Internal photoemission metrology of inhomogeneous interface barriers

Valery Afanas'ev^{*1}, Nadiia Kolomiets¹, Michel Houssa¹, and Andre Stesmans¹

¹ Laboratory of Semiconductor Physics, Department of Physics and Astronomy, University of Leuven, Celestijnenlaan 200D, box 2417, B-3001 Leuven, Belgium

Received ZZZ, revised ZZZ, accepted ZZZ

Published online ZZZ (Dates will be provided by the publisher.)

Keywords: Interface barrier, effective work-function, internal photoemission, polarization layer, interface dipole.

* Corresponding author: valeri.afanasiev@fys.kuleuven.be, Phone: +32 16 327167

Interfaces of heterogeneous solids, ranging from polycrystalline materials to composites, are frequently encountered in nanotechnology. Electron transport in these materials and across their interfaces critically depends on the energy barriers electrons encounter on their way. Because of electrode structural heterogeneity, the barriers may exhibit significant spatial variations resulting in a broad distribution of barrier heights and built-in potentials. Quantification of the distributed interface barriers represents a formidable experimental challenge since direct association of interface properties with those of a free surface is generally inaccurate. Here we present a methodology enabling quantification of electron barriers at interfaces of semiconductors and metals with insulators using the field-dependent Internal Photo-Emission (IPE) of electrons. We will show that practically-relevant interfaces may contain “patches” with differences in barrier height (or the effective work function) of up to 1 eV which makes the electrode heterogeneity a crucial factor in designing electron devices suitable for low-voltage operation.

Effective work-function (EWF) differences between different grains in top electrode give rise to contact fields promoting electron photoemission from high-EWF “patches” while suppressing IPE from low-EWF areas.

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1 Introduction Lowering of the operation voltage represents the mainstream trend in development of a broad spectrum electron devices aiming at reducing power consumption and dissipation. With International Technology Roadmap for Semiconductors (ITRS) 2.0 [1] predicting the Complementary Metal-Oxide-Semiconductor (C-MOS) circuitry to operate at 0.4 to 0.5 V power supply in the coming decade, the need to ensure tight control of electric fields in complex device structures is obvious. However, the latter requires not only stability of the externally applied voltages but, which is probably even more challenging, equally tight control of built-in voltages (V_{bi}) associated with contact potentials arising due to work-function

(WF) differences between device electrodes [2]. The built-in voltage unavoidably adds to the externally applied one thus modifying electrical response of a device. In the case of MOS transistors V_{bi} directly leads to the threshold voltage (V_{th}) shift. As a result, V_{th} needs to be adjusted to ensure optimal operation at low external voltage. Furthermore, V_{bi} remains applied even if the external power supply is turned off. In this case, particularly relevant for non-volatile memory devices, the electrode WF difference affects not only the cell set/reset characteristics as has already been reported for resistive switching memory stacks [3,4] but, also, the retention behaviour since non-zero electric field influences stability of the conducting filament.

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Taking into account that WF difference between electrodes can easily reach 1 eV [5] while the “stress” and “read” bias voltages of 0.2 V and 0.1 V, respectively, are used in the reliability tests [3], the impact of V_{bi} on the cell operation can hardly be ignored.

Taking into account the obvious significance of contact potentials, two issues become important if addressing the device electrostatics which is determined by the properties of interfaces rather than those of surfaces. First, the vacuum WF values are generally determined by the combination of the bulk (inner) chemical potential and the surface dipole contribution [6]. While the former represents the intrinsic property of a material, the surface component is sensitive to the crystallographic orientation (and reconstruction) since the surface atom density affects the electron spill out into vacuum [7]. Nevertheless, both bulk and surface components are determined by the electrode material itself and may be expected to be well reproducible and stable as long as no chemical or structural modification occurs. By contrast, at the interface between two solids, an array of (possibly polar) chemical bonds will terminate the electrode surface leading to WF variation. The well known WF sensitivity to the adsorption of foreign atoms at the surface provides good illustration to this effect [6].

Furthermore, while no free charges can be stabilized in vacuum above the electrode surface, it is well possible at the interface. This charge-containing *polarization layer* [8] includes various contributions stemming from electronic and/or ionic charges and may be expected to be highly sensitive to the physical and chemical properties of the second phase, i.e., will be influenced by factors not necessarily related to the electrode itself. Finally, chemical interaction between two phases in the interface region can hardly be excluded particularly taking into account that electron device processing includes a number of high-temperature annealing steps. All in one, it can be expected that the interface dipole WF component at an interface with a dissimilar phase will not remain the same as at the electrode surface. To account for this effect, the effective WF (EWF) is introduced which includes additional components relevant to particular interface. Obviously, if considering the V_{bi} problem in multi-layered device stacks, EWF must be used instead of vacuum WF.

