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Ionization potential and electron attenuation length of titanium dioxide deposited by atomic layer deposition determined by photoelectron spectroscopy in air

Francisco C. Marques^{a,*}, Jacek J. Jasieniak^{b,c}

^a Universidade Estadual de Campinas, Unicamp, Instituto de Física “Gleb Wataghin”, 13083-859 Campinas, SP, Brazil

^b Monash University, Department of Materials Science and Engineering, Exciton Science, Clayton, Victoria, 3800, Australia

^c ARC Centre of Excellence in Exciton Science, Clayton, Victoria, 3800, Australia



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ABSTRACT

Photoelectron emission spectroscopy in air (PESA) has been used to investigate titanium dioxide (TiO₂) deposited by atomic layer deposition (ALD). A procedure has been developed to unambiguously determine the photoemission threshold energy (also referred to as the “ionization potential”) of TiO₂ thin films, avoiding inherent artifacts due to photoelectron emission from the substrate, which supplies misleading results. This has been achieved using PESA measurements performed as a function of TiO₂ film thickness on two substrates with different work functions. We find that proper measurements of the photoemission threshold energy (including work function and ionization potential) of thin films by PESA require the use of films much thicker than their electron attenuation length (EAL). A photoemission threshold energy of 5.0 ± 0.2 eV is obtained for TiO₂ and has been attributed to a trap level due to oxygen vacancies, which lie within the band gap of the TiO₂. The analysis of the photoemission decay with film thickness also provides a method for determining a “practical” (or effective) EAL at excitation energy slightly above the photoemission threshold energy of the material. We extract an EAL for the deposited TiO₂ of 0.65 ± 0.02 nm (at 0.5 eV). The procedure can also be adopted for determining the thickness of extremely thin films, provided their thickness is smaller than their EAL.

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1. Introduction

TiO₂ is one of the world’s most produced pigments, being commonly used in paints, sunblock and toothpaste [1]. It is also a high dielectric and high band gap semiconductor ($E_g = 3.2$ eV) that has been used in applications ranging from solar cells [2,3], memory devices [4], capacitors [4,5] to self-cleaning surfaces [6]. For many of these applications, it is the unique surface structure and the desirable optoelectronic properties of TiO₂ that enable its use in such a versatile manner.

An understanding of TiO₂’s precise electronic structure is at the core of its adoption in optoelectronic applications. Typical methods for studying such structures have been based on high-vacuum, including X-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS) and Auger Electron Spectroscopy (AES) [7–11]. More recently, photoelectron spectroscopy in air

(PESA) has emerged as a suitable tool to investigate the ionization potential of semiconductors and metal oxides, and the work function of metals at the low excitation energy level range of 3–6 eV [12–17]. It has also been used as a powerful technique for the determination of the thickness of very thin SiO₂ films (1 monolayer up to about 10 nm thick) and other properties related with the interface of film/atmosphere, such as friction, oxidation, and mechanical deformation [13]. In this technique, the photon excitation energy is continuously varied and measurements are performed in air atmosphere. The incident ultraviolet (UV) light beam excites electrons from the sample to oxygen molecules in air, which are then detected by an open counter [13].

Despite the obvious advantage of PESA being performed in air, there are also a number of drawbacks. As for any photoelectron technique, PESA is very sensitive to the surface since the probed photoelectrons are extracted from a very thin layer at the surface, usually less than 10 nm. For this reason, surface contamination stemming from air exposure is a big concern. This factor can result in the ionization potential of some materials determined by PESA to differ from those reported by ultra-high vacuum

* Corresponding author.

E-mail address: marques@ifi.unicamp.br (F.C. Marques).

techniques measurements [12,13,18]. Notably, because PESA is an air based technique, it is ideal for studying metal oxide materials, which cannot undergo secondary oxidation processes during the measurement. Another potential problem related to PESA measurements is concerned with charging effects. In XPS a beam of electrons may be used to neutralize charging in insulating materials due to photoelectron emission, which is not adopted in PESA. However, the very low excitation intensities ($<1000 \text{ nW/cm}^2$ for PESA) ensure that the use of sufficiently conductive substrates, such as indium tin oxide coated glass, soda-lime glass, as well as many deposited thin films, minimize these effects.

