Optical properties and electronic band lineup on Si of amorphous zirconium modified $\text{Bi}_2\text{Zn}_{2/3}\text{Nb}_{4/3}\text{O}_7$ thin films

Sudheendran Kooriyattil^{1,2}, Shojan P. Pavunny^{1*}, Esteban Fachini³, and Ram. S. Katiyar^{1*}

¹*Department of Physics and Institute for Functional Nanomaterials, University of Puerto Rico, P.O. Box 70377, San Juan, PR 00936-8377, USA*

²*Department of Physics, Sree Kerala Varma College, Thrissur-680011, India*

³*General Studies College, University of Puerto Rico, San Juan, PR 00931, USA*

Abstract

We have investigated optical and band alignment properties of pulsed laser deposited amorphous thin films of bismuth based monoclinic pyrochlore $\text{Bi}_2\text{Zn}_{2/3-x/3}\text{Nb}_{4/3-2x/3}\text{Zr}_x\text{O}_7$ (Zr-BZN) where $x=0.4$ on quartz and silicon substrates, respectively. The optical parameters, such as complex refractive index ($n - jk$), energy bandgap (E_g), complex dielectric function ($\epsilon' - j\epsilon''$), and complex conductivity ($\sigma' - j\sigma''$) and associated dispersion parameters were estimated from the UV-Visible transmission spectra. The analysis of refractive index dispersion confirmed the Wemple–Di Domenico single-effective-oscillator model for the direct inter-band transition. The valence band of Zr-BZN is found to be ~ 0.1 eV above that of silicon. The numerical values for conduction band offset ΔE_C on silicon and optical bandgap E_g were estimated to be ~ 2.46 eV and ~ 3.46 eV, respectively for Zr-BZN samples. We determined a complete electron band offset dominated type II staggered band lineup of this high-k dielectric/semiconductor heterostructure, where a straight forward spatial confinement of electrons and holes is facilitated. These important results can play critical role and provide key insight for the practical applications of Zr-BZN material, especially in CMOS (complementary metal-oxide-semiconductor) logic and memory devices.

Keywords: Optical properties; Band offset; Amorphous thin films; High-k dielectric

*Corresponding authors: electronic mail rkatiyar@hpcf.upr.edu (R.S.K.), shojanpp@gmail.com (S.P.P.); Tel-787 751 4210; Fax-787 764 2571

1. Introduction

Transparent electronic materials have gained considerable research interest for future technological developments, such as electronic sheets and flexible displays [1,2,3]. Transparent thin film transistors based on wide bandgap materials were reported more than a decade ago which lead to enhanced research and development activities on transparent insulating oxides for gate insulator applications [4]. The performance and stability of the device depends upon the quality of the gate insulator being used. Moreover, reduction of the gate oxide thickness has emerged as the most difficult challenge associated with the device scaling. Ultra-thin gate dielectric layers suffer from unacceptably high amount of tunnel leakage currents [5,6]. The gate leakage must be reduced without compromising the current drive (I_{ON}) of the transistor. Consequently, it was necessary to replace the conventional gate insulator, SiO_2 , with a "high-k" (high permittivity) material for low power consumption and dense integration [7]. According to the international technology road map for semiconductors, linear dielectrics with permittivity greater than 25 will be needed by the end of this decade in order to simultaneously meet the aggressive scaling goals and to keep the gate leakage currents within the tolerable limits ($10 \mu A/cm^2$) [8]. Introduction of new material systems, in addition to continuous process control improvement are expected to break the scaling barriers.

