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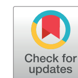
Electromodulation of wide-bandgap semiconductors



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ABSTRACT

In this work, we explored the functionality of the electromodulation technique to determine the energy gaps of wide band gap oxides which lie in the ultraviolet region. Oxides like Er_2O_3, Ga_2O_3, HfO_2, Ta_2O_5 and ZrO_2 were analyzed in this study with their band gaps determined through the spectrophotometric as well as with the electromodulation method. Contrary to the spectrophotometric method, where extrapolation was required to find the band gap of the material, the electromodulation spectrum of each oxide clearly revealed the critical points associated with the optical transitions in the material. Keeping in view the large variations produced by the spectrophotometric method in the band gap values due to extrapolation, and the potential limitations faced by other band gap determination techniques, like electron energy loss spectroscopy, x-ray photoelectron spectroscopy and internal photoemission, in terms of their availability, demands of ultra-high vacuum and low signal to noise ratio, this study proves to be valuable in considering the electromodulation as an efficient substitute for the above mentioned experimental techniques to determine the energy gaps of wide band gap materials.

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1. Introduction

Wide band gap oxides such as Er_2O_3, Ga_2O_3, HfO_2, Ta_2O_5 and ZrO_2 constitute a special class of semiconductors which found importance in several optical, photocatalytic, electronics and optoelectronics applications. For example, because of their high thermal stability and wide spectral transparency, they can be efficiently used in optical applications like beam splitters, filters, antireflection coatings [1] as well as selective absorber coating materials for solar thermal applications [2]. The favorable positions of their valence band maxima and conduction band minima make some of these wide band gap oxides prominent candidates for water splitting applications [3–5]. Moreover, due to their characteristics of high dielectric constant and large band gap, these oxides are being considered as an efficient solution to the large leakage current problem faced by silicon-based CMOS devices [6–9]. The large energy gap of these oxides provides high band offsets between the stacking of oxide and metals and results in a low leakage current [10]. Therefore, knowledge of the band gap for these oxides is an important factor prior to their use in CMOS based electronics applications.

Although, the band gap of a material depends on several factors such as its fabrication method, nature of the synthesized product (bulk, thin film or nanostructures), and its crystal structure. However, in the case of wide band gap oxides, the existence of the band gap in the ultraviolet (UV) region poses a serious concern on the validity of the experimental techniques used to determine the band gaps. Table 1 lists the band gap values of the above mentioned oxide thin films obtained through different techniques.

It can be seen from Table 1 that significant variations occur in the reported band gap values of these oxides. Besides the sample preparation method, nature of synthesis, and crystal structure, the other important factor which results these variations is the inadequacy of the experimental techniques used to find the band gap of these oxides. For example, the spectrophotometric technique may not be an acceptable tool for measuring the band gaps of reduced dimensional structures like thin films, quantum dots or nanocrystals. This is because of the fact that the extrapolation associated with this method is not as good for reduced dimensional forms as it is for the bulk form of the materials [65]. Spectroscopic

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ellipsometry (SE) is another widely available technique to determine the band gap of materials. However, its potential in determining the band gap is severely limited due to the lack of a standard band gap extraction model from the data. In fact, it was found by Di et al. [10] on the basis of SE analysis, that employing different models can lead to a variation of more than 69% in the band gap values of HfO_2 films. Hence, retrieving the band gap value from the ellipsometry is always compromised. Besides the extrapolation and the lack of a standard model, the existence of the band gaps of the above mentioned oxides within the UV region turned attention to some more sophisticated techniques which can perform efficiently in the UV region. These include electron energy loss spectroscopy (EELS) [17,33,34,56,61,62], internal photoemission (IPE) [45], and x-ray photoelectron spectroscopy (XPS) [30,31]. However, these techniques are not widely available, often demand ultra-high vacuum to achieve the required measurements, and suffer large background problems in the analysis due to multiple physical phenomena such as scattering of electrons having energies less than the fundamental transition energy [66].

While considering the problems of the experimental techniques related to band gap measurement of wide band gap oxides, the insufficiency related to the theoretical techniques cannot be ruled out. Theoretical calculations based on density functional theory (DFT) are considered as efficient tools to predict the nature of transitions involved in a material. However, DFT based calculations like generalized gradient approximation (GGA) or local density approximation (LDA) always underestimate the band gap of a material by more than 30% [67]. Therefore, an appropriate approximation or functional approach is always required to overcome this band gap underestimation. So far, numerous studies based on DFT calculations were performed using different approximations or functional approaches to compute the accurate band gaps of wide band gap oxides. Some of these include GGA plus on-site coulomb interaction (GGA + U) [68–71] or hybrid density functionals (PBE, HSE, B3LYP) [3,72–74]. Even with these more accurate functional approaches, the band gap value is not accounted as a true one due to the problem of ignorance of derivative discontinuity [3,67].