Second, as already mentioned, different crystallographic faces may exhibit different WFs in vacuum [5,7]. Therefore, in the case of polycrystalline electrodes a *lateral* variation of the WF across the electrode surface can be expected. This WF lateral non-uniformity is well known and can be observed using, for example, the Kelvin-probe microscopy [9,10]. Then it is logical to expect that similar effect will also be encountered in the EWF with additional (not intrinsic) sources of non-uniformity added. For instance, interaction with hydrogen may cause laterally non-uniform WF variations as revealed by photoemission microscopy [11]. In this case one has to consider electron transfer between differently oriented crystallites [10,12,13]

which gives rise to lateral variations of electrostatic potential along the electrode interface (cf. Fig. 18 in Ref. 6). These lateral variations of EWF will directly be reflected in the lateral variations of V_{bi} leading to variability of threshold voltages and degrading sub-threshold slope of transistor transfer characteristics [14-17]. Again, the question arises concerning applicability of the vacuum WF variability values known from surface microscopy studies to the electrostatics of the interfaces. As it will be demonstrated by experimental results discussed below, the EWF values can differ from the vacuum WF by as much as 1 eV. Therefore, there are no reasons to accept variability of vacuum WF as the measure of EWF and V_{bi} lateral non-uniformity.

In this overview we will address methodology of the EWF determination and evaluation of its non-uniformity using Internal PhotoEmission (IPE) spectroscopy. Since technicalities of the IPE experiments have been addressed elsewhere [18-21], here these will be described only briefly. Then we will show results of several case studies addressing interfaces of metals and semiconductors with insulating oxides relevant to C-MOS devices aiming at evaluation of the possible EWF deviations from the vacuum WF values and on the evaluation of lateral EWF variations at the interface. We will show that for the technologically-relevant processing conditions up to 1 eV EWF variations can be observed with lateral EWF non-uniformity reaching ≈ 0.5 -1 eV. These variations are in the same range as the prospected on-device voltages [1] mandating experimental determination of the EWF as a function of processing conditions. As we will show, the IPE metrology provides the much needed solution.

2. Experimental approach

2.1 EWF measurements Determination of EWF at the interfaces of metals and semiconductors with insulating layers generally follows the paths used to measure WF at solid surfaces. First, observation of electron emission from an electrode allows one to estimate the barrier height electrons encounter at the surface or interface. The most straightforward analogy exists between external electron photoemission and IPE: As illustrated in Fig. 1, escape of an excited electron from the metallic photoemitter into vacuum or into insulating material becomes possible when the energy of the exciting photons $h\nu$ exceeds WF or interface barrier height Φ_e , respectively. This allows one to directly associate the spectral threshold of photoemission with the height of electron barrier (Φ_{VAC} or Φ_e in Fig. 1). In the ideal case $\Phi_{VAC} = WF = EWF$, and difference between the barriers for electron emission into vacuum and into a solid exactly corresponds to the energy of the conduction band bottom E_C of the latter with respect to the vacuum level E_{VAC} , i.e., to the electron affinity of the insulator χ_{INS} . The only difference between these two photoemission cases consists in the necessity to apply electric field F ensur-

ing drift of electrons photoinjected into the insulating layer towards opposite collector electrode: As opposed to electron photoemission into vacuum, electron-phonon scattering prevents ballistic transport in the conduction band of a solid insulator [22]. In its turn, EWF can be calculated by adding χ_{INS} to the electron IPE barrier height Φ_e . The electron affinity values can reliably be determined by comparing the IPE barrier at interfaces insulators with semiconductor crystals, such as silicon, to the vacuum photoemission threshold of the same semiconductor because electrical neutrality of these interfaces can accurately be verified using capacitance-voltage (CV) technique [23] or photo-voltage measurements [24].

Figure 1 Schematic comparison of electron transitions during photoemission from a metal electrode into vacuum (a) and internal photoemission into an insulator (b).

Potentially, one can also use thermionic emission of electrons to determine WF or EWF [5]. However, applications of this method are limited to relatively low barriers (less than 1 eV) which are encountered, for example, in metal/semiconductor contacts [25]. In the case of barriers of larger height, temperatures required to observe measurable rate of thermally-stimulated electron transitions exceed the range of interface thermal stability.

Second group of methods evaluates WF by observing electrostatic potential difference caused by electron transfer between materials with different WF [2]. In the Kelvin probe method, the voltage required to make the sample potential equal to that of the reference electrode is directly associated with the WF difference between these two materials. In the similar spirit, zero electric field condition in semiconductor (flat band point) can be reached in MOS structure when applying the corresponding voltage to the metal electrode [23]. The value of this flat-band voltage (V_{FB}) contains contributions stemming from the EWF difference between metal and semiconductor as well as from the charges present in the insulating (oxide) film. The latter

contribution can be eliminated by measuring a series of samples with different insulator thickness d_{ins} and then extrapolating the $V_{\text{FB}}(d_{\text{ins}})$ dependence to $d_{\text{ins}}=0$ which would give $V_{\text{FB}}(0)=V_{\text{bi}}$. Unfortunately, the essential condition of application of this method consists in the absence of other interfaces between metal and semiconductor electrodes which potentially can result in artefacts in the EWF difference determination. Furthermore, semiconductor/insulator interface of high quality is required to allow for accurate V_{FB} determination from CV curves. Finally, this method is inapplicable to the frequently encountered metal-insulator-metal (MIM) structures. As a result, despite technical complexity as compared to CV measurements, the IPE approach represents the most reliable way to find the EWF.

