Fiber optical laser spot microscope: A new concept for photoelectrochemical characterization of semiconductor electrodes

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A fiber optical laser spot microscope, which allows the simultaneous measurements of photocurrent and reflected light intensity or the measurement of laser spot photocurrent under the illumination of other light sources, has been developed to study semiconductor/electrolyte interfaces. The capability of this microscope was demonstrated on as-cleaved and Pt-treated *p*-InSe. The Pt treatment increased the photocurrent and improved the lateral resolution due to the increase of surface reaction rate. The higher photocurrent was observed at the spot where the reflectivity was higher. This behavior is considered to be due to an uneven distribution of platinum. The laser spot photocurrent image under the illumination of other light sources provided useful information to clarify whether the rate was controlled by surface or bulk properties of InSe.

The photoelectrochemical properties of semiconductor electrodes are to a large extent determined by surface morphology. The presence of scratches, grain boundaries, and in layered compounds steps are known to reduce the photocurrent as they induce recombination. The scanning laser spot (SLS) technique permits laterally resolved studies of the photoelectrochemical properties of semiconductors and it is possible to visualize the effect of these defects on the photocurrent.[1-8] SLS can also be used to make images on semiconductors by photoetching and photodeposition.[4]

The normal experimental solution to implement the SLS technique on a photoelectrochemical system is based on standard optical components. The laser beam is focused on the electrode with a microscope lens through a window of the photoelectrochemical cell. The scanning is usually accomplished with a step motor controlled *X-Y* coordinate table or scanning mirrors. Such a system is quite sensitive towards mechanical vibrations and is usually set up on an optical table. The system presented in this letter is based on fiber optical components, a new concept compared to other SLS systems. The advantages are that the optical alignment is simple, no special optical table is required, the system is less sensitive towards mechanical vibrations, and is cheap and compact. The system also permits a simultaneous measurement of both the laser spot photocurrent and the reflected light intensity. It is thus possible to make microscopic pictures of the surface. It is always a problem in the SLS technique to relate a certain photocurrent image with the surface structure but our technique offers a way to do so. This optical configuration also makes it possible to illuminate the electrode surface with another light source while the laser spot photocurrent is recorded. This technique gives information about the surface properties when the surface state is occupied and how it affects the charge transfer and conductivity. The usefulness of the system is demonstrated on as-cleaved and Pt-treated *p*-InSe in this letter.

The spatial resolution of the SLS technique is not entirely determined by the spot size but also depends on the photoelectrochemical properties of the system. The light spot generates electron-hole pairs which diffuse outwards from the illuminated area and create a charged semisphere which is much larger than the light spot and moves along with it. The magnitude of the photocurrent is determined by electrochemical charge transfer kinetics and surface and bulk properties of the semiconductor. If the charge transfer rate increases, the size of the charged semisphere decreases and the spatial resolution is improved.

The optical system is shown in Fig. 1 and consists of a single-mode optical fiber and a Selfoc micro lens (Nippon Sheet Glass Co. Ltd.). The single-mode fiber used is tuned to 632 nm and has a core diameter of 4 μm. The micro lens is cylindrical with a graded index of refraction which decreases with the square of the radial distance from the optical axis. The laser spot on the electrode is approximately a 1:1 image of the fiber core and the smallest spot diameter obtained was 4.15 μm. A bundle ($d = 8.5$ mm) of fibers is arranged around the micro lens in order either to collect the reflected light or to illuminate the electrode by another light source through these fibers.

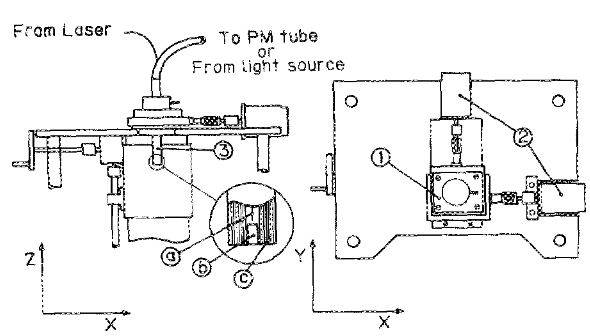

FIG. 1. Experimental configuration. (1) *X-Y* coordinate table. (2) Step motors. (3) Laser spot probe with (a) single-mode optical fiber, (b) Selfoc microlens, and (c) assembly of optical fibers.

