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Preparation of WSe_2 surfaces with high photoactivity

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Layered dichalcogenide semiconductors (LS) are studied intensively for photovoltaic applications. It is generally accepted that the smooth van der Waals face ($\perp c$) is most suitable for this purpose. Recombination centers have been associated with surface steps (exposing $\parallel c$ facets) or near-surface dislocations. Efforts to passivate the recombination centers had, until now, only limited success. In contrast to this approach, a method of surface preparation of LS, leading to rough surfaces that exhibit high photoactivity with high reproducibility, is presented. The physical principles underlying this technique are discussed in detail.

The atomically smooth van der Waals (vdW) surface of LS serves as a model system for the study of the physical properties of semiconductors and, consequently, it has received appreciable attention recently.[1-3] Further interest in these materials stems from the prospect of using them in high-efficiency photoelectrochemical (photovoltaic) cells for solar-energy conversion.[4-7] It was generally accepted that the collection efficiency of minority carriers and hence the conversion efficiency of light to electricity of those crystals depends on the quality of the exposed vdW surface ($\perp c$). Recombination centers within the material were associated with dangling bonds of W and Se atoms at $\parallel c$ edges.[8-11] Thus suitable photovoltaic efficiencies were obtained only after careful screening of samples.[1] Considerable effort was diverted towards surface modification of the $\parallel c$ facets, leading to electrical passivation of those defects, which, however, yielded only limited gain.[12-15]

Since it is generally accepted that the preferential diffusion of carriers within the material bulk occurs along the $\perp c$ direction (parallel to the cleavage plane)[3] it is strongly desirable to produce an efficient junction over the crystal edges rather than trying to "block" them. At the same time, theoretical and experimental considerations suggest that the highest absorption coefficient of the material, in the visible and near-infrared region of the spectrum, occurs on the vdW planes.[16-19] Thus, the optimal configuration for light-to-electricity conversion must combine both $\parallel c$ and $\perp c$ planes in an active junction.

The smooth, defect-free vdW face of n-type WSe_2 is inert towards oxidation, corrosion, and anodic decomposition.[20-22] Since organized patterns ought to be engineered, dislocations, which serve as nucleation sites[22] for the controlled anisotropic corrosion (CAC) process, were *deliberately introduced* by mechanical indentation. CAC was carried out in 1M HCl solution at +500 mV vs Pt electrode, under oxygen bubbling[21] and auxiliary illumination. Subsequently, the samples were carefully rinsed and soaked in hot 2M KOH (60 °C) to remove insoluble WO_3 and occluded selenium oxides.

A light-beam-induced current (LBIC) was used to map the quantum efficiency of the crystal surface prior, during, and after CAC. The experiment was carried out using a standard laser-scanning setup, with a spatial resolution of less than 15 μm. Light intensity was measured with a calibrated Si detector. Using liquid junctions for the LBIC experiment, the evolution of specific defects, during CAC could be followed.

A decay up to 50% of the measured signal was observed whenever an untreated defect was crossed by the laser beam. Thus, as anticipated,[6,8] mechanical defects and crystal edges behave as strong recombination sites, before the treatment. Contrarily, exceedingly high photovoltaic activity of the entire surface including the edges can be observed after CAC. Enhanced quantum efficiency (q_{eff}) of about 80% was obtained over large areas, as shown in Fig. 1. Note the increased optical activity near a treated edge, considered until now to be the main cause for electrical losses within LS. The measured quantum efficiency was not corrected for liquid absorption or surface reflectivity. Measured losses are ca. 20% of the visible and 25% of the infrared light for the CAC treated surface. For the cleaved surface the reflectivity is some 5% higher in the visible region. This difference increases beyond 960 nm, likely due to light trapping by multiple reflections from the steps of the CAC treated surface (see inset in Fig. 2), which are 1–4 μm wide. Thus internal collection efficiencies approaching unity were achieved, on large areas, according to this method of surface preparation. Note that the dark current did not change appreciably after CAC (the freshly cleaved samples exposed rather smooth vdW before indentation). As a result the fill factor, open circuit voltage (V_{oc}), short circuit current (I_{sc}), and conversion efficiency went up substantially due to CAC and reached the values 0.69, 610 mV, 29 mA/cm^2, and 12.4%, respectively.

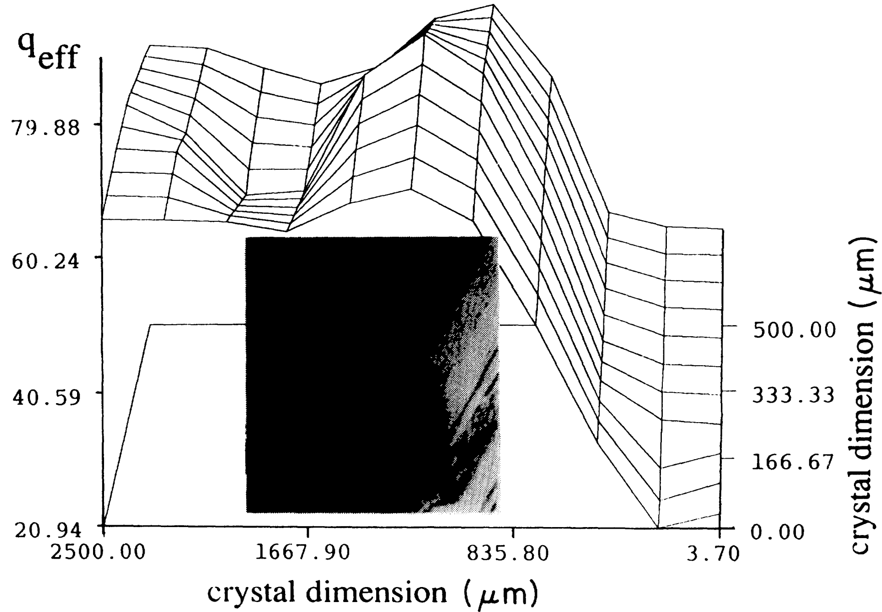

FIG. 1. Laser scanning image of native edge of WSe_2 in polyiodide solution, after CAC. In the inset a secondary electron (SE) image of the treated edge is shown.

Band-structure calculations indicated that different selection rules apply to the optical transitions on the $\parallel c$ and $\perp c$ faces.[18,19] Specifically, the lowest indirect transition is forbidden on the $\parallel c$ face ($E \parallel c$).[17] To confirm this hypothesis, careful optical measurements were performed on samples having thick $\parallel c$ (photoetched) facets exposed to a focused beam. The shift of the photoresponse edge to shorter wavelengths, as compared with freshly cleaved surfaces (see Fig. 2, curves *B* and *C*) together with the steepness of the photoresponse curve suggest that the first indirect transition is indeed forbidden on the $\parallel c$ face. However, the photoresponse of samples that were submitted to CAC, i.e., "mixed" surfaces, showed an appreciable shift to longer wavelengths (see Fig. 2, curve *A*). A redshift of the photoresponse from exposed edges was reported before but was always associated with low overall collection efficiency.[8] This is not surprising since such surfaces were prepared by cutting the crystal with a sharp blade, thus introducing extensive damage and high surface recombination velocity. Note that for this material

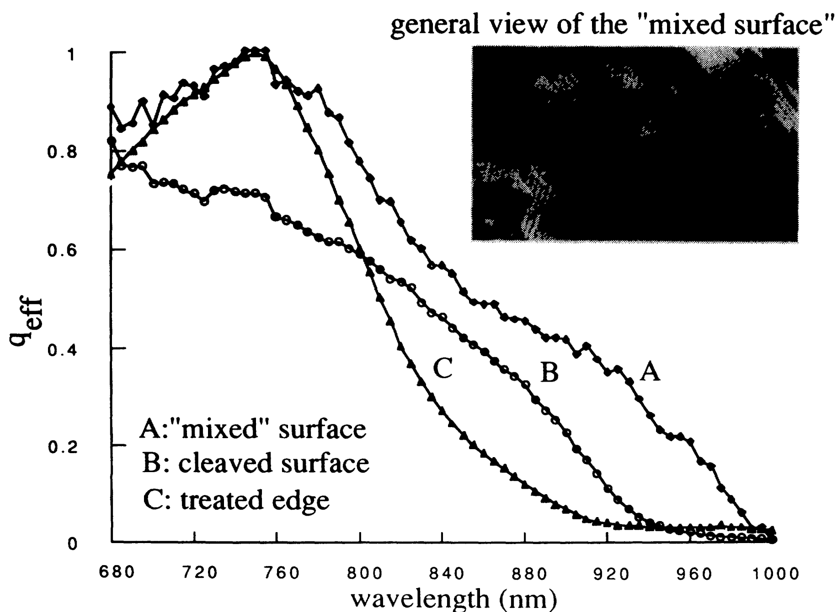

FIG. 2. Spectral response (after correcting for reflectivity losses) for "mixed" surface of *n*-type WSe_2 in KI/I_2 solution (curve *A*); freshly cleaved surface (*B*); CAC treated edge (*C*). SE image of a mixed surface is shown in the inset.

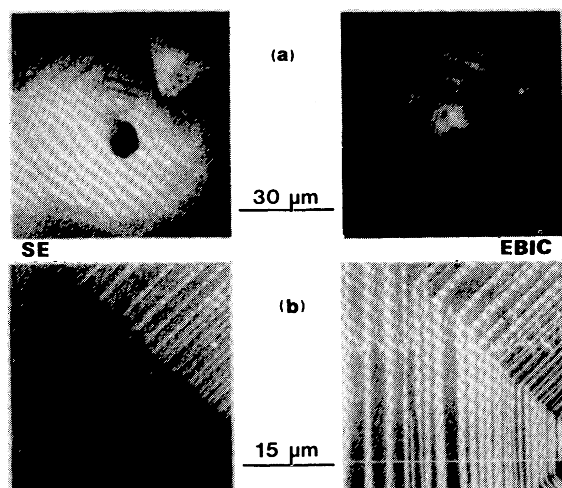

FIG. 3. SE-EBIC pair images taken at 30 kV at (a) room temperature and (b) 140 K. (a) The Schottky contact is confined on the etch pit only. The sharp tip of a needle that realizes the electrical connection to the current amplifier is seen up in the right corner. (b) Magnified fragment of a big etch pit. The sample is inclined 45° with respect to the primary electron beam to ensure equal illumination of both $\parallel c$ and $\perp c$ facets; therefore differences in EBIC signal on $\parallel c$ and $\perp c$ facets cannot be ascribed to geometrical reasons. The signal profile and zero lines are also shown on the EBIC image.

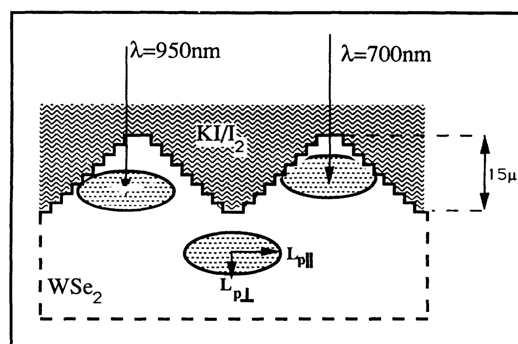

FIG. 4. Schematic representation (to scale) of a "mixed" WSe_2 surface under illumination. Carriers generated by 700-nm light are effectively collected through the slanted architecture produced by CAC. Carriers generated by 950-nm light are only partially collected by the mixed surface. Such carriers are doom to recombine on the smooth vdW face [see the role of the anisotropic diffusion length (L_p)]. This explains the redshift observed with the mixed surfaces.

the "effective" indirect band gap was found to vary from 1.3 eV prior to photoetching (PE) to 1.2 eV after PE [see Ref. 7(b)].

In order to deconvolute the "global etching effect" observed under visible light, electron-beam-induced-current (EBIC) measurements were performed. Schottky barriers for the EBIC experiments were obtained by gold evaporation (for n-type crystals). To increase the signal-to-noise ratio, the Schottky contact areas were considerably restricted. A special experimental technique was developed to fabricate Schottky microcontacts covering single etch pits only; first, the etched crystal surface has been covered with a gold layer (ca. 25 nm thick), afterwards the top layer of the crystal (a few micrometers thick) was removed by cleavage. Since the etch pits were usually very deep (ca. 20 μm), the junction was confined to the etch pit area. Figure 3(a) shows the preferential collection of minority carriers on the $\parallel c$ facets inside a single etch pit, at room temperature.

Striking enhancement of the EBIC signal was observed by lowering the specimen temperature. This is in sharp contrast with other materials [e.g., Si (Ref. 23)], where influence of temperature on the EBIC signal is considerably weaker. This effect, probably related with the crystal anisotropy, enabled us to reduce significantly the electron-beam spot size, and, consequently, to improve the achievable spatial resolution. Thus in Fig. 3(b) enhanced collection efficiency from the $\parallel c$ facets is clearly seen. Further advantage for using the EBIC at low temperatures is the reduced beam damage.

The above results suggest that the topmost layers on the $\parallel c$ facets of the mixed surface are chemically different from the vdW planes. Recent measurements using small area photoelectron spectroscopy and nuclear reaction analysis (with O^{18}), indicate the existence of an intimate semiconductor/oxide interface on the $\parallel c$ facets.[21] Such interfaces are probably not very different from other oxide-terminated surfaces (see Si/SiO_2 interface), which exhibit low surface recombination velocity. The wide-band-gap oxide serves to open the energy gap at the interface thus pushing the surface states, previously eminent on this facet, out of the forbidden gap.

The enhanced activity of those surfaces could be attributed to a synergistic effect between the high absorption coefficient of the illuminated vdW surface; longer lifetime and diffusion length of minority carriers, collected through the $\parallel c$ face; passivation of recombination centers of any kind; and light trapping in the infrared. The geometrical configuration which yields the ideal combination between the two surfaces ($\parallel c$ and $\perp c$) is a network of etch pits as obtained by CAC (a schematic representation is shown in Fig. 4).

The difficulties in controlling the surface chemistry and structure of the $\parallel c$ face of layered semiconductors, in general, and the metal dichalcogenides, in particular, are manifested through the fact that, to our knowledge, no high-efficiency (ca. 10%) polycrystalline solar cell was reported in the literature. This is in sharp contrast with many other families of semiconductors for which such cells were reported. The present study shows that based on a judicious chemistry one may possibly achieve that goal in the future.

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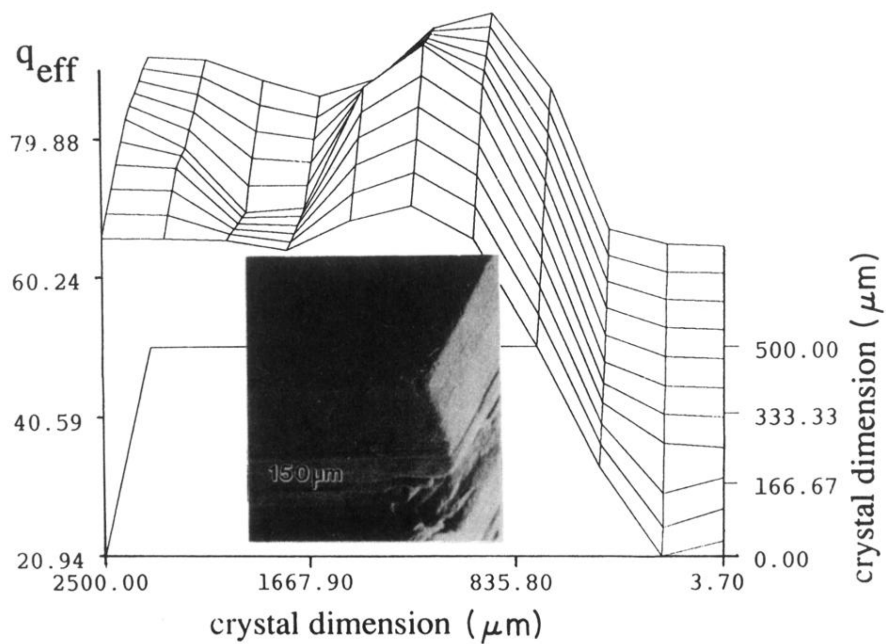

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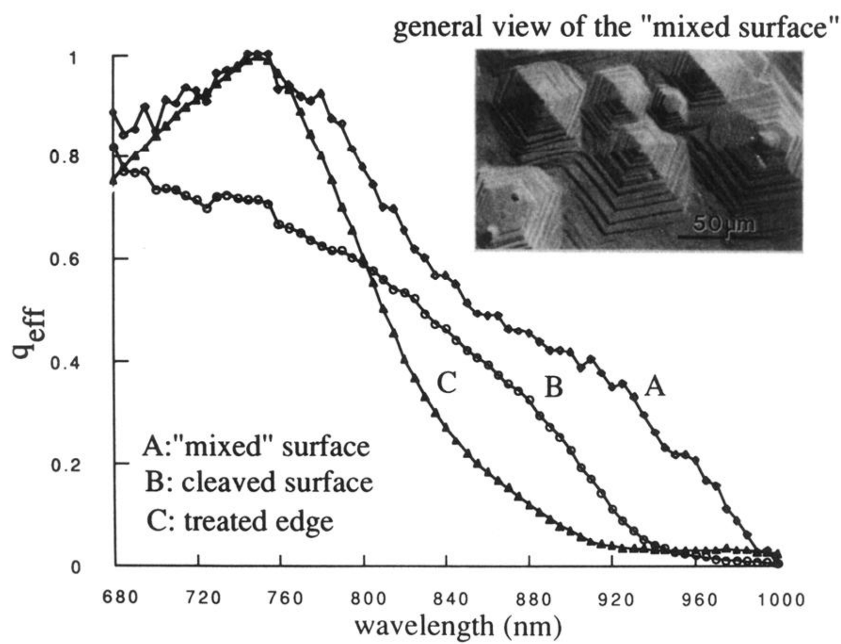

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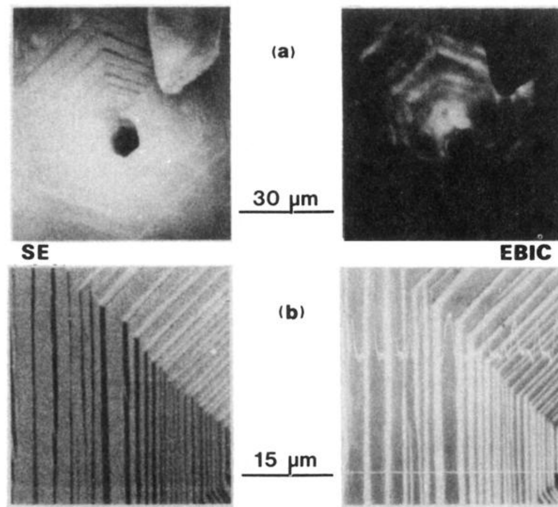

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