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Investigation of acceptors in p-type WS_2 by standard and photo-assisted scanning tunneling microscopy/spectroscopy

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Abstract

Current imaging tunneling spectroscopy (CITS) and photo-assisted scanning tunneling spectroscopy (STS) is used to characterize dopants in p-type WS_2 single crystals. While the local charge distribution at ionized acceptor sites give rise to topographic depressions on a nm scale, CITS measurements reveal an additional bright ring. On the base of a one dimensional metal–insulator–semiconductor (MIS) model, the topographic contrast and the ring structure are explained by two competing current mechanisms involving tunneling into unoccupied states of the valence and the conduction band. Local surface photovoltage (LSPV) imaging allows to directly measure the local potential. We observe a nonoscillating reduction of the tip-induced bandbending in the vicinity of the acceptors and correlate this with the lateral extension of the topographic depressions and the ring structures observed in CITS measurements. In addition, photoinduced tunneling current (PITC) measurements do not show an enhanced minority charge carrier recombination at acceptor sites.

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1. Introduction

Recently, scanning tunneling microscopy (STS) has been widely used to study the electronic structure of surface and subsurface defects on a large variety of semiconductors. Especially on semiconductors with a low surface state density, such as the (110) surface of III–V semiconductors [1–16], the (1010) and the (1120) surface of wurtzite II–VI semiconductors [17] or the (0001) surface of the layered semiconductors MX_2 (M = W or Mo, X = S or Se) [18–21], the localized charge distribution in the vicinity of an ionized dopant results in a nm scale topographic depression or hillock superimposed on the atomically resolved lattice. Using a low temperature STM at 4.2 K, van der Wielen et al. [22] showed that positively charged Si donors in GaAs cause oscillations in the local charge distribution resulting in an oscillating contrast in constant current images. These oscillations were interpreted in terms of Friedel oscillations. Scattering states of ionized

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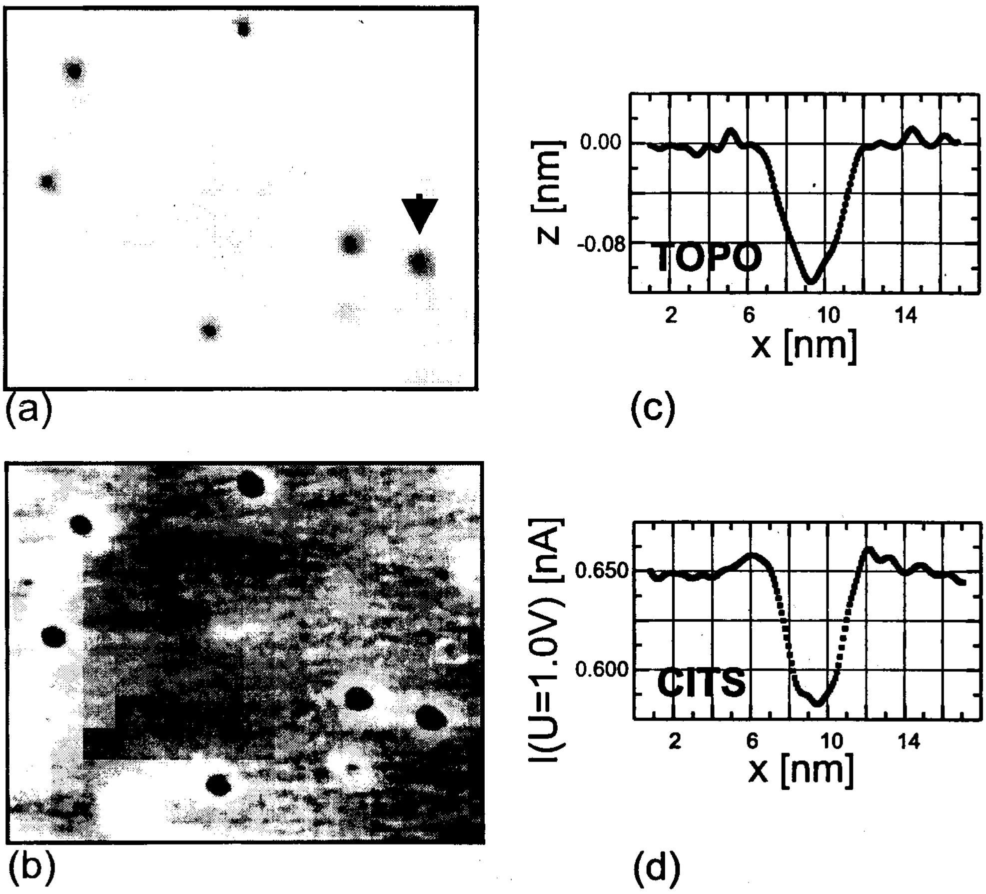

Fig. 1. Topography ($U_{sample} = 1.3$ V, $I_{ref} = 2.1$ nA, scan area 85 nm × 69 nm, $\Delta z = 0.15$ nm) (a) and simultaneously measured CITS-image ($U_{CITS} = 1.0$ V, $I = 0.57$–0.71 nA) (b) showing acceptors in a p-type WS_2 single crystal. (c) and (d) show corresponding cross-sections for the topography and the CITS-image respectively across the acceptor site marked by an arrow in (a).

neling of electrons from the tip into unoccupied states in the conduction band (J_{CB}). [1]

The dotted lines in Fig. 3a describe the situation if the tip is located close to an acceptor site. The additional screened Coulomb potential at the acceptor site results in a local increase of the majority carrier concentration in the valence band. Therefore, J_{VB} will increase at an acceptor site, while J_{CB} is reduced due to the acceptor-induced bandbending. The depressions observed in the topographic measurements (Fig. 1a) indicate that J_{CB} dominates for $U_{sample} = 1.3$ V. In the constant current mode, the STM tip has to approach the surface to keep the tunneling current constant.

Compared to our investigations on p-type WS_2, most of the experiments on p-type GaAs samples were done on highly doped semiconductors, where the majority carriers (J_{VB}) dominate the tunneling current, resulting in hillocks at the dopant sites.

The ring structures, observed in the CITS measurements for lower sample voltages (Fig. 1b) can be explained by the competing contributions of J_{VB} and J_{CB} to the tunneling current. When the tip approaches the acceptor site, J_{VB}, measured at 1.0 V, increases due to the enhanced majority carrier concentration resulting in the bright ring-shaped contrast

[1] This seems to be not compatible with the $I-V$ spectra in [25]. However those have been acquired using mechanically cut PtIr tips without an additional cleaning procedure. A dielectric contamination layer on these tips will cause the transition from J_{VB}- to J_{CB}-dominated tunneling to more positive sample voltages. For more details see: Th. W. Matthes, PhD thesis, Hartung-Gorre, Konstanz, Germany, 1998.

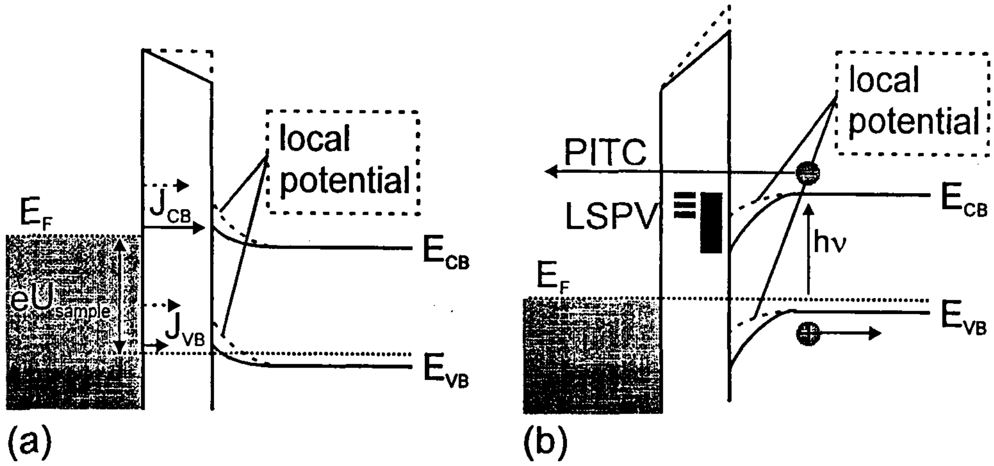

Fig. 3. (a) Schematic band alignment for the tunneling tip above the p-type WS_2 surface for an applied voltage of $U_{sample} = 1.3$ V. Tunneling paths involving the conduction band (J_{CB}) and the valence band (J_{VB}) of the semiconductor are given by arrows. The band alignment and currents for the tip located over an acceptor site is given by dotted lines. (b) Schematic band alignment for the tunneling tip above the p-type WS_2 surface for an applied voltage of $U_{sample} = 0$ V and optical excitation of the semiconductor. Photogenerated electron-hole pairs are separated within the electrical field of the tip-induced space charge region, leading to a (negative) photocurrent (PITC) and the local surface photovoltage (LSPV), which is given as gray bar. The conditions for the tip above an acceptor site is given by dotted lines and the dotted bar.

in Fig. 1b, while J_{CB}, measured at 1.3 V, does not change significantly and no topographic contrast is observed. When the tip gets closer to the acceptor site, the additional bandbending at the acceptor site reduces the potential drop in the tunneling barrier, resulting in a reduced tunneling transmission factor T through the tunneling barrier and an upward shift of the conduction band with respect to the Fermi energy of the tip. The tunneling feedback will therefore reduce the tip–sample separation to maintain a constant tunneling current at 1.3 V. As a consequence of the reduced tip–sample separation, the I–V curve is getting steeper and a black dot centered at the acceptor site is observed. Indeed this can be simulated by one dimensional calculations as described in Ref. [25]. However, this simple model only yields the experimentally observed behavior for J_{CB}, while the contribution of J_{VB} is overestimated.

These qualitative interpretations of the contrast mechanisms in constant current and CITS images of acceptor sites are supported by the additional information obtained in photo-assisted scanning tunneling spectroscopy.

The PITC, measured at negative sample voltages, shows no correlated contrast. The measurements and calculations in Ref. [25] indicate that in this voltage range the PITC is limited by bulk diffusion of the photogenerated minority carriers and nearly independent of bias voltage (*quasi-saturation regime*). A small change in the surface potential due to the ionized acceptor does not influence the collection of the minority carriers. As shown in Ref. [24], strong recombination centers, such as deep levels due to dangling bonds at non van der Waals surfaces, are needed to change the PITC.

However, the LSPV, which measures the local tip-induced bandbending (Fig. 3b; for a detailed discussion see, Ref. [25]), is sensitive to small changes in the local surface potential caused by the ionized acceptor (Fig. 2c). The lateral extension of the contrast in the LSPV image corresponds to the depression in the topographic contrast, supporting the interpretation that the reduced bandbending is responsible for the observed depression in constant current images. Since no oscillating behavior is observed in Fig. 2c, we conclude that the acceptor causes a nonoscillating screened Coulomb potential at room temperature. The ring structure and topographic hillocks, as observed in CITS images (Fig. 1b) and the results of some other investigations