The X-Y scan was accomplished with a coordinate table equipped with step motors and the minimum step width was $0.5\ \mu m$. The data acquisition and control were handled by a personal computer (NEC PC 8801 MR). The photoelectrochemical measurements were potentiostatically controlled (Nikko Keisoku Potentiostat) and the bias in the experiments was -0.6 V vs Ag/AgCl. The light from a He-Ne laser (NEC, 5 mW) was chopped and the photocurrent and photomultiplier tube (PMT) output of the reflected light were amplified with a lock-in amplifier (NF, LI-574). The electrolytes were prepared from reagent grade chemicals and Milli-Q purified water. The Pt deposition on InSe was carried out by dipping InSe into 20 mM H_2PtCl_6 for 5 min followed by rinsing with water.

Since InSe is a layered compound, the characteristic surface morphology is steps between adjacent layers. This type of compound is especially well suited for SLS studies as ordered surface structures are very easy to prepare by lifting off layers with a sticking tape. The two-dimensional electronic structure of InSe results in high conductivity parallel to the planes and low conductivity perpendicular to them. The electrodes must therefore be very thin so the potential drop over the electrode does not become too large. The laser spot (LS) photocurrent which was observed when the spot was swept over a step is shown in Fig. 2. The upper line scan shows the photocurrent after Pt dip treatment and the lower before Pt treatment. The step influences the photocurrent over a much larger distance compared to the dimension of the step and the light spot. After Pt treatment the drop in the photocurrent becomes sharper and more localized at the step. It is a well known fact that Pt treatment improves the photocathodic current on p-type semiconductors by its catalytical effect on the hydrogen evolution reaction.[9-11] As the Pt treatment increases the photocathodic charge transfer reaction rate, the charged sphere diameter decreases and the resolution increases. A similar effect was observed when the electrode was illuminated with white light through the surrounding bundle of fibers, as is shown in Fig. 3. The SLS image becomes sharper if the electrode was illuminated with white light. The relative magnitude of the photocurrents in

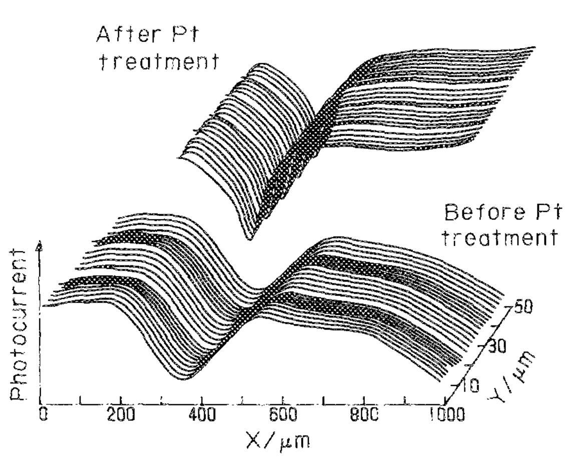

FIG. 2. Line plot showing the laser spot photocurrent across a step on an InSe electrode before (lower lines) and after Pt treatment (upper lines).

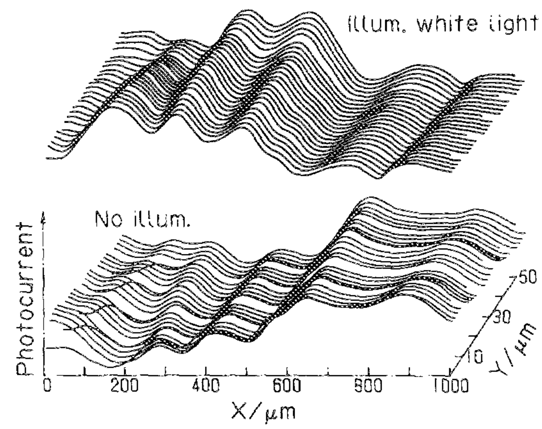

FIG. 3. Line plot of the laser spot photocurrent when the electrode is simultaneously illuminated with white light (upper lines) and without white light illumination (lower lines).

the left part in Fig. 3 compared to the right part is higher in the nonilluminated case and lower in the illuminated case. This is related to changes of the bulk properties during illumination and to variations in the electrochemical rate constant. It is known that the photocurrent of p-InSe becomes constant at higher light intensities at potentials, positive of -0.9 V vs Ag/AgCl due to the slow electron transfer.[11] The anisotropic properties of InSe could also result in local variations of the conductivity during illumination. The shift of the relative magnitudes of the photocurrent during white light illumination is related to these two properties of InSe. The resolution is apparently better in the illuminated case. The reason for this behavior could be found in the fact that during illumination the recombination current through surface steps is not affected until the light spot is much closer to the surface defects. The result is that the drop of photocurrent due to structural defect appears sharper, as clearly seen in the left part in Fig. 3.

The SLS probe with an array of optical fibers around the central emitting fiber makes it possible to record both the reflected light intensity and the photocurrent at the same time. With this optical arrangement it is possible to observe light which has been reflected by irregularities, diffracted or emitted as photoluminescence. Due to construction considerations there is a "dead zone" around the central emitting fiber where the reflected light cannot be detected. If the system is properly aligned, the specularly reflected or slightly deflected light returns towards this "dead zone" and will not be recorded. Figure 4 shows an example of the SLS image of the reflected light intensity and laser spot photocurrent at an InSe electrode which was dip treated in a H_2PtCl_6 solution. In this case, it was confirmed that light detected was not photoluminescence because no light was detected if a long pass filter ($\lambda > 690$ nm) was placed in front of the PMT. The electrode surface was first observed by an optical microscope and the increased reflected light image in Fig. 4 is associated with a folded surface layer which rises like a hill over the surrounding surface. The two main peaks in the reflected light image are due to reflection at the slopes of the hill and

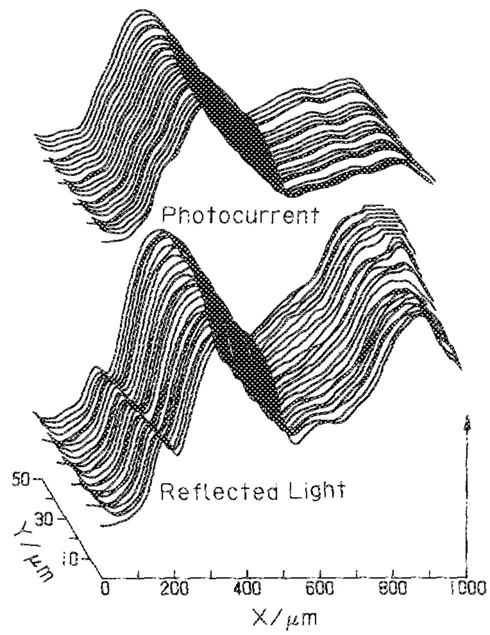

FIG. 4. Reflected light (lower lines) and laser spot photocurrent (upper lines) from the same area. The increase in photocurrent is correlated with an increase in the intensity of the reflected light.

the minimum between them is the reflectivity at the top of the hill. In the left part of the reflected light image in Fig. 4 there is a sharp hump in the intensity which is related to a step. The increase in the photocurrent might be related to the fact that the light spot covers a larger area at the slopes of the hill. Another possible explanation is the uneven distribution of Pt. We have studied this effect by putting a drop of approximately 1 mm in diameter of the Pt solution for 5 min on the electrode surface. The electrode was rinsed with water and analyzed with SLS. We observed much higher photocurrent at the area which has been covered with the Pt drop compared to the surface which has been untreated. Further experiments are required to explain the reason for the increased photocurrent observed in Fig. 4.

In summary, a new fiber optical concept for SLS studies of a photoelectrochemical system which combines laser spot photocurrent measurement with measurement of the reflected light intensity or under simultaneous illumination of the electrode surface with another light source has been developed. It was demonstrated that this combination makes it possible to relate the reflectivity with photocurrent or the influence on the photocurrent by illuminating the electrode with another light source and to provide much useful information on the structure and reactivity of semiconductor electrodes.

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