In this work we utilize PESA to investigate the photoelectron properties of TiO_2 . This material has been previously deposited by different techniques, such as atomic layer deposition (ALD) [19,20], sputtering [21], solution processing [22] and thermal evaporation [23]. Whilst each has specific benefits, we have chosen to focus on the use of ALD due its highly controllable monolayer-by-monolayer deposition approach.

Significant work has been previously carried out towards understanding the band structure of TiO_2 using electrochemical and photoelectron spectroscopies [24,25]. From these, it is clear that this material is n-type and has a deep valence band at a value relative to vacuum of greater than 7 eV. Interestingly, the ionization potential of TiO_2 , as determined by PESA, was reported by Nakano et al. [24] as 5.2 eV. This suggests that significant electron density exists within the band-gap region, which has the capacity to dominate the optoelectronic performance of this material. In this work, we clarify the origin of this electron density.

We also propose a procedure to measure the photoemission threshold energy (also referred to as the “ionization potential”) that avoids inherent artifacts of PESA when studying very thin films. This is based on the measurement of the photoemission threshold energy of thin films with different thicknesses that have been deposited on two substrates with different work function. Additionally, we develop a procedure to extract a “practical” electron attenuation lengths (EAL), which is an important parameter in studies of solid surface using photoemission electron spectroscopy and other surface electron spectroscopies [26,27]. It is used to estimate the information depths of analyses performed by XPS/UPS/AES and is one of the correcting factors in quantitative measurements. It is also used in determining specimen thickness by electron energy loss spectroscopy (EELS) [26]. We demonstrate here that the EAL determined by PESA is also important in the determination of the work function and the ionization potential of thin films and can be used in determining the thickness of very thin film.

2. Experimental

The TiO_2 films were deposited in an ALD Cambridge Savannah S100 reactor, at a temperature of 250°C . Titanium tetrachloride (TiCl_4) and water (H_2O) were used as the precursors with pulse duration of 0.01 s and 0.05 s, respectively. A 5 s argon pulse between each precursor pulse was used to clean the chamber from the previous precursor. Every layer was 0.08 nm thick, which is consistent with the atomic layer deposition phenomenon and with previous data reported in literature for films deposited with the same precursors, TiCl_4 and H_2O [19,20].

PESA measurements were performed using an AC-2 Riken Keiki spectrometer model, which allows measurements in the 3.4–6.2 eV range. To avoid contamination from the surface after deposition, the films were kept under inert atmosphere and PESA measurements were performed within two days of film deposition. Using this procedure, one reduces contribution from impurities on the surface of the film, which has been one of the problems that give contradictory results in measurements realized by this technique.

3. Results

3.1. PESA of TiO_2

The band gap of TiO_2 is 3.2 eV, thus ultraviolet light (UV) is partially absorbed by a TiO_2 coating and, for sufficiently thin films, potentially partly absorbed by the underlying substrate. During PESA, the emitted electrons stem from both of these contributions, with that of the substrate being highly dependent on the thickness of the TiO_2 coating. In order to experimentally solve the origin of the PESA signal, we developed a procedure that consists of determining the photoemission threshold energy as a function of the film thickness from the same film, but deposited on two different substrates with different work function. This enables us to remove the contributions of the substrate. In this work we adopted aluminum (work function in the 3.0–4.4 eV range, depending on the air exposure time and the probing technique [12,13,18]) and CdTe (work function = 5.2 eV), Fig. 1. The inset in Fig. 1 displays the procedure for determining the photoemission threshold energy. It shows the emission intensity (I) as a function of the excitation energy. The signal is zero (or, better, equal to the background) for energy smaller than the ionization potential and increases linearly when one plots $I^{1/3}$ (for semiconductor, as in the inset) or $I^{1/2}$ (for metals) as a function of energy [13]. The intersection of the slope of that curve with the background supplies the photoemission threshold energy.

