Applied Surface Science 256 (2010) 2602–2605

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Pitfalls in measuring work function using photoelectron spectroscopy

M.G. Helander *, M.T. Greiner, Z.B. Wang, Z.H. Lu

*Department of Materials Science and Engineering, University of Toronto, 184 College St., Toronto, Ontario, Canada M5S 3E4*

A R T I C L E  I N F O

*Article history:*
Received 17 August 2009
Received in revised form 30 October 2009
Accepted 2 November 2009
Available online 10 November 2009

*Keywords:*
Ultraviolet photoelectron spectroscopy
Work function
Secondary electron cut-off
Fermi level

A B S T R A C T

Accurate measurement of work function is essential in many areas of research and development. Despite the importance of photoelectron spectroscopy as a technique for measuring work function, there has been relatively little discussion in the literature of how to conduct accurate measurements. We review the basic technique of measuring work function using ultraviolet photoelectron spectroscopy and discuss several common sources of error related to the experimental setup. In particular, the sample-detector geometry is found to be a key experimental parameter; accurate results are only obtained when the sample is perpendicular to the electron detector. In addition, we demonstrate that photoelectron work function values correspond to the minimum work function "patch" on a non-uniform surface, in contrast to the average work function measured by other techniques, such as the Kelvin probe method.

## 1. Introduction

Work function (i.e., the minimum energy required to remove an electron from the surface of a solid) is an important parameter in the study of surfaces and interfaces [1]. Many interfacial chemical and electrical properties are related to the work function of a material. Hence, experimental determination of work function is critical to many scientific endeavours and engineering applications. Photoelectron spectroscopy (PES) is one of the most commonly used techniques used to measure the *absolute* work function of a sample [2]. Most reliable tabulated work function values are from PES measurements [3]. However, despite the importance of this technique, there is relatively little discussion in the literature of how to conduct accurate work function measurements using PES [4]. Arguably, PES is a mature enough technique that such discussion should be readily available in textbooks. However, the frequency of errors in reported PES work function measurements highlights the need for an up-to-date discussion of common pitfalls. PES is extremely sensitive to subtle changes in the experimental conditions [5,6]. As a result, there is significant disagreement in the literature over reported work function values, even for well-controlled sample surfaces (e.g., Ag single crystal [7–9]). In this paper we review the general theory related to measuring work function using PES and discuss several common sources of error related to the experimental setup.

## 2. Theory

PES relies on the analysis of the kinetic energy of photoelectrons emitted from the surface of a sample upon irradiation by a mono-energetic photon source. The kinetic energy of the emitted electrons is typically measured using an electron energy analyzer (spectrometer), such as a spherical capacitance analyzer (SCA) equipped with an electrostatic lens system to more efficiently collect and focus the emitted photoelectrons. X-ray photoelectron spectroscopy (XPS) uses soft X-rays as the photon source, such as monochromatic Al K$\alpha$ ($h\nu = 1486.7$ eV). XPS is the most common form of PES and is often used to study surface chemical composition. Ultraviolet photoelectron spectroscopy (UPS) is another commonly used variation of PES that utilizes lower energy vacuum ultraviolet (VUV) photons, such as He I$\alpha$ ($h\nu = 21.22$ eV). UPS is more commonly used than XPS for work function measurements due to the superior line width and high photon flux from laboratory VUV sources, such as noble gas discharge lamps [10–12].

Before we begin the discussion of work function measurements, we must first review the basic concepts concerning the electron work function. The work function of a uniform surface of a conductor is defined as the minimum energy required to remove an electron from the interior of the conductor to just outside the surface, where "just outside" refers to a distance that is large enough that the image force is negligible, but small compared to the physical dimensions of the crystal (typically $\sim 10^{-4}$ cm)

---

* Corresponding author at: Department of Materials Science and Engineering, University of Toronto, 184 College St., Room 140, Toronto, Ontario, Canada M5S 3E4.
*E-mail addresses:* michael.helander@utoronto.ca (M.G. Helander), zhenghong.lu@utoronto.ca (Z.H. Lu).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.11.002

