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LETTER TO THE EDITOR

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LETTER TO THE EDITOR

The high-efficiency (17.1%) WSe_2 photo-electrochemical solar cell

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Abstract. WSe_2 crystals (photo-electrodes) have been grown via a vapour transport technique, employing $SeCl_4$ as transporter. Photo-electrochemical (PEC) solar cells with n-WSe_2/I^-, I_2/Pt have been fabricated. In order to improve upon the efficiency, the effective WSe_2 crystal surfaces have been etched in aqua-regia. We have obtained a high PEC conversion efficiency, up to 17.1%. This corresponds to the most efficient WSe_2-based PEC solar cell reported so far. Evidence and arguments have been presented to show that the high efficiency (~17.1%) is achieved due to the combined effect of improved crystal quality, obtained through a $SeCl_4$ transporter, and a decrease in the density of surface steps consequent to photo-etching.

MX_2-type layered chalcogenides having corrosionless d–d phototransitions (e.g. WSe_2) are of special significance in the fabrication of viable photo-electrochemical solar cells (Tributsch 1977, Tributsch and Bennett 1977, Gobrecht *et al* 1978). However, the achieved conversion efficiencies are far behind the expected optimum ones (Gerischer 1977). Many attempts have been made to improve the conversion efficiencies. These include surface cleaving, surface modification, photo-etching etc (Kline *et al* 1981, White *et al* 1982, Tenne and Wold 1985, Tenne *et al* 1985). Of these photo-etching seems to be more promising because of the fact that this process leads to higher conversion efficiencies (Ellis *et al* 1976, Hodes 1980, Tenne *et al* 1984). Among the various photo-electrodes of transition metal dichalcogenides, tungsten diselenide has recently received special attention because of its higher conversion efficiencies and stability in fabricating photo-electrochemical solar cells (Fan *et al* 1980, Parkinson 1984, Tenne *et al* 1985, Tenne and Wold 1985). The recent advancement in the growth of n-WSe_2 crystals using a new transporter ($SeCl_4$) has led to further advances in the direction of achieving higher conversion efficiencies by improving the crystal quality (Azaiez *et al* 1986). In this Letter we report the conversion efficiency of 17.1% obtained by using $SeCl_4$-grown WSe_2 crystals modified through photo-etching as photo-anodes in WSe_2/I^-, I_2/Pt PEC solar cells. This conversion efficiency appears to be the highest reported so far for WSe_2-based PEC cells.

The single crystals of WSe_2 using $SeCl_4$, which is a transporter having an ingredient (Se) native to WSe_2, were grown by a chemical vapour transport technique (Prasad *et al* 1986). The transporter was added to pre-synthesised tungsten diselenide powder in a concentration of 0.2 mg cm^{-3}. A temperature gradient of 2 °C cm^{-1} was maintained for 170 h in the growth furnace. Large single crystals having dimensions up to $0.5 \times 0.5 \times 0.1$ cm^3 were obtained after growth. Crystals were attached to a platinum wire, which was fused in a narrow tube containing a mercury pool. The back contact of the crystals was provided with an In–Ga alloy. The electrolyte used for electrochemical studies corresponded to IMKI + 0.05 MI_2 (pH ~ 9). All experiments were carried out using Princeton Applied Research (PAR) electrochemical equipment. A fresh crystal surface, obtained through cleaving with adhesive tape, was used for the fabrication of PEC cells. Illumination was provided with a tungsten lamp with an intensity of 60 mW cm^{-2} (after correction to solution absorption) for both photo-etching and electrochemical measurements. Typical PEC efficiencies of the order of 10% were observed with the as-grown crystals. Photo-etching was carried out in 0.1 mol l^{-1} aqua-regia in forward-bias conditions. Several different etchants like perchloric acid, orthophosphoric acid, chromic acid and aqua-regia were used for photo-etching. It was found that the best results with regard to the enhancement of efficiency were obtained in aqua-regia.

Figure 1 (curve A) shows *I–V* characteristics of a WSe_2 crystal before photo-etching. Figure 1 (curve B) is the corresponding characteristic after photo-etching.

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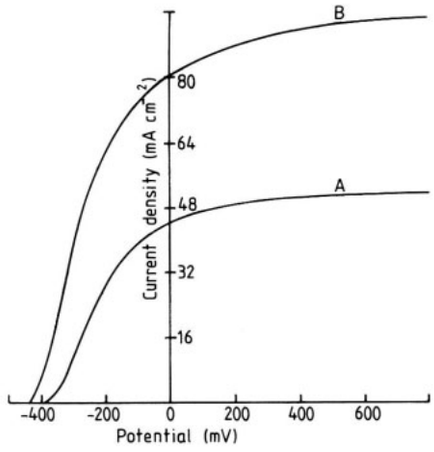

Figure 1. *I–V* characteristics of the WSe_2/I^-, I_2/Pt PEC solar cell before (curve A) and after (curve B) photo-etching.

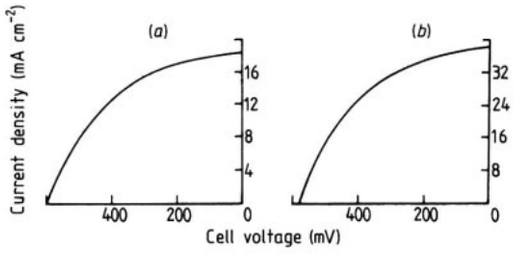

Figure 2. The power characteristics of a cell with as-grown WSe_2 crystal before (*a*) and after (*b*) photo-etching in 0.1 mol l^{-1} aqua-regia. The crystal area is 0.0125 cm^2.

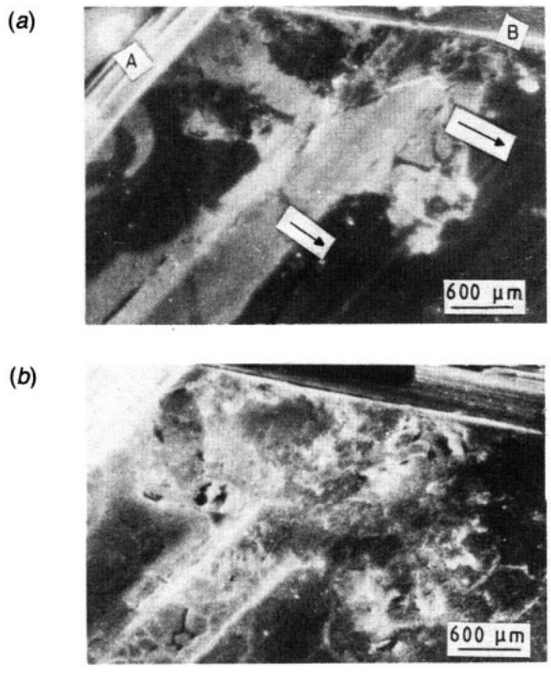

Figure 3. (*a*) A scanning electron micrograph (secondary-electron image) of the as-grown crystal. The edges of the crystals are outlined as A, B. Notice the presence of steps on the effective surface in the as-grown crystals—some of these are marked by arrows. After photo-etching, several of these surface steps disappear (*b*).

Figure 2 shows the power characteristics of the crystal before and after photo-etching. The PEC conversion efficiency before photo-etching is ~8.3% (figure 2(*a*)) and this changes to 17.1% (figure 2(*b*)) after photo-etching. This efficiency is one of the highest reported efficiencies for WSe_2-based PEC solar cells. It should be mentioned that the said efficiency (~17.1%) was obtained for a specifically good crystal exhibiting rather significant changes in surface microstructure on photo-etching for WSe_2. Conversion efficiencies of about 17.1% could be obtained on some other crystals also. Efficiencies in the range of 13 to 15% were generally obtained.

A possible factor which is likely to contribute to the enhancement of conversion efficiency may come about from the growth parameters adopted in the present study. Unlike many other previous WSe_2 growth experiments, where a $TeCl_4$ transporter is used, we have employed $SeCl_4$ as the transporter. Here Se atoms are involved which are native to WSe_2 crystals. Thus, unlike the case with Te, incorporation of Se in the growing crystal would not result in the creation of additional recombination-type energy states (gap states) in the band gap. Analytical explorations of these crystals through the EDAX technique, in the scanning electron microscope mode, and resistivity measurements confirmed the improved quality of $SeCl_4$-grown crystals.

In order to explore the influence of photo-etching on the microstructural characteristics of the surface, the effective crystal surface was characterised by employing the scanning mode of an electron microscope (Philips EM-CM12). The crystal surfaces of several crystals where PEC measurements had been carried out were explored. Figures 3(*a*) and 3(*b*) represent the surface characteristics of the crystal obtained in the secondary-electron scanning mode corresponding to the PEC characteristics shown in figure 1 (curves A and B), before and after photo-etching. A noticeable feature brought out by this (figure 3(*b*)) is the disappearance of several surface steps (see figure 3(*a*)) consequent to photo-etching. The surface steps are known to be detrimental in the PEC conversion process through the energy states (recombination levels) which they produce in the electronic band structure (Lewerenz *et al* 1980). A reduction in the density of surface steps would produce an enhancement in the PEC efficiency. This would be mostly apparent through an increase in the photocurrent. This is what has actually been observed in the present investigation (figure 2(*b*)). It has been surmised in earlier works that photo-etching may lead to an increased PEC efficiency through a decrease of the surface reflectivity also (Tenne *et al* 1983, Decker *et al* 1987). It is not known to what extent this contributes to the enhancement of conversion efficiency. However, the photo-etching treatment did not appear to produce any significant decrease in reflectivity of the WSe_2 (0001) crystal surface in the present investigation.

In conclusion, therefore, it may be said that the

present studies reveal that improved crystal quality, through the use of $SeCl_4$ as a transporting agent, and surface modification, through photo-etching which results in a decrease of the density of steps on the surface, leads to a high-conversion-efficiency WSe_2 photo-electrochemical solar cell. Further studies on the crystal growth characteristics and the role of the chemical vis-à-vis photo-etching modifications are in progress and results are forthcoming.

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