Influence of organic material and sample parameters on the surface potential in Kelvin probe measurements

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Abstract

Scanning Kelvin probe is a method for material surface studies. It is used to determine the work function of metals. In the case of organic semiconductors, the measured surface potential is considered to be the Fermi level of the material which has been shown in some cases. But in most papers, the surface potential dependence on the metal electrode or film thickness was observed. Material properties and their influence on the measured surface potential and its relation to the Fermi level previously have not been systematically studied.

In this work, the surface potential was measured for different materials- metal, organic dielectric material, and organic semiconductors. In most of the cases, the obtained surface potential was dependent on the metal electrode work function. This dependence decreased with the increase in electrical conductivity of the material. Several materials were chosen for studies where sample thickness was varied. Results showed that for most of the studied semiconductors the sample thickness of around 1.5- 2 µm was required to obtain surface potential values which do not depend on the electrode work function.

Introduction

Scanning Kelvin probe (SKP) method is a relatively simple method, often used in material surface analysis. Kelvin probe principle was described by Lord Kelvin in 1898 [1]. It states that when two metals are connected with the electrical circuit and brought close to each other, electrons from metal with lower work function flow to the metal with higher work function until their work functions (Fermi levels) are equal. It results in one surface being negatively charged and other surface being positively charged. In that case, a parallel plate capacitor with an electric field that is equal to the difference in the work function of the metals is created. In 1932 Zisman made a system with vibrating probe [2]. As the probe vibrates, the capacity of the capacitor changes and the alternating current flows. It is possible to apply a backing potential which stops the flow of current. The applied voltage is equal to the work function difference between both metals. If the work function value of the probe is known, the work function of the sample can be easily calculated.

SKP is a simple and well-explained method when it comes to metal work function measurements. It is possible to use SKP not only to determine the work function of pure metals but also to measure the changes of work function, caused by external effects, for example, changes of indium tin oxide (ITO) work function caused by the UV radiation [3, 4].

In the case of organic materials, layered samples (substrate/ metal electrode/ organic material) are always made due to their poor electrical conductivity. In this way, a parallel plate capacitor similar to the pure metal samples is obtained.

In some cases, SKP has been successfully employed in organic material studies. Particularly, researching the interaction between metal and polymer [5] as well as in the Fermi level energy level "mapping" in perovskite solar cells [6]. In the latter case, it was possible to combine a Kelvin probe with ultraviolet photoelectron spectroscopy (UPS) to understand the energy level alignment at the interface between the materials. N.Hayashi et al. show that there is almost no influence of metal work

function on C_{60} surface potential at the metal/C_{60} interface [7]. Similar results were obtained by T. R. Ohno et al., who have studied C_{60} on various substrates using UPS [8]. Authors conclude that Fermi level pinning is achieved and obtained results describe the Fermi level of C_{60} thin film.

On the contrary, E.Kinbara et al. discovered that for some poly(3-arylthiophene) derivatives the measured surface potential value was proportional to the metal work function during the investigation of these materials and their interfaces with metal electrodes in the air [9]. Similar surface potential dependence on metal work function was reported by Y.Harima et al. [10]. Such results are explained by poor charge carrier exchange at the metal/ organic interface due to the blocking layer on the metal electrode, rather than effect originating from the properties of organic material. By measuring the diffusion potential and applying it as a correction according to the Schottky-Mott rule [11], the surface potential dependence on metal work function could be reduced in the cases of phthalocyanines. Yet for some materials, there was a considerable difference between surface potential obtained by SKP and surface potential obtained from Schottky-Mott rule and diffusion potential measurements. This difference was explained by the oxygen and moisture induced surface states which SKP is sensitive to.

In the studies of metal/ TPD interfaces, the surface potential dependence on the metal work function was observed [12, 13]. Authors give two possible explanation of this phenomenon: 1) the system is in thermal equilibrium and the Fermi level of metal and TPD align, but the obtained surface potential is not a value that characterizes material, but rather than the system; 2) the system is not in thermal equilibrium and the work function of metal and a Fermi level of TPD do not align due to the poor charge carrier exchange between both materials [14].

There is a variety of obtained results as well as a variety of given possible explanations and effects. Yet there still has not been systematic research to show what characteristics of the material itself will determine the results obtained by Kelvin probe and their dependence on other factors, like metal work function, film thickness, etc. Till now, the results are explained in a case-by-case manner. This has led to situation, where SKP is often used in relative measurements, testing gas (for example, hydrogen) diffusion in materials [15, 16] as well as in the research of different metal

alloys and their corrosion [17–19], instead of being well explained and understood method for absolute measurements, like Fermi level determination of organic materials.

