately the same region as that contained in Fig. 1a, after the oxygen processing. For electrical analysis, electron-beam induced current (EBIC) measurements have provided a comparative analysis of grain boundaries for electrical activity [1,2]. In conventional EBIC, the transverse electron beam induced current is measured through a sample as the high-energy electron beam is scanned across it. Thus, spatial resolution of the response, usually the minority carrier current, is obtained, but the resolution is limited by the generation volume (typically 0.5-1.0 μm for usual conditions). The STM provides the facility for these electrical evaluations. However, since the voltages can be reduced substantially, the very near surface region can be more effectively evaluated. For an applied voltage of 10 V, the generation volume is estimated to be about 5 nm [2]. For such examinations, it has been noted that higher tip-surface voltages result in more stable and reproducible signals due to the larger generation volume. Thus, the effect of the oxygen processed onto the surface of the $CuInSe_2$ can be evaluated not only directly, but in the same instrument providing the nanoprocessing and atomic imaging.

Figure 2 shows the nano-EBIC (NEBIC) signal measured on the grain boundary of Fig. 1 before oxygen processing. The grain boundary is initially active, as indicated by the change in the NEBIC current through the depletion region provided by the grain boundary. The loss in minority current observed in the unprocessed grain boundary is significantly reduced, with the NEBIC response almost constant over the defect region. The signal has a higher noise content and is somewhat less stable, but the fact is that the large change in the NEBIC current associated with the loss in minority carriers in the defect region has been reduced.

3. ATOMIC-LEVEL ENGINEERING OF SEMICONDUCTORS

The capability to change the composition of materials atom-by-atom is technologically significant for the control of the electronic properties of semiconductors and the characteristics of electronic devices. As discussed in the previous sections, the STM permits the imaging on the atom-level, but the initial experiments aimed at placing single atoms at pre-selected spots (e.g., voids, substitutional impurities, etc.) have been limited by the design and operational characteristics of the conventional STM probe. This section presents the initial experiments on the atomic engineering of $CuInSe_2$ surfaces, using a specially-designed tip configuration to overcome of these problems.

The nature of the new tip uses three major design changes: (1) a catheter wire (3-5 mil diameter, with a <1 mil coaxial opening) is used to introduce the oxygen gas onto the surface [6]. This arrangement confines the oxygen to directly to the region being processed, and allows for better control of the effluence; (2) the gas flow through the catheter opening is pulsed so that it is only directed onto the surface when the electronic pulse for processing is applied to the tip; (3) two tips are nanofabricated on the coaxial catheter, separated by several hundred Å and electrically isolated from each other. The first probe, used for imaging, is some 10-30Å closer to the surface than the following tip, used for the processing. The operation of this more complex probe arrangement is as follows. The first tip operates as the conventional STM probe, using the same biases and tip-surface separations to provide the imaging. This time scans a region of the semiconductor surface and the image is used to allow the operator to select a specific atomic region (e.g., a void) for processing. The spatial coordinates of the selected region are fed back to the following processing probe--whose separation from the imaging tip is known exactly. The processing probe is then advanced to the region, and at the defined coordinates, the gas pulse is introduced at the same time the required electrical bias is applied to the tip (also pulsed). The region can then be re-imaged to determine the success of the operation. Difficulties in positioning and tracking the probe have been discussed previously. These relate primarily to misinterpretation of the probe separations/positions and thermal drift.