Bi_2O_3 - ZnO - Nb_2O_5 (BZN) based pyrochlore system with the general formula $A_2B_2O_7$ is known to have high dielectric constant (ϵ') and relatively low dielectric loss which make them a potential class of materials for microelectronic and microwave applications [9,10]. Monoclinic $Bi_2Zn_{2/3}Nb_{4/3}O_7$ (m-BZN) is one of the prominent compositions in this material system which exhibit both temperature and field independent dielectric properties [11,12]. Recently amorphous bismuth zinc niobate thin films have gained considerable attention due to their potential application in thin film transistors as a transparent high-k gate insulator [13]. It has been reported that the dielectric properties of this compound can be further improved by suitable substitution at A or B sites [14,15]. Ideal gate dielectric needs to have relatively high dielectric constant and a wide bandgap, the later parameter should be large enough than that of the semiconductor channel materials to achieve a desirable conduction and valence band offsets.

The bandgap and the alignment of bands with semiconductor channel are the two important parameters which determine the ability of the alternative high-k material in acting as an efficient energy barrier for charge carriers in CMOS devices [16,17,18]. Ideally, the band offset should be more than 1 eV to block current conduction that may occur by tunnelling through the dielectric (either Fowler–Nordheim or direct tunnelling), excitation to the oxide band states (Schottky emission) or by hopping through via defect states (Poole–Frenkel) and to avoid the unwanted shifts in the effective flat-band voltage and threshold voltage of the transistor device [19-20,21,22]. In addition a precise estimation of the index of refraction and extinction coefficient is essential for the better understanding of the electronic structure of the gate oxide materials as well as for screening their potential technological applications in optics and microelectronics [23]. Even though there are many reports on integration of bismuth zinc niobate thin films into silicon devices [24,25], surprisingly there is no systematic experimental study available in literature on the energy band alignment of this class of electronic materials with Si. In this paper, we report fabrication, characterization, and the interfacial band line-up properties of amorphous Zr-BZN thin films fabricated by pulsed laser deposition (PLD) on p-type silicon (100) substrates in order to critically evaluate the feasibility of employing Zr-BZN as a potential high-k dielectric in logic and memory devices. Thin films grown on quartz substrates were characterized using UV/visible spectroscopy and their optical parameters such as bandgap, refractive index, extinction coefficient, etc. were determined.

2. Experimental

Ceramic target of Zr-BZN was prepared using solid state reaction route and the details of the procedure have been reported earlier [26]. In order to estimate the optical parameters and the band offset, thin films of Zr-BZN were deposited on quartz (0001) and p-Si (100) substrates using an excimer (KrF) laser (LPX-210 Lambda Physik GmbH) configured for 248 nm radiation with a pulse energy of 250 mJ (energy density 2 J/cm^2) and operating at a pulse repetition rate of 10 Hz. The PLD chamber was evacuated to a base vacuum of $\sim 5 \times 10^{-6}$ mTorr prior to the depositions and during depositions, the high purity oxygen partial pressure in the chamber and the substrate temperature were maintained at 50 mTorr and 300 °C, respectively. In this work, we report on three different Zr-BZN films with thicknesses 650 nm, 500 nm, and 350 nm on quartz deposited using 3000, 2500, and 2000 number of pulses, respectively. The reflection high-

