

Qualitative Change of the Electronic Properties of a Semiconductor Surface by Chemical Treatment Using Polyelectrolytes

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In the present study we demonstrate the ability of changing the electronic properties of a semiconductor surface by adsorbing polyelectrolytes. For this purpose polyethylenimine (PEI) polymers were adsorbed onto the van der Waals surface of the layered structure semiconductor WSe₂. For comparison the surface properties of the as grown and chemically treated surface were investigated by standard and photoassisted tunneling spectroscopy. In the case of the chemically treated sample a strong change in the *I/V* characteristics could be observed.

Introduction

The chemical treatment of semiconductor surfaces by different chemical substances to stabilize, improve, or even tune their electronic properties is a field of large interest. A prominent example in this area is the surface passivation of silicon by hydrogenation. Concerning the layered structure transition metal dichalcogenides, several experiments are reported in the literature which aim to increase the quantum efficiency of optoelectronic devices.^{1,2} On these semiconductors the chemical treatment by EDTA (ethylenediaminetetracetic acid) or NaI/I₂ results in a passivation of defects which could also be detected as an increase in the photoinduced tunneling current using photoassisted scanning tunneling spectroscopy/microscopy.^{3,4} However no qualitative change of the electronic surface properties could be observed. In this study we report for the first time on the chemical treatment by adsorbing polyelectrolyte molecules (polyethylenimine, PEI) on the layered structure semiconductor WSe₂. On the basis of their large charge density in aqueous solution, pure and modified polyethylenimine polymers are widely used in the paper industry as effective drainage and retention aids. In these applications polyethylenimine allows the control of flocculation in stock suspensions.^{5–7} Due to this large charge density they are expected to act indirectly as electron donor with respect to the surface of a p-type semiconductor. This might result in additional band bending and could increase the open circuit voltage of optoelectronic devices.

Experimental Section

For our measurements we used a single crystal of the transition metal dichalcogenide WSe₂ (p-type), which was grown by chemical

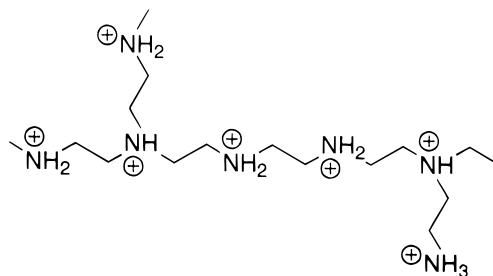


Figure 1. Chemical structure of the PEI molecule, used for the chemical treatment of WSe₂.

vapor transport. To allow a direct comparison of the results, the (0001) surface of the same crystal was investigated prior to and after the chemical treatment by standard and photoassisted scanning tunneling spectroscopy. After the initial measurements on the as grown sample, polyethylenimine polymers (Figure 1) with a molecular weight of 6200 g/mol (BASF AG Ludwigshafen, Germany) were diluted in deionized water (50 vol %) and dropped onto the crystal surface. After repeatedly rinsing the surface with deionized water, it was dried in a stream of nitrogen.

For the investigation of surface properties, we used a standard scanning tunneling microscope which was operated in high vacuum (10⁻⁶ Torr). Using mechanically prepared PtIr tips, *I/V* characteristics were measured under dark and illuminated conditions (HeNe laser, 633 nm, 500mW/cm²). In order to measure both *I/V* characteristics with and without illumination while keeping identical tunneling conditions, we used the following setup: The incident light is modulated by a chopper at a frequency of 500 Hz. During the first half of the dark period, the *z*-feedback is set active to adjust the tip-sample separation for a given reference voltage *U*_{ref} and reference current *I*_{ref}. The *z*-feedback is then switched off and during the second half of the dark period the tunneling current is measured at a fixed tunneling voltage *U*_t. The light then turns on and the current at *U*_t is measured under illumination. In the first half of the next dark period the tip-sample distance is readjusted at the reference voltage *U*_{ref} and reference current *I*_{ref} and so on. By variation of *U*_t the *I/V* curves under dark and illuminated conditions are thus measured simultaneously for a tip-sample separation that is solely determined by *U*_{ref} and *I*_{ref} under dark conditions. A more detailed description of this setup will be given elsewhere.⁸

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(1) Hodes, G.; *Appl. Phys. Lett.* **1989**, *54*, 2085.
(2) Razzini, G.; Peraldo Bicelli, L. *Electrochem. Solar Cells* **1981**, *128*, 2134.
(3) Akari, S.; Lux-Steiner, M. Ch.; Glöckler, K.; Schill, T.; Heikamp, R.; Koslowski, B.; Dransfeld, K.; *Ann. Phys.* **1993**, *2*, 141.
(4) Akari, S.; Friemelt, K.; Glöckler, K.; Lux-Steiner, M. Ch.; Bucher, E.; Dransfeld, K. *Appl. Phys.* **1993**, *A57*, 221.
(5) Horn D.; Linhart, F. *Paper chemistry*; Roberts, J., Ed.; Blackie: Glasgow and London, **1991**; pp 44–61.
(6) Tanka, H.; Oedberg, L.; Wagberg, L.; Lindström, T. J. *Colloid Interface Sci.* **134**, **1990**, 219.
(7) Akari, S.; Schrepp, W.; Horn, D. *Langmuir* **1996**, *12*, 857.

(8) Matthes, Th. W.; Sommerhalter, Ch.; Boneberg, J.; Leiderer, P.; Lux-Steiner, M. Ch. To be published.

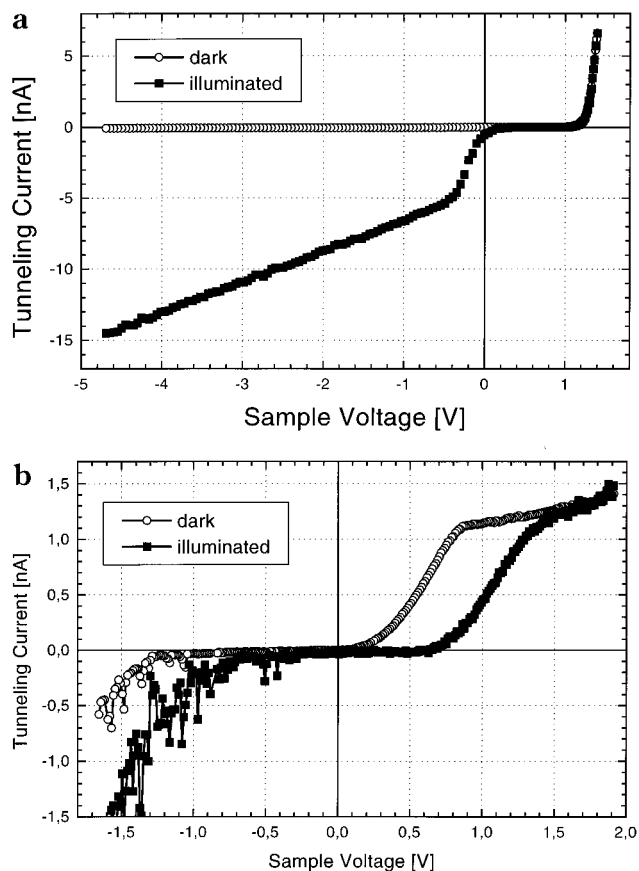


Figure 2. I/V characteristics for the as grown (a) and PEI adsorbed (b) WSe_2 single crystal measured by photoassisted tunneling spectroscopy. The tip-sample separation is adjusted under dark conditions for an applied reference sample voltage $V_{ref} = 1.3$ V and reference current $I_{ref} = 1.2$ nA. I/V curves under dark conditions are given by open circles. I/V curves under illumination (HeNe laser, 633 nm, 500 mW/cm²) are given by filled squares.

Results

Prior to the spectroscopic measurements, the surfaces of the as grown and the chemically treated crystal were imaged in the constant current mode. Atomic resolution could be obtained on both surfaces showing the hexagonal structure of the $WSe_2(0001)$ surface. While for the untreated sample voltages $> +0.8$ V had to be applied, the treated surface could be atomically resolved at voltages $> +0.2$ V. At negative sample voltages no stable imaging conditions could be obtained for both cases. Up to now our attempts to image the PEI molecules themselves failed.

The measured I/V curves for the as grown and chemically treated surface are shown in parts a and b of Figure 2, respectively. For the untreated surface the dark I/V curve exhibits an ideal rectifying behavior. While in the negative voltage range no current could be detected, it increases exponentially in the positive voltage range. The I/V curve under illumination is identical to the dark curve for voltages between $+1.4$ and $+0.3$ V. At $+0.3$ V we observe the onset of a photoinduced tunneling current, which increases rapidly for decreasing voltage and reaches a regime of smaller linear increase at about -0.5 V.

The results on the treated surface were completely different (Figure 2). Under dark conditions we observed an exponential increase in the positive voltage range up to 0.8 V followed by an almost linear regime of much smaller slope for higher voltages. In the negative range an onset of the tunneling current occurs at about -1.0 V. We should note however that in the negative voltage range the tunneling current was much less stable compared to positive voltages. A shift by about 0.5 V to more positive

voltages is observed under illumination. At 1.5 V both curves coalesce and no significant photoinduced effect was measured for higher voltages.

Discussion

In spite of the fact that the measured I/V curves were completely different after the adsorption of PEI molecules, atomic resolution of the WSe_2 lattice could be obtained. Possibly for the applied tunneling conditions the tip penetrates the adsorbed PEI layer until tunneling into the semiconductor can occur. The change of the bias regime at which atomic resolution could be observed reflects the influence of the adsorbed layer onto the semiconductor surface. However, at this stage of experiments and due to the insufficient knowledge about the electronic properties of the PEI molecules an explanation can be given here.

To understand the change of the I/V curves due to the adsorption, we will first sketch the basic physical interpretation for the as grown surface. The (0001) van der Waals surface of WSe_2 is a typical representative for a semiconductor surface with a very low surface density of states. Due to the layered structure all bonds of the (0001) surface are saturated and no intrinsic surface states have been reported up to now.⁹ As a consequence, the scanning tunneling microscopy (STM) configuration can be described as a metal-insulator-semiconductor junction with a thin insulating gap. In the proximity of the metallic tip, the band bending at the semiconductor surface is essentially determined by the work function difference between tip and sample and the externally applied tunneling voltage. The band diagrams for different applied potentials are shown in Figure 3. For voltages $< +0.3$ V the bands are bent downward. Light-generated minority charge carriers are partially driven to the semiconductor surface, where they can be detected as an additional light-generated (negative) tunneling current or they are lost by backdiffusion and recombination in the bulk. The regime of quasi-saturation of the photoinduced tunneling current (below -0.5 V) is reached, when the amount of minorities that are lost by backdiffusion becomes negligible due to the extended space charge region. In this situation all minority charge carriers which are driven to the space charge region will contribute to the photoinduced tunneling current. At voltages $> +0.3$ V the bands are bent upward. Now the holes are driven to the surface, while the electrons are driven into the bulk. The fact that no positive photoinduced current is detected can be explained by the negligible photoinduced change of the majority charge carrier concentration for moderate or high doping levels. A more detailed discussion as well as a one-dimensional model calculation will be given in ref 10¹⁰ for the case of the isostructural WS_2 .

For the case of the PEI-adsorbed WSe_2 surface, we can give only a preliminary interpretation.

From our experiments we can conclude that the main effect of the adsorbed layer is a transfer of electrons into the p-type semiconductor. Since in the presence of water molecules the polyethylenimin (basic substance) is a proton acceptor, the excess of negatively charged OH groups might act as electron donator. However one could also think of a direct electron transfer which solely involves the PEI molecules themselves. Up to now we do not know whether a water layer is still present under the high vacuum conditions, that we used for the STM measurements.

(9) Mayer, T.; Klein, A.; Lang, O.; Jägermann, W. *Surf. Sci.* **1991**, *269/270*, 909 and references herein.

(10) Sommerhalter, Ch.; Matthes, Th. W.; Boneberg, J.; Leiderer, P.; Lux-Steiner, M. Ch. Submitted to *J. Vac. Sci. Technol. B*.

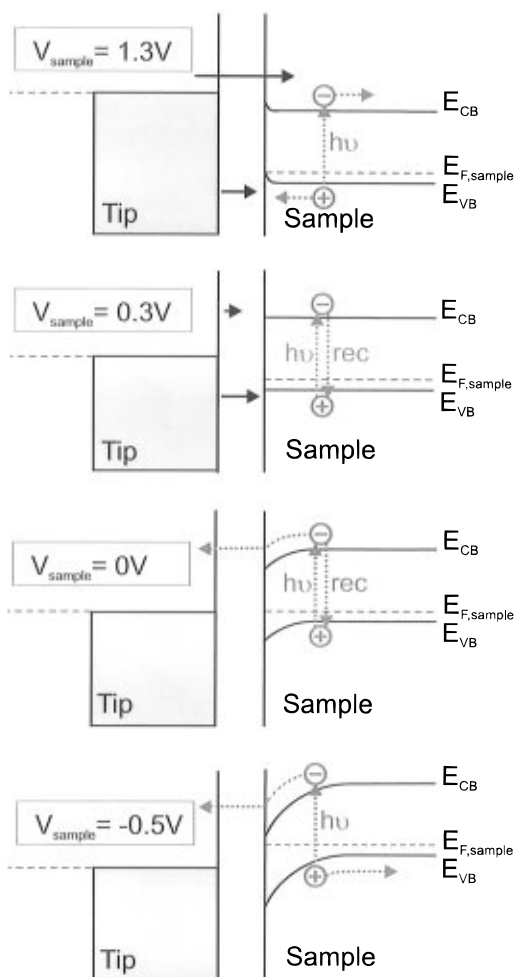


Figure 3. Band diagrams for the tip/vacuum/p-WSe₂ system prior to the PEI treatment. The charge carrier transport channels are given by arrows (black solid arrows for transport that occurs under dark conditions as well as gray dotted arrows for transport that involves light generated charge carriers). Under illumination and in case of upward band bending (upper diagram) electrons are driven to the bulk and holes to the surface; in the case of downward band bending (lower diagrams) electrons are driven to the surface and holes to the bulk. In both cases a photoinduced tunneling current is resulting.

In both cases an additional downward band bending at the semiconductor surface is expected. Extrinsic surface states can be created at the PEI–semiconductor interface, which act as recombination centers and effectively pin the semiconductor Fermi level. As a consequence the I/V characteristic should be comparable to that of a conventional semiconductor surface with Fermi level pinning due to intrinsic surface states (for example Si(111)-(7 × 7)¹¹). Under these conditions, the applied voltage essentially drops within the tunneling gap. The band diagram for zero applied voltage is shown in Figure 4. By variation of the tunneling voltage, the tunneling current probes the available density of states, i.e., the empty states in the semiconductor's conduction band at positive sample voltages and the density of filled states in the valence band at negative voltages. Therefore the measured low current regime corresponds to the semiconductor bandgap in this model.

Under illumination an additional surface photovoltage shifts the $I-V$ curve to more positive potential. The band bending is reduced due to the photogenerated minority charge carriers which are subsequently trapped and recombine via surface states. The shift of the $I-V$ curve

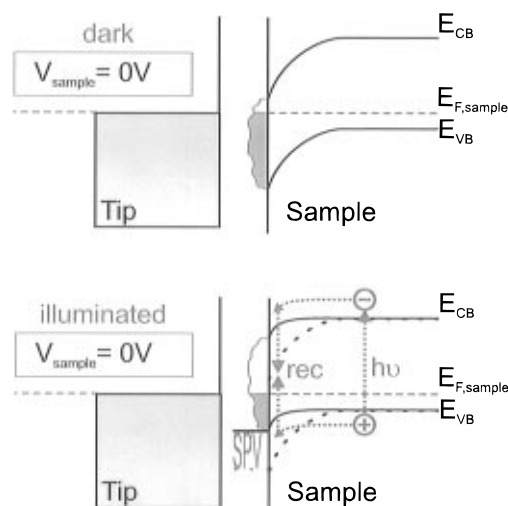


Figure 4. Band diagram for the case of the PEI-treated surface. The semiconductor Fermi level is effectively pinned by surface states. Under illumination the band bending is reduced due to the photogenerated minority charge carriers which are subsequently trapped and recombine via surface states due to the PEI treatment. SPV corresponds to surface photo voltage and rec to recombination.

under illumination gives a lower limit for the band bending due to the adsorption of PEI.

The behavior of the dark current in the voltage range between 0.9 and 1.5 V might be a consequence of the minority injection from the tip.¹² If the current density of electrons, which are injected into the conduction band of the semiconductor by the tunneling current, increases toward higher voltages, some of these charge carriers can return to the surface. There they will be trapped by surface states and reduce the band bending in the same way as electrons, which are created by photoexcitation.

If our simple model is valid, the shift of the $I-V$ curves under illumination should depend on the light intensity and the coalescence of dark and illuminated curve at high positive voltages should depend on the magnitude of the tunneling current. However, at this stage of our investigations we cannot exclude that the observed behavior might also be associated with tunneling via the electronic states of the PEI molecules. Further detailed experiments are necessary to clarify the responsible process.

Conclusions

In summary we have demonstrated that the adsorption of PEI molecules onto the van der Waals surface of a p-type WSe₂ single crystal essentially changes the electronic surface properties. From the results of our photoassisted scanning tunneling spectroscopy investigations, we can conclude that the adsorption of PEI induces a strong downward band bending at the semiconductor surface, which might be of interest for the optimization of electronic and optoelectronic devices. Further experiments will be necessary to clarify the underlying electronic processes and to investigate the technological potential of the observed effects.

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(11) Kuk, Y.; Becker, R. S.; Silverman, P. J.; Kochanski, G. P. *J. Vac. Sci. Technol.* **1991**, *B9*, 545.

(12) Cahill, D. G.; Feenstra, R. M. *J. Vac. Sci. Technol.* **1993**, *A11*, 792.