2.2 EWF non-uniformity evaluation In vacuum, evaluation of the WF lateral non-uniformity can be done by a variety of techniques ranging from scanning-probe methods (Kelvin probe [10], ballistic electron microscopy, BEEM, [26]) to electron emission imaging methods such as photoelectron emission microscopy (PEEM) [11], surface ionization methods [5] and photoemission from adsorbed probe-atoms [27, 28]. However, in the case of interface barriers, detection of lateral non-uniformity represents considerable challenge. Though scanning light spot methods have been proposed long ago to realize IPE [29-31], their lateral resolution remains in the micron range [32,33] making impossible detection of non-uniformities on the nanometer scale. Similarly, lateral resolution of the CV method is determined by the Debye length of chosen semiconductor and is usually of the order of 0.1 μm [23]. Significantly better lateral resolution of interface barrier quantification can be achieved by BEEM [26, 34-36]. However, in order to achieve sufficiently high electrode transparency, most of these works focus on relatively low metal/semiconductor barriers. Applicability of this approach to insulating oxides has been demonstrated in the past [37-39] but the use of ultrathin (3-5 nm) noble metal electrodes makes these of little relevance to most of the C-MOS issues though the revealed large barrier variation across the electrode area indicates significance of the effect.

Analysis of interface barrier non-uniformities on the basis of IPE spectral distributions was first addressed in relationship to inhomogeneous Schottky barriers [40]. Worth of adding here is that the light penetration depth is much larger than the mean free path of electrons in BEEM experiments. As the result, IPE methodology can be applied to electrodes with thicknesses ranging from 5 to ≈ 40 nm which is in the range of metal thicknesses typically used to control the EWF. In the IPE approach contributions of interface “patches” with different barrier height to the photoinjection current are separated by differentiating the experimental IPE quantum yield spectra. Under assumption that the yield (Y) of electron IPE from a metal strictly follows the Fowler law $Y \approx \text{const}(\hbar\nu - \Phi_e)^{1/2}$ [41,42], the “patches” with same barrier height Φ_e should provide a

plateau on the spectral plot of the first derivative of the yield logarithm as has been demonstrated for Schottky barriers [40]. However, when applied to metal/insulator barriers [43] it delivers spectral plots with no distinguishable plateau region(s). This observation suggests continuous distribution of barrier heights across the electrode area rather than the presence of spots with several well defined barrier values. In fact, the latter conclusion would also be consistent with continuous BEEM threshold distributions recently reported on metal/silicon interfaces [35, 36].

Figure 2 Schematics of electrostatic potential variations (a) caused by electric transfer between grain boundaries in a laterally inhomogeneous electrode (b) giving rise to contact electric fields between the grains with different EWF values, $EWF1 > EWF2$. Depending on the externally applied bias V , IPE from only high-EWF grains or from all grains becomes possible leading to the shift of spectral curves schematically illustrated in panel (c). Meaning of the symbols is explained in the text.

To find more reliable IPE-based solution of the inhomogeneous barrier characterization problem, let us consider IPE of electrons from a laterally inhomogeneous electrode taking into account the presence of contact potentials related, for example, to the electrode grain boundaries, as illustrated in Fig. 2: Due to electron transfer from a low EWF2 grains to “patches” with higher EWF1 the low-EWF regions acquire positive charge resulting in potential distribution illustrated in panel (a). Since the charge transfer occurs across all grain boundaries, within one grain the potential remains constant (see Fig. 18 in Ref. 6 illustrating this electrostatic effect).

Next, depending on the ratio between the insulator film thickness d_{ins} and characteristic size of differently charged grains L , two scenarios are possible: In the case of large “patches”, i.e., $L > d_{ins}$, the system represents two capacitors with different EWF of top electrode in parallel circuit. If the externally applied voltage V is sufficient to compensate the EWF difference between top electrode (EWF1) and the bottom electrode (EWF_{BE}), photoinjected electrons will drift across the insulator towards bottom electrode, e.g., semiconductor device channel, and give rise to the IPE current with spectral threshold $\Phi_{e1} = EWF1 - \chi_{ins}$. At the interfaces of grains with lower EWF2 this will happen when the bias voltage will become sufficient to compensate the difference $EWF2 - EWF_{BE}$ yielding the IPE spectral band with lower threshold $\Phi_{e2} = EWF2 - \chi_{ins}$. The difference between voltages at which IPE from high- and low-EWF grains becomes observable corresponds to the difference between EWF1 and EWF2.

In the case $L < d_{ins}$, the potential difference between grains with different EWF give rise to contact fields as illustrated in panel (b). At interfaces of the grains with larger EWF with insulator the contact field “helps” the excited electrons to drift from the interface region into the insulating film. By contrast, the contact field prevents electron IPE from the low EWF “patches” because it will not allow them to drift across the insulating layer toward the opposite bottom electrode. Only if the externally applied electric field becomes sufficient to overcompensate the effect of the local contact field, electron photoemission from the low-EWF “patches” becomes possible.