energy electron diffraction (RHEED) patterns were recorded *in situ* at 24 keV beam energy and 1.4 A filament current after deposition by one ($\sim 2 \text{ \AA}/\text{shot}$ growth rate), two, three, etc. laser ablation shots and after completion of deposition to identify the growth and crystal structure of the Zr-BZN thin films. The structural properties of the films were examined by x-ray diffraction (XRD) method by using Cu-K α 1 radiation from a Rigaku D/Max Ultima III x-ray diffractometer functioning in Bragg-Brentano geometry. The surface morphology of the films was investigated by atomic force microscopy (AFM, Veeco). The transmission spectra in 190–800 nm wavelength range were recorded for the samples and the bare substrate at normal incidence with background and zero scans using a double beam, Perkin-Elmer UV-VIS spectrometer. Refractive index and extinction coefficient were estimated following a procedure reported by Manifacier *et al.* [27]. In this method, envelopes are drawn through the maxima and minima of the transmittance spectra and the calculation proceeds on the assumption that these envelopes correspond to the transmittance of integral half wave and quarter wave thicknesses. The bandgap was calculated from Tauc plot. To determine the band alignment of Zr-BZN with Si, amorphous films were deposited on the hydrofluoric acid (HF) last dipped p-Si(100) substrates having $\sim 0.1\text{--}1 \text{ }\Omega\text{cm}$ resistivity by PLD with the same deposition parameters as for quartz. High-resolution x-ray photoelectron spectroscopy (XPS) measurements were performed at photoelectron take-off angles of 45° with a PHI 5600 Multisystem to record the shallow core level and valence band spectra of HF treated Si and Zr-BZN/Si heterostructures of dielectric thicknesses $\sim 3 \text{ nm}$ and $\sim 70 \text{ nm}$, respectively. Al K α (1486.6 eV) radiation from a monochromatized x-ray source operating at 350 W was used. The base vacuum during measurements was maintained in the 5×10^{-10} Torr range. Multiple scans were carried out in order to obtain better spectra and the charging effects were corrected using the neutralizer. All XPS spectra were calibrated by referencing to the extrinsic carbon 1s core-level peak position at 285 eV to address the sample charging issues.

3. Results and discussion

3.1. Structural and microstructural characteristics

RHEED pattern along 0001 azimuth of bare quartz substrate kept at deposition conditions prior to commencement of laser ablation are displayed in Fig. 1 (a) showing visible Kikuchi lines. Figs 1 (b), (c), and (d) demonstrate the *in situ* evolution of featureless RHEED image corresponding to the disordered phase after the growth of Zr-BZN by one, two, and three laser

pulses, respectively. The continued amorphous pattern at the end of ~500 nm thick deposition can be seen in Fig. 1 (e). The x-ray diffraction patterns for the Zr-BZN thin films are shown in Fig. 2 (a) – (c) along with that of the bulk ceramic target [Fig. 2 (e)] used for high energy laser plasma ablation. The observed x-ray diffraction patterns of the Zr-BZN polycrystalline ceramic target showed the formation of a monoclinic pyrochlore phase with $C2/c$ space group. The XRD spectra of the quartz (0001) substrate used for deposition are also shown in Fig. 2 (d) for comparison. The obtained XRD scans of Zr-BZN thin films [Fig. 2 (a) – (c)] do not have any Bragg diffraction peaks other than that of quartz substrate which are represented by the ‘*’ symbol. This confirmed the findings from RHEED study that as fabricated layers used in this investigation are in amorphous phase with higher entropy and weak inter atomic interaction. From a careful look at these diffractograms, one can conclude that the low intense peaks at $2\theta=33.2^\circ$ and 45.5° appearing in thinner films of thicknesses 500 nm and 350 nm and the intense peak present at $2\theta=50.7^\circ$ in all three films belong to quartz substrate. It is generally observed that as the thickness of the disordered film (quantity of Zr-BZN) increases, the amount of x-ray signals (peak intensity) collected from the substrate decreases. The reason for the quartz peaks not having the same intensity ratios in Figs (c) and (d) is probably due to the difference in amount/degree of slight misalignment of the surfaces of the two thin films with respect to x-ray beam during measurement.

The microstructure of these films measured using atomic force microscopy is presented in Fig. 3. AFM plane views ($XY = 5\mu\text{m} \times 5\mu\text{m}$ and $Z = 15\text{ nm}$) demonstrate smooth surface topography of the samples owing to their disordered phase even though particulates are present due to inherent shortcoming of the PLD method employed. The root mean square (RMS) roughness of the dielectric layers of thickness 350 nm, 500 nm, and 650 nm were 0.37 nm, 0.55 nm, and 0.61 nm, respectively. These figures confirm that the films are essentially smooth enough for the error free determination of the optical parameters [28] and are grown perfectly continuous on quartz substrate. No significant dependence of roughness on thickness was observed for these disordered networks.