Fig. 1 shows that the photoemission threshold energy for very thin TiO_2 films deposited on CdTe is different from those deposited on aluminum. This arises because, for very thin films, most of the PESA signal comes from the substrate. Thus, for TiO_2 deposited on CdTe, the photoemission threshold energy of very thin films tends to be similar to the effective ionization potential obtained for solution processed CdTe ($5.2 \pm 0.2 \text{ eV}$). On the other hand, it tends to be similar to that of aluminum (4.2 eV) for very thin TiO_2 films deposited on aluminum (with an inherent native oxide coating).

As the TiO_2 film gets thicker, the PESA signal tends to originate predominantly from the film. One can observe in Fig. 1 that the photoemission threshold energy for TiO_2 films that are thicker than 60 monolayers ($\sim 5 \text{ nm}$) on both substrates approaches the same value ($5.0 \pm 0.2 \text{ eV}$). Thus, Fig. 1 indicates that there are some filled electronic levels in TiO_2 at about 5 eV. These electronic levels cannot be associated with the ionization potential of TiO_2 , since the ionization potential of pure semiconductor should be the level determined by the top of the valence band, 7.2 eV, see Fig. 2. On the other hand, it has been observed by XPS that oxygen vacancies in TiO_2 generate electronic levels close to the conduction band. The experimental data of the density of electronic states (DOS) of the oxygen vacancy band as a function of energy reported by Nakano et al. [24] is also displayed in the inset of Fig. 2. It is centered at 1.18 eV below the bottom of the conduction band (see value of E_{OV} in Fig. 2). The determination of the photoemission threshold energy determined by PESA as $5.0 \pm 0.2 \text{ eV}$, is consistent with the ionization of oxygen vacancy levels within the TiO_2 .

These defect states have been associated with important optoelectronic characteristics of TiO_2 . For instance, it is well known that TiO_2 is considered a n-type semiconductor due to its tendency for oxygen deficiency [28–30]. Oxygen vacancies in TiO_2 can, however, act as a charge trap, recombination centers and work-function pinning levels, which may strongly affect the use of films deposited by ALD in optoelectronic devices such as in solar cell [31] and solar-hydrogen generation [29]. Thus, PESA can be used to investigate oxygen vacancy states in TiO_2 to identify synthetic conditions that minimize such states for optoelectronic applications.

Another important conclusion from the analysis of the result displayed in Fig. 1 is that reliable measurements of the photoemission threshold energy (including the ionization potential and the

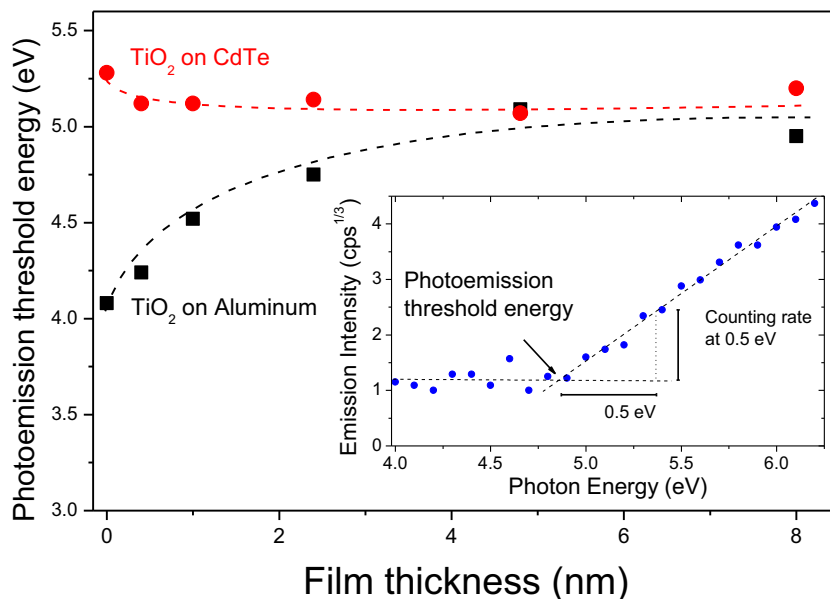


Fig. 1. Photoemission threshold energy of TiO₂, determined through PESA measurements, as a function of the thickness of the films deposited on CdTe (red circle) and aluminum (black square) substrates. The inset shows a typical PESA measurement indicating the procedure to determine the photoemission threshold energy and the counting rate for electrons emitted with 0.5 eV. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

work function) of any thin film (semiconductor or metal), requires a film much thicker than its practical electron attenuation length.

