APPLIED PHYSICS LETTERS VOLUME 80, NUMBER 16 22 APRIL 2002

High-resolution work function imaging of single grains of semiconductor surfaces

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(Received 6 December 2001; accepted for publication 19 February 2002)

The size reduction of modern electronic devices creates a growing demand for characterization tools to determine material properties on a nanometer scale. The Kelvin probe force microscope is designed to obtain laterally resolved images of the sample's work function. Using a setup in ultrahigh vacuum, we were able to distinguish work function variations for differently oriented crystal facets of single grains on a semiconductor surface. For the tetragonal solar cell material $CuGaSe_2$ the experiments demonstrate differences as low as 30 meV between (102) and (111) oriented surfaces and up to 255 meV between $(\bar{1}\bar{1}\bar{2})$ and (110) surfaces. This influences the band bending of solar cell heterostructures and consequently also the solar power conversion efficiency. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1471375]

The work function is an important property in many scientific disciplines: in semiconductor physics[1–3] it governs the band alignment in heterostructures used in solar cells[4] or laser diodes, in organic and polymer light emitting diodes[5,6] it directly influences the light output efficiency, and in electrochemistry[7,8] it controls the efficiency of catalytic reactions. The Kelvin probe force microscope[9,10] is based on the atomic force microscope (AFM) and designed to obtain laterally resolved images of the sample's work function (Φ) in addition to the surface topography. However, for quantitative studies of Φ, ultrahigh vacuum (UHV) conditions are essential, since it is well known that adsorbates can strongly alter Φ of a surface.[11,12] Distinct Φ values for differently oriented surfaces have previously been observed by photoemission spectroscopy experiments on several semiconductors in single crystalline form;[13,14] the energy resolution is typically no better than ~100 meV. That the band offset in heterostructures depends on Φ, and thus on the crystal orientation at the interface, was recently shown by photoemission spectroscopy[14] on CdTe–CdS interfaces.

Our Kelvin probe force microscope (KPFM) is a modified[15,16] UHV-AFM (Omicron). Applying an ac voltage (frequency f_2) to the sample results in an oscillating electrostatic force between the conductive AFM tip and the sample. Compensation of the electrostatic forces at this frequency (f_2) is achieved by adjusting a dc bias to exactly match the contact potential difference (CPD) between tip and sample.[9,10] Knowing the work function of the cantilever, the work function of the sample can be determined ($\Phi_{\text{sample}} = \Phi_{\text{cantilever}} + \text{CPD}$). In the present setup[15,16] in UHV the use of small ac voltages (~100 mV) allows application to semiconductors, where large ac voltages would falsify measurements by induced band bending below the tip. Under these conditions we obtain extremely high energy (~5 meV) and lateral (~25 nm) resolution. Measurements were performed using conductive PtIr coated Si cantilevers whose work function ($\Phi = 4.28 \pm 0.07$ eV) was determined by calibration with reference samples prepared in UHV.

The present study was conducted on p-type $CuGaSe_2$ thin films, a material relevant for thin film solar cells based on chalcopyrite semiconductors.[17] We studied an oriented $CuGaSe_2$ thin film grown on the ZnSe(110) surface by metalorganic vapor phase epitaxy.[18] Fig. 1 shows the surface of this $CuGaSe_2/ZnSe$ sample. Two-dimensional (2D) colorscale images of the topography and the work function are shown in Figs. 1(a) and 1(b), respectively. In Fig. 1(c) both images are merged into one three-dimensional representation; the 3D image reveals the topographical information, whereas the magnitude of Φ is given by the color scale. It is clearly seen that different crystal facets exhibit distinct values of the work function. From x-ray diffraction measurements the [220] direction is known to be perpendicular to the sample surface. Since AFM data supply truly 3D information; the crystal orientation of the different facets can be indexed using an analysis of the angles between the facets of single grains and the surface normal. To illustrate this procedure, Fig. 2 shows the topography and the work function along the line in Fig. 1(a). Comparison between the topography and the work function clearly shows that for each facet Φ adopts a distinct and constant value. Comparing the angles of the facets with those expected for the $CuGaSe_2$ crystal structure (tetragonal) results in an assignment of the crystallographic orientation of the facets. The result of the analysis of several grains is included in Fig. 1(b). The (112) surface develops preferentially during crystal growth[19] and thus, is likely to be found frequently in the present sample. The (112) plane is metal terminated, whereas the $(\bar{1}\bar{1}\bar{2})$ plane is Se terminated. Using the Pauling electronegativities, the Se termination of the $(\bar{1}\bar{1}\bar{2})$ surface results in a higher work function due to the surface dipole [as indexed in Fig. 1(b)].

For solar cell fabrication a ~2-μm-thick absorber layer (i.e., $CuGaSe_2$) is deposited onto Mo-covered soda lime glass, where the Mo serves as the back contact in the solar cell pn heterostructure. The deposition of a thin buffer layer (usually CdS or ZnSe) is followed by a n-type ZnO window layer. To compare the previous result to a sample on a tech-

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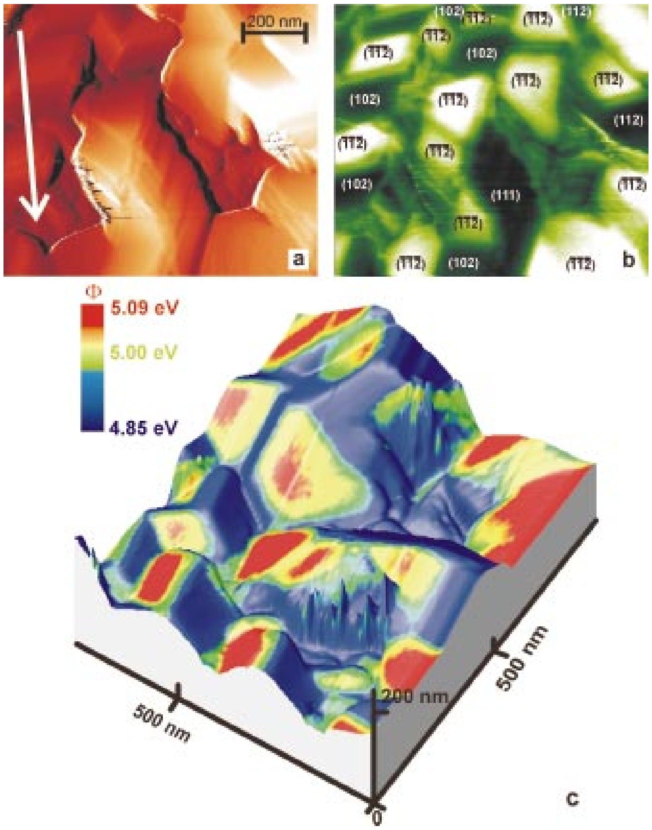

FIG. 1. (Color) KPFM measurement of a $CuGaSe_2$ thin film grown on a freshly cleaved single crystalline ZnSe(110) substrate. (a) The topography image shows distinct crystal facets on the (220) oriented $CuGaSe_2$ film. The color scale corresponds to height differences of 384 nm. The line gives the location of the linescan shown in Fig. 2. (b) Representation of the simultaneously measured work function ($\Phi = 4.85...5.09$ eV). The crystallographic orientation of the facets is assigned based on the angles to other facets and to the surface normal. (c) three-dimensional image merging the topography (as the 3D effect) and the work function represented by the color scale. The origin corresponds to the lower left corner in the 2D images.

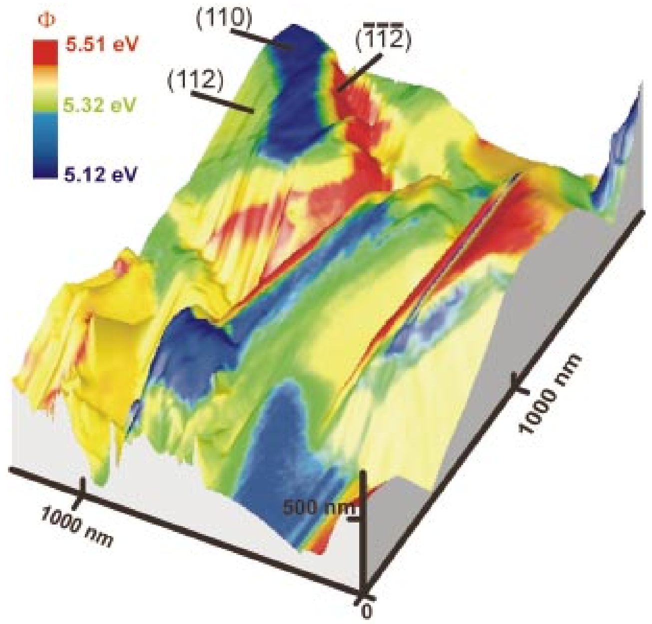

FIG. 3. (Color) KPFM measurement of a $CuGaSe_2$ thin film grown on a Mo/glass substrate. Three-dimensional image merging the topography (as the 3D effect) and the work function represented by the color scale. Also for this polycrystalline film it is clearly visible that the different facets assume distinct values of the work function.

nologically relevant substrate, we also performed a KPFM study on the surface of a $CuGaSe_2$ thin film grown by chemical vapor deposition on a Mo/glass substrate.[20] Fig. 3 shows a 3D representation in which the image reveals the topographical information and the work function is given by the color scale. Here it is also clearly observed that Φ assumes distinct values for different facets of the $CuGaSe_2$ grains. In this case a direct identification of the orientation of the crystal facets is not possible due to a lack of a preferential direction. For one particular grain we are able to infer the orientation of the crystal facets by also taking the work function results of the $CuGaSe_2/ZnSe$ sample in Fig. 1 into account. The absolute values of Φ of the two samples do not correspond exactly, probably the result of different doping levels from differing preparation techniques. However, for both samples the difference between the work function of the facets agrees well. The various work function values for different facets can be explained by a surface dipole characteristic for each orientation.[21] The atomic arrangement at the surface, i.e., surface relaxation and reconstruction, varies with surface orientation. Therefore the atoms and ions will form a surface dipole which depends on the orientation. Table I gives an overview of the work function values for the crystal orientations determined from Figs. 1 and 3. We would like to point out that for the observation of small work function differences, as for example the difference of 30 meV between the (111) and the (102) planes, the KPFM represents an ideal tool which in addition to its high energy resolution

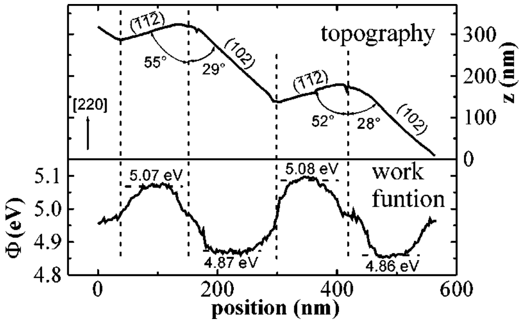

FIG. 2. Topography and work function along the line in Fig. 1(a). It is clearly seen that the work function assumes a constant value on the crystal facets. The orientation of the facets is indicated in the upper plot and was calculated from the angles of the facet to the surface normal and to other facets of the same grain.

TABLE I. Work function values for different crystallographic surface orientations of $CuGaSe_2$. The assignment of the orientation is based on an analysis of the angles of the facets to other facets of the same grain and to the surface normal (as determined from the topographical images). The work function was calculated using the work function of the tip ($\Phi = 4.28 \pm 0.07$ eV).

Sample	Surface orientation	CPD (mV)	Work function (eV)
$CuGaSe_2/ZnSe$	$(\overline{112})$	778 ± 22	5.06 ± 0.07
	(1 1 2)	590 ± 10	4.87 ± 0.07
	(1 0 2)	590 ± 10	4.87 ± 0.07
	(1 1 1)	560 ± 10	4.84 ± 0.07
$CuGaSe_2/Mo/glass$	$(\overline{112})$	1185 ± 12	5.47 ± 0.07
	(1 1 2)	1019 ± 7	5.30 ± 0.07
	(1 1 0)	930 ± 5	5.21 ± 0.07

(~5 meV) also provides exceptional lateral resolution (~25 nm).

Previous studies of work function differences for differently oriented surfaces employed photoemission spectroscopy on single crystals,[13,14] with inferior energy resolution (100–300 meV). In view of the application of semiconductors in heterostructures, the observation of laterally different work function values is of importance because the energy band alignment (i.e., band offsets) in these heterostructures will vary with the exposed surface.[22] This can have a detrimental effect on the efficiency of solar cell devices.[4] The record efficiency of 18.8% for a $Cu(In,Ga)Se_2$ solar cell was achieved using an absorber material with a (220)/(204) preferential orientation.[23] Thus, according to our present results on the related material $CuGaSe_2$, the orientation could be an important criterion for obtaining record efficiencies, for example due to an improved band alignment.

The present results demonstrate for the first time the work function dependence on the facet orientation in single grains of a semiconductor thin film. For the observation of small work function differences (~30 meV) on a nanometer scale, the Kelvin probe force microscope is the ideal tool. Studies of laterally varying work function values are also important for other fields: the performance of organic light emitting diodes,[5] for example, depends sensitively on the barrier height between the light emitting material and the electrodes.[6] In electrochemistry and catalysis, and its application in fuel cells, the electron transfer process is influenced by the work function.[7,8]

The authors thank A. Meeder and D. Fuertes Marrón for the preparation of the $CuGaSe_2$/Mo/glass sample and U. Fiedeler and S. Siebentritt for the preparation of the $CuGaSe_2$/ZnSe sample. Financial support from the German ministry for science and education BMBF is acknowledged.

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