3.2. *Optical characteristics*

The three phase (air/film/substrate) optical model structure Air/a-Zr-BZN layer/ SiO_2 (0001) employed is depicted in inset of Fig. 4. The room temperature UV-Visible spectral transmission

curves of the amorphous Zr-BZN thin films along with that of quartz substrate are shown in Fig. 4. The selection of the substrate was based on the fact that it possesses a wider bandgap (8.9 eV) [29] than the material under investigation and hence no absorption edge (the abrupt transition from the weak absorption/high transmission at long wavelength to strong absorption/low transmission at short wavelength) will be present from it in the measurement window of 1.5 – 4 eV. All three transmission spectra showed oscillations (Fabry-Perot resonances) which were originated due to interference at the air- and substrate-film interfaces. The sharp fall in transmission and disappearance of the fringes at the shorter wavelengths are due to fundamental absorption by the dielectric films. The deposited films were quite transparent (80%) in the visible region. The spectral transmission curves show a small dependence of the optical band edge on the thickness of the films. The absorption edge shifted to the longer wavelength region with increasing layer thickness indicating that the optical bandgap E_g decreased with increasing thickness.

Optical bandgap E_g of the thin film material can be determined from the absorption coefficient α , which in turn can be calculated from the measured transmission spectra as a function of incident photon energy E for a direct allowed transition. The scattering losses dominate the fundamental absorption at shorter wavelength regions close to the optical bandgap. For this region the absorption coefficient α at a given wavelength λ can be written as [30],

$$\alpha = -\ln(T/d), \quad (1)$$

where, d is the film thickness and T is the transmittance at λ . The thickness range of all three films studied were selected considering the following two criterion [31]: (1) thickness of the layer must be ≤ 1000 nm in order to have an absorption coefficient of $\geq 10^5$ cm⁻¹ for an accurate estimation of band gap and (2) films must be thick enough to provide ample amount of oscillations (Fabry-Perot resonances) in the transmission spectra for the error free determination of complex index of refraction ($n - jk$).

The direct bandgap (E_g), a figure of merit in identifying an alternative high-k dielectric was calculated from the modified square law based bandgap calculations using $(\alpha h\nu)^2$ versus $(h\nu)$ plots, by extrapolating the linear portion of the absorption to the x-axis as shown in Fig. 5. It can be observed that the absorption edge shifts towards higher energy (blue shift) with the decrease

in layer thickness which indicates an increase in bandgap. The calculated bandgap for the film of thickness 640 nm was 3.40 eV while it was 3.48 eV and 3.50 eV for the films of thicknesses 500 nm and 400 nm, respectively. The observed bandgap was comparable with the earlier reported numerical values for similar compositions [32].

The changes in energy bandgap could occur due to many reasons, such as lattice strain, grain size, presence of impurities, structural defects, and disorders [33]. All of the films used for the current study were grown under the same process parameters and the films are amorphous in nature. So, we can easily rule out the effects of strain, grains, and impurities to the observed changes in the bandgap.

The measurement of the band edge is a versatile tool to estimate the level of frozen in structural disorder in amorphous solids. It reflects the local atomic structure undetected by the XRD. For these disordered materials, the intrinsic absorption edge contains two separate regions named as (i) Tauc region and (ii) Urbach region described as follows [34].

The Tauc region is described by the equation

$$\alpha h\nu = B(h\nu - E_g)^n, \quad (2)$$

where, $n = 0.5, 1.5, 2$ or 3 for allowed direct, forbidden-direct, allowed-indirect and forbidden-indirect electronic transitions, E_g represents the optical gap which is close to the energy bandgap, the energy separation between the conduction and valence band mobility edges, and the constant B , also known as the transition matrix element, is given by the relation:

$$B = \frac{1}{nc\epsilon_0} \left(\frac{e}{m_e^*} \right)^2 \left(\frac{2\pi^3 L (m_e^* m_h^*)^{3/2}}{h^3} \right) \quad (3)$$

where, m_e^* and m_h^* are effective masses of electrons and holes, respectively, L represents the average interatomic separation in the sample, and n is the index of refraction.