The aim of this work was to study the properties of organic materials, which can determine the obtained surface potential dependence on metal work function.

Experimental

All of the investigated thin films were made on ITO covered glass. At first, ITO was etched using hydrochloric acid (HCl) and zinc (Zn), leaving 5mm wide electrode at the side of the substrate. Other electrodes- aluminum (Al), silver (Ag), gold (Au), or copper (Cu) - were thermally evaporated in the vacuum by Edwards Auto 306. Electrodes were deposited at the $1 \cdot 10^{-5}$ mbar pressure with the speed of about 0.2 nm s^{-1}. Each electrode was 5 mm wide with about 1 mm wide gaps between them. The placement and shape of each electrode were obtained using shadow masks. In this way, a substrate covered by four electrodes with various work function values was obtained (see Fig. 1).
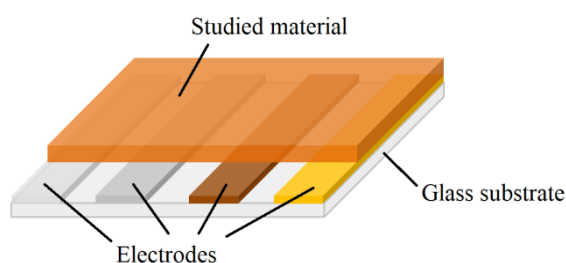

Fig. 1 Scheme of the studied samples

For this research, various materials were chosen. Most of the studied materials were commercially available organic semiconductors. Poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS) which is charge carrier transport material, poly(methyl methacrylate) (PMMA) which is a dielectric polymer, and metal (Al) were also included. These materials are not organic semiconductors but exhibit extremely different electrical properties.

Additionally, two original indandione derivatives – 2-(4-[N,N-dimethylamino]-benzylidene)-indene-1,3-dione (DMABI) and its derivative 2-(4-

(bis(2-(trityloxy) ethyl)amino)benzylidene)-2H-indene-1,3-dione (DMABI-6Ph) – were included. Their synthesis has been described elsewhere [20, 21] and their energy level values have been determined previously [22].

Thin films of such organic materials as DMABI, fullerenes (C_{60}, phenyl-C61-butyric acid methyl ester ($PC_{61}BM$), phenyl-C71-butyric acid methyl ester ($PC_{71}BM$)), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and N,N′-bis(3-methyl phenyl)-N,N′-diphenyl benzidine (TPD) were made by thermal sublimation in vacuum using self-built thermal evaporation system. The deposition rate was between 0.2 and 0.5 nm s^{-1} and was monitored by pre-calibrated quartz resonators. The pressure during evaporation was $1 \cdot 10^{-5}$ mbar or lower. Only half of the sample surface was covered with the studied material during the thermal evaporation in vacuum to measure the work function of the metal as well as the surface potential of the organic material above each electrode. Scheme of the obtained samples is shown in Fig. 1.

In other cases, the samples were made using the spin-coating method. To obtain the solution, the necessary amount of organic compound was dissolved in chloroform. Spin coating parameters were: rotation speed- 400 rpm; acceleration- 400 rpm s^{-1}; rotation time- 40 s. Afterward, the samples were dried on a hotplate at 70°C for 15 minutes. In this way DMABI-6Ph and polymer (poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(9-vinylcarbazole) (PVK), PMMA) samples were obtained.

Scanning Kelvin probe (KP Technology SKP5050) was used as equipment of surface potential and work function measurements. Probe vibration frequency was 79 Hz with 80 data points per one full vibration. Measurements for organic materials were done at several points above each electrode for 30- 60s at each point. By averaging these points, the surface potential difference between the probe and the sample was obtained. To determine the absolute value of work function/ surface potential, a highly oriented pyrolytic graphite (HOPG) was used as reference material with a known work function of 4.93±0.03eV [10]. Surface potential measurements were done in the air at room temperature.

The electrical conductivity of the studied materials was measured using 4-probe method employing the samples and procedure described previously in [23]. Measurements were done for 700 nm – 1 μm thick samples. It was assumed that the

specific electrical conductivity (S/cm) of each material is constant regardless of the thickness of the sample.

