Work Function and Photothreshold of Zirconium Sulfoselenide Transition Metal Dichalcogenides

M. Moustafa, C. Janowitz, and R. Manzke

***Abstract*—Single crystals of ternary layered transition metal dichalcogenide zirconium sulfoselenide compounds (ZrS_xSe_{2-x}) were grown by the chemical vapor transport technique and characterized employing different methods such as dispersive x-ray spectroscopy (EDX), the low energy electron diffraction (LEED), and Laue diffraction. The work function and photothreshold values of different compositions of the ZrS_xSe_{2-x} family have been measured by high resolution angle-resolved photoemission spectroscopy (ARPES). The photothreshold values are found to follow an ascending trend from $ZrSe_2$ towards ZrS_2. Additionally, the obtained values of the end members, i.e. ZrS_2 and $ZrSe_2$, are compared with the existing values based on various band models and previously experimental results.**

***Index Terms*— Work function and photothreshold, transition metal dichalcogenides, layered materials, photoemission and photoelectron spectra**

I. INTRODUCTION

Work functions and photothresholds are considered to be important physical quantities which characterize material surface properties. The work functions play an essential role in various phenomena such as electron emission from materials and charge transfer at interfaces. The latter determine the properties of the interface between two materials. Therefore, determining such surface parameters is important when employing layered structure materials for fabrication such as Schottky-barrier and Ohmic contacts. Work function and photothreshold values can be determined by different techniques such as the photoemission spectroscopy (PES) and the Kelvin probe (KP) [1, 2]. Kelvin probe is a non-contact vibrating capacitor device used for measuring the work function difference between a specimen and a vibrating electrode brought in close proximity. While the PES allows the measurement of the absolute values, KP only gives the contact potential difference (CPD) between the actual probe and the sample surface. Calibration with reference material allows turning KP results into absolute values.

The family of the transition metal dichalcogenides (TMDCs) represents a class of important layered materials [3-5]. They possess a batch of rich remarkable features leading to a wide range of interesting physical properties and suitability for various applications. They display the whole spectrum of electronic properties covering the range from metals and semi-metals to large and narrow band gap semiconductors to insulators [6, 7]. The compounds of this family have in common the chemical formula MX_2 where M stands for a transition metal and X for a chalcogen atom: S, Se, or Te of group IVa. The most significant structural character of these compounds is that they crystallize in a quasi 2-D structure consisting of a sheet of metal atoms lying between two sheets of chalcogens forming X-M-X layers or sandwiches. Inside the layers, the bonding is of strong mixed covalent-ionic character depending on the electronegativity χ of the elements, while the adjacent layers are loosely coupled by relatively weak Van der Waals forces. The family of ZrS_xSe_{2-x} TMDCs belongs to the group IVb crystallizes in 1*T* structure in which the transition metal is octahedral coordinated by six chalcogenides, as shown in Fig. 1 (a).

The highly anisotropic structure of these materials, in combination with different *d* orbital occupations in different transition metal elements, give rise to a lot of unique physical properties in a number of their electronic, optical, and chemical properties [8, 9]. Additionally, TMDC semiconductors were introduced for different types of applications, e.g. p-n junctions [10], high mobility field-effect transistors [11], switching and memory effects [5], and photovoltaic applications [5, 12]. The energy gap range of the TMDCs matches the solar spectrum very well. The energy gap range of the TMDC materials matches the solar spectrum very well, in addition to the reported high absorption and strong anisotropy of the transport properties. Therefore, TMDC semiconductors are considered to be promising candidates for the implementation in photovoltaic applications and for efficient solar energy conversion among many other semiconductor compounds proposed for this field. Some of them, like WSe_2 [13, 14], $MoSe_2$ [13], and WS_2 [15] have been already successfully explored for potential use in the fabrication of solar cell applications.

Electronic properties of the TMDC materials have been investigated by many groups using different approaches.

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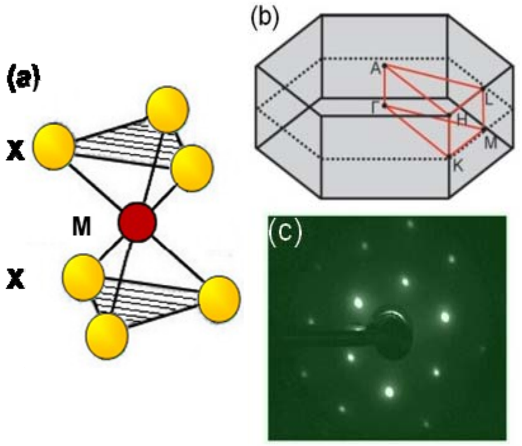

Fig. 1. (a) 1-*T* crystal structure (b) Corresponding Brillouin zone (BZ) with different high symmetry points and directions (c) LEED pattern of ZrS_2 taken at an electron energy of 102 eV

Early, the band structure calculations of Murray et al. [16, 17] using the semi-empirical tight binding approach of the linear combination of atomic orbitals (LCAO) method. The calculations of Bullett [18] based on the chemical pseudopotential methods. Most recently, novel calculations of the band structure were performed based on density functional theory (DFT) method and with the inclusion of the spin-orbit interactions [19, 20]. Ghafari et al. [19] reported on the electronic structure of ZrS_2 and $ZrSe_2$ crystals as well as for the ternary ZrSSe compound. Jiang reported for four simple TMDC materials using *GW* approximation method [20]. Additionally, the electronic properties of layered TMDCs have been studied by many various experimental techniques, including optical absorption, [21- 24] direct and inverse photoemission spectroscopy (PES/IPS) [19, 25, 26]. In spite of these intensive theoretical and experimental efforts, still much less has been known about the work functions and the photothresholds of TMDCs and in particular for the family of ZrS_xSe_{2-x}. This work focuses on the experimental measurements of work function and photothreshold values of the ZrS_xSe_{2-x} series by the photoemission spectroscopy. The obtained values are discussed and compared with the existing values found in the literature.

II. EXPERIMENTS

All single crystals of ZrS_xSe_{2-x} used for this study were grown by the chemical vapour transport (CVT) technique using iodine as the transport agent. The stoichiometric quantities of 99.999% pure sulfur and selenium powder, and 99.8% pure zirconium were placed in quartz ampoules. 99.999% pure iodine was added to provide an iodine concentration of (5 mg cm^{-3}) of the ampoule volume. The charged ampoules were evacuated and sealed at a pressure of ~10^{-5} Torr, for more details about the crystal growth referee to [21], with the reagents maintained at liquid nitrogen temperature preventing sublimation or evaporation of the ampoule contents and retaining volatile impurities. Crystal growth took place in a 4-zone oven including two zones for buffering at both ends to avoid temperature variation caused by the environmental temperature during the growing process. The crystals obtained had naturally clean mirror-like faces and were thick enough enabling good cleavage in ultrahigh vacuum (UHV) in the direction perpendicular to the *c*-axis. This character is of high impotence when they are subjected to experiments such as the photoemission spectroscopy measurements.

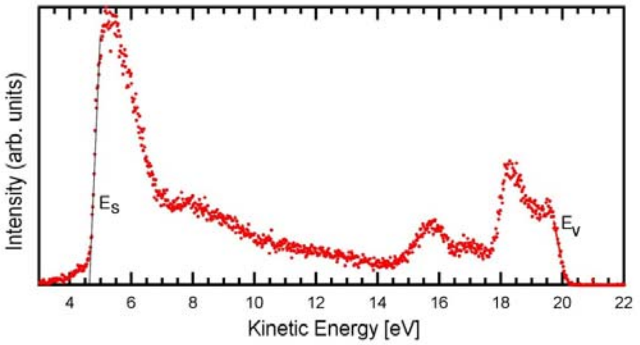

Fig. 2. EDC spectrum of $ZrS_{0.8}Se_{1.2}$ crystal taken at the A point of the BZ taken with energy of 22 eV. For the determination of the photothreshold, bias voltage has been applied to accelerate the slowest kinetic energy electrons and accordingly the secondary cut-off is measured.

The stoichiometric compositions of the grown crystals were determined using energy dispersive x-ray spectroscopy (EDX) for crystals of the ZrS_xSe_{2-x} series. For a qualitative determination of the crystal structure we used the low energy electron diffraction (LEED) which showed a clear hexagonal array. Fig. 1 (b) and (c) represent the corresponding Brillouin zone (BZ) of the octahedral structure with different high symmetry points and directions and a LEED pattern of ZrS_2 taken at energy of 102 eV, respectively. LEED in addition to Laue diffraction patterns used to orientate the crystals. High resolution photoemission spectroscopy spectra were measured at the Helmholtz-Zentrum Berlin for materials and energy (HZB). The measurements were performed under ultra high vacuum ($p \leq 2 \times 10^{-10}$ mbar). The resulting photoelectrons were energy analysed using a hemispherical analyser. Values of work function Φ and the photothreshold E_P were taken after saturation, i.e. no significant changes are observed. Usually, a bias voltage is applied on the sample to accelerate the slowest kinetic energy emitted electrons to beyond the spectrometer's minimum energy and accordingly the secondary cut-off is measured.

III. RESULTS AND DISCUSSION

The work function Φ, the photothreshold E_p, and the electron affinity parameters can be determined precisely utilizing the photoemission spectroscopy. This technique has an advantage of allowing the measurement of the absolute values without need of calibration, contrary to e.g., the Kelvin probe method.

A typical photoemission spectrum has two thresholds: The higher energy cut-off which is determined by the Fermi level E_F or by valence band maximum E_v of metals or semiconductors, respectively, and the lower energy cut-off, or secondary edge E_s, as formed by the secondary electrons with the minimum energy required for escaping from the

TABLE I
WORK FUNCTION (Φ) AND PHOTOTHRESHOLD (E_P), DETERMINED BY PHOTOEMISSION SPECTROSCOPY, FOR VARIOUS COMPOSITIONS OF THE SERIES ZrS_xSe_{2-x}

ZrS_xSe_{2-x} x	Φ [EV]	E_P [eV]
0.0	5.22 ± 0.18	6.12 ± 0.14
0.4	5.35 ± 0.26	6.43 ± 0.26
0.8	5.36 ± 0.31	6.54 ± 0.30
1.2	5.26 ± 0.11	6.65 ± 0.15
1.5	5.27 ± 0.20	6.74 ± 0.12
2.0	5.20 ± 0.14	6.90 ± 0.12

solid surface. Fig. 2 depicts an example of the obtained energy distribution curve (EDC). Since the length of the spectrum is known, the work functions or the photothresholds are determined as:

$$\Phi = h\nu - (E_F - E_s) \qquad (1)$$

$$E_P = h\nu - (E_V - E_s) \qquad (2)$$

where $h\nu$ is the photon energy. E_s is the lower energy cut-off, E_V and E_F are the higher cut-offs for semiconductors and metals, respectively. Usually, a bias voltage is required to be applied on the sample to accelerate the slowest kinetic energy emitted electrons to beyond the spectrometer's minimum energy and accordingly the secondary cut-off is measured. The measurements have been performed by applying various bias voltages in the range between 2.5 eV and 5 eV for each sample. Values of work function and the photothreshold were taken after saturation, i.e. no significant changes are observed. The experimentally determined values of the work function and photothreshold for the whole series of ZrS_xSe_{2-x} are summarized in Table I. The work function of the gold of ~5.1eV was found, in consistent with other reported values, which confirms the accuracy of the results.

First, we compare the present results of the end members of the group i.e. $ZrSe_2$ and ZrS_2 with the measurements by other groups. This is not possible for the mixed compositions due to the scare results for them. For $ZrSe_2$, the reported work function Φ=5.22 eV agrees well with experimental value of 5.2 eV [27] and slightly higher of 4.8 eV [18]. The photothreshold of 6.12 eV is in a very good agreement to the reported values, both experimentally e.g. [22] and from ab initio tight binding calculations after subtracting the energy offset value of 6.1eV [28]. Values of photothreshold obtained from photoemission spectroscopy is 0.9 eV compared to 1.25 eV complied by Willams [29]. The difference is most likely due to the self-intercalated character of the $ZrSe_2$ which is due to the excess metal for Se-rich compounds. This is interpreted in correspondence of the phase limit of a good-stoichiometric character of the crystals. The phase limits of good and poor-stoichiometric zirconium diselenide samples have been placed as $ZrSe_{(1.945\pm0.03)}$ and $ZrSe_{(1.850\pm0.03)}$, respectively, for crystals grown by the CVT technique [30, 31]. The ratio of Se/Zr (1.945) leading to more additional zirconium atoms which occupy the vacancies left by the chalcogens (S or Se). We assume that a similar analogy is valid for the ternary compositions crystals since they come from the same growth batch, or at least have been grown under very similar conditions.

TABLE II
IONIZATION POTENTIALS (IN UNITS OF EV) OF OBTAINED FROM THE KOHN-SHAM (KS) AND (*GW*) CORRECTIONS OF THE EXCHANGE-CORRELATION FUNCTIONALS AND FROM THE (EN) MODEL. ATOMIC IONIZATION POTENTIALS AND ELECTRON AFFINITIES (IN UNITS OF EV) USED THE EN MODEL [32]

Materials	$(I^{(KS)})$	$(I^{(GW)})$	$(I^{(EN)})$	atom	*I*	*A*
$ZrSe_2$	5.56	6.04	5.58	Se	9.75	2.02
ZrS_2	6.28	6.76	6.10	S	10.36	2.08
				Zr	6.84	0.43

For ZrS_2 little differences have been observed, the work function and the photothreshold were found to be of 4.95 eV and 6.05 eV, respectively [33]. This may be due to the high discrepancy of the band gap determination of ZrS_2 due to the so-called band gap problem, i.e., the band gaps of many semiconductors and insulators are systematically underestimated by 30-100% [34]. Experimentally, the band gap values of ZrS_2 are reported to vary from 1.7 eV [5, 21] to 2.48 eV [26]. Theoretical calculations for ZrS_2 using *GW* approximation of the Density functional theory (DFT) reveal that the band gaps of the ZrS_2 change from 1.8 eV to 2.61 eV [20]. The ionization potential for these materials has been estimated to fall in the range from 6.1 eV to 7.1 eV. Recent band structure properties from first principle calculations report on ionization potentials. Table II shows the ionization potentials of the $ZrSe_2$ and ZrS_2 TMDC materials obtained from the Kohn-Sham density functional theory (KS-DFT) corrections of the exchange-correlation functionals model calculations ($I^{(KS)}$), and the *GW* correction calculations ($I^{(GW)}$), and the electronegativity model ($I^{(EN)}$) [20, 35, 36]. Experimental data for ionization potentials of these materials are very scant. As obvious from the data, the ionization potentials of these materials are mainly determined by anions. This is, of course, mainly due to the fact that the VBM states can be attributed to *p* states on anions. Based on the previous review, the experimentally obtained photothreshold value of (6.90 ± 0.12 eV) is in good agreement with the theoretical calculations. Additionally, the obtained values of the photothreshold follow an ascending trend from $ZrSe_2$ towards ZrS_2. This is in accordance with the hypothesis, observed for other semiconductor systems, that the thresholds are determined mainly by the electronegativity of the chalcogen (anion) atoms. This is mainly due to the fact that the valence bands are derived from *p*-states of the anions. Experimental values of the photothresholds of selenides and sulfides differ by 0.78 eV, which is close to the difference values between ionization potential of S (10.27 eV) and Se (9.53 eV) chalcogen atoms of 0.74 eV [37], which is in good agreement to the obtained experimental values. It is interesting to consider some of the consequences of the values of photothreshold determined for these materials. Furthermore, since the energy gap values and the photothreshold are known and assuming no band bending near the surface, the electron affinity values of $ZrSe_2$ and ZrS_2 are (5.02± 0.18 eV) and (4.88±0.14 eV), respectively. The obtained surface parameter values are of particular interest for developing an optimized alternative structure for solar cell application, such as Schottky-barrier solar cells.