The Urbach region is described by the relation,

$$\alpha(E,T) \propto \exp\left(\frac{E - E_g}{E_u(x)}\right) \quad (4)$$

where, E_g is the optical energy gap also known as Urbach focus, $E_u(X)$ is the characteristic width parameter also termed as the Urbach tail energy and X describes the structural disorder at ambient temperature. The width parameter is normally found to be larger for amorphous phase than crystalline phase. The characteristics of the Urbach tail or the value of E_u is an indicator of the degree of disorder in an amorphous structure.

The absorption coefficient as a function of photon energy is depicted in Fig. 6 along with its Urbach fit in the range $(E_g - 0.5) < E < E_g$ using the form:

$$\alpha = \alpha_g \exp\left(\frac{E - E_g}{E_u}\right), \quad (5)$$

where, α_g is the absorption coefficient at the bandgap E_g . In disordered materials, there is no abrupt termination of conduction and valence bands. Instead, some electronic states called tail states trespass in to the forbidden gap forming a quasi-gap. Optical absorption near the absorption edge is characterized by three types of optical transitions as illustrated in Fig. 6. In the first region (I) where, the energy $E < (E_g - 0.5)$, the optical transitions between the tail and the tail states occur, the second region, called Urbach region (II) $[(E_g - 0.5) < E < E_g]$ denotes optical transitions between tail and extended valence/conduction bands, and the region with energy $E > E_g$ (III), corresponds to transitions between extended states (valence band-conduction band electron transition) available within the band structure of amorphous materials. Unlike in a crystalline material, only energy - not the crystal momentum of an electron (involved in an optical transition) - needs to be conserved in an amorphous material.

The parameters obtained from Urbach simulation are presented in Table 1. From the table it can be seen that as the thickness increases the Urbach energy and the optical bandgap decreases. The analysis revealed that the slope of the absorption edge increased and hence the amount of structural disorder (E_u) decreased with the rise in film thickness. Also one may note that the amount of subgap absorption below the Urbach tail (region I and II in Fig. 6), decreased progressively with thickness increase, indicating reduction of the deep gap state density N_D [35].

A qualitative estimation of defect concentration was carried out using Jackson-Amer postulate which has been proved experimentally in many cases. The law states that the defect density is proportional to the integrated sub gap absorption and can be represented by the equation:

$$N_D \propto \int \alpha dE \quad (6)$$

The integrated subgap absorption α_{int} is given by the area under the absorption curve shown in Fig. 6 over the excitation energy interval of 1.37 eV to E_g . The α_{int} values for the three samples under investigation are given in Table 1. From these values it is evident that the defect density N_D is inversely proportional to the thickness. This result also shows that decreasing layer thickness results in a slight increase in defect density. So, this study confirmed that the process driven higher degree of amorphousness and larger defect density could be the reasons for the observed higher bandgap in thinner films compared to thicker films. In a disordered network, there exist allowed states/vacancy levels near the bottom of the conduction band edge in the forbidden energy region caused by the presence of oxygen vacancies and point defects which is quantified by the Urbach energy. In thicker films, these allowed localized electronic levels combine with conduction band and result in the bandgap reduction.