Let us further consider the expected evolution of the IPE spectra while increasing the externally applied bias V (panel b). In the low-bias range only contribution stemming from the “patches” with high EWF1 will be present because electrons photo-emitted from the grains with low EWF2 will be prevented from leaving the interface by the contact field. Therefore, at the *lowest* bias allowing IPE detection, the observed spectral threshold again corresponds to the contribution of grains with the *largest* EWF1 present at the interface [$\Phi_{e1} = EWF1 - \chi_{ins}$ as shown in panel (c)]. With increasing bias V , the external field will overcompensate the contact fields thus allowing photoinjection of electrons from the grains with lower EWF. As the result, the IPE spectra will exhibit progressively lower spectral

thresholds corresponding to the grains with lower EWFs. Eventually, when the strength of the external electric field $F=V/d_{\text{ins}}$ becomes larger than the strength of the contact field, even “patches” with lowest EWF will contribute to the IPE current yielding spectral threshold $\Phi_{e2}=\text{EWF2}-\chi_{\text{INS}}$ as illustrated in panel (c). Since the EWF difference between “patches” can be estimated from the difference between electron IPE thresholds Φ_{e1} and Φ_{e2} , the strength of the contact field will be related to the characteristic lateral size L of the low-EWF areas as $(\Phi_{e1} - \Phi_{e2})/L$. Because we compensate this field by applying bias V externally, the characteristic size of the low-WF spots L can be estimated by equalizing two fields:

$$\frac{\Phi_{e1} - \Phi_{e2}}{qL} \approx \frac{\Delta V}{d_{\text{ins}}}, \quad (1)$$

where q is the elemental charge and ΔV corresponds to the difference between minimal voltages required to observe the highest and lowest IPE thresholds. In this case one may expect that ΔV will exceed difference between EWF1 and EWF2. In practice, IPE currents can reliably be detected in samples with insulating film thickness d_{ins} as low as 5-10 nm which enables detection of low-EWF “patches” of few nm in size. Finally, since the IPE yield is linearly proportional to interface area fraction occupied by grains with particular EWF, one can attempt to evaluate this fraction in the same spirit as in Ref. 40. Nevertheless, care should be taken if the EWF non-uniformity is associated with the presence of near-interface charges because the latter may affect electron scattering [19,20].

2.3 Experimental realization The measurements presented in this work were performed on MIM or MOS samples with semitransparent top electrodes. More detail about sample fabrication will be given when discussing particular results. IPE spectra were measured at room temperature in the dc current mode using a Keithley 6517 or 617 electrometers. The IPE current was determined as the difference between the photocurrent measured under illumination and the one measured in darkness. The optical scheme has been discussed elsewhere [18-20]; The absolute calibration of the light intensity at the exit was attained using NIST-traceable Si ($\lambda > 300$ nm) and SiC ($\lambda < 400$ nm) photodiodes. The spectral resolution was fixed at 2 nm which corresponds to a monochromator slit energy width of about 15 meV at $h\nu = 3$ eV. The relative quantum yield Y was defined in terms of the photocurrent normalized to the incident photon flux. More details concerning the measurement procedure can be found elsewhere [18-21].

Analysis of the spectral curves follows Powell’s model [42] in which the spectral threshold of IPE is determined from linear extrapolation of the yield spectra to zero yield in $Y^{1/p}$ - $h\nu$ coordinates ($p=2$ for IPE from a metal, $p=3$ for IPE from a semiconductor). Spectra are usually taken at incremental gate bias until increase of leakage current makes quantification of IPE impossible. In all the dis-

cussed cases electron IPE is observed, i.e., photoemission from the bottom electrode under positive gate bias or from the top electrode under negative gate bias. This conclusion is made on the basis of trapped charge polarity measurements performed after electron photoinjection.

3 Effective workfunction and inhomogeneous barriers

Experimental results discussed below are grouped in two sections: First, the EWF determination from IPE data will be discussed aiming at evaluation of the possible differences between vacuum WF and EWF in the technologically relevant structures. In particular, we will explore mechanisms responsible for EWF variations at electrode/insulator interfaces. In the second part the field-dependent IPE spectra indicative of interface barrier non-uniformity will be discussed. Again, we will evaluate the EWF “contrast” of several electrode materials on the basis of lowest and highest IPE thresholds and address possible origin of the lateral barrier variations.

3.1 EWF versus WF The issue of systematic differences between vacuum WF and EWF at an interface with insulator has been overlooked for a long time because thermally grown oxide on silicon has been used as the “test vehicle” to evaluate EWF. Indeed, the difference between WF and EWF at the metal/SiO₂ interface appears to be very close to the electron affinity of SiO₂. The latter can be evaluated to be about 0.9-1.0 eV by comparing ionization energy of clean cleaved Si (5.15-5.4 eV, depending on crystal face [44]) to the barrier height of electron IPE from the valence band (VB) of Si into the conduction band (CB) of SiO₂ (4.25±0.05 eV for (100) Si and 4.32±0.05 eV for (111)Si [45]). Indeed, in the case of Au (WF=5.16-5.33 eV [46]) the repeatedly reported electron IPE threshold of 4.1 eV [42,45,47] yields EWF of 5.0-5.1 eV which agrees with vacuum WF within the measurement error [46]. The general agreement between WF and EWF values for SiO₂ is also observed for other metals: The threshold of electron IPE from copper (3.8 eV [18, 47]) yields EWF=4.8-4.9 eV coinciding with the known vacuum WF values [5,47].