3.2. Electron attenuation length

The EAL is defined as the distance travelled by electrons in the material with a probability e^{-1} without inelastic scattering, or:

$$I = I_0 \exp\left(-\frac{d}{\lambda}\right) \quad (1)$$

where I_0 is the initial intensity and d is the film thickness. The EAL's of a large variety of elements and compounds has been widely determined adopting Eq. (1) and using mainly XPS and UPS [32]. These techniques are very powerful because of the use of an electron energy analyzer to determine the kinetic energy of photoelectrons emitted from the film/substrate composite. This allows probing of specific element inherent to the substrate, underneath the film, *i.e.* electrons that will travel through the complete thickness of the film. For this reason, EAL determined by XPS/UPS adopts a procedure by choosing appropriate substrates composed of elements with electron binding energy in the range of interest. For instance, Bain and Whitesides [33] used a thin layer of gold underneath a hydrocarbon film to determine the EAL of the film for the energies of the Au 4p_{3/2} (kinetic energy, KE = 940 eV), Au 4d_{5/2} (KE = 1151 eV) and Au 4f_{7/2} (KE = 1402 eV). Different substrates can be used to determine the EAL of any materials at different energies following the same procedure.

That is a great advantage over PESA, which does not use an electron energy analyzer. In PESA the signal is proportional to the sum of all electrons emitted with energies in the zero to the excitation energy range. Thus, one cannot select a specific kinetic energy associated with atoms from the substrate, as can be done by using standard XPS/UPS systems. Therefore, in PESA measurements one cannot adopt the procedure described above. Thus, in order to find a way to extract the EAL of a thin film, one needs to treat a single signal composed of a mixture of photoelectrons extracted from all elements of the film and of the substrate with different energies. In spite of that, we demonstrate here that one can still determine a "practical" (or effective) electron attenuation length by PESA measurement.

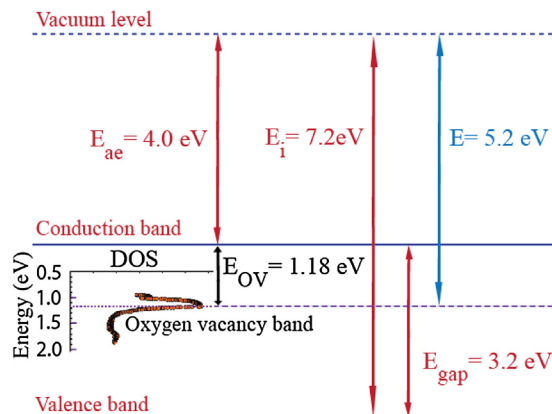


Fig. 2. Band diagram of TiO₂ showing the main electronic levels (electron affinity $E_{ae} = 4.0$ eV; ionization potential $E_i = 7.2$ eV; band gap $E_g = 3.2$ eV; oxygen vacancy level $E_{OV} = 1.18$ eV, below the bottom of the conduction band, and the expected PESA signal for the oxygen vacancy level $E = 5.2$ eV). The inset (in between the conduction and valence bands) shows the density of states (DOS), obtained by photocapacitance transient, as a function of energy for the oxygen vacancy level in TiO₂. (Adapted from Ref. [24]).

If the electron attenuation length, λ , is much smaller than the light penetration depth, $\frac{1}{\alpha}$ (where α is the absorption coefficient), *i.e.* $\lambda \ll \frac{1}{\alpha}$, the intensity of the PESA signal can be given by the equation:

$$I = I_f + (I_0 - I_f) \exp\left(-\frac{d}{\lambda}\right) \quad (2)$$

where, I_f and I_0 are constants and d is the film thickness. In this case, I_f is equivalent to the PESA signal expected from a very thick film ($d \gg \lambda$), while I_0 is the signal of the substrate only, similar to Eq. (1). The difference between Eqs. (1) and (2) is the presence of the constant term I_f and a different pre-exponential factor ($I_0 - I_f$) in Eq. (2).

Eq. (2) can be used in photoemission spectroscopy using an excitation light source for which the analyzed material has low absorption coefficient. Considering typical values of λ (1–10 nm) and α ($<10^{-6} \text{ cm}^{-1}$) reported in literature, the condition $\lambda \ll \frac{1}{\alpha}$

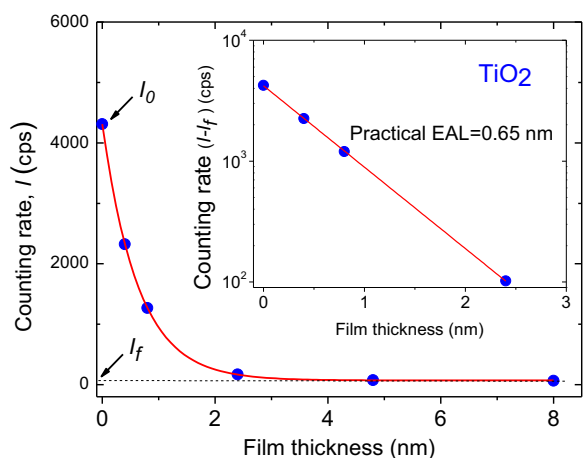


Fig. 3. Counting rate as a function of the thickness of TiO₂ films deposited on CdTe. The inset shows the procedure to extract the EAL by the slope of the curve adopting Eq. (3), supplying EAL = 0.65 nm.

is met for most materials. In case of semiconductors, this condition is met at the onset of the absorption coefficient, where α is $<10^4 \text{ cm}^{-1}$. In addition, the signal is a collection of all electrons, with different energies, emitted from the sample. However, considering the limited range of energy usually adopted in PESA, one can use Eq. (2) to extract a number that represent an effective EAL of that range of energy. In practice this energy range is limited to approximately 1 eV, after subtracting the threshold energy (see the inset in Fig. 1). That limits the EAL measurement to excitation photon energy slightly above the onset of the film absorption edge. On the other hand, that is an energy range of high interest, since it is the energy harvested in photovoltaic devices. In Fig. 3 we plot the intensity (counting rate) of the PESA signal at 0.5 eV above the ionization threshold as a function of the thickness of TiO₂.

One can rewrite Eq. (2) to obtain an equation similar to Eq. (1):

$$I - I_f = (I_0 - I_f) \exp\left(-\frac{d}{\lambda}\right) \quad (3)$$

Thus, if one plots $\ln(I - I_f)$ as a function of thickness, d , one should get a straight line, whose slope is $(-1/\lambda)$. In order to be able to apply this equation one needs the PESA intensity of a thick film, I_f , (i.e. without contribution of photoelectrons emitted by the substrate). The PESA signal of the film with thickness in the 5–8 nm range (see Fig. 1) is approximately due to the film only, representing a thick film. So, it is reasonable to assume that its intensity is approximately I_f . Taking the average of the two thickest samples, we applied Eq. (3), see the inset in Fig. 3. We observe that the experimental data in fact follows a linear relation, given support to Eq. (2). From the slope of the straight line we obtain an EAL = 0.65 nm. The same number can be extract from the raw data by adopting a fitting procedure of Eq. (2).

We could not find any other reported value of EAL for TiO₂ in literature for the sake of comparison. But there are a number of EAL's reported for other materials at low energy which are much smaller than that of the universal curve [7,34,35].

If one measure PESA of a transparent material, no signal is expected from the film, but only from the substrate. That would be the case, for instance, of SiO₂, with band gap of about 7 eV, while PESA usually works in the 3–6 eV range. In this case, the entire signal would originate from the substrate. Thus, if there is no signal from the film, $I_f = 0$, and Eq. (2) becomes equal to Eq. (1) for transparent materials.

Another important result that can be extract from Fig. 3 is that one can use it to experimentally determine the thickness of extremely thin films, thinner than their EAL. In order to do that one

needs first to determine the PESA signal of the film as a function of its thickness adopting a different technique for determining thickness, such as ellipsometry. In fact, this procedure has already been used to determine the thickness of silicon dioxide (SiO₂) [13], using a graph similar to the inset in Fig. 3. Here, we extrapolate this procedure to absorbing material as well. In addition, if one determines the EAL of the film one can extract its thickness using Eqs. (2) or (3).

4. Conclusion

The photoemission threshold energy (or effective ionization potential) of TiO₂ deposited by ALD was obtained by PESA through the adoption of a procedure consisting of using TiO₂ films with varied thickness on two different substrates that possessed different work functions. A photoemission threshold energy value of $5.0 \pm 0.2 \text{ eV}$ was determined, which was attributed to oxygen vacancy levels within the band gap and not to the ionization potential (top of the valence band) of TiO₂, as reported previously. The existence of this energy state within ALD deposited TiO₂ can have a profound impact on its use within optoelectronic applications, for instance, it can act as charge trap, recombination center and work-function pinning level. The use of PESA provides a convenient approach to study such low-electron density levels.

Beyond the identification of this electronic state, we determined a formalism to extract the electron attenuation length using PESA. For this purpose, we showed that one requires the attenuation length at the desired energy to be much smaller than the correspondent light penetration depth. This condition can be met through the use of an excitation source with small energy, slightly above the photoemission threshold. Adopting this formalism, we have experimentally extracted a practical attenuation length for TiO₂ deposited by ALD of $\sim 0.65 \text{ nm}$. In addition, this procedure can also be used for the determination of extremely thin films (absorbing or transparent), as long as their thickness is smaller than their corresponding EAL.

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References

- [1] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, Chem. Rev. 107 (2007) 2891–2959, <http://dx.doi.org/10.1021/cr0500535>.
- [2] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films, Nature 353 (1991) 737–740, <http://dx.doi.org/10.1038/353737a0>.
- [3] H. Yu, S. Zhang, H. Zhao, G. Will, P. Liu, An efficient and low-cost TiO₂ compact layer for performance improvement of dye-sensitized solar cells, Electrochim. Acta 54 (2009) 1319–1324, <http://dx.doi.org/10.1016/j.electacta.2008.09.025>.
- [4] S.K. Kim, W.-D. Kim, K.-M. Kim, C.S. Hwang, J. Jeong, High dielectric constant TiO₂ thin films on a Ru electrode grown at 250 °C by atomic-layer deposition, Appl. Phys. Lett. 85 (2004) 4112–4114, <http://dx.doi.org/10.1063/1.1812832>.
- [5] K.M. Kim, B.J. Choi, Y.C. Shin, S. Choi, C.S. Hwang, Anode-interface localized filamentary mechanism in resistive switching of TiO₂ thin films, Appl. Phys. Lett. 91 (2007) 12907, <http://dx.doi.org/10.1063/1.2749846>.
- [6] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Light-induced amphiphilic surfaces, Dis. Colon Rectum. 19 (1997) 1–24, <http://dx.doi.org/10.1038/41233>.
- [7] D. Briggs, M.P. Seah, Practical Surface Analysis, Auger and X-ray Photoelectron Spectroscopy, 2nd ed., Wiley, Michigan, 1990, p. 186.
- [8] C.J. Powell, W.S.M. Werner, W. Smekal, Refined calculations of effective attenuation lengths for SiO₂ film thicknesses by x-ray photoelectron spectroscopy, Appl. Phys. Lett. 89 (2006) 252116, <http://dx.doi.org/10.1063/1.2422903>.

- [9] M.P. Seah, S.J. Spencer, Energy dependence of the electron attenuation length in silicon dioxide, *Meas. Sci. Technol.* 22 (2011) 115602, <http://dx.doi.org/10.1088/0957-0233/22/11/115602>.
- [10] A.W. Blackstock, R.H. Ritchie, R.D. Birkhoff, Mean free path for discrete electron energy losses in metallic foils, *Phys. Rev.* 100 (1955) 1078–1083, <http://dx.doi.org/10.1103/PhysRev.100.1078>.
- [11] D.E. Eastman, Photoelectric work functions of transition, rare-earth, and noble metals, *Phys. Rev. B* 2 (1970) 1–2, <http://dx.doi.org/10.1103/PhysRevB.2.1>.
- [12] H. Kirihaata, M. Uda, Externally quenched air counter for low-energy electron emission measurements, *Rev. Sci. Instrum.* 52 (1981) 68–70, <http://dx.doi.org/10.1063/1.1136448>.
- [13] M. Uda, Open counter for low energy electron detection, *Jpn. J. Appl. Phys.* 24 (1985) 284, <http://dx.doi.org/10.7567/JJAPS.24S4.284>.
- [14] D. Yamashita, Y. Nakajima, A. Ishizaki, M. Uda, Photoelectron spectrometer equipped with open counter for electronic structures of organic materials, *J. Surf. Anal.* 14 (2008) 433–436 <http://www.sas.jp/JSA/CONTENTS/vol.14.4/Vol.14No.4/Vol.14No.4.433-436.pdf>.
- [15] K. Tada, S. Takaishi, M. Onoda, In-situ measurement of oonization potential of conjugated polymer during electrochemical doping using photoelectron spectroscopy in air, *Appl. Phys. Express* 1 (2008) 71801, <http://dx.doi.org/10.1143/APEX.1.071801>.
- [16] J. Jasieniak, M. Califano, S.E. Watkins, Size-dependent valence and conduction band-edge energies of semiconductor nanocrystals, *ACS Nano* 5 (2011) 5888–5902, <http://dx.doi.org/10.1021/nn201681s>.
- [17] Z. Yu, I.R. Perera, T. Daeneke, S. Makuta, Y. Tachibana, J.J. Jasieniak, A. Mishra, P. Bäuerle, L. Spiccia, U. Bach, Indium tin oxide as a semiconductor material in efficient p-type dye-sensitized solar cells, *NPG Asia Mater.* 8 (2016) e305, <http://dx.doi.org/10.1038/am.2016.89>.
- [18] M. Uda, Y. Nakagawa, T. Yamamoto, M. Kawasaki, A. Nakamura, T. Saito, K. Hirose, Successive change in work function of Al exposed to air, *J. Electron Spectrosc. Relat. Phenom.* 88–91 (1998) 767–771, [http://dx.doi.org/10.1016/S0368-2048\(97\)00237-5](http://dx.doi.org/10.1016/S0368-2048(97)00237-5).
- [19] J. Aarik, A. Aidla, T. Uustare, K. Kukli, V. Sammelselg, M. Ritala, M. Leskelä, Atomic layer deposition of TiO₂ thin films from TiI₄ and H₂O, *Appl. Surf. Sci.* 193 (2002) 277–286, [http://dx.doi.org/10.1016/S0169-4332\(02\)00497-X](http://dx.doi.org/10.1016/S0169-4332(02)00497-X).
- [20] J. Aarik, A. Aidla, T. Uustare, V. Sammelselg, Morphology and structure of TiO₂ thin films grown by atomic layer deposition, *J. Cryst. Growth* 148 (1995) 268–275, [http://dx.doi.org/10.1016/0022-0248\(94\)00874-4](http://dx.doi.org/10.1016/0022-0248(94)00874-4).
- [21] C.J. Tavares, J. Vieira, L. Rebouta, G. Hungerford, P. Coutinho, V. Teixeira, J.O. Carneiro, A.J. Fernandes, Reactive sputtering deposition of photocatalytic TiO₂ thin films on glass substrates, *Mater. Sci. Eng. B* 138 (2007) 139–143, <http://dx.doi.org/10.1016/j.mseb.2005.11.043>.
- [22] A.M. Peiró, J. Peral, C. Domingo, X. Domènech, J.A. Ayllón, Low-temperature deposition of TiO₂ thin films with photocatalytic activity from colloidal anatase aqueous solutions, *Chem. Mater.* 13 (2001) 2567–2573, <http://dx.doi.org/10.1021/cm0012419>.
- [23] M.W. Pyun, E.J. Kim, D.-H. Yoo, S.H. Hahn, Oblique angle deposition of TiO₂ thin films prepared by electron-beam evaporation, *Appl. Surf. Sci.* 257 (2010) 1149–1153, <http://dx.doi.org/10.1016/j.apsusc.2010.08.038>.
- [24] Y. Nakano, T. Morikawa, T. Ohwaki, Y. Taga, Origin of visible-light sensitivity in N-doped TiO₂ films, *Chem. Phys.* 339 (2007) 20–26, <http://dx.doi.org/10.1016/j.chemphys.2007.05.031>.
- [25] V.E. Henrich, G. Dresselhaus, H.J. Zeiger, Observation of two-dimensional phases associated with defect states on the surface of TiO₂, *Phys. Rev. Lett.* 36 (1976) 1335–1339, <http://dx.doi.org/10.1103/PhysRevLett.36.1335>.
- [26] C.-W. Lee, Measurement of mean free paths for inelastic electron scattering of Si and SiO₂, *J. Electron Microsc. (Tokyo)* 51 (2002) 143–148, <http://dx.doi.org/10.1093/jmicro/51.3.143>.
- [27] A. Jablonski, C.J. Powell, Relationships between electron inelastic mean free paths, effective attenuation lengths, and mean escape depths, *J. Electron Spectrosc. Relat. Phenom.* 100 (1999) 137–160, [http://dx.doi.org/10.1016/S0368-2048\(99\)00044-4](http://dx.doi.org/10.1016/S0368-2048(99)00044-4).
- [28] R.N. Blumenthal, P.W. Lee, R.J. Panlener, Studies of the defect structure of nonstoichiometric cerium dioxide, *J. Electrochem. Soc.* 118 (1971) 123, <http://dx.doi.org/10.1149/1.2407923>.
- [29] J. Nowotny, T. Bak, M. Nowotny, L. Sheppard, Titanium dioxide for solar-hydrogen II. Defect chemistry, *Int. J. Hydrogen Energy* 32 (2007) 2630–2643, <http://dx.doi.org/10.1016/j.ijhydene.2006.09.005>.
- [30] M.K. Nowotny, P. Bogdanoff, T. Ditttrich, S. Fiechter, A. Fujishima, H. Tributsch, Observations of p-type semiconductivity in titanium dioxide at room temperature, *Mater. Lett.* 64 (2010) 928–930, <http://dx.doi.org/10.1016/j.matlet.2010.01.061>.
- [31] W. Niu, X. Li, S.K. Karuturi, D.W. Fam, H. Fan, S. Shrestha, L.H. Wong, A.I.Y. Tok, Applications of atomic layer deposition in solar cells, *Nanotechnology* 26 (2015) 64001, <http://dx.doi.org/10.1088/0957-4484/26/6/064001>.
- [32] V.W. Ballarotto, M. Breban, K. Siegrist, R.J. Phaneuf, E.D. Williams, Photoelectron emission microscopy of ultrathin oxide covered devices, *J. Vac. Sci. Technol. B* 20 (2002) 2514–2518, <http://dx.doi.org/10.1116/1.1525007>.
- [33] C.D. Bain, G.M. Whitesides, Attenuation lengths of photoelectrons in hydrocarbon films, *J. Phys. Chem.* 93 (1989) 1670–1673, <http://dx.doi.org/10.1021/j100341a095>.
- [34] F. Offi, S. Iacobucci, L. Petaccia, S. Gorovikov, P. Vilmercati, A. Rizzo, A. Ruocco, A. Goldoni, G. Stefani, G. Panaccione, The attenuation length of low energy electrons in Yb, *J. Phys. Condens. Matter* 22 (2010) 305002, <http://dx.doi.org/10.1088/0953-8984/22/30/305002>.
- [35] F. Gerken, A.S. Flodström, J. Barth, L.L. Johansson, C. Kunz, Surface core level shifts of the lanthanide metals Ce^{5s}–Lu⁷ⁱ: a comprehensive experimental study, *Phys. Scr.* 32 (1985) 43–57, <http://dx.doi.org/10.1088/0031-8949/32/1/006>.