The envelope method was used to determine the real (n) and imaginary (k) parts of refractive index of all three films from their respective transmittance spectra. In order to compute the dispersion in refractive index, the maximum (T_{max}) and minimum (T_{min}) at a particular wavelength was identified from the envelope and was used along with the corresponding literature data of quartz (substrate) refractive index [36]. The refractive index (n), a physical parameter that determines propagation velocity in the dielectric medium is given in Fig. 7 (a) as a function of measured wave length, the spectral region far from any absorption lines. The refractive index of the films was estimated to be in the range of 2.06 to 2.4. The observed trend in refractive index with decreasing film thickness implies that there might exist an interlayer of silicates with a higher refractive index at the Zr-BZN/SiO₂ interface and this transitional region possesses a larger percentage of the film as the film thickness decreases. Extinction coefficient (k), a measure of the total optical losses caused by absorption (more significant) and scattering, for the Zr-BZN films in the 450-800 nm wavelength window is displayed in Fig. 7 (b). Optical losses were very low (k ranged from 0.11×10^{-3} to 0.34×10^{-3}) for the high quality films in the

visible and near IR spectral region. Here the increased values of film thickness parameter corresponds to reduced values for k ; probably due to lower amount of defect density present in thicker films as inferred from Jackson-Amer fitting.

The dispersion in refractive index of Zr-BZN samples was analyzed using the Single term Sellmeier equation or DiDomenico and Wemple single electronic oscillator model [37,38] formulated as,

$$\frac{1}{n_{\lambda}^2 - 1} = \frac{1}{S_0 \lambda_0^2} - \frac{1}{S_0 \lambda^2}, \quad (7)$$

where, S_0 is the average oscillator strength of the particular oscillator and λ_0 is average position of this oscillator. The linearity in the $1/(n^2-1)$ vs $1/\lambda^2$ experimental data plots (Fig. 8) in the 1.5–3.4 μm^{-2} range indicates the applicability of the one term Sellmeier formula in the high transparency spectral region far from resonances. The oscillator strength and average oscillator position were estimated to be in the range of 0.651–0.759 and 201.62–225.65, respectively, from the slope and infinite-wavelength intercept of the straight line fit. The oscillator peak energy $E_0 = hc/e\lambda_0$, refractive index dispersion parameter E_0/S_0 and dispersion energy $E_d = (S_0/E_0)h^2c^2$ determined for the samples are listed in Table 2. The estimated value for the term $A = (1/S_0)$, a measure of dispersion, falls within the reported limits ~ 40 to $260 \times 10^{-16} \text{ m}^2$ [39] and indicates “normal dispersion”. The long wavelength refractive index $n_{\infty} = \sqrt{1 + S_0 \lambda_0^2}$ that represents the electronic transitions and the numerical values of corresponding electronic (dynamic or optical) dielectric constant $\epsilon_{\infty} = \epsilon_e = n_{\infty}^2$ are given in Table 2. The dielectric constant (which gives rise to polarizability) of a material essentially consists of electronic and lattice components ($\epsilon_r = \epsilon_e + \epsilon_l$). Electronic dielectric constant arises from the dielectric response of the valence electrons and constitutes electronic dipoles, whereas the lattice dielectric constant represents the

dielectric response of the lattice vibrations and causes ionic dipoles. These two polarization components are important for high-k dielectrics as they follow a high clock frequency (0.1-10 GHz) used in advanced CMOS devices. The measured high value of ϵ_e is in good agreement with the observation that the electronic dielectric constants increases with higher-k materials of comparatively less large energy bandgap [40]. The pinning factor or slope parameter, S , a dimensionless physical parameter that gives a measure of the degree of alignment or pinning caused by the interface states at an insulator (wide band gap semiconductor) / semiconductor stack is given by the Monch empirical relation [41], $S = [1 + 0.1(n_\infty^2 - 1)^2]^{-1}$. The value of S ranges between 0 and 1. A value of '0' suggests strong pinning (the Bardeen limit) and a value '1' represents ideal unpinned Schottky limit. The mid-range pinning factor obtained for Zr-BZN samples by substituting n_∞ in the Monch relation is listed in Table 2 and is found to follow the theoretical variation in S with ϵ_∞ .