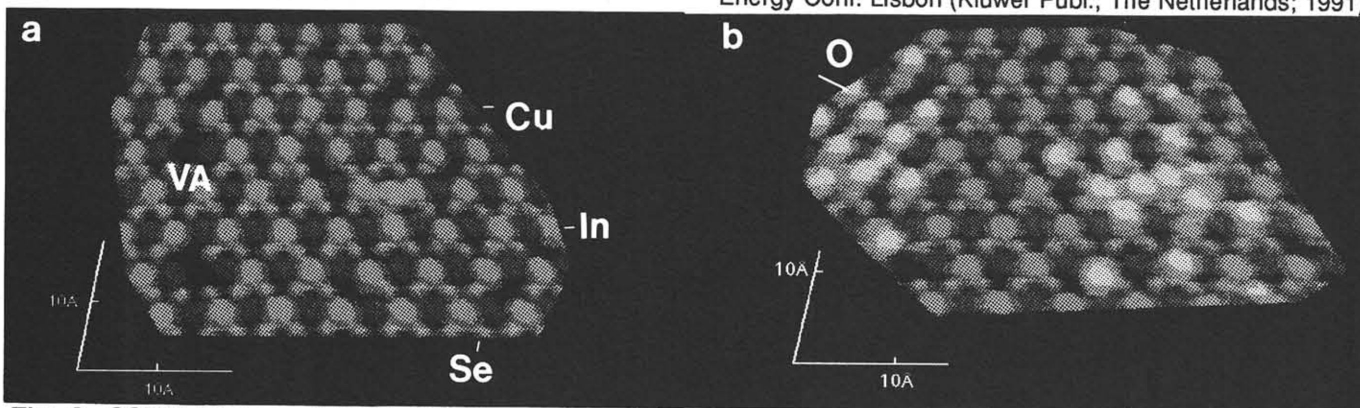

Fig. 3 SSTM images of (220) $CuInSe_2$ surface: (a) before processing; (b) after processing and reprocessing with oxygen at predetermined target point.

Figure 3a shows the atomic region used to define the nanoprocessing. The void at VA was selected for the introduction of the oxygen. In the first attempt, the oxygen atoms were introduced at a location some 4-6 atomic sites away from the preselected void (seen in Fig. 3b at A). Some observation should be made about these data. *First,* the oxygen is confined to a much smaller region (approximately 20 Å in diameter) compared to that in the single probe case of Fig. 1. This confinement is a major improvement over what was possible before, and could certainly provide for the study of passivation of single defects on such $CuInSe_2$ surfaces on atomic scales. *Second,* the initial placement within some *20 Å of the pre-selected site* is an exceptional when considering the thermal, electrical, optical, mechanical and control problems of the experiment. With the re-definition of the area provided by the oxygen placement, the area was re-processed. The computer control provides the result shown in Fig. 3b with the oxygen now covering the pre-selected void at VA.

This paper presents the first atomic engineering results on a semiconductor surface. The process involves: (1) the identification of specific atoms to be removed from the surface; (2) the the removal of those atoms; (3) the placement of individual, extrinsic atoms at those locations ; and (4) the comparison of the results on a bulk basis (using conventional EBIC) and on the nanoscale using NEBIC. These results are presented in Fig. 4. For this case, the placement of two oxygen atoms at Se-vacancies show no effect on the electrical activity from the micron-resolution of the bulk EBIC. However, on the atomic scale, the region is shown to be electrically passivated by the placement of only these two atoms.

<u>*Acknowledgements*</u>: The author gratefully acknowledges the support of the SERI Director's Development Fund and the U.S. Department of Energy (under Contract Number DE-AC02-83CH10093) for this portions of this project.

1) T.J. Coutts, L.L. Kazmerski and S. Wagner, Eds., Solar Cells, *Spec. Iss. on Copper Indium Diselenide* 16, 1-640 (1986)
2) L.L. Kazmerski, J. Vac. Sci. Technol. B 9, 1549 (1991).
3) M..A. McCord and R.F.W. Pease, J. Vac. Sci. Technol. B 4, 86 (1986).
4) E.E. Ehrichs and A.L. de Lozanne, J. Vac. Sci. Technol. A 8, 571 (1990).
5) L.L. Kazmerski, Solar Cells 24, 387 (1988).
6) L.L. Kazmerski, Proc. Tenth E.C. Photovoltaic Solar Energy Conf. Lisbon (Kluwer Publ., The Netherlands; 1991).

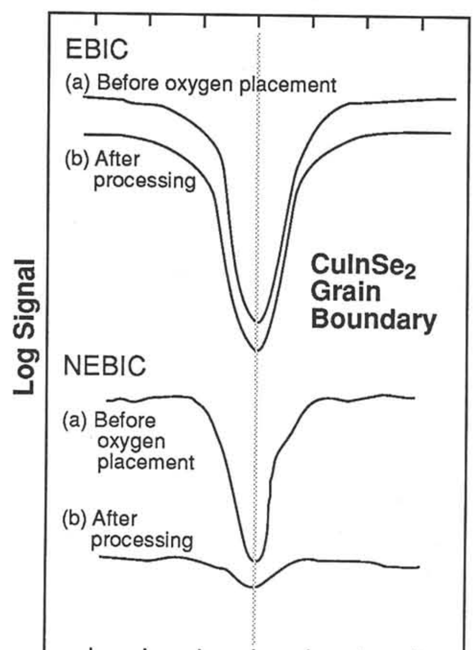

Fig. 4 Comparison of EBIC and NEBIC response from same grain boundary before and after placement of three oxygen atoms on defect.