Results and discussion

At first, the surface potential of the electrodes was measured. From that, the work function (WF) of each electrode was obtained. These values were: $\Phi_{Al} = 3.80$ eV, $\Phi_{Ag} = 4.28$ eV, $\Phi_{ITO} = 4.78$ eV, $\Phi_{Cu} = 4.83$ eV, $\Phi_{Au} = 4.95$ eV. Between separate measurement sessions and sample series, the work function of the electrodes was stable within the uncertainty of the experiment ($\pm$ 0.03 eV). The work function of metals can vary depending on the technique used to measure WF, the crystal plane of metal, etc. WF values obtained in this work using SKP were in good agreement with the values found in the literature [24].

Next, a surface potential of studied materials above each of the four electrodes was measured. In this way, the surface potential dependence on the electrode work function for each studied material was obtained (Fig. 2 a). As it can be seen, in the case of Al the obtained surface potential does not depend on the metal beneath it. On the other hand, in the case of PMMA, there is a constant difference between the surface potential of polymer and the work function of the metal beneath it. Based on this, we can introduce the so-called slope coefficient (S), which describes the relation between surface potential and metal work function. Slope coefficient can be defined as

$$S = \frac{d\Phi_{surf.}}{d\Phi_{met}} \tag{1}$$

where $d\Phi_{surf.}$ is the change of the surface potential of the studied material ($\Phi_{surf.}$) and $d\Phi_{met}$ is the change of metal work function (Φ_{met}). If S= 0, the surface potential of the material does not depend on the electrode beneath the thin film. This is the case of Al. If S= 1, there is a direct correlation with the constant difference between the surface potential of the sample and the metal work function. S= 1 was obtained for PMMA. This shows that insulating material works as a surface "modificator" for the metals. In the cases of organic semiconductors, the slope coefficient S was between 0 and 1, depending on the material (see Fig. 2 a). Generally, the obtained surface potential and metal work function are related as

$$\Phi_{surf.} = S \cdot \Phi_{met} + C \tag{2}$$

where C is a constant, depending on studied material.

As S= 0 for metal (Al), S= 1 for dielectric material (PMMA), and 0< S <1 for other materials, one parameter which affects the slope coefficient could be an electrical conductivity of studied material. In Fig. 2 b, the relation between slope coefficient and the electrical conductivity of the material is shown. When the electrical conductivity of the material increases, the slope coefficient (the surface potential dependence on metal electrode work function) decreases. The thickness of the studied samples was in the range from 300- 800nm. Such thickness was enough to avoid the problems related to the coverage of the substrate surface [22] or band bending at the interface.
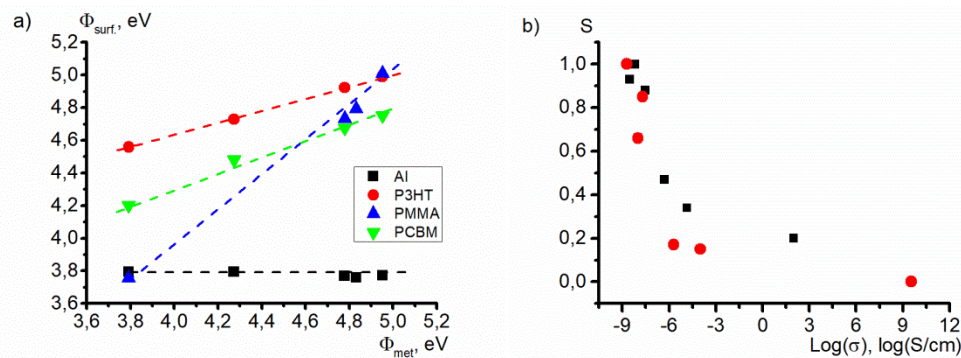

Fig. 2 a) Surface potential dependence on metal work function for different materials. Dashed lines are guides for eyes; b) Slope coefficient dependence on the electrical conductivity of the materials. Red data points represent the materials chosen for further studies

As the thickness of the samples in all cases was not the same, several materials were chosen for further studies. These materials represent the full range of electrical conductivity (round data points in Fig. 2 b): the polar opposites- metal (Al) and dielectric polymer PMMA-, semiconducting polymers P3HT and PVK, and two fullerene derivatives- C_{60} and $PC_{71}BM$. For each these materials, samples with various thicknesses were made.

In the case of Al, no surface potential dependence on metal work function was observed (Fig. 3 a) within the limits of measurements precision. On the other hand, Fig. 3 b and c show that the surface potential of PMMA depends not only on the metal work function but also on the film thickness. As the film thickness increases, the difference between Φ_{PMMA} and metal work function increases as well, while the slope coefficient stays the same and is S= 1. By modifying Eq.(2), the surface potential of PMMA can be written as

$$\Phi_{PMMA} = \Phi_{met} + C(d) \tag{3}$$

where C(d) is thickness-dependent constant. In Fig. 3 c, PMMA surface potential dependence on film thickness for different electrodes is shown. Here, the surface

potential is inversely proportional to the film thickness (d), which is proportional to the capacitance of the sample (C_0):

$$\Phi_{PMMA} = \Phi_{met} + A\frac{1}{d} = \Phi_{met} + BC_0 \qquad (4)$$

where A and B are constants. According to M. Pfeiffer et al., SKP can be applied to samples with low conductivity if: 1) the adjustment of the applied voltage is slow enough to allow the sample to dielectrically relax; 2) the capacity of the sample is larger than the capacity of the medium between the probe and the sample. [25] Usually these conditions are easily met. However, when the sample thickness is in the range of several micrometers (µm), one should be cautious, as the capacity of the sample decreases with increased film thickness. In this case, the capacity of air between the probe and sample is not negligible anymore and can influence the obtained results. Second, the SKP used in this research is based on so-called "peak-to-peak voltage" principle, which was developed by I.D.Baikie. Here the applied voltage (V_b) is changed in large amplitude and the resulting voltage (V_{ptp}) is measured. [26] While in the "zero-current" method the applied voltage is adjusted within the range of tens or couple of hundred of Hz, the direction of peak-to-peak voltage is being changed with the frequency of over 10 kHz, which may be too fast for dielectric material.

Electrical conductivity for PVK, obtained by the 4-probe method, was σ_{PVK}= $2 \cdot 10^{-8}$ S cm^{-1}. In this case, the slope coefficient decreased with the increase of the film thickness. As can be seen in Fig. 4, the changes in slope coefficient were not great- in the case of 70 nm thick film S= 1, while in the case of 1.8 µm thick film S= 0.82.
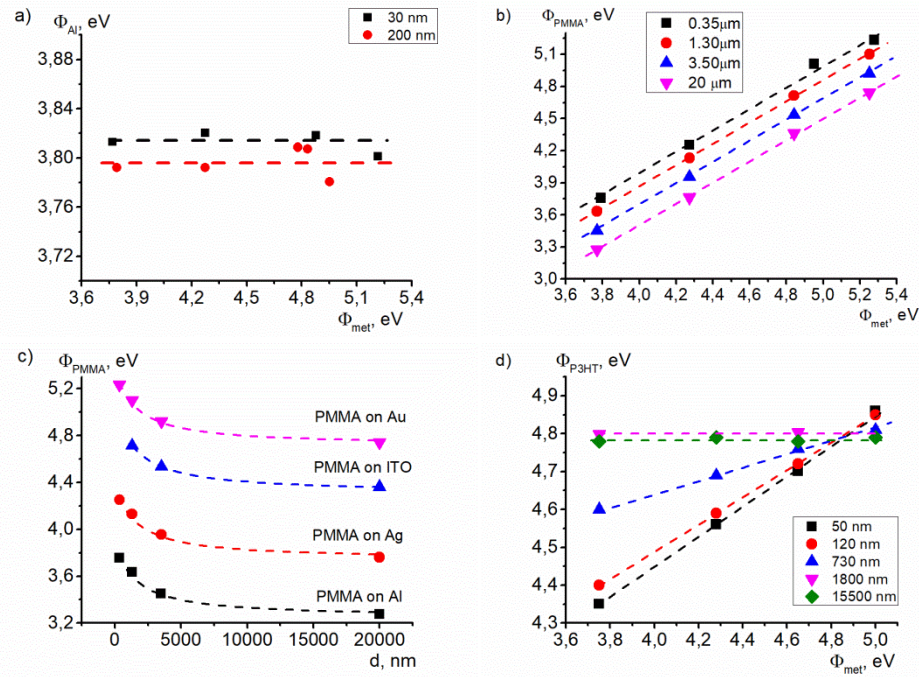
Fig. 3 a) Al work function dependence on metal work function; b) PMMA surface potential dependence on metal work function for samples with various thickness, c) PMMA surface potential dependence on film thickness with various electrodes under the PMMA layer; d) P3HT surface potential dependence on metal work function for samples with various thickness. Dashed lines are guides for eyes

In the case of fullerene C_{60}, it was possible to obtain the surface potential value which did not depend on the electrode work function. While thinnest C_{60} sample had S= 0.15, by increasing sample thickness to almost 2 μm S= 0 was achieved (Fig. 4). Similar results were obtained for another fullerene derivative- $PC_{71}BM$. While the thinnest sample (95 nm) had S= 1, by increasing sample thickness to 850 nm the slope coefficient was reduced to only S= 0.18. Further increase in sample thickness (1.45 μm and 2.50 μm) allowed obtaining metal-independent surface potential (see Fig. 4). As the energy levels of the fullerenes is similar (I_{C60}= 6.2 eV, $E_{a,C60}$= 3.6 eV [7] and I_{PC71BM}= 6.1 eV, $E_{a,PC71BM}$= 4.2 eV [27]), the differences in slope coefficient cannot be explained by the metal/ organic interface effect, but rather by the material properties. The measured electrical conductivity for C_{60} was higher than that of $PC_{71}BM$ (σ_{C60}= $1 \cdot 10^{-4}$ S cm^{-1} and σ_{PC71BM}= $1 \cdot 10^{-8}$ S/cm, respectively), the slope coefficient S for C_{60} samples was lower at small sample thickness, following the trend shown in Fig. 2 b.

Similarly to the fullerenes, in the case of P3HT a strong slope coefficient dependence on film thickness can be observed (Fig. 3 d). For the 50nm thick P3HT film S= 0.42. As the thickness of the film increases, the slope coefficient decreases. At the thickness of around 1.8μm the slope coefficient S= 0, meaning that the surface

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potential of the film becomes independent on the metal electrode work function. Further increase in the film thickness did not change the obtained surface potential (see Fig. 3 d). The obtained surface potential value for P3HT, which does not depend on metal work function, was Φ_{P3HT}= 4.80 eV. Our previous research shows that the ionization energy of P3HT is I_{P3HT} = 4.54 eV [28]. It means that the obtained surface potential value is around 0.25 eV higher than the ionization energy of P3HT molecules and its relation to the Fermi level of P3HT is questionable.
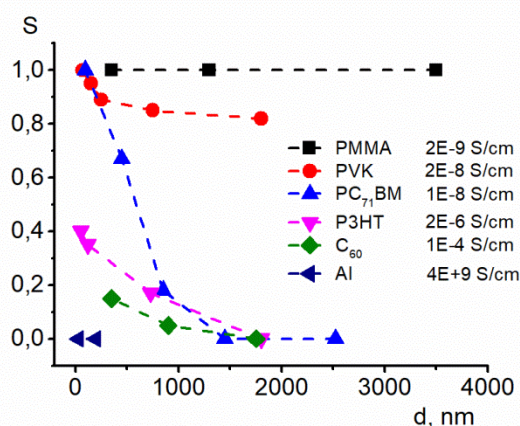

Fig. 4 Slope coefficient S dependence on film thickness for various materials. Dashed lines are guides for eyes

In Fig. 4 a summary of slope coefficient dependence on film thickness for the studied materials is shown. Two tendencies can be observed. One, with increased film thickness, the slope coefficient decreases and reaches S= 0 at a certain point. The exceptions are polymers with a poor electrical conductivity: PMMA (S stays at 1 for all of the samples) and PVK whose slope coefficient seems to "saturate" at the value of around 0.80. Second, as the electrical conductivity of the material increases, S is lower even at thinner films and allows obtaining metal-independent surface potential.

As the P3HT and fullerene derivatives showed, the film thickness of around 1.5 - 2 μm is required to obtain S= 0 and to avoid the electrode work function influence on the measured surface potential.

Conclusions

It was shown that for studied materials there is a surface potential dependence on electrode work function. In the case of Al, no such dependence was observed. On

the other hand, dielectric material (PMMA) works as a "surface modificator", meaning that at a fixed film thickness there is a fixed difference between the surface potential of the sample and work function. This could be related to the capacity effects of the film.

In the case of P3HT electrode-independent surface potential was obtained. Its relation to the Fermi level of P3HT is questionable as it is 0.25 eV higher than the molecule ionization energy, while in all other cases, the obtained surface potential values were between molecule ionization energy and electron affinity level of studied materials.

For organic semiconductors surface potential dependence on metal work function decreased by the increased electrical conductivity of studied material as well as by increased film thickness. P3HT and fullerene derivatives showed that around 1.5- 2 μm thick organic semiconductor film is required to obtain a surface potential value that does not depend on metal work function. In that case, the obtained surface potential describes the studied material itself, instead of the metal/organic material system. Further studies to show the relation between electrode-independent surface potential and the Fermi level of the material should be done.

Conflicts of interest. Authors have no conflicts of interest to declare.

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