The real ($\epsilon' = n^2 - k^2$) and imaginary ($\epsilon'' = 2nk$) parts of the wavelength dependent complex dielectric function ($\epsilon^* = \epsilon' - j\epsilon''$) of Zr-BZN layers are illustrated in Fig. 7. These parameters follow the same trend with photon energy ($E = hc/\lambda$) as that of complex index of refraction. The real part of the dielectric constant measured at optical frequencies 0.37-0.67 PHz (450-800 nm) is in the range of ~4-6 and it originates mainly from the electronic polarization as ions respond more slowly than electrons at these very high frequencies. These numbers are comparable with the earlier reported values for films of similar compositions [42]. Optical conductivity is termed as the electronic conductivity that originates in the presence of an alternating electric field of the incident light beam (electromagnetic wave). In this study optical conductivity of Zr-BZN films were estimated in the 0.37 to 0.67 PHz range. Complex optical conductivity is given by the relation $\sigma^* = \sigma' - j\sigma''$ where the real part is $\sigma' = \omega\epsilon''\epsilon_0$ and the imaginary part is $\sigma'' = \omega\epsilon'\epsilon_0$. In Fig. 9, we have plotted the real and imaginary (σ' and σ'') parts of complex optical conductivity for the dielectric samples investigated using transmission

experiment and these show that σ' is two orders lower than σ'' in the visible and near IR spectral region.

3.3. Zr-BZN/Si band offset

Another material property considered in selecting a gate dielectric is sufficiently large barrier height (> 1 eV for electrons and holes) with the semiconductor channel. Alternative high- k dielectrics help in achieving enhanced capacitance density or electrostatic control and reduced gate oxide leakage or standby power. The simplified formulation that governs the tunnelling current, J_g , through a dielectric is given by [43]

$$J_g \propto \exp\left(-\frac{4\pi\sqrt{2qm^*\Delta E}}{h} \frac{k}{3.9} t_{EOT}\right), \quad (8)$$

where, q , m^* , ΔE , k , h , and t_{EOT} represent the elementary charge, effective tunnelling mass of the carrier, the energy barrier height formed at the gate dielectric/substrate interface, dielectric constant of the gate insulator, Plank's constant, and equivalent oxide thickness, respectively. From the above relation it is evident that the gate oxide leakage currents can be minimized (exponential inverse relation) by using an alternative dielectric material having large energy band offset, and high relative permittivity. The energy barrier height for holes (ΔE_v) reported in this paper was determined by employing XPS along with Kraut analysis method [44].

In order to determine the Zr-BZN (amorphous)/Si valence band offset, XPS spectra were collected from three samples: (1) HF (hydrofluoric acid)-last pre-cleaned p-Si(100) substrate to measure the core level ($2p^0$) binding energy and the valence band maximum (E_v) of bare Si (hereafter referred as bulk Si) [Fig. 10 (a)], (2) 70 nm thick Zr-BZN (wide bandgap semiconductor) on Si (hereafter referred as bulk Zr-BZN) to measure the core level binding energy of Bi ($5d_{5/2}$) and the E_v of Zr-BZN [Fig. 10 (b)], and (3) ~3 nm thick Zr-BZN on Si (hereafter referred as ultra-thin Zr-BZN) to simultaneously measure the binding energies of Bi ($5d_{5/2}$) and Si ($2p^0$) core levels in the Zr-BZN/Si heterostructure [Fig. 10 (c)]. The energy corresponding to E_v of bulk Si and Zr-BZN samples with respect to the surface Fermi level were