The absence of derivative discontinuity from the optical response of a material is the fundamental problem that also leads to the limitations in the experimental methods used to measure the band gap of a material. Optical transitions related to the band gap or defect level transitions appear as a derivative discontinuity or singularity in the optical response of a material, and they are also known as the critical points of the material. In the case of experimental methods like spectrophotometry or ellipsometry, these critical points do not have any physical location in the optical spectra, and hence, the extraction of such critical points is graphical or model-dependent. In fact, it was found by Feng et al. [65] that the model of finding the band gap is itself adjusted to find the location of the critical point (band gap in this case) in the absorption coefficient of the material. The EELS based techniques can reveal these critical points in terms of sharp edges or peaks on their intensity spectrum [75]. However, these points are extremely suppressed by the background of the spectrum [32,66]. Moreover, in some cases, the observed EELS spectra of the wide band gap oxides spread over wider energies [55,76]. This leads to the problem of indistinguishability of the fundamental transition from the defect level transition that may exist close to it.

Due to the limitations suffered by the above mentioned experimental techniques, and the fundamental problem of the lack of information about the derivative discontinuity faced by the theoretical as well as the experimental methods, another technique is demanded to elucidate the critical points and thus determine the band gaps of materials. Electromodulation (EM) has been used as an independent technique for the accurate determination of the band gaps of semiconductors. In this technique, a periodic perturbation in the form of an electric field is applied to the sample, which consequently destroys the crystal translational symmetry [77]. As a result, the optical response of the material, in the presence of the electric field, exhibits sharp third derivative-like features, with strongly enhanced critical points and highly suppressed featureless background [78]. This property makes EM more robust as compared to other techniques in a sense that the observed spectra correspond to the optical transitions around the critical points with no background interference. If the changes in the reflected light are detected due to the electric field, the method is called electroreflectance (ER). The ER mode of EM avoids complications related to the passage of light through the material, especially when opaque metallic electrodes are used to apply the perturbing electric filed. The sensitivity of the technique to the surface of the material is eliminated by the fact that the electric field is only efficient at the critical points. The high resistive nature of the wide band gap oxides creates an additional difficulty in calculating their band gaps by the spectrophotometric methods, where only light is used as an external perturbation, and might not be as efficient to lift the electrons from the valence band into the conduction band. If an electric field is combined with the photon energies as a source of perturbation, it accelerates the electrons against the high resistive nature of the material to enable the optical transitions. Therefore, a large amplitude of the electric field is an important requirement to measure the band gap of the wide band gap oxides. In case of ER, the different geometries which are designed to achieve different modes of electroreflectance, such as Transverse electroreflectance or surface barrier electroreflectance, provide a high flexibility for achieving the necessary strength and direction of the electric field [77]. Taking into consideration the above mentioned advantages offered by ER over other experimental band gap determination techniques, we employed the ER technique for the determination of critical points associated with the wide band gap oxides listed in Table 1, which serve as examples of the superiority of the technique and its applicability to other wide band gap materials. The materials studied were in thin film form, which enabled high magnitudes of the electric field of the order $10^4 - 10^5$ V/cm. To the best of our knowledge, this is the first application of this technique to this class of materials.

Table 1
A brief survey of the reported band gap values of thin films of wide band gap metal oxides obtained through different experimental methods.

Material	Band gap value (eV)	Technique	Ref.
Erbium oxide (Er_2O_3)	4.17–5.8	SP	[11,12]
	4.7–5.45	SE	[13,14]
	7.6	XPS	[15]
Gallium oxide (Ga_2O_3)	4.46–4.74	SE	[16]
	4.5–4.6	EELS	[17–19]
	4.63–5.16	SP	[20–29]
Hafnium oxide (HfO_2)	5.25	XPS	[30,31]
	5.25–5.7	EELS	[6,32–35]
	5.27–5.82	SE	[2,36–38]
	5.45–5.82	SP	[1,39–44]
	5.6	IPE	[45]
Tantalum oxide (Ta_2O_5)	4.13–5.43	SE	[46–49]
	4.2–4.56	SP	[50–54]
	4.4–4.6	EELS	[55,56]
Zirconium oxide (ZrO_2)	3.85–6.07	SP	[1,7,57–60]
	4–5.3	EELS	[34,61,62]
	4.93–5.2	SE	[63,64]

SP: spectrophotometry, **SE**: spectroscopic ellipsometry, **EELS**: electron energy loss spectroscopy, **IPE**: internal photoemission, **XPS**: x-ray photoelectron spectroscopy.

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