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Kelvin probe force microscopy on III–V semiconductors: the effect of surface defects on the local work function

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Abstract

The application of Kelvin probe force microscopy (KPFM) in ultra high vacuum (UHV) allows to determine the absolute work function of surfaces with a very high energy (< 5 meV) and lateral (< 20 nm) resolution. We present measurements on different UHV cleaved III–V compound semiconductors. The (110)-surface shows work function variations due to defect states at step edges. We observed band bending on the (110)-surface of GaAs from surface photovoltage measurements. Finally, we discuss the influence of the previous effects on KPFM measurement of a UHV cleaved GaP pn-homojunction. Due to the long range nature of the electrostatic forces the geometry of the tip, cantilever and sample plays an important role in KPFM.
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Keywords: Kelvin probe force microscopy; Gallium arsenide; Gallium phosphide; Surface defects; Work function; Surface photovoltage

1. Introduction

Due to their technological importance, III–V compound semiconductors have been widely studied. While extensive work has been done on their geometric and electronic structure, Kelvin probe force microscopy (KPFM) in ultra high vacuum (UHV) opens the possibility to study the electronic structure of the surfaces on a nanometer scale. The work function is one of the most important parameters characterizing the property of a surface. Chemical and physical phenomena taking place at the surface are strongly affected by the work function. In turn, the work function varies sensitively reflecting the physical and chemical changes of surface conditions [1]. For example, due to a localized dipole at atomic steps on a metal surface, the averaged work function decreases in proportion to the step density [2]. If molecules or atoms are adsorbed on a surface, the work function changes depending on the magnitude of the electric dipole formed by the adsorbates [1]. Although the work function is defined as a macroscopic concept, it is necessary to consider its microscopic local variations in understanding the details of the formation of semiconductor interfaces and device behavior. Ebert et al. presented various scanning tunneling microscopy (STM) investigations especially on InP(110) surfaces with the focus on the behavior of charged surface defects [3–5]. Heinrich et al. [6] presented detailed studies on InP(110) step edges also probed by STM. They have shown that steps carry charges and have localized defect states in the band gap. Furthermore, the magnitude of the charge is a function of the orientation and atomic termination of the step. Sommerhalter et al. [7] presented, for the first time, KPFM measurements on GaAs(110) surfaces, which qualitatively show surface band bending at step edges.

One of the oldest techniques for determining relative changes in the work function is measuring the work function difference between two materials forming the two sides of a parallel plate capacitor. Prior to connection the metals are electrically neutral, no electrical field between the plates arises and the two materials share the same vacuum level. After connection, charge flows from the metal with the smaller work function to the metal with the higher one until the Fermi levels are equal. This

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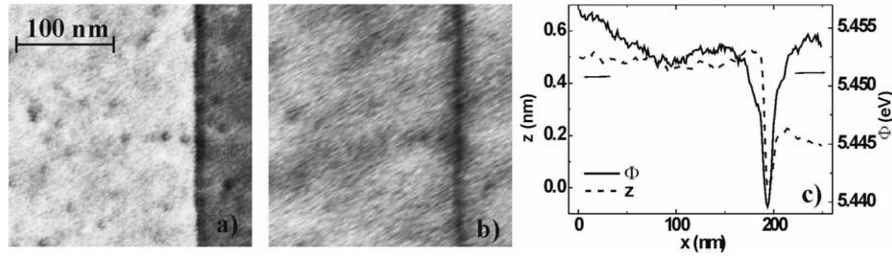

Fig. 1. KPFM measurement on UHV cleaved p-type doped GaAs(110) surface. The topography (a) shows a monolayer step (grey scale = 0.55 nm). The simultaneously measured work function (b) shows a downward band bending at the step edge ($\Phi = 5.44$–5.46 eV). The profiles in (c) show an average value of the data perpendicular to the step edge.

results in an electric field between plates and a drop in the local vacuum level across the gap. This potential energy drop is equal to the difference in work function of the two metals and is called contact potential difference (CPD). Lord Kelvin suggested that the CPD may be measured directly by a null-method [8]. If the spacing between the two capacitor plates is varied the resulting capacitance change induces a current in the external circuit. Thus, the CPD may be easily found by determining the external bias for which no currents are observed. With a noncontact atomic force microscope (NC-AFM) it is possible to measure the electrostatic force between the 'plates' (sample and cantilever) and minimize it by applying a d.c. bias, which corresponds to the CPD. Knowing the work function of the cantilever one can determine the work function of the sample. This direct method of measuring the work function with a spatial resolution in the nm range and with a relative energy resolution of ≈ 2 meV is then called KPFM [9]. The Kelvin probe technique can also be applied for semiconducting samples, however, surface band bending may change the work function. Measurements of illumination induced changes of the work function can be used to determine the surface photovoltage (SPV) [10,11].

We investigated the surfaces of UHV-cleaved n- and p-type doped GaAs and GaP with the KPFM. In this paper, we will focus on the work function variations at step edges; for p-type materials we found an increase and for n-type doped semiconductors a decrease of the work function at step edges. Finally, we discuss the impact on the work function difference measured at a UHV cleaved GaP pn-homojunction.

2. Experimental

The UHV-KPFM used in this study is a modified Omicron UHV-AFM/STM ($p < 10^{-10}$ mbar) capable of simultaneously measuring topography and CPD [7,12,13]. For all measurements, PtIr coated Si cantilevers were used. To obtain absolute work function values, we calibrated each cantilever on highly oriented pyrolytic graphite (HOPG). The principle of KPFM in vacuum and the experimental setup is described elsewhere [7,12–14]. To measure the electrostatic forces a a.c.-bias voltage ($V_{ac} = 100$ mV) at the second resonance frequency of the cantilever is superimposed on the tip-sample voltage. This setup allows the independent and energy sensitive determination of the CPD. Furthermore, with this low a.c.-voltages, a significant tip induced band bending at semiconductor surfaces can be excluded [7,13]. The noise level for all work function values is $\sigma_{rms} < 5$ meV. To determine the SPV of the semiconductors, defined as the work function difference between the dark and illuminated sample surface, we illuminated the sample with a HeCd laser ($\lambda = 442$ nm) or a laser diode ($\lambda = 675$ nm). All other measurements were performed under dark conditions.

Well defined III–V semiconductor (110) surfaces were obtained by cleavage in UHV. The (110) cleavage plane of GaAs is known to be free of intrinsic surface states in the forbidden band gap [15]. Doping concentration of the samples were $p \approx 2 \times 10^{18}$ and $n \approx 1 \times 10^{17}$ cm^{-3} for the p- and n-type material, respectively. GaP p- and n-type material had doping concentrations of $p \approx 1.5 \times 10^{18}$ and $n \approx 5 \times 10^{17}$ cm^{-3}, respectively. The GaP pn-homojunction was also cleaved in UHV and both sides of the junction were in electrical contact.

3. Results

Figs. 1 and 2 show the topography and the work function of the KPFM measurements on p- and n-type doped GaAs(110) surfaces, respectively. Additionally, line profiles are plotted. These profiles are averaged values from all lines through the images perpendicular to the step edges. It is clearly seen that the work function changes are associated with the step, we observe a work function depression on the p-type sample, whereas the n-type GaAs(110) shows a work function increase along the step edge. This indicates that the steps are the source of a localized charge-induced downward or upward

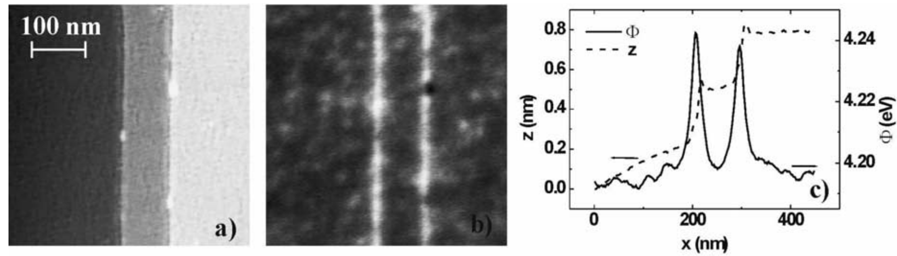

Fig. 2. KPFM measurement on UHV cleaved n-type doped GaAs(110) surface. The topography (a) shows two separate monolayer steps (grey scale = 0.83 nm). The simultaneously measured work function (b) shows an upward band bending at the step edges ($\Phi = 4.19$–4.24 eV). The profiles in (c) show an average value of the data perpendicular to the step edge.

band bending. Thus, on the samples investigated the steps are found to be positively charged on p-type doped and negatively charged on n-type doped materials. Up to now it was only possible to measure this effect with indirect methods like STM analysis [6] but with the KPFM it is possible to measure the potential, induced by charges localized at step edges, directly. The monolayer step on p-GaAs (Fig. 1) shows a reduction of the work function by $\Delta\Phi = -15$ meV, with a width (full width at half maximum) $w = 15$ nm. The work function of the step free surface was determined to be $\Phi = 5.45$ eV. Under illumination with a laser diode ($\lambda = 675$ nm) we determined a SPV = 50 meV. The work function of n-GaAs (Fig. 2(b)) increases at the step edges by about $\Delta\Phi = 45$ meV with a width $w = 25$ nm. The work function of the flat surface is $\Phi = 4.20$ eV and under illumination it changes to lower values, SPV = −70 meV.

At the step edges of GaP(110) surfaces we found a similar behavior. The work function for the p-type (n-type) material was found to be $\Phi = 5.61$ eV ($\Phi = 4.21$ eV), the work function variation at the step edges to be $\Delta\Phi = -130$ meV ($\Delta\Phi = 40$ meV) and the width to be $w = 35$ nm ($w = 20$ nm), respectively. Fig. 3(c) shows averaged profiles perpendicular to the step edge from the work function image of p-GaP (Fig. 3(b)) with and without illumination. In contrast to the results of p-GaAs, the work function of p-GaP shifted under superbandgap illumination to lower values, SPV = −100 meV. In addition, in Fig. 3(c) it can be seen that under illumination the work function difference at the step edge also decreases ($\Delta\Phi = -90$ meV). For the n-type doped GaP(110) we found a small increase, SPV = 25 meV, also in contrast to the n-type GaAs surface.

In Fig. 4 we present KPFM images of a UHV cleaved GaP pn-homojunction. In the topography the two sides can be distinguished due to a different morphology. The n-type doped side shows atomically flat areas between a few steps, whereas the p-type side exhibits a large number of steps; we attribute this morphology difference to the liquid phase epitaxy growth of the p-type side. The work function difference between the two sides averages $\Delta\Phi_{p-n} \approx 1.20$ eV; in comparison with the measurements on the singly doped surfaces presented above, this is about 200 meV smaller. Possible reasons for these discrepancy are different doping concentration of the materials, a different concentration of cleavage induced surface defects and an averaging effect of the cantilever itself [16,17]. We illuminated the pn-junction with a HeCd laser; with increasing intensity we observed a reduction of the potential drop across the pn-junction. Fig. 4(c) shows the averaged work function profiles perpendicular to the interface for three different light intensities. With the maximum intensity available we got nearly flat band conditions across the interface.

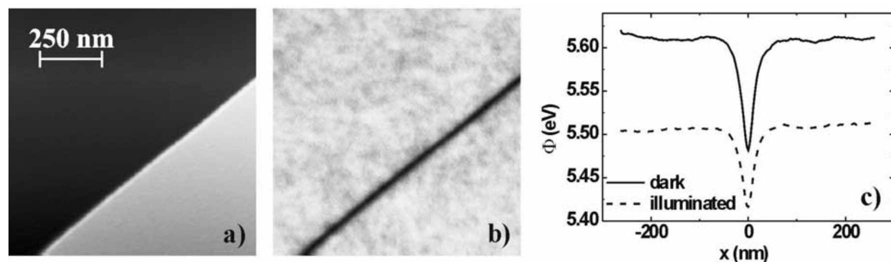

Fig. 3. KPFM measurement without illumination on a UHV cleaved p-type doped GaP(110) surface. The topography (a) shows a diagonal step (grey scale = 6.97 nm). The simultaneously measured work function (b) shows a downward band bending at the step edge ($\Phi = 5.48$–5.62 eV). The profiles in (c) show an average value of the work function data perpendicular to the step edge measured under dark and illuminated conditions.

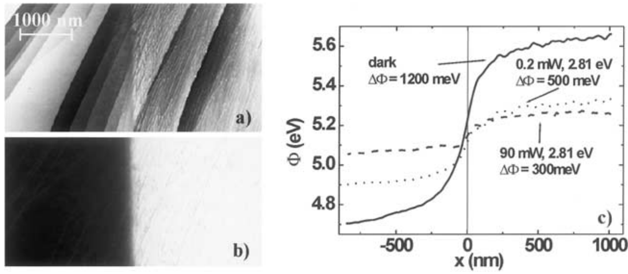

Fig. 4. KPFM measurement on UHV cleaved GaP pn-homojunction without illumination. The topography (a) shows two different morphologies indicating the different doping types (grey scale = 6.53 nm). The simultaneously measured work function (b) shows the band bending at the pn-homojunction ($\Phi = 4.54–5.82$ eV). The profiles in (c) shows an average value of the work function data perpendicular to the step edge. We illuminated the sample with a HeCd laser ($\lambda = 442$ nm) with two different intensities.

4. Discussion

The reason for the work function variation at the step edges of the semiconducting samples with the different behavior between n- and p-type doped material can be explained by means of the schematic band diagram in Fig. 5. Due to a relaxation of the surface atoms no surface states exist within the band gap for most (110) surfaces of III–V semiconductors [18]. This means that the position of the Fermi energy at the surface will be determined by the bulk doping; the surface is in flat band condition. In contrast, surface states within the band gap appear at the step edges. Due to localized charges in these defect states a band bending occurs, influencing the work function; in the case of n-type material the work function is increased (Fig. 5(a)). Consistent with the measurements on p-GaAs (Fig. 1) and p-GaP (Fig. 3) on p-type material the work function at step edges is reduced (Fig. 5(b)). van Laar et al. proposed a defect state near the conduction band which would imply a stronger band bending for n-type material [19]. This can also be confirmed in our measurements presented in Figs. 1 and 2. We found the increase of the work function at a monolayer step on n-GaAs to be $\Delta\Phi = 45$ meV and the decrease on a p-GaAs monolayer step to be $\Delta\Phi = -15$ meV. STM measurements of vacancy concentrations at step edges with different orientation on p-InP(110) [6], point out that the density of states and the captured charge depend on the termination and therefore also on the orientation of the step. Within our measurements we found only small variations of up to 10 meV between different steps. Except for n-GaP all (110) surfaces of III–V semiconductors should be free of surface states within the band gap and therefore we should find flat band conditions at the surface [15,18,19]. For p- and n-type doped GaAs we found a SPV of 50 meV and −70 meV, respectively which is attributed to a surface band bending [11]. We assume that this small SPV can be explained by cleavage defects and adsorbates induced by the cleavage process. But under illumination we should nearly get flat band conditions at the surface and therefore the bulk values. We derived values for the difference in Fermi level position in the bulk $\Delta E_{fb} = 1.37$ eV and at the surface $\Delta E_{fs} = 1.25$ eV which are in excellent agreement with the doping concentrations and the values given by van Laar et al. [19]. For GaP we measured a negative SPV for the p-type sample and a positive for n-type material. This could be explained by a band inversion at the surface, but further investigation is necessary. We therefore determined only the difference in Fermi level position at the surface to be $\Delta E_{fs} = 1.40$ eV. In comparison with the band gap energy of the bulk, $E_g = 2.26$ eV and the doping concentrations of the samples this seems to be too small. Huijser et al. [18] found in photoemission measurements, that the band gap on GaP(110) surfaces is free of filled surface states and a band of empty surface states starting at 0.55 eV below the conduction band edge. On n-type material the Fermi energy at the surface is pinned at this position. We therefore expect only a difference in Fermi level position of $\Delta E_{fs,max} = 1.76$ eV. Taking the doping concentrations into account the determined value by our KPFM measurements is slightly to small.

With this knowledge we can also explain the measured GaP pn-homojunction. At the interface between the materials a band bending of up to the band gap energy is expected. As can be seen in Fig. 4 at the surface

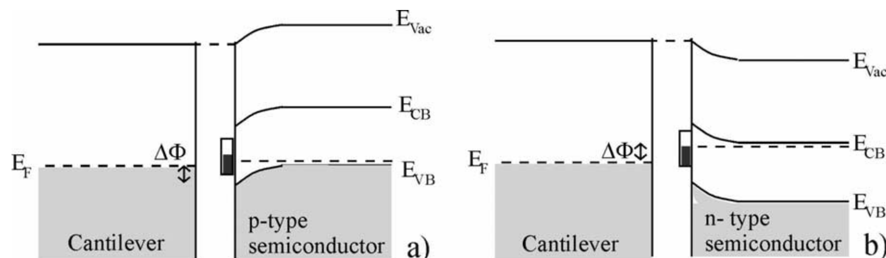

Fig. 5. Schematical band diagram for an ideal p-type (a) and n-type (b) GaAs(110) surface in the region of a step with defect states within the band gap.

we can only determine a built-in voltage of 1.20 eV. The main reason of this reduction is of course the pinning of the Fermi energy at the defect level within the band gap of the n-type doped material as we discussed above. A further reduction of the potential difference is caused by the heavily stepped surface of the p-type doped side. Furthermore, the influence of the cantilever should be considered. Due to the long range nature of the electrostatic force an averaging effect of the whole cantilever is possible [16,17]. Detailed theoretical models for the interaction of the cantilever with a semiconducting surface are up to now not available.

5. Conclusion

In conclusion, high resolution UHV-KPFM measurements on GaAs(110) and GaP(110) compound semiconductor surfaces were presented. We have shown that monolayer cleavage steps on these surfaces create localized defect states in the band gap. Captured charges within these defect states induce an upward band bending for n-type and a downward band bending for p-type surfaces. The magnitude of this effect is found to be stronger for the n-type doped semiconductors, explained by the position of the defect state near to the conduction band. Furthermore, we presented SPV measurements on a UHV cleaved GaP pn-homojunction which show a decreasing voltage drop across the pn-junction for increasing illumination intensity.

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