determined to be 0.5 ± 0.05 eV and 2.4 ± 0.05 eV, respectively, by extrapolating the leading edge of the valence band (broad spectral feature) of each spectrum to their respective base line (background) as illustrated by the intersection points in insets of Fig. 10 (a) and (b), respectively and this process contributes mostly to the uncertainty in the offset value. The core line positions in all three samples were determined by carrying out Voigt (Mixed Gaussian-Lorentzian functions) modelling after Shirley background correction. The energy difference between $2p^0$ (represents Si-Si bonding) core level and E_v of the clean bulk Si substrate was determined to be ~ 99 eV [45]. In a similar way, values for $(E_{Bi5d_{5/2}} - E_v)$ and $(E_{Si2p^0} - E_{Bi5d_{5/2}})$ terms in bulk Zr-BZN and ultra-thin Zr-BZN samples were estimated to be $\sim 23.7 \pm 0.05$ eV and $\sim 75.4 \pm 0.05$ eV, respectively. By substituting the above numbers in Eq. (9), the valence band offset for Zr-BZN/Si heterointerface or the total energy gain for the hole transfer was calculated to be -0.1 ± 0.07 eV, where, the uncertainties were combined using root sum square relationship [19].

$$\Delta E_v = (E_{Si2p^0} - E_v)_{Bulk Si} - (E_{Bi5d_{5/2}} - E_v)_{Bulk Zr-BZN} - (E_{Si2p^0} - E_{Bi5d_{5/2}})_{Zr-BZN / Si} \quad (9)$$

The conduction band discontinuity is given by,

$$\Delta E_C = E_{g(Zr-BZN)} - E_{g(Si)} - \Delta E_v \quad (10)$$

where, $E_{g(Zr-BZN)}$ is the bandgap of Zr-BZN and $E_{g(Si)}$ is that for silicon. Substituting the values of average bandgap of Zr-BZN (3.46 ± 0.05 eV) obtained from spectrophotometric measurements and the corresponding parameter for silicon (1.1 eV) the conduction band discontinuity (ΔE_C) was estimated to be 2.46 ± 0.08 eV. The electron affinity of Zr-BZN was determined to be 1.59 ± 0.08 eV by subtracting electron barrier height from electron affinity of silicon. The schematics of the resulting type II staggered energy band alignment at the Zr-BZN/Si heterostructure under flatband condition is depicted in Fig. 11, where, the valence and conduction bands of the smaller-gap material (Si) lie below than the corresponding band edges of larger-gap material (Zr-BZN) and interface excitons (electrons/holes) are confined in the (smaller-gap/larger-gap) material. Even though the conduction band offset, determined for Zr-BZN/Si interface, is calculated to be sufficiently large enough (> 1 eV) to inhibit electron tunnelling between Zr-BZN high-k dielectric and Si channel, the overall type II (nested) energy level configuration with electron-

hole charge separation reveals the inefficiency of Zr-BZN to act as a potential gate oxide to ensure low gate induced drain leakage and better threshold voltage stability in MOSFET devices based on it. These numbers reveal that some compromise needs to be effected between high-k and large bandgap since the later parameter has a tendency to decrease with increasing dielectric constant. However, the wide bandgap and the associated optical characteristics divulged from spectrophotometric analysis suggests that this material can be a good choice to act as a charge storage/resistive layer in MIM capacitor structures for potential device applications such as: radio frequency (RF) coupling and bypass capacitors in oscillators and resonator circuits, filter and analog capacitors in analog/mixed-signal (AMS) circuits, decoupling capacitors for microprocessors (MPUs), and storage capacitors in dynamic random access memory (DRAM) and resistive random access memory (RRAM) devices. The fabrication of Zr-BZN sandwiched MIM devices on suitable substrates is in progress in order to evaluate the feasibility of this material for such applications.

4. Conclusions

In short, spectrophotometric and XPS characterizations were found to be complementary in determining the wide bandgap and the band discontinuity on silicon of Zr-BZN high-k dielectric for miniaturization of the future generations of CMOS devices. The pulsed laser deposited films exhibited good optical transparency with low optical losses. The complex optical functions, namely refractive index, dielectric constant, and conductivity were determined for the samples by the envelope method. The DiDomenico model for the interband transition with single electronic oscillator was validated and various associated optical parameters like long wave length refractive index, oscillator peak energy, dispersion energy, average oscillator strength, average oscillