



Full Length Article

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

ARTICLE INFO

Article history:

Received 18 April 2017

Received in revised form 24 May 2017

Accepted 5 June 2017

Keywords:

Photoelectron emission spectroscopy in air

Atomic layer deposition

Ionization potential

Electron attenuation length

Titanium dioxide

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.

© 2017 Elsevier B.V. All rights reserved.

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 nW/cm² 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 TiO₂. 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 TiO₂ 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 TiO₂, 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 TiO₂ films were deposited in an ALD Cambridge Savannah S100 reactor, at a temperature of 250 °C. Titanium tetrachloride (TiCl₄) and water (H₂O) 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, TiCl₄ and H₂O [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 TiO₂

The band gap of TiO₂ is 3.2 eV, thus ultraviolet light (UV) is partially absorbed by a TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 ± 0.2 eV). On the other hand, it tends to be similar to that of aluminum (4.2 eV) for very thin TiO₂ films deposited on aluminum (with an inherent native oxide coating).

As the TiO₂ 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 TiO₂ films that are thicker than 60 monolayers (~ 5 nm) on both substrates approaches the same value (5.0 ± 0.2 eV). Thus, Fig. 1 indicates that there are some filled electronic levels in TiO₂ at about 5 eV. These electronic levels cannot be associated with the ionization potential of TiO₂, 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 TiO₂ 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 ± 0.2 eV, is consistent with the ionization of oxygen vacancy levels within the TiO₂.

These defect states have been associated with important optoelectronic characteristics of TiO₂. For instance, it is well known that TiO₂ is considered a n-type semiconductor due to its tendency for oxygen deficiency [28–30]. Oxygen vacancies in TiO₂ 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 TiO₂ 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

Download English Version:

<https://daneshyari.com/en/article/5347567>

Download Persian Version:

<https://daneshyari.com/article/5347567>

[Daneshyari.com](https://daneshyari.com)