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Surface Photovoltage Spectroscopy and Mapping by Atomic Force Microscopy

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We have adapted an atomic force microscope (AFM) for the purpose of performing surface photovoltage (SPV) spectroscopy. SPV spectra were obtained from p-type Si (100) and TiO_2 (100) test samples over a wavelength region between 300-800 nm. Simultaneous AFM topography and SPV mapping was also conducted. The boundary between a polymer coating and bare Si substrate was used to test the mapping capability.

Within the last few years, there has been considerable attention paid toward combining scanning probe microscopy (SPM) techniques with optical related phenomena. For instance, when light impinges on a semiconductor surface with an energy greater than its band gap, electron-hole pairs are produced and separated in the space-charge region near the surface. The accumulation of extra charge carriers at the surface will induce band bending which will manifest itself in the form of a (photo)voltage or as a (photo)current in the case of charge transport. Optical spectroscopy combined with a SPM probe can determine locally important information of the physics and chemistry of surfaces, such as the band gap and photoconductive properties in materials, on the nanometer-scale. Scanning tunneling microscopy (STM) has been used to measure photoenhanced tunneling current[1-6] and surface photovoltage (SPV)[7-11] in highly doped semiconductors. However, one serious drawback of using a scanning tunneling technique is the inability to systematically investigate lightly doped or wide band gap semiconductors. In order to circumvent this problem, we report on using a modified atomic force microscope (AFM) to acquire SPV spectroscopy as well as detect local spatial variation in the SPV signal.

Figure 1 shows a schematic diagram of the experimental setup. For the SPV spectroscopy, a 500-W Xe lamp with a monochromator was used as the light source. The monochromatic light was focused onto the sample beneath

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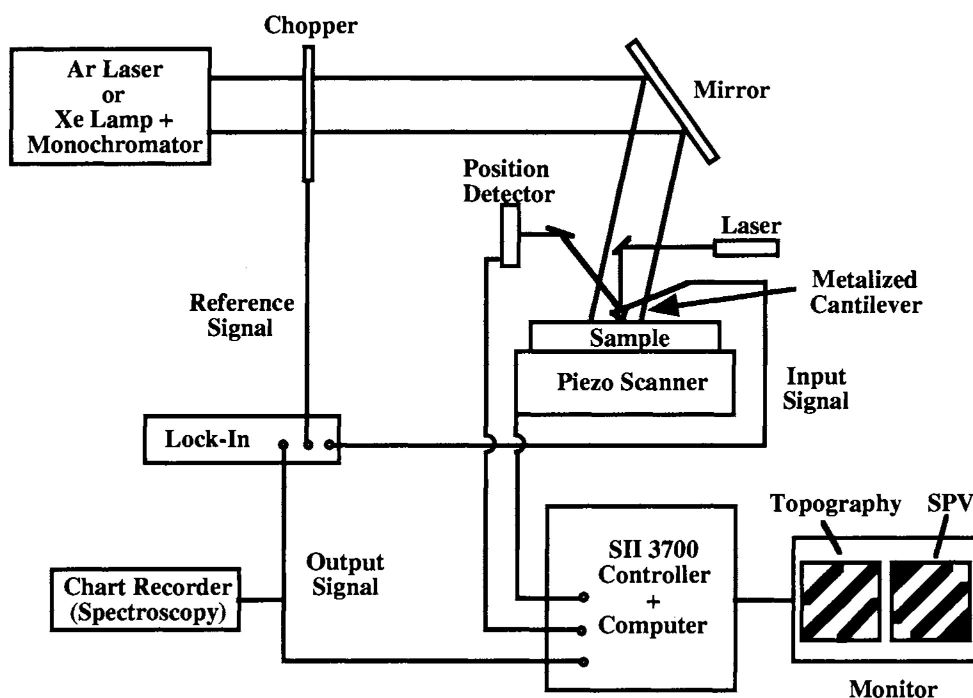

Fig. 1. Schematic diagram for acquiring SPV spectroscopy and mapping with an AFM.

a double-sided, metal coated, Si_3N_4 AFM probe (OMCL-TR-800PB-1, Olympus) at ~45° angle from the sample normal, using a short focal length lens. The light was modulated via a mechanical chopper at a frequency of 70 Hz. The SPV signal was measured using a lock-in amplifier (Model 850, Stanford Research Systems) and the output signal was recorded on a chart recorder. For the SPV mapping, a 40 mW Ar laser (Ion Laser Technology), chopped at 4 kHz, was used to illuminate the sample slightly off-normal to the surface and the SPV output signal was sent directly to an auxiliary channel in the SPM controller (SPI 3700, Seiko Instruments, Inc.). In this manner, simultaneous topographical and SPV measurements could be performed.

Single crystal Si and TiO_2 substrates were used as test samples for the spectroscopy experiments. The substrates were simply rinsed in a methanol solution followed by distilled water (18 MΩ•cm) before use. For the mapping experiment, a drop of Nafion (20 µl) was simply placed on a clean Si substrate and allowed to dry before being imaged with the AFM.

Figure 2 shows typical SPV spectra of (a) p-type Si (100) and (b) TiO_2 (100) taken with the AFM. To the best our knowledge, these are the first SPV spectra taken with an AFM. For these measurements, the AFM probe was placed in contact with the sample and held stationary during the acquisition of the SPV signal. For Si, the SPV signal is fairly constant in the visible region then rapidly decreases for wavelengths below 420 nm. This decrease in SPV signal is associated with the transparency of Si in the UV region. In the case of TiO_2, hardly any SPV signal

could be detected in the visible region due to the lack of band bending from sub-band gap illumination. The onset of a peak at approximately 400 nm is due to photoexcitation of carriers across the band gap of TiO_2 (3.1 eV); while the rapid decrease below 340 nm results from the lack of absorption in the TiO_2 sample. These spectra are in good agreement with those reported in the literature.[12,13)]

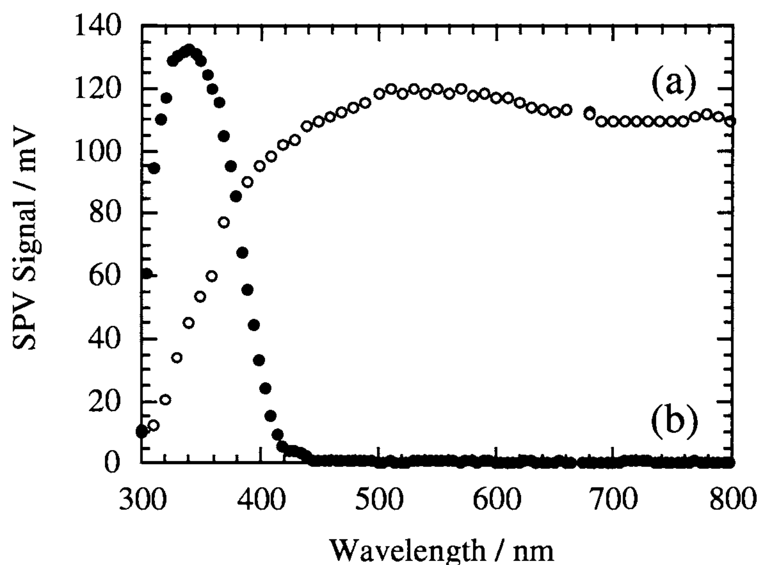

Fig. 2. SPV spectroscopy of (a) p-type Si (100) and (b) TiO_2 obtained with an AFM probe.

Lastly, we have also attempted simultaneous topography and SPV imaging with the present set up. We have been able to detect signals as small as a few μV, although at this level the electrical line noise from the lock-in amplifier becomes noticeable. Moreover, there is a compromise between sensitivity and acquisition speed since a long time constant is needed to acquire a small SPV signal. We have observed small variations in a Si substrate, but it is difficult to assign the origin of these variations (i.e., defects, impurities, stress, etc.) without having a well-characterized sample for comparison. Weaver and Wickramasinghe[14)] have imaged SPV variations in well-charaterized semiconductors using a non-contact AFM. In order to clearly distinguish that SPV variations corresponded to real topographic features in our images, we decided to examine the boundary between a polymer filmand bare Si surface. Figure 3a shows a 40 μm x 40 μm AFM image taken over such a boundary region. The bright areas indicate the location of the polymer film while the dark areas indicate the bare Si surface. Figure 3b shows the SPV image obtained simultaneously with the topographic image. The image shows similar bright and dark areas which are of opposite phase to the topographic image. In other words, regions of high SPV represent areas of exposed Si while low SPV signal indicates regions with a polymer coating. This result is reasonable since the SPV signal will decrease when the AFM probe is further away from the Si surface. A decrease in SPV signal can also occur by reducing the amount of the light reaching the surface. Absorption measurements of the polymer film showed no absorption peaks in the UV-visible region and hence the reduction in SPV signal is attributed to the increase in the probe/sample separation distance. We have also performed spectroscopy over such regions and have observed a corresponding decrease in SPV signal over the coated regions. At present, it is difficult to determine the ultimate limit of this technique with the present sample. We are currently fabricating features with

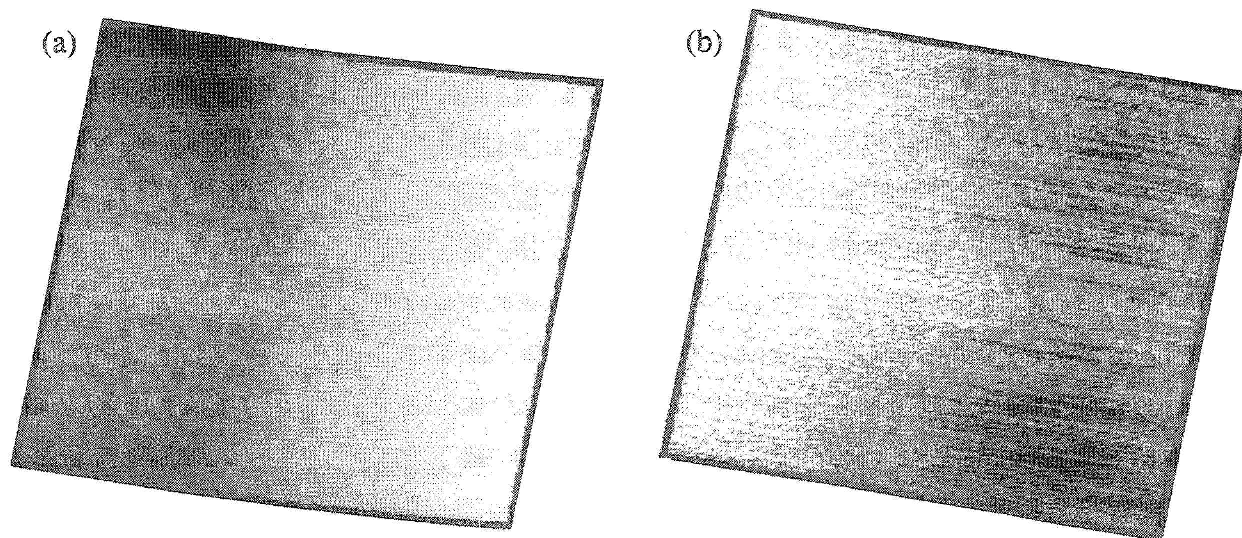

Fig. 3. (a) AFM topographic image of a bare Si/polymer boundary and (b) SPV mapping over the same region.

smaller line width patterns to help resolve this issue.

The present design of this system also allows for the possibility of conducting photocurrent spectroscopy as well as photocurrent mapping. For such measurements, two types of experiments are possible: a) the bias applied between the AFM probe and sample is fixed while the wavelength of light is varied, or b) the wavelength of light is fixed and the applied bias is varied. Such studies are in progress and will be the topic of forthcoming publications.

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