III. CONCLUSION

Single crystals of layered transition metal semiconductors of ZrS_xSe_{2-x} were grown by the CVT. They are n-type degenerate semiconductors exhibiting a 'self-intercalated' character due to little deviation from the exact-stoichiometry. The work function and the photothreshold values of the ZrS_xSe_{2-x} were determined by angle-resolved photoemission spectroscopy. The photothreshold values are found to follow an ascending trend from $ZrSe_2$ towards ZrS_2 from 6.12 eV to 6.90 eV, respectively. The ternary TMDC semiconductors ZrS_xSe_{2-x} can be introduced as promising materials for solar cell applications.

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REFERENCES

[1] L. Kelvin, "Contact electricity of metals", Phil. Mag. 46, 1898, pp. 82-121.

[2] W. A. Zisman, "A new method of measuring contact potential differences in metals", Rev. Sci. Instrum., vol. 3, 1932, pp. 367-370.

[3] R. H. Friend and A. D. Yoffe, "Electronic Properties of Intercalation Complexes of the transition metal dichalcogenides", Adv. Phys. vol. 36, 1987, pp. 1-94.

[4] J. A. Wilson and A. D. Yoffe, "The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties", Adv. Phys. vol. 18, 1969, pp. 193-335.

[5] P. A. Lee, G. Said, R. Davis, and T. H. Lim, "On optical properties of some layer compounds", J. Phys. Chem. Solids 30, 1969, pp. 2719-2729.

[6] R. Manzke and M. Skibowski, "*Photoelectron Spectra of Layered Compounds*", Landolt-Börnstein, New Series, Group III. vol. 23 b, Pt. 84 Springer-Verlag, Berlin, 1994.

[7] J. C. E. Rasch, T. Stemmler, B. Müller, L. Dudy, and R. Manzke, 1T-$TiSe_2$: Semimetal or Semiconductor?", Phys. Rev. Lett. 101, 2008, pp. 237602.

[8] J. A. Wilson, F. J. D. Salvo, and S. Mahajan, "Charge-density waves and superlattices in the metallic layered transition metal dichalcogenides", Adv. Phys. 50, 2001, pp. 1171–1248.

[9] C. O. Oriakhi and M. M. Lerner, "*Handbook of Layered Materials, edited*" by S. M. Auerbach, K. A. Carrado, and P. K. Dutta (Marcel Dekker, New York, 2004), pp. 509.

[10] R. Späh, U. Elrod, M. Lux-Steiner, E. Bucher, and S. Wagner, "pn junctions in tungsten diselenide", Appl. Phys. Lett. 43, 1983, pp. 79–81.

[11] V. Podzorov, M. E. Gershenson, C. Kloc, R. Zeis, and E. Bucher, "High-mobility field-effect transistors based on transition metal dichalcogenides", Appl. Phys. Lett. 84, 2004, pp. 3301–3304.

[12] H. Tributsch, "Photo-Intercalation: possible application in solar energy devices", Appl. Phys. 23, 1980, pp. 61-71.

[13] G. Kline, k. kam, D. Canfifld, and B. A. Parkinson, "Efficient and stable photoelectrochemical cells constructed with WSe_2 and $MoSe_2$", Solar Energy Mater. 4, 1981. pp. 301-308.

[14] M. K. Agarwal, V. V. Rao, and V. M. Pathak, "Growth of n-type and p-type WSe_2 crystals using $SeCl_4$ transporter and their characterization", J. Cryst. Growth 97, 1989, pp. 675-679.

[15] D. N. Gujarathi, G. K. Solanki, M. P. Deshpande, and M.K. Agarwal, "PEC behaviour of mixed single crystals of tungsten sulphoselenide grown by a CVT", Solar Energy Materials & Solar Cells 90, 2006, pp. 2630-2639.

[16] R. B. Murray, R. A. Bromley, and A. D. Yoffe, "The band structures of some transition metal dichalcogenides. III. Group VIA: trigonal prism materials", J. Phys. C 5, 1972. pp. 759-778.

[17] R. B. Murray and A. D. Yoffe, "The band structures of some transition metal dichalcogenides: band structures of the titanium dichalcogenides", J. Phys. C 5, 1972, pp. 3038-3046.

[18] D. W. Bullett, 'Electronic band structure and bonding in transition metal layered dichalcogenides by atomic orbital methods", J. Phys. C 11, 1978, pp. 4501-4514.

[19] A. Ghafari, A. Bouchani, C. Janowitz, and R. Manzke, "Electronic structure of ZrS_xSe_{2-x} by Tran-Blaha modified Becke-Johnson density functional", Phys. Rev. B 84, 2011, pp. 125205.

[20] H. Jiang, "Structural and electronic properties of ZrX_2 and HfX_2 (X = S and Se) from first principles calculations", J. Chem. Phys. 134, 2011, pp. 204705.

[21] M. Moustafa, T. Zandt, C. Janowitz, and R. Manzke, "Growth and band gap determination of the ZrS_xSe_{2-x} single crystal series", Phys. Rev. B 80, 2009, pp. 035206.

[22] K. Terashima and I. Imai, "Indirect absorption edge of ZrS_2 and HfS_2", Solid State Commun. 63, 1987, pp. 315-318.

[23] L. Roubi and C. Carlone, "Resonance Raman spectrum of HfS_2 and ZrS_2", Phys. Rev. B 37, 1988, pp. 6808.

[24] A. Reshak and S. Auluck, "Theoretical investigation of the electronic and optical properties of ZrX_2 (X=S, Se and Te)" Physica B 353, 2004, pp. 230-237.

[25] M. Moustafa, A. Ghafari, A. Paulheim, C. Janowitz, and R. Manzke, "Spin orbit splitting in the valence bands of ZrS_xSe_{2-x}: Angle resolved photoemission and density functional theory", J. Electron Spectrosc. Rel. Phenom. 189, 2013, pp. 35-39.

[26] H. E. Brauer, H. I. Starnberg, L. J. Holleboom, and H. P. Hughes, "The electronic structure of ZrSe2 and CsxZrSe2 studied by angle-resolved photoelectron spectroscopy", J. Phys. C 6, 1995, pp. 7741-7760.

[27] T. Shimada, F. S. Ohuchi, and B. A. Parkinson, "Work Function and Photothreshold of Layered Metal Dichalcogenides", Jpn. J. Appl. Phys. 33, 1994, part 1, pp. 2696- 2698.

[28] W. Jaegetmann and C. Pettenkofer, "Stability of Photoelectrodes Controlled by Electronic Factors: Layered Chalcogenides of Group IV b" Ber. Bunsenges. Phys. Chem. 92, 1988, pp. 1354-1358.

[29] P. W. Williams: Optical and Electrical Properties, ed. P. A. Lee (D. Reidal, Dordrecht), 1976, pp. 273.

[30] A. Gleizes and Y. Jeannin, "Nonstoichiometry in the $ZrSe_2$ phase" J. Solid State Chem. 1, 1970, pp. 180-184.

[31] C. R. Whitehouse and A. A. Balchin, "Non-stoichiometry in ZrS_2 and $ZrSe_2$", Phys. Stat. Sol. (a) 47, 1978, K173-K176.

[32] Lange's Handbook of Chemistry, edited by J. H. Dean, 15th ed. (McGraw-Hill, New York, 1992).

[33] R. Murray and R.Williams: "The band structures and photoe-mission of transition metal dichacogenides", In: Philos. Mag. 29:3, 1974, pp. 473.

[34] F. Aryasetiawan and O. Gunnarsson, "The GW method", Rep. Prog. Phys. 61, 1998, pp. 237.

[35] R. S. Mulliken, "A New Electroaffinity Scale; Together with Data on Valence States and on Ionization Potential and Electron Affinities", J. Chem. Phys. 2, 1934, pp. 782–793.

[36] A. Nethercot, "Prediction of Fermi Energies and Photoelectric Threshold Based on Electronegativity Concepts", Phys. Rev. Lett. 33, 1974, pp. 1088-1091.

[37] W. A. Harrison, Applied Quantum Mechanics (World Scientific, Singapore, 2000)