Contact Potential Difference and Photo Voltage
Comparing the Kelvin Probes

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January 6, 2014

For the Cahen group

1   Introduction

The purpose of this manual is to outline the measurements I did to compare the three Kelvin Probes (KPs) in 618, 301 and 101. The one in 618 measures in ambient, 301 in the glove box ($\rightarrow$ nitrogen atmosphere) and the one inside the Lakeshore in 101 (referred to as the 'Mc Allister') can measure in ambient, argon atmosphere & in vacuum with temperature dependence. Next to measuring the contact potential difference (CPD), all three KPs can be used surface potential voltage (SPV) by illuminating the sample.

A standard reference with known and stable work-function, HOPG, is used to calibrate the probe, i.e. to find the work function of the probe head. To compare the three probes, I used Si–H as a relatively stable and well understood sample.

1.1   (Brief-)Theory

When two (semi-)conductors with dissimilar fermi-levels are electrically connceted from their back-side with a gap between them, charge will flow from the material with the lower work function (WF) to the one with the higher WF [1]. Electrons will stop flowing when equilibrium is established. As long as there is a gap between the materials, an electrical field will develop in the gap due to the difference in the local vacuum level across this gap. The potential drop across the gap is known as the contact potential difference or CPD. When the work functions are expressed in Electron-Volts, the CPD is directly equal to the difference of the WFs:

$$|\text{CPD}| \;=\; |\varphi_{\text{Probe}} - \varphi_{\text{Sample}}| \,. \tag{1}$$

Here, I use the absolute value because the sign of the CPD is ultimately dependent on how the measurement system, the Kelvin Probe, is set up. The materials then behave as a parallel plate capacitor, where the potential drops over the space between the two samples. In such a capacitor, the potential drop is given by

$$V \;=\; \frac{Q}{C(d)} \,, \tag{2}$$

where $C(d)$, the capacitance, is inversely proportional to the distance between the plates d, Q is the charge on the surfaces and V is the potential set the difference in local vacuum levels.

The CPD is measured by mechanically vibrating the probe-head, thus periodically changing the size of the gap. This causes the capacitance to change as well and according to Equation (2), charge qill again flow from one material to the other resulting in a steady state alternating current. This DC current is nulled by an external current source with known impedance from which the equivalent DC voltage needed to null the current can be calculated. This voltage is equal and opposite to the CPD. Thus, if φ_{Probe} is known, φ_{Sample} can easily be calculated from Equation (1).

The work function of a semiconductor (with molecular surface modification) is composed of the electron affinity χ [2], plus the position of the Fermi level in the semiconductor band-gap ζ and a surface-charge dependent band-bending term BB. ζ in turn is dependent on the doping level of the semiconductor and is approximately given by:

$$E_{f,n} = E_i - kT \ln \frac{n}{n_i} \quad (3) \qquad \text{and} \qquad E_{f,p} = E_i + kT \ln \frac{p}{p_i} \quad (4),$$

for n- and p-type semiconductors respectively. The band-bending term can be neutralised by illuminating the sample, thus creating (more) free carriers to neutralise the surfacecharges. The

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[1] The work function is defined as the energy needed to remove an electron from a solid to a point in vacuum immediately outside of it

[2] Difference between vacuum-level and bottom of conductionband

difference in CPD of one sample between light and dark is called the surface-potential-voltage or SPV.

2   Procedure

A fresh HOPG-surface is prepared by rubbing adhesive tape onto a piece and tearing it off evenly. The piece is mounted onto a sample-holder and the CPD is measured.

n-Si–H (100) with different resitivities/doping-levels is prepared according to a slightly modified standard cleaning procedure. Pieces of suitable size are cut, swiped off with ethyl-acetate and successively sonicated for six minutes each in ethyl-acetate, acetone, methanol and water. The pieces are ashered at 100W with $1l/minO_2$ and $1.5l/minAr$ for 3 minutes, rinsed with water, etched in 2% HF, rinsed with water and ashered again as before. The pieces are etched as before, back-contacts are created by applying InGa-eutectic to a scratched back surface. The piece is mounted onto a sample holder and the CPD is measured for at least two minutes each on three different spots per piece. The time the sample is subjected to ambient after etch and before each measurment is recorded and used in a linear fit '$\Delta(CPD)/\Delta t$' to find the – arguably somewhat hypothetical – CPD each spot on each piece had right after the etch.

p-Si–H(100) is prepared as n-Si–H, but the 2% HF-etch is replaced by a three minutes etch in 5% buffered-oxide-etch (BOE), a solution of 10:1 NH_4F/HF.

Alumina-passivated silicon was used as obtained from Nir, aluminium coated silicon was used as obtained from Igal.

3   Results & Discussion

3.1   Callibration with HOPG and general remarks

General   The noise peak-to-peak distance is typically on the order of 10 mV, good measurements can be obtained with a signal peak-peak-distance of three times that value. For HOPG and Si–H distances of as high as 90-120 mV can be reached.

The work function of freshly cleaved HOPG changes with -0.9 to -1.2 mV per minute. The difference in measured CPD between successively cleaved HOPG surfaces is of the order of ∼10 mV. The difference of the work function of the probe-head on different dates can be greater [3], up to 100 mV. With good noise-reduction [4] the machine noise level can be brought down to ±10 mV.

Mc Allister   A jump of 20-40 mV can be observed when switching on the weak pump and a similar jump of ∼10 mV is often observed when switching on the turbo pump. These jumps are inconsistent in size and direction and can thus best be interpreted as a displacement of the probe head over the sample. The CPD of HOPG in the Mc Allister is independent of temperature to within 10 mV, measured over the range of 50K to 300K, in steps of 50K, in both directions.

Glove box   The difference in CPD between HOPG cleaved inside the glove box and HOPG cleaved outside and brought into the box is 60 ± 30 mV. The work function of HOPG when cleaved outside is lower than when cleaved inside, consistent with the observed degradation of HOPG in ambient, i.e. its decrease in WF. Thus, for calibration, HOPG has a WF of 4.65 ± 0.01 eV when cleaved in an inert atmosphere and 4.59 ± 0.06 eV when cleaved in air.

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[3]Someone else – or I, for that matter – measured a CPD and touched their sample with the probe...

[4]If necessary, turn off lights and air-conditioning in the room

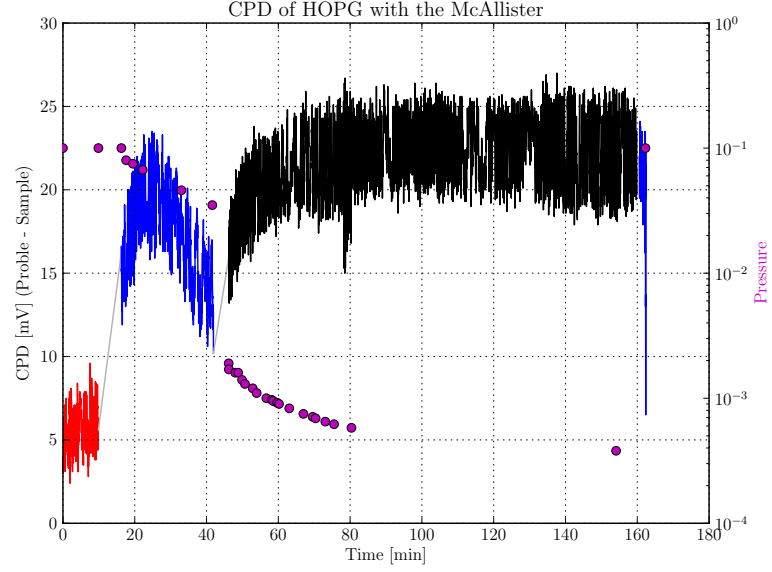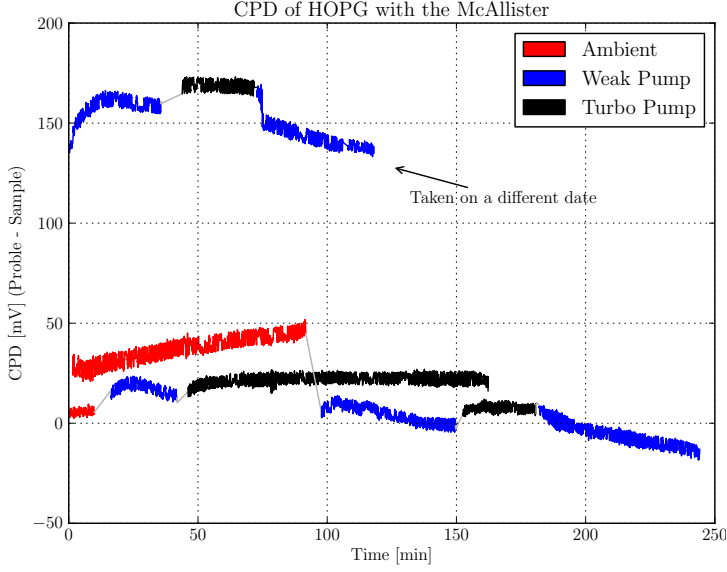Figure 1: HOPG measurements in the Mc Allister

3.2 Comparison

n-Si–H The standard deviation of measured CPD between spots of the same piece is comparable to that between pieces, so all obtained values were averaged. The values obtained across the three systems agree very well with each other and in the case of mid- and high-resistivity silicon also with theory, see Figure 2. A three, instead of only one, minute long HF etch did not influence the CPD obtained for the low resistivity sample. Here, frankly, the wafers were old and the box might have been mislabelled. Another explanation for the deviation from theory might be that the method fails because the surface-reactivity of silicon increases with doping-level. Thus for highly-doped silicon, the linear extrapolation could be more 'hypothetical' than for the other two conditions.

p-Si–H

Alumina and aluminium coated silicon The WF of alumina passivated silicone was found to be 4.41 eV in 618 and 4.37 eV in the Mc Allister. SPV was 540 ± 10 mV in 618 and 520 ± 10 mV in the Mc Allister using the same illumination set-up. Using an LED, the bend bending was observed to be as high as 600 mV. We assume that our Halogen-lamp set-up doesn't always saturate the sample and that heat-effects come into play. This will be investigated further.
The work function of (hydrophillic) aluminium coated silicon was 4.0 ± 0.1 eV in 618 and $4.17\pm$ X eV in the Mc Allister. Apart from the mentioned 'jump', the CPD did not change when the sample was cooled to 250 K, confer Table XXX. Apparently, no ice forms on the surface. This stroke of luck might be because the sample is not the coolest point in the Mc Allister.
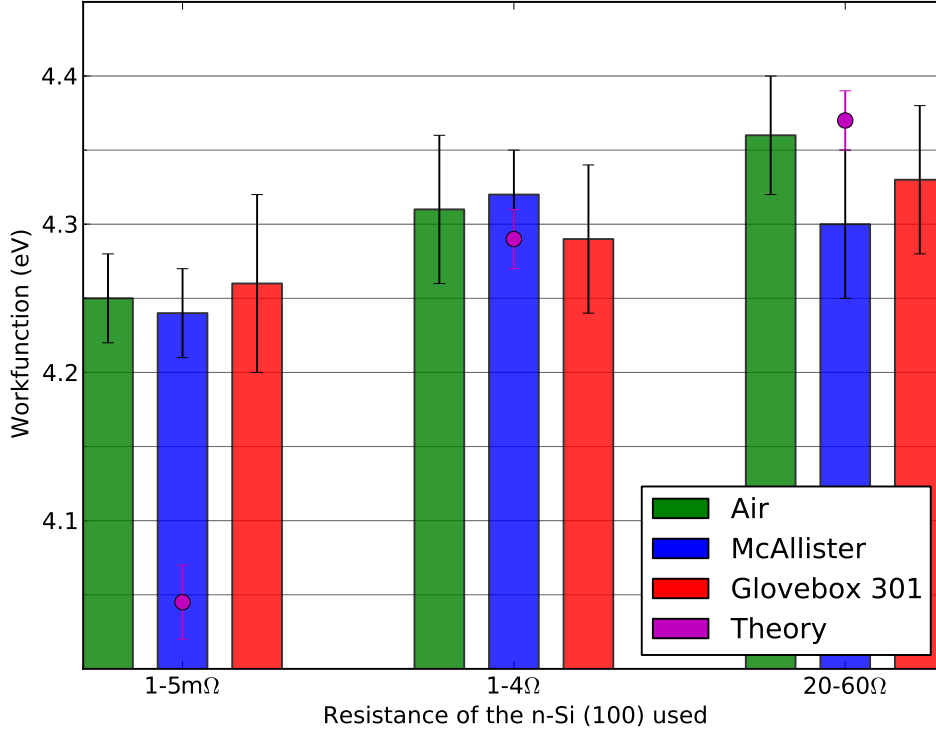
Figure 2: Summary of the measured work functions for the n-Si–H samples used. Indicated errors include deviations in the samples & the inaccuracy of calibration with HOPG.

4 Conclusion

Si–H is a good system to check and compare Kelvin Probes. It is easily prepared and we have great practical knowledge about it.

The three KPs in use agree with each other and (mostly) with theory as well. Reliable measurements can be done with each individual probe. If absolute values, i.e. work functions, are needed, special care has to be taken to calibrate. I advise to calibrate once before measuring and once after, to check if the probe-head has changed during measurement. Temperature dependent SPV will soon be a reality, the effect of warmth on SPV has to be investigated further.