However, the picture changes dramatically if addressing other insulators [18,48]: Electron photoemission yield spectra from Cu into atomic-layer deposited (ALD) Al₂O₃ shown in Fig. 3 indicate the spectral threshold to be close to $\Phi_e=3.5$ eV. Taking into account that the electron IPE threshold from the (100)Si VB into alumina is shifted down by 1 eV as compared to the earlier discussed SiO₂ case (3.25 eV vs. 4.25 eV [49]), the electron affinity of ALD Al₂O₃ should be close to 1.9-2 eV. This would correspond to EWF=5.5 eV which exceeds vacuum WF by more than 0.5 eV. This enhancement of the EWF as compared to SiO₂ suggests additional contribution to the barrier stemming from the insulating layer.

Figure 3 Semilogarithmic spectral plots of the IPE quantum yield measured in p-Si/Al₂O₃(20 nm, thermal ALD)/Cu(10 nm) capacitors under different negative voltages applied to the metal electrode corresponding to the indicated average strength of electric field in the oxide. The inset shows the corresponding Fowler plots and the scheme of the observed electron transitions. Lines illustrate determination of the IPE spectral threshold Φ_e .

Very similar behaviour is observed for practically important Cu_{0.6}Te_{0.4} electrodes used as ion injector in conducting-bridge memory cells [50]. As can be seen from the IPE spectra shown in Fig. 4, Cu_{0.6}Te_{0.4} films identically prepared on top of SiO₂ and ALD-Al₂O₃ insulators exhibit spectral thresholds of electron IPE which differ by only 0.1-0.2 eV. Indeed, the spectral thresholds found from the $Y^{1/2}$ - $h\nu$ (Fowler) plots shown in Fig. 5 indicate the difference of only ≈ 200 meV which would translate in the EWF increase of Cu_{0.6}Te_{0.4} on Al₂O₃ by more than 0.5 eV as compared to SiO₂ or the vacuum WF indicating formation of significant polarization layer at the interface [48]. Obviously, the vacuum WF values of Cu or Cu_{0.6}Te_{0.4} cannot be used to analyse electrostatics of these stacks.

There is significant number of observations indicating that EWF at a particular interface can be affected by a wide range of factors ranging from the composition of materials to the fine details of sample processing. Here we will illustrate this point by addressing TiN materials widely used in the metallization of electron devices. In Fig. 6 are shown semilogarithmic yield spectral plots (a) and the corresponding Fowler plots (b) used to determine spectral thresholds of electron IPE from TiN electrodes into crystalline (cubic) γ -Al₂O₃ film in seemingly symmetric TiN/ γ -Al₂O₃/TiN sandwich structure. There is, however, a well detectable (≈ 200 meV) difference between IPE thresholds of top and bottom electrodes. This asymmetry may be caused by different oxygen distribution at two interfaces since the observed incorporation of oxygen in the near-interface layer of the top TiN electrode suggests partial oxidation of TiN due to oxygen scavenging from γ -Al₂O₃

Figure 4 Semilogarithmic plots of the IPE quantum yield spectra measured in p-Si/Al₂O₃(20 nm, thermal-ALD)/Cu_{0.6}Te_{0.4}(10 nm) and p-Si/SiO₂(20 nm)/Cu_{0.6}Te_{0.4}(10 nm) capacitors under different negative voltages applied to the metal electrode corresponding to the indicated average strength of electric field in the oxides.

Figure 5 Fowler plots of the IPE quantum yield spectra measured on p-Si/Al₂O₃(20 nm, thermal-ALD)/Cu_{0.6}Te_{0.4}(10 nm) and Si/SiO₂(20 nm)/Cu_{0.6}Te_{0.4}(10 nm) capacitors illustrating determination of the electron IPE spectral thresholds.

[51]. What is interesting, however, is the EWF of TiN evaluated from the 3.0 and 3.2 eV interface barriers (Fig.6) taking into account a ≈ 0.5 eV upshift of the CB bottom in γ -Al₂O₃ as compared to the as-deposited amorphous ALD-alumina [52] yields EWF estimates for bottom and top interfaces of 4.5 and 4.7 eV, respectively which practically coincides with the known WF of TiN [12]. Apparently,

Figure 6 Semi-logarithmic (a) and Fowler (b) plots as measured on the TiN/ γ -Al₂O₃(17 nm)/TiN sample under indicated bias voltage applied to the top TiN electrode. The observed signal corresponds to electron IPE from the bottom and top electrodes, respectively, as illustrated in the inset in panel (b).

the influence of polarization layer in the case of TiN is not as significant as for the above discussed Cu-containing electrodes.

One of the hypothesis frequently discussed in the literature relates the EWF lateral variations in polycrystalline electrodes to the WF difference between differently oriented crystallites [10, 12, 13]. In order to evaluate significance of this crystallographic effect we compared electron IPE spectra from TiN layers deposited on top of thermally-grown SiO₂ film using ionized metal plasma (IMP) or cathodic arc evaporation (ARC) physical vapour deposition (PVD) methods. As revealed by the X-ray diffraction scans shown in the inset in Fig. 7 (b), these layers have predominantly (100) and (111) grain orientation, respectively. The (100)-face of TiN is expected to have EWF of 4.6 eV as compared to 4.4 eV for (100) face [10,12]. However, interface barriers obtained from the IPE spectra shown in Fig. 7 indicate the opposite trend: For the (100)-oriented IMP TiN the barrier height is by ≈ 100 meV lower than for the (111)-oriented ARC TiN layer. What is even more striking is the difference observed between these two barriers and the barrier for the earlier studied TiN electrodes prepared

Figure 7 Semi-logarithmic (a) and Fowler (b) plots as measured on the Si/SiO₂/TiN samples prepared using different PVD methods under indicated bias voltage applied to the top TiN electrode. The inset in panel (b) shows X-ray diffraction scans revealing different orientation of the TiN crystallites.

by PVD in N₂/Ar plasma [53]. The corresponding spectra are also shown in Fig. 7 for comparison. In the last case, a 0.8 eV higher barrier is found suggesting that the method of TiN electrode deposition plays by far more important role than the crystallography of the film. Apparently, nitrogen concentration in the TiN film represents the key factor determining the EWF. It needs also be noticed that using $\chi_{\text{INS}} = 0.9$ eV for SiO₂ the EWF ranging from 4.2 to nearly 5 eV can be inferred indicating the range of the potential processing-induced TiN EWF variations.

In addition to the electrode composition changes, the EWF of TiN can also be affected by oxygen deficiency of the underlying oxide insulator [54,55]: The IPE spectra shown in Fig. 8 indicate that incorporation of a thin Hf layers between TiN_x($x \approx 1$) and HfO₂ leads to significant (≈ 0.5 eV) electron barrier lowering at the *opposite* TiN/HfO₂ interface suggesting this is due to the effect of *remote oxygen scavenging*. On the other hand, as compared to the reference TiN/HfO₂/TiN sandwich structure, replacement of the bottom TiN electrode by a thin SiO_x layer on top of Si crystal enhances the barrier by ≈ 200

meV [cf. blue symbols in Fig. 8(b)]. These observations point towards O balance at the interface as the significant factor influencing the TiN/HfO₂ barrier height.

Finally, another significant factor affecting interface barrier height needs to be mentioned: Annealing in hydrogen of metal electrodes on top of insulating layers may lead to formation of a *hydrogen-induced dipole*. This phenomenon is well documented for platinum group metal electrodes such as Pt and Pd on top of insulating oxides at which hydrogen exposure leads to electron barrier lowering [56, 57]. Since the value of the dipole varies with partial pressure of hydrogen or H-containing molecules in the ambient, interaction of H with metal surface is seen as the microscopic mechanism of dipole formation [56]. At the same time, for H₂ pressure of about 1 atm., the 0.4-0.5 eV dipole is well reproduced at interfaces of Pt with different oxide insulators (SiO₂, Al₂O₃, HfAlO_x, HfO₂,...) which allows one to associate the dipole with layer of protons located right above metal surface plane at the Pt/oxide interface [57]. Furthermore, this is not the only way how hydrogen may induce a dipole thus affecting EWF and the barrier height. It has been demonstrated recently [58] that in structures with ALD HfO₂ grown from metallo-organic precursor a negative dipole can be formed compensating

Figure 9 Semi-logarithmic spectral plot of the IPE quantum yield measured on Si/SiO₂/HfO₂/Pt capacitors annealed in vacuum (10⁻⁸ Torr) or in hydrogen (1.1 atm.) for 15 min at 400 °C, with ALD HfO₂ deposited by using HfCl₄ (circles) or TDMA-Hf (squares) precursors. The vertical arrow marks the onset of intrinsic photoconductivity in the oxide. Horizontal arrows indicate the direction of the spectral curve shift due to annealing in H₂.

the positive metal-related dipole at the Pt side of Pt/HfO₂ interface. Since this negative dipole exhibits clear sensitivity to the HfO₂ synthesis chemistry, it can be associated with formation of negatively charged states in the near-interface oxide layers which, in combination with a thin polarized layer at the metal surface, forms interface dipole layer affecting the barrier height. What is remarkable in this observation is that otherwise identically processed Pt/HfO₂ interfaces can exhibit ≈1 eV difference in the electron barrier height depending on the oxide growth path. The corresponding range of the EWF variation from 4.5 to 5.6 eV significantly exceeds the known vacuum WF variation range (cf. Table II in Ref. 46). Obviously then, not only the vacuum WF values of the electrodes are irrelevant to the interfaces but, also, the range of the expected EWF variations is significantly larger than that of WF due to the influence of additional factors affecting variation of electrostatic potential across the interface. Therefore, the EWF values should be determined for the particular material system under processing relevant conditions.

3.2 EWF non-uniformity evaluation

The results presented in the previous section point towards multiple factors affecting the interface barrier height ranging from chemical modification of the contacting solids to generation of charges in the near-interface regions and formation of dipoles. Since these processes are expected to be sensitive to the local atomic structure of the solids in the interface region, it is highly unlikely that the barrier heights and EWF will remain uniform across the polycrystalline electrode area. Furthermore, even in the case of single-crystal electrodes, chemical interactions may result in a “patchy” (in terms of WF) surface as happens, for instance, at (100)Pt surface upon hydrogen exposure [11].

Figure 8 Semi-logarithmic (a) and Fowler (b) plots as measured on the TiN/HfO₂(10 nm)/TiN samples with or without Hf interlayer inserted at the top or bottom interface. Blue symbols in panel (b) show the spectrum obtained on the Si/SiO_x/HfO₂/TiN stack under the same -1 V bias on the top TiN electrode.

Figure 10 Semi-logarithmic spectral plot of the IPE quantum yield measured at the indicated metal bias on Si/SiO₂/HfO₂(17 nm)/Ru capacitors annealed in hydrogen (1.1 atm.) (a) or in vacuum (10⁻⁸ Torr) (b) at 400 °C for 20 min. The vertical arrow marks the onset of intrinsic photoconductivity in the oxide.

The first case study addresses interfaces of polycrystalline ruthenium electrodes with insulating oxide (HfO₂ in this case). Ruthenium represents an attractive material for high-EWF electrodes thanks to the possibility to deposit this metal by ALD [59] and the fact that the oxidized Ru is also metallic and delivers EWF approaching 6 eV [60]. The IPE from a 10-nm thick PVD Ru electrodes capped with 10 nm TiN protective layer are shown in semi-logarithmic and Fowler plots in Figs. 10 and 11, respectively. The results in panels (a) and (b) correspond to samples annealed in hydrogen (1.1 atm.) or in vacuum (10⁻⁸ Torr) at 400 °C for 20 min, respectively. The spectral curves exhibit significant “red shift” with increasing voltages which can hardly be explained by image-force barrier lowering since the latter does not exceed few tens meV in the used range of electric fields [cf. Fig. 9 in Ref. 21 showing IPE spectra from the VB of (100)Si into HfO₂]. Therefore, the shift of the spectral curves reflects lateral non-uniformity of the electron barrier (and EWF) at the Ru/HfO₂ interface. In both H₂ and vacuum annealed samples the spectral thresholds observed in low fields are 0.4-

0.5 eV higher than those found at highest fields as can be seen from the Φ_e -F^{1/2} (Schottky) plot shown in Fig. 12. This figure also shows the behavior of the threshold of electron IPE at the opposite (100)Si/HfO₂ interface measured under positive metal bias affirming the marginal impact of image-force effects. Therefore, because the transition from IPE stemming from high-WF “patches” at the Ru/HfO₂ interface to the IPE from low-EWF areas requires application of 3-4 V bias across 17-nm thick insulator, one can use Eq.(1) to estimate the typical low-barrier “patch” size to be ≈2 nm.

The second effect revealed by these IPE spectra concerns the impact of H₂ anneal: After this processing step the electron barrier height decreases by 300-450 meV as indicated by horizontal arrows in Fig 11. Taking into account that the bandgap of HfO₂ remains unchanged as indicated by the same photoconductivity spectral threshold

Figure 11 Fowler plots of the IPE quantum yield measured at the indicated metal bias on Si/SiO₂/HfO₂(17 nm)/Ru capacitors annealed in hydrogen (1.1 atm.) (a) or in vacuum (10⁻⁸ Torr) (b) at 400 °C for 20 min. Horizontal arrows indicate the direction of the spectral threshold shift due to annealing in H₂.

Figure 12 Schottky plot of the IPE spectral thresholds found in Si/SiO₂/HfO₂/Ru capacitors annealed in hydrogen (1.1 atm.) or in vacuum (10⁻⁸ Torr) at 400 °C for 20 min. The behavior of the spectral threshold of electron IPE from the (100)Si VB into HfO₂ is also shown for comparison.

(cf. vertical line in Fig. 10), the effect of hydrogen can be associated with formation of interface dipole. Interestingly, the data shown in Figs 11 and 12 suggest that the “patches” with higher barrier (and EWF) are affected by this dipole more significantly than the interface areas with lower barrier. This observation would be consistent with sensitivity of hydrogen surface ionization to local EWF of the electrode. If considering the EWF values, in the vacuum-annealed samples EWF is in the range 4.75-5.2 eV which is close to the range of vacuum WFs reported in the literature (see, e.g., Table 1 in Ref. 5). Importantly, however, the IPE results presented here reveal that this whole spread of EWFs is observed at the interface of the same Ru electrode. Upon annealing in H₂ representing the processing step routinely used in semiconductor manufacturing, EWF is lowered to the range 4.4-4.8 eV which is inconsistent with vacuum WFs. However, significant lateral non-uniformity remains present even after H₂ anneal.

Another example of IPE from laterally non-uniform electrodes is illustrated by Figs. 13 and 14 which show the yield spectra measured at the interfaces of Ge doped (5% or 20%) Cu_{0.6}Te_{0.4} electrodes with Al₂O₃ insulator. While the electron IPE spectra from undoped Cu_{0.6}Te_{0.4} exhibit virtually no field dependence as can be seen from Fig. 4, doping with Ge leads to strong field dependence with ≈500 meV “red shift” of the spectra. The threshold of low-field IPE is close to that of pure Cu_{0.6}Te_{0.4} (note that this IPE is observed at positive gate bias voltages due to large EWF difference between Cu_{0.6}Te_{0.4} and n⁺-Si bottom electrode) but in the high-fields the IPE threshold appears close to the

energy barrier between the VB of pure Ge and amorphous alumina (2.85-2.9 eV, see ref. 61) which can also be seen from the corresponding spectrum shown in Fig. 14(a). Since the increase of Ge doping level from 5 to 20 % results in the increase of the yield without shift of the spectral threshold (Fig. 14) it is likely that Ge is segregated at the interface with Al₂O₃ forming low-barrier “patches”. Using the observed IPE threshold difference and approximately 3 V external bias required to “switch” the IPE from the high-barrier areas to that from the low-barrier ones, the average lateral size of the Ge “islands” can be estimated as ≈3 nm.

Finally, in order to demonstrate the possible range of the interface barrier non-uniformity, we addressed stacked Hf/TiN electrode deposited on top of amorphous Al₂O₃ layers [62]. As can be seen from the IPE yield spectra shown in Fig. 15, interlayer of Hf allows one to lower the

Figure 13 Semi-logarithmic (a) and Fowler (b) plot of the IPE quantum yield measured on n⁺-Si/Al₂O₃/Cu_{0.6}Te_{0.4}Ge(5%) capacitors under the indicated bias voltage applied to the CuTe electrode as compared to the undoped Cu_{0.6}Te_{0.4} electrode. Horizontal arrow in panel (b) indicates “red shift” of the IPE spectra.

Figure 14 Semi-logarithmic (a) and Fowler (b) plot of the IPE quantum yield measured on n^+ -Si/Al₂O₃/Cu_{0.6}Te_{0.4}Ge(5% or 20%) capacitors when applying the indicated bias voltage applied to the CuTe electrode and compared to the IPE from undoped Cu_{0.6}Te_{0.4} electrode or (100)Ge crystal.

IPE threshold as compared to the “standard” TiN electrodes [53]. In low fields spectral threshold close to 2.2 eV is systematically found. Its weak field dependence suggests IPE to occur from the interface area with similar barrier height and EWF. However, as the field strength increases to 1 MV/cm (-2 V bias voltage), the spectral threshold shift by ≈ 1 eV to the lower photo energies indication IPE from “patches” with much reduced EWF. If evaluating the typical size of the latter using Eq. (1) one comes to the value of ≈ 10 nm, which is comparable to the thickness of the Hf interlayer, i.e., coincides with the expected grain size in cubic Hf polycrystalline electrode. On the other hand, the quantum yield of electron IPE from the low-EWF regions appears to be larger than the yield from high-EWF islands by approximately factor of 10^2 which would mean that the latter occupy only few percent of the interface area. Taken together, these observations allow us to hypothesize that appearance of high-EWF regions is caused by local oxidation of Hf in the grain boundary regions while the rest of the interface corresponds to metallic Hf. Nevertheless, the revealed lateral EWF variations will give rise to contact fields which may significantly affect electron transport.

Figure 15 Semi-logarithmic (a) and Fowler (b) plot of the IPE quantum yield in p^+ -Si/TiN(30 nm)/Al₂O₃(20nm)/Hf(10 nm)/TiN(10 nm) capacitors as measured under the indicated bias voltage applied to the top Hf/TiN electrode stack.

4 Conclusions

In this paper we briefly overviewed the ideas underlying the IPE-based metrology of inhomogeneous electrodes in MOS and MIM systems. The basic advancement is related to combination of spectrally resolved measurements with compensation of the built-in fields by externally applied voltages. Three important conclusions can already be reached: First, the EWF may differ significantly (up to 1 eV) from the commonly accepted vacuum WF values which, therefore, cannot be used for device electrostatics analysis. Second, the processing-induced EWF variations of 0.5-1 eV can be encountered mandating the EWF determination as affected by interface preparation. Finally, lateral variations of EWF may reach 0.5-1 eV which should be taken into account when considering electron transport analysis. It is also demonstrated that the presented IPE approach allows one to successfully quantify both the EWF and its lateral variations.

Acknowledgements This work was supported by Fonds Wetenschappelijk Onderzoek – Vlaanderen (Project G.OCO5.13) and by Internal Fund project C14/16/061.

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