

In situ preparation and interface characterization of TiO₂/Cu₂S heterointerface

Cite as: Appl. Phys. Lett. **82**, 2269 (2003); <https://doi.org/10.1063/1.1565507>

Submitted: 21 October 2002 • Accepted: 07 February 2003 • Published Online: 02 April 2003

Guangming Liu, T. Schulmeyer, A. Thissen, et al.



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Detailed photoluminescence studies of thin film Cu₂S for determination of quasi-Fermi level splitting and defect levels

Journal of Applied Physics **114**, 233506 (2013); <https://doi.org/10.1063/1.4850955>

Photovoltaic Properties of Cu₂S–CdS Heterojunctions

Journal of Applied Physics **41**, 3731 (1970); <https://doi.org/10.1063/1.1659500>

Reactive magnetron sputtering of Cu₂O: Dependence on oxygen pressure and interface formation with indium tin oxide

Journal of Applied Physics **109**, 113704 (2011); <https://doi.org/10.1063/1.3592981>



Webinar
Quantum Material Characterization
for Streamlined Qubit Development



Zurich
Instruments

Register now

***In situ* preparation and interface characterization of TiO₂/Cu₂S heterointerface**

Guangming Liu,^{a)} T. Schulmeyer, A. Thissen, A. Klein, and W. Jaegermann
*Department of Materials Science, Darmstadt University of Technology, Petersenstrasse 23,
D-64287 Darmstadt, Germany*

(Received 21 October 2002; accepted 7 February 2003)

The electronic structures and interface properties of the TiO₂/Cu₂S interface have been *in situ* studied after each growth step by x-ray and ultraviolet photoelectron spectroscopy. The *p*-doped Cu₂S films (BE_{VBM}=0.1 eV) were grown on the highly *n*-doped chemical vapor deposition prepared TiO₂ (BE_{VBM}=3.4 eV) films by thermal evaporation in a multistep growth procedure. The conduction band offset (0.7 eV), valence band offset (2.9 eV) and interface dipole (0.5 eV) were determined based on the quantitative examination of band bending occurring in the Cu₂S films at higher coverage, leading to a staggered energy level configuration. © 2003 American Institute of Physics. [DOI: 10.1063/1.1565507]

Solid state injection type solar cells with different absorbers in contact to TiO₂ are considered as a new photovoltaic cell using an extremely thin absorber (ETA) with low cost production.^{1,2} Cu₂S thin films as one of the most promising absorbing materials have been widely investigated as represented in the CdS–Cu₂S system during recent decades.^{3–6} The stability of this system has been proven to be a fatal problem due to the diffusion of Cu into the CdS layer, which resulted in a degradation of photovoltaic performance. However deposition of Cu₂S onto TiO₂ surface as an alternative substrate would be expected to produce a stable device without such interface diffusion. In this research, we will present results of ultrahigh vacuum (UHV) evaporation of Cu₂S films with well controlled thickness and composition on the surface of *in situ* chemical vapor deposition (CVD) prepared TiO₂ films.

The electronic properties at the interfaces of solid state injection type solar cells are essential for the photovoltaic behavior of thin film based devices, especially the band alignment of the different phases is very important in design and optimization of photovoltaic devices with high conversion efficiencies. After previous work determining the band alignment of CdTe/TiO₂,⁷ the deposition of Cu₂S films on the TiO₂ substrate surface was investigated after each growth step by photoelectron spectroscopy in this work. The basic interface properties and possible application perspectives of such materials combination in solid state injection type photovoltaic device will also be discussed based on the *in situ* combined XPS and UPS measurements.

The experiments were performed in an integrated ultrahigh vacuum (UHV) system consisting of a multitechnique surface analysis system (Physical Electronics 5700) photoelectron spectrometer (XPS), (UPS) and a preparation chamber. The apparatus allows *in situ* characterization of the prepared films and surfaces at a base pressure below 1×10^{-9} Torr. The XP spectra of the samples were measured

using monochromatized AlK α radiation. He(I) ($h\nu = 21.2$ eV) discharge lamp was used as excitation sources for UPS measurements. The position of the Fermi energy (E_F) was determined from the Fermi edge of a freshly sputtered thick Au film. The binding energy scale was calibrated against Cu 2*p*_{3/2} (932.67 eV), Ag 3*d*_{5/2} (368.26 eV), and Au 4*f*_{7/2} (84.00 eV). In order to obtain stoichiometric Cu₂S films with symmetric core level spectra, the vacuum evaporation conditions of Cu₂S were optimized at a source temperature of 1100 °C and substrate temperature of ~250 °C.⁸ The film thickness of Cu₂S was evaluated by the intensity attenuation ratio of substrate core level lines by assuming a uniform growth mode. Chemical vapor deposition of TiO₂ films was performed in an ultrahigh vacuum preparation chamber. The films were deposited on SnO₂ transparent conductive oxide (TCO) glass substrate by the pyrolysis reaction of titanium isopropoxide–Ti(OPr^{*i*})₄ precursor. Details of the preparation and characterization of the TiO₂ films are described elsewhere.^{7,9} No contamination on the CVD prepared TiO₂ surface under UHV conditions could be detected before and after evaporation of Cu₂S films within the resolution limits of our XPS system.

Figure 1 shows the evolution of the core level spectra of Cu₂S overlayer and TiO₂ substrate during the stepwise deposition process. With increasing Cu₂S film thickness, the Ti 2*p* and O 1*s* emission lines of the TiO₂ substrate were gradually attenuated while the Cu 2*p* and S 2*p* emission lines of the Cu₂S overlayer increased in intensity until the substrate related emissions completely vanished at 150 min deposition. More intriguing, Ti 2*p* and O 1*s* binding energy values shifted from 459.4 and 530.6 eV without deposition of Cu₂S (0 min) to lower values of 459.2 and 530.4 eV (30 min deposition time), respectively. Meanwhile Cu 2*p* (933.2 eV) and S 2*p* (162.2 eV) emission of the Cu₂S films evaporated can be easily distinguished after 0.25 min deposition time and also shifted to lower values of 932.6 and 161.8 eV at 150 min deposition time, respectively. These core level binding energy shifts can be ascribed to band bending developed at the interface of TiO₂/Cu₂S due to the initially dif-

^{a)}Author to whom correspondence should be addressed; present address: Department of Chemistry, University of California, Riverside, CA 92521; electronic mail: gmlu@mail.ucr.edu

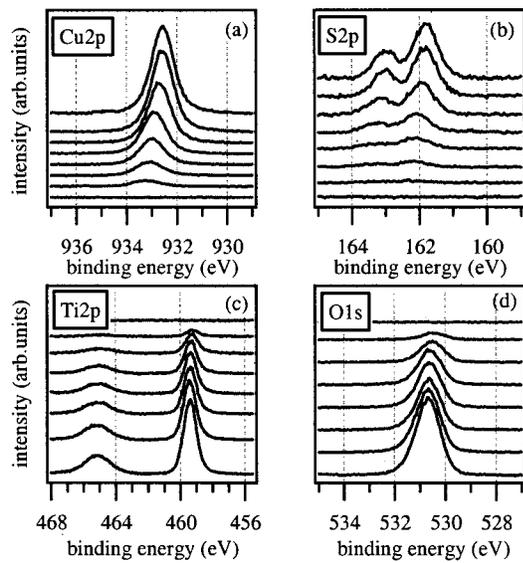


FIG. 1. XPS core level spectra of Cu 2p (a), S 2p (b), Ti 2p (c) and O 1s (d) emission lines obtained during the stepwise deposition of Cu₂S films on CVD prepared TiO₂ substrate. Spectra from bottom to top correspond to the deposition times 0, 0.25, 0.75, 1.75, 4, 10, 30, and 150 min, respectively.

ferent Fermi level positions on both sides of the junction (see discussion below).

In Fig. 2, the valence band region (~ 0 – 8 eV) of the XP spectra (a) as well as UP spectra (He I) (b) after each growth step clearly shows the variation of TiO₂ band structures to Cu₂S. The valence band of the TiO₂ mainly shows two peaks from O 2p orbitals: a broad one centered at ~ 6 eV (π non-bonding) and a narrow one at ~ 8 eV (σ bonding).¹⁰ With increasing Cu₂S film thickness, a broad signal about 8 eV wide with a relatively narrow peak superposed at about 3 eV arised which is due to the strong overlap of the S 3p and Cu 3d orbitals, dominating the valence band spectra of the Cu-rich compound.^{11,12} The VBM of TiO₂ (0 min) and bulk Cu₂S films (150 min) were determined to be 3.4 and 0.1 eV (below the Fermi level) by linearly extrapolating the low binding energy edge in the UP spectra, which are also consistent with our previous results and reported values.^{4,7} The work function of the sample after each step was determined

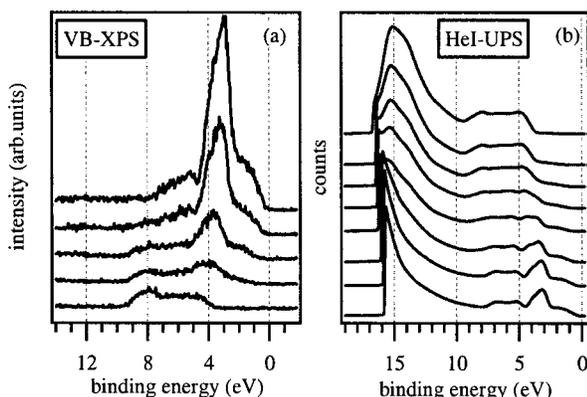


FIG. 2. Development of valence band (a) and UP (He I) (b) spectra of the vacuum evaporated Cu₂S films grown on TiO₂ surface during the stepwise deposition process: (a) spectra from bottom to top refer to the deposition times 0, 0.75, 1.75, 10, 150 min, respectively; (b) spectra from top to bottom denote the deposition times 0, 0.25, 0.75, 1.75, 4, 10, 30, and 150 min, respectively.

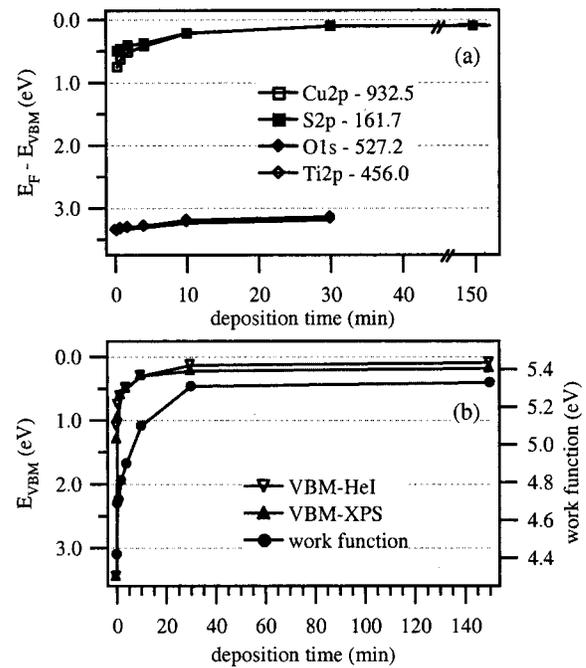


FIG. 3. Evolution of (a) the valence band position ($E_F - E_{VBM}$) determined from core level binding energies; (b) VBM and work functions of the substrate TiO₂ and overlayer Cu₂S with the deposition time.

by subtracting the secondary electron onset (SO) position of the UP spectra from the excitation energy (21.2 eV). From the top (0 min) and the bottom (150 min) He I UP spectra, the work functions of the substrate TiO₂ and bulk Cu₂S films were determined to be 4.4 ± 0.1 and 5.3 ± 0.1 eV, respectively.

Figure 3 summarizes the shifts of all relevant features in the XP and UP spectra as a function of the deposition time. The VBM positions of the TiO₂ substrate and the Cu₂S overlayer with respect to Fermi level can be determined from the corresponding core level binding energies during growth. Figure 3(a) shows that there is a parallel binding energy shift of -0.2 eV in VBM of TiO₂ determined by Ti 2p and O 1s core levels, indicating the band bending (eV_{bb}) in the TiO₂ substrate. The band bending occurring in the overlayer Cu₂S cannot unambiguously be determined based on the core level shifts, because the binding energy shifts of the VBM determined by Cu 2p and S 2p exhibit a large difference (0.2 eV) at the first growth steps of Cu₂S and then is parallel to each other at higher coverage. We cannot yet, conclusively assign this effect based on the present data but this difference may tentatively be ascribed to strain at the interface from the mismatch of the lattice structure or stoichiometry variation of Cu_xS at early deposition. At higher coverage (>4 min), the VBM of Cu 2p and S 2p lines shift parallel by -0.3 eV after 150 min deposition and no further shift can be observed with increasing Cu₂S overlayer thickness. The overlayer shift exhibits contributions both from the substrate and overlayer. The band bending in the Cu₂S at higher coverage is determined to be -0.1 eV after subtracting the substrate band bending of -0.1 eV observed at this region. We should note here that the band bending occurring in the initial interface region of the Cu₂S films (<10 Å) cannot be identified, although a larger band bending is expected to be formed in the more weakly *p*-doped Cu₂S overlayer ($BE_{VBM} = 0.1$ eV)

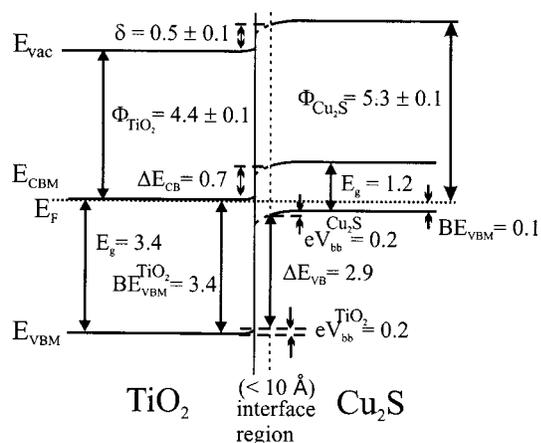


FIG. 4. UHV experimentally determined schematic energy level diagram of the TiO₂/Cu₂S heterojunction.

than in the highly *n*-doped TiO₂ substrate (BE_{VBM} = 3.4 eV) since the amount of band bending is usually distributed across a heterojunction inversely proportional to the doping densities on both sides.¹³ The chemical composition of the substrate TiO₂ and overlayer Cu₂S films grown is very stable during the deposition process. Even at the high growth temperature of 250 °C for the substrate, there is no evidence of an interface reaction between Cu₂S and TiO₂ since no chemical shifts can be observed in the core levels lines.

Figure 3(b) also shows that the variation of VBM positions obtained from the He I and XP spectra are nearly the same. The valence band offset between the substrate TiO₂ and the bulk overlayer Cu₂S (150 min) is calculated to be 3.3 eV. Therefore, the valence band offset ΔE_{VB} between the interface of TiO₂ and Cu₂S at higher coverage is obtained by subtracting the corresponding band bending on both side:

$$\begin{aligned} \Delta E_{VB} &= -3.3 \text{ eV} - (-0.2 \text{ eV}) - (-0.2 \text{ eV}) \\ &= -2.9 \text{ eV}. \end{aligned} \quad (1)$$

The corresponding conduction band offset can be determined by subtracting the band gap difference from ΔE_{VB}; the band gap of Cu₂S (1.2 eV) and TiO₂ (3.4 eV) are mainly from our recent results and literature:^{4,6,7}

$$\Delta E_{CB} = -2.9 \text{ eV} - (1.2 \text{ eV} - 3.4 \text{ eV}) = -0.7 \text{ eV}. \quad (2)$$

From Fig. 3(b) the work function difference ΔΦ between the bulk substrate TiO₂ (4.4 ± 0.1 eV) and overlayer Cu₂S (5.3 ± 0.1 eV) is calculated to be -0.9 ± 0.1 eV. Thus the interface dipole δ, due to charge transfer at the interface of two semiconductors with different electronic structures, can be determined:

$$\begin{aligned} \delta &= \Delta\Phi - eV_{bb} \\ &= -0.9 \text{ eV} - (-0.4 \text{ eV}) \\ &= -0.5 \pm 0.1 \text{ eV}. \end{aligned} \quad (3)$$

The experimentally determined band alignment at the interface of TiO₂/Cu₂S is shown in Fig. 4. The band discontinuities are crucial for high solar cell efficiencies. It is expected that best efficiencies using *p*-type absorbers are obtained for conduction band offsets close to zero.¹⁴ For the TiO₂/Cu₂S interface a staggered band alignment is observed where the TiO₂ conduction band minimum is considerably below that of Cu₂S (ΔE_{CB} = 0.7 eV). It can be concluded that such heterojunction device favors electron transfer from the Cu₂S absorber to the TiO₂ semiconductor while it also exhibits a large energy loss due to the pronounced cliff formed in the conduction band, which limits the performance of a solar cell device. Further experiments are needed to check if a more reasonable band alignment with a smaller conduction band offset and interface dipole can be obtained. Since different preparation conditions of the films most likely leads to a different band alignment,¹⁵ it seems necessary to modify interface electronic properties by changing the interface formation conditions.

In summary, ultrahigh vacuum evaporated Cu₂S layered semiconductor films were grown on CVD prepared TiO₂ surface in several growth steps. The interface properties and electronic structures of TiO₂/Cu₂S heterojunction were *in situ* characterized by ultraviolet and x-ray photoemission spectroscopy. A staggered band alignment was determined based on these measurements, the conduction band offset ΔE_{CB} = 0.7 eV and the valence band offset ΔE_{VB} = 2.9 eV indicate that the given combination of TiO₂/Cu₂S is not good interface for solar energy conversion without further modification of its band line up by appropriate interface engineering procedures.

The authors acknowledge financial support of this work by the Alexander von Humboldt Foundation in Germany.

- ¹I. Kaiser, K. Ernst, Ch.-H. Fischer, R. Könenkamp, C. Rost, I. Sieber, and M. Ch. Lux-Steiner, *Sol. Energy Mater. Sol. Cells* **67**, 89 (2001).
- ²K. Ernst, R. Engelhardt, K. Ellmer, C. Kelch, H.-J. Muffler, M.-Ch. Lux-Steiner, and R. Könenkamp, *Thin Solid Films* **387**, 26 (2001).
- ³J. A. Bragagnolo, A. M. Barnett, J. E. Phillips, R. B. Hall, A. Rothwarf, and J. Meakin, *IEEE Trans. Electron Devices* **ED-27**, 645 (1980).
- ⁴A. L. Fahrenbruch and R. H. Bube, *Fundamentals of Solar Cells* (Academic, New York, 1983).
- ⁵P. F. Linquist and R. H. Bube, *J. Appl. Phys.* **43**, 2839 (1972).
- ⁶W. D. Gill and R. H. Bube, *J. Appl. Phys.* **41**, 3731 (1970).
- ⁷S. Tiefenbacher, C. Pettenkofer, and W. Jaegermann, *J. Appl. Phys.* **91**, 1984 (2002).
- ⁸B. Rezig, S. Duchemin, and F. Guastavino, *Sol. Energy Mater.* **2**, 53 (1979).
- ⁹J. Lu and R. Raj, *J. Mater. Res.* **6**, 1913 (1991).
- ¹⁰R. Sanjinés, H. Tang, H. Berger, F. Gozzo, G. Margaritondo, and F. Lévy, *J. Appl. Phys.* **75**, 2945 (1994).
- ¹¹D. Schmid, M. Ruckh, and H. W. Schock, *Appl. Surf. Sci.* **103**, 409 (1996).
- ¹²J. C. W. Folmer and F. Jellinek, *J. Less-Common Met.* **76**, 153 (1980).
- ¹³S. M. Sze, *Semiconductor Devices: Physics and Technology* (Wiley, New York, 1985).
- ¹⁴H. J. Hovel, in *Semiconductor and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1975), p. 131.
- ¹⁵A. Klein, T. Löher, C. Pettenkofer, and W. Jaegermann, *Appl. Phys. Lett.* **70**, 1299 (1997).