[13–18]. In other words, the work function is the difference betweeen the electrochemical potential $\bar{\mu}$ of electrons in the bulk and the electrostatic potential energy $-e\Phi_{\rm vac}$ of an electron in the vacuum just outside the surface [19],

$$e\phi_{\rm m} = -e\Phi_{\rm vac} - \bar{\mu}. \tag{1}$$

The energy-level corresponding to $-e\Phi_{\rm vac}$ is referred to as the *local* vacuum level $E_{\rm vac}$ and is not to be confused with the vacuum level at infinity $E_0$, which represents an electron at rest at infinity (i.e., zero potential energy) [20,21]. Since the Fermi level $E_{\rm F}$ relative to the vacuum level at infinity $E_0$ is the electrochemical potential of electrons in the conductor [22],

$$E_0 - E_{\rm F} = -\bar{\mu}, \tag{2}$$

the work function given by Eq. (1) is equivalent to the difference in potential energy of an electron between the local vacuum level $E_{\rm vac}$ and the Fermi level,

$$e\phi_{\rm m} = E_{\rm vac} - E_{\rm F}. \tag{3}$$

From Eq. (3) it is clear that if the local vacuum level $E_{\rm vac}$ varies across a sample, as is the case for the different faces of a single crystal, the work function will also vary [19].

Now that we have reviewed the basic concepts related to the electron work function we can move on to discuss PES work function measurements. From the photoelectric effect the maximum kinetic energy of a photoelectron is given by,

$$E_{\rm K,max} = h\nu - e\phi_{\rm m}, \tag{4}$$

where $E_{\rm K}$ is kinetic energy and $h\nu$ is the photon energy. This maximum kinetic energy occurs for a photoelectron emitted from the Fermi level. In principle, work function can be measured by varying the photon energy and determining the threshold photon energy required for the onset of photoemission. This method was in fact one of the original techniques used to measure work function [19]. However, in PES measurements typically only a single photon energy is used and hence another methodology is required.

Based on Eq. (4) the kinetic energy of a photoelectron emitted from an energy-level with binding energy $E_{\rm B}$ below the Fermi level is given by,

$$E_{\rm K} = h\nu - E_{\rm B} - e\phi_{\rm m}, \tag{5}$$

where $E_{\rm B}$ is the binding energy of the electron referenced to the Fermi level. In PES measurement the sample is in electrical contact with the spectrometer, resulting in a contact potential difference $\Delta\phi = (\phi_{\rm m} - \phi_{\rm s})$ due to the difference in local vacuum level between the sample and spectrometer, where $\phi_{\rm s}$ is the work function of the spectrometer [17,18]. The *measured* kinetic energy of a photoelectron in PES is therefore given by,

$$E_{\rm K}^{\rm meas} = h\nu - E_{\rm B} - e\phi_{\rm m} + \Delta\phi = h\nu - E_{\rm B} - e\phi_{\rm s} \tag{6}$$

As a result, the measured kinetic energy $E_{\rm K}^{\rm meas}$ of a photoelectron in PES is *independent* of the sample work function. This effect is schematically depicted in Fig. 1(a). Nonetheless, the work function of the sample can still be determined by correcting for the built-in potential $\Delta\phi$ (i.e., by taking the width of the photoelectron spectrum) [27],

$$e\phi_{\rm m} = h\nu - \left(E_{\rm K,max}^{\rm meas} - E_{\rm K,min}^{\rm meas}\right), \tag{7}$$

where $E_{\rm K,max}^{\rm meas}$ is the maximum measured kinetic energy of an electron emitted from the Fermi level and $E_{\rm K,min}^{\rm meas}$ is the minimum measured kinetic energy in the photoelectron spectrum (i.e., the zero of the kinetic energy scale relative to the sample), as shown in Fig. 2. For semiconductors the Fermi level typically falls in the band gap, which means that $E_{\rm K,max}^{\rm meas}$ must be determined from a metal sample in electrical contact (i.e., the Fermi levels are aligned) with the semiconductor sample.

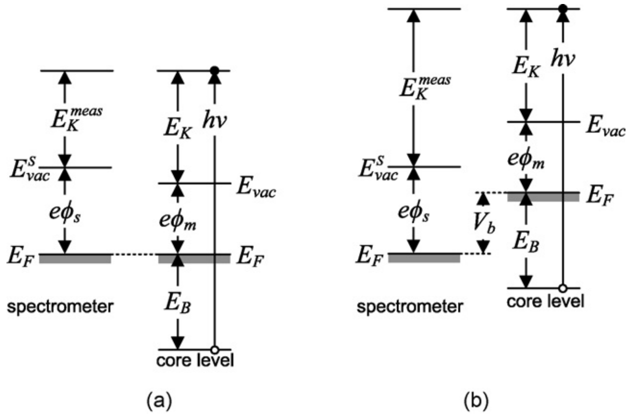


**Fig. 1.** Schematic energy-level diagram for a conductive sample in electrical contact with the spectrometer, (a) photoemission process for an electron excited from a core level with binding energy ($E_{\rm B}$), and (b) the effect of an applied bias ($V_{\rm b}$) between the sample and spectrometer. The Fermi level ($E_{\rm F}$), local vacuum level of the sample ($E_{\rm vac}$), sample work function ($\phi_{\rm m}$), local vacuum level of the spectrometer ($E_{\rm vac}^{\rm S}$), spectrometer work function ($\phi_{\rm s}$), photon energy ($h\nu$), kinetic energy of the emitted photoelectron ($E_{\rm K}$), and measured kinetic energy of the emitted photoelectron ($E_{\rm K}^{\rm meas}$) are as shown.

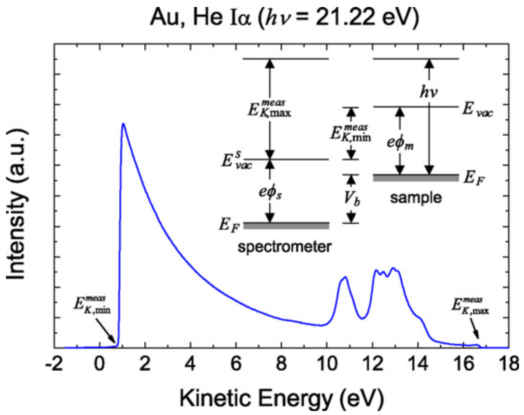


**Fig. 2.** He Iα ($h\nu$ = 21.22 eV) valence band spectrum of an Ar$^+$ sputter cleaned Au film on Si(1 0 0). The spectrum was collected with a photoelectron take-off angle ($\theta$) of 90° and with a −10 V bias ($V_{\rm b}$) applied to the sample. The kinetic energy scale has already been corrected for the applied bias. The high intensity peak at low kinetic energy corresponds to the SEC region of the spectrum. $E_{\rm K,max}^{\rm meas}$ (Fermi level) and $E_{\rm K,min}^{\rm meas}$ are as shown. The inset of the figure shows the corresponding schematic energy-level diagram for the sample and spectrometer.

The point of minimum kinetic energy in a photoelectron spectrum $E_{\rm K,min}^{\rm meas}$ occurs in the region of the spectrum typically referred to as the secondary electron cut-off (SEC) since (i) the majority of the signal is comprised of low kinetic energy secondary electrons, and (ii) in this region the spectrum is suddenly "cut-off" due to the local vacuum level. In other words an electron leaving the sample with energy less than $E_{\rm vac}$ has insufficient kinetic energy to escape, and hence does not contribute to the photoelectron spectrum. This implies that the electrons of interest leave the sample with zero kinetic energy. However, it is extremely difficult, if not impossible, to measure electrons leaving the sample with zero kinetic energy. Even electrons with near zero kinetic energy may have insufficient kinetic energy to make it into the spectrometer. Therefore, a small negative bias is typically applied to the sample when measuring the SEC region of the spectrum. This bias helps accelerate the lowest kinetic energy electrons into the spectrometer (and also helps to overcome the contact potential difference), as schematically shown in Fig. 1(b). Since an applied bias offsets all of the energy levels in the sample, Eq. (7) is still valid.

## 3. Experiment

The UPS measurements were performed using a PHI 5500 Multi-Technique system with a base pressure of ~$10^{-10}$ Torr equipped with a He discharge lamp (SPECS UVS 10/35). The spectrometer (hemispherical analyzer) was calibrated using XPS with monochromatic Al K$\alpha$ ($h\nu = 1486.7$ eV) as per ISO 15472 [23]. All UPS measurement were performed with a pass energy of 2.95 eV and with the electrostatic lens of the analyzer configured for an analysis area of 500 $\mu m^2$ (800 $\mu$m diameter circle) and a photoelectron acceptance angle of ±5°. The energy resolution for UPS measurements was ~135 meV determined from the width of the Fermi edge of Ar$^+$ sputter cleaned Au thin film. The substrates used were the same as those used in Ref. [24], namely 200 nm thick Au film on native oxide terminated Si(1 0 0) deposited by radio frequency (rf) magnetron sputtering. Freshly deposited films were loaded into the analysis chamber and Ar$^+$ sputter cleaned (3 keV ions) at 75° until the C 1s and O 2p signals vanished and singular SEC spectra were obtained.

## 4. Results

Fig. 2 shows a typical He I$\alpha$ ($h\nu = 21.22$ eV) valence band spectrum for an Ar$^+$ sputter cleaned Au film. The high intensity peak at low kinetic energy corresponds to the SEC region of the spectrum. The positions of $E_{\mathrm{K,max}}^{\mathrm{meas}}$ (Fermi level) and $E_{\mathrm{K,min}}^{\mathrm{meas}}$ used in Eq. (7) are indicated on the spectrum. The inset of the figure shows the corresponding schematic energy-level diagram for the sample and spectrometer. Using Eq. (7) the calculated work function of the sample is 5.33 ± 0.05 eV, consistent with values in literature for Ar$^+$ sputter cleaned Au [25].

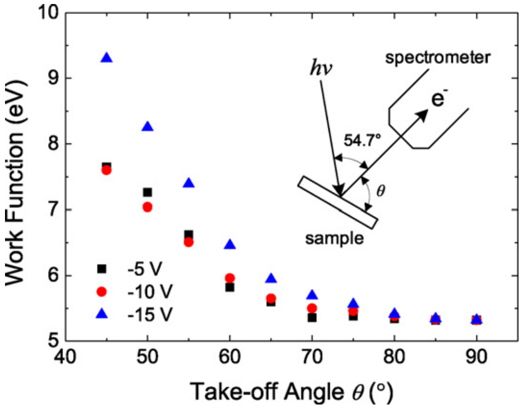
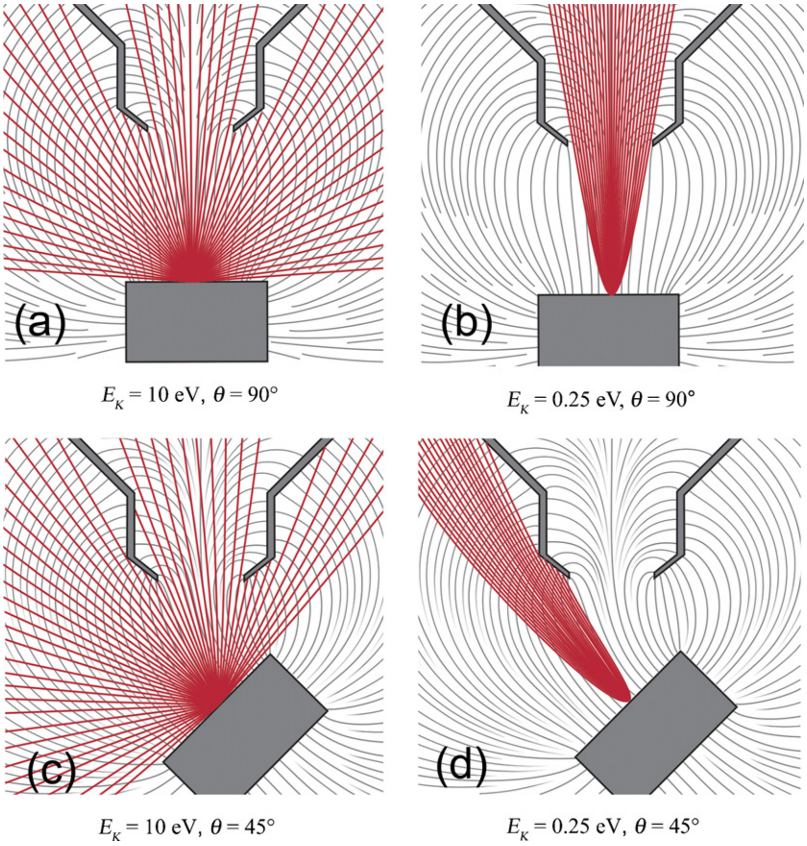


**Fig. 3.** Measured work function of Ar$^+$ sputter cleaned Au film using Eq. (7), as a function of photoelectron take-off angle ($\theta$) and applied sample bias ($V_b$). The inset shows the geometry of the sample relative to the photon source (He discharge lamp) and spectrometer. The measured work function deviates significantly and shows a strong dependence on the applied bias for photoelectron take-off angles less than 90°. This highlights the importance of measuring work function with the sample perpendicular to the detector (i.e., at a photoelectron take-off angle of 90°).

As discussed above, measuring work function using PES relies on accurate determination of $E_{\mathrm{K,min}}^{\mathrm{meas}}$ at the low kinetic energy edge of the SEC region. However, since the SEC region of the spectrum is derived from electrons with near zero kinetic energy, its shape and



$E_K = 10$ eV, $\theta = 90°$

$E_K = 0.25$ eV, $\theta = 90°$

$E_K = 10$ eV, $\theta = 45°$

$E_K = 0.25$ eV, $\theta = 45°$

**Fig. 4.** Finite element simulation of the electric field between a conductive sample and the grounded lens of the spectrometer, with an applied bias of −15 V. The electron trajectories from a point source at the sample surface are also shown. The angular distributions of the electron point sources are identical at the sample surface, however the trajectories of the slow (0.25 eV) electrons are severely distorted by the electric field, such that at a photoelectron take-off angle of 45° none of the slow electrons is directed into the lens. Note that the trajectories of the higher kinetic energy electrons are not significantly affected by the electric field.

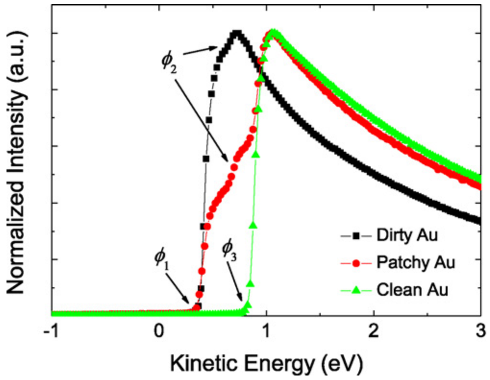


**Fig. 5.** SEC region of the UPS spectrum of a laterally inhomogeneous "patchy" Au film. The sample was prepared by partially $Ar^+$ sputter cleaning an air exposed Au film for several seconds. Reference spectra for air exposed Au (dirty) and $Ar^+$ sputter cleaned Au (clean) are also shown. The spectra were collected with a photoelectron take-off angle ($\theta$) of 90° and with a $-15$ V bias ($V_b$) applied to the sample. The kinetic energy scale has already been corrected for the applied bias. Three distinct peaks are observed in the spectrum corresponding to patches with different work functions, namely: $e\phi_1 = 4.9$ eV, $e\phi_2 \approx 5.1$ eV, and $e\phi_3 \approx 5.3$ eV. The two lower work function values correspond to dirty Au, while the third value is for clean Au.

position can be significantly influenced by subtle changes in the local electromagnetic field. Of particular importance is the direction of the electric field at the surface of the sample relative to the trajectory of an emitted photoelectron. Since the electric field at the surface of a conductor (sample) is perpendicular to the surface, only electrons emitted normal to the surface will experience a purely tangential acceleration. As a result, the sample must be perpendicular to the detector in order to prevent the lowest kinetic energy electrons from experiencing a normal acceleration away from the detector.

Fig. 3 shows the measured work function of the same Au film from Fig. 2 as a function of applied sample bias and photoelectron take-off angle. As expected the work function measurements deviate significantly (and are bias dependent) for photoelectron take-off angles less than 90° (see inset of Fig. 3). For photoelectron take-off angles less than 90° the emitted photoelectrons experience a normal acceleration away from the spectrometer since the electric field at the surface of the sample points away from the spectrometer. The lowest kinetic energy photoelectrons are therefore swept away from the spectrometer due to the normal acceleration, resulting in $E_{\mathrm{K,min}}^{\mathrm{meas}}$ shifting to higher kinetic energy, which incorrectly yields a higher work function value. This effect is shown in Fig. 4. Also, for higher applied sample bias the electric field at the surface of the sample is also higher, resulting in an even more significant normal acceleration away from the spectrometer.

Work function measurements using PES must therefore always be taken with the sample perpendicular to the detector (i.e., at a photoelectron take-off angle of 90°). This necessary condition has often been overlooked in previous discussions of PES work function measurements.

## 5. Discussion

Finally we discuss the case for a non-uniform or "patchy" surface (i.e., a sample with laterally inhomogeneous work function). Based on Eq. (7) it is clear that $E_{\mathrm{K,min}}^{\mathrm{meas}}$ scales with work function. Hence the signal from the SEC of a patch with lower work function will tend to bury the signal from a patch with higher work function. Therefore, PES measurements tend to yield the lowest work function patch on a non-uniform surface. Fig. 5 shows the SEC region for a patchy Au film. The signal from the high work function (clean) patches is almost completely buried by that from the lower work function (dirty) patches. Since nearly all surfaces, including single crystals, exhibit some degree of patchiness [19] this is an important point to consider, particularly when comparing PES work function measurements to values obtained by other techniques, such as Kelvin probe [26], which measure an average value of work function. As a result the shape of the SEC region of the spectrum is an extremely sensitive indication of surface cleanliness. Since adsorbed contaminates tend to lower the work function of clean metals, the presence of any low kinetic energy tail in the SEC region of the spectrum is an indication of residual contaminates, which may be below the detection limit of other techniques such as XPS. Such tail features in the SEC region are often found in many spectra of apparently "clean" surfaces reported in literature, but have been largely ignored.

## 6. Summary

In summary, we have reviewed the basic theory related to measuring work function using PES. With careful consideration of the experimental setup, common errors arising from the sample-detector geometry can be minimized by ensuring that the sample is perpendicular to the detector. PES has also been shown to measure the minimum work function from a non-uniform "patchy" surface, which is typically of most samples.

## Acknowledgement

We wish to acknowledge funding for this research from Natural Sciences and Engineering Research Council (NSERC) of Canada.

## References

[1] W. Mönch, Semiconductor Surfaces and Interfaces, Springer, Berlin, 2001.
[2] D.P. Woodruff, T.A. Delchar, Modern Techniques of Surface Science, Cambridge University, Cambridge, 1994.
[3] H.B. Michaelson, J. Appl. Phys. 48 (1977) 4729.
[4] O. Klyushnikov, J. Struct. Chem. 39 (1998) 944.
[5] M.P. Seah, I.S. Gilmore, G. Beamson, Surf. Interface Anal. 26 (1998) 642.
[6] M.P. Seah, I.S. Gilmore, S.J. Spencer, Surf. Interface Anal. 26 (1998) 617.
[7] M. Uda, A. Nakamura, T. Yamamoto, Y. Fujimoto, J Electron Spectrosc. Relat. Phenom. 88–91 (1998) 643.
[8] A.W. Dweydari, C.H.B. Mee, Phys. Sat. Sol. (a) 27 (1975) 223.
[9] M. Chelvayohan, C.H.B. Mee, J. Phys. C 15 (1982) 2305.
[10] J.E. Rowe, S.B. Christman, E.E. Chaban, Rev. Sci. Instrum. 56 (1985) 759.
[11] J.E. Rowe, S.B. Christman, E.E. Chaban, Rev. Sci. Instrum. 44 (1973) 1675.
[12] J.K. Cashion, J.L. Mees, D.E. Eastman, J.A. Simpson, C.E. Kuyatt, Rev. Sci. Instrum. 42 (1971) 1670.
[13] C. Kittel, Introduction to Solid State Physics, Wiley, New York, 1996.
[14] S.M. Sze, K.K. Ng, Physics of Semicondcutor Devices, Hoboken, John Wiley & Sons, New Jersey, 2007.
[15] N.W. Ashcroft, N.D. Mermin, Solid State Physics, Harcourt, Philadelphia, 1976.
[16] D.R. Lide, CRC Handbook of Chemistry and Physics, Taylor and Francis, Boca Raton, 2004.
[17] S. Hüfner, Photoelectron Spectroscopy: Principles and Applications, Springer, Berlin, 2003.
[18] D. Briggs, M.P. Seah, Practical Surface Analysis, Wiley, New York, 1992.
[19] C. Herring, M.H. Nichols, Rev. Mod. Phys. 21 (1949) 185.
[20] H.D. Hagstrum, Surf. Sci. 54 (1976) 197.
[21] A.H. Marshak, IEEE Elec. Dev. Lett. 6 (1985) 128.
[22] P. Van Rysselberghe, J. Chem. Phys. 21 (1953) 1550.
[23] M.P. Seah, Surf. Interface Anal. 31 (2001) 721.
[24] M.G. Helander, M.T. Greiner, Z.B. Wang, Z.H. Lu, Appl. Surf. Sci. 255 (2009) 9553.
[25] J.E. Lyon, A.J. Cascio, M.M. Beerbom, R. Schlaf, Y. Zhu, S.A. Jenekhe, Appl. Phys. Lett. 88 (2006) 222109.
[26] W.A. Zisman, Rev. Sci. Instrum. 3 (1932) 367.
[27] J. Sitte, Chem. Phys. Lett. 42 (1976) 131.