

## Abstract

In this thesis electrochemical and photoelectrochemical investigations on n-molybdenum disulfide and p-tungsten diselenide are presented. These compounds are layer type group VI transition metal dichalcogenides which exhibit strong anisotropic characteristics parallel and perpendicular to the *c*-axis of the crystal. They have good physical (e.g. high absorption coefficient) and chemical (inert van der Waals surface) preconditions to be used in thin layer solar cells. So far the major drawback for the technical application are the surface states induced by unsaturated bonds (so called dangling bonds) at the crystal edges which lower the efficiency of such modules. Electrochemical and photoelectrochemical investigations on the characteristics of this semiconductor surface were carried out. Photoelectrochemical microwave reflection measurements were mostly applied for the investigations on the illuminated semiconductor surface. This technique can detect the light induced change of excess charge carriers at the semiconductor electrolyte interface. For the measurements mainly n-type molybdenum disulfide (natural and synthetic crystals) and some p-type tungsten diselenide (synthetic) samples were used. As basic characterisation the back contact was tested. With AFM (atomic force microscopy) and XPS (x-ray photoelectron spectroscopy) the surface was investigated. Hall and conductance measurements were performed for the electronic parameters and cyclic voltammetry and DEMS (differential electrochemical mass spectroscopy) were carried out to test the electrochemical behaviour. The characteristics of these crystals under illumination were investigated using the combinatoric technique of simultaneous measurement of the photocurrent and the microwave reflection. By this method it is possible to detect the excess charge carriers that reach the external circuit (photocurrent) and the ones that remain in the semiconductor (microwave reflection). The measurement of the periodically illuminated crystal reflected microwave radiation provides the light induced change in photoconductance. This change in conductance is proportional to the number of excess charge carriers that remain in the semiconductor whereby their behaviour can be studied under different experimental conditions. The measurements were performed potential controlled in a three electrode setup with different electrolytes (electrochemically inert and with redox system) and at different excitation wavelengths. By the variation of the concentration of the redox couple in the electrolytes the border cases of inhibited and

uninhibited charge transfer could be approximated. Thereby conclusions on the charge transfer itself and surface recombination could be drawn. Furthermore the behaviour of charge carriers in the bulk and in space charge region could be explored separately analysing different penetration depth of different wavelengths. After showing that the basic assumptions of photoelectrochemical microwavereflection can be applied to this system, the impact of adsorbates on the molybdenum disulfide surface has been examined. To passivate the unsaturated bonds at the crystal edges, the surface was treated with different molecules (cysteine, EDTA and Tween 80) and the impact on photo corrosion, charge transfer and recombination was investigated. Tween 80 showed an effective reduction of dark and photo corrosion in electrochemical inert electrolyte, whereas the photocurrent was enhanced by this treatment in electrolyte with redox system. Similar results were revealed by the treatment with EDTA but to a smaller extent. If the surface was treated with amino acid cysteine the photocurrent was also enhanced in analogy the results of the other adsorbed compounds. In electrochemical inert electrolyte along with the reduction of photo corrosion a quenching of excess charge carriers in the semiconductor was observed. This is a basic difference to EDTA and Tween 80 where the remaining excess charge carriers could be detected measuring the microwave reflection. By the adsorption of cysteine an additional process is revealed. While the adsorption at the unsaturated bonds at the crystal edges (which results in a reduction in photo corrosion current) cysteine is interacting with the  $4d_{z^2}$  orbital which is forming the valence band edge of  $\text{MoS}_2$  and is protruding deeply in to the van der Waals surface. In this way cysteine extracts the holes from the valence band. By the positive charge which is forming at the cysteine the molecule acts as an effective recombination centre at the surface and reduces the amount of remaining excess charge carriers in the semiconductor. Finally the sensitivity factor of the microwave reflection was calculated measuring at 875 nm illumination wavelength. In addition this sensitivity factor could be used to calculate a charge transfer constant for holes under conditions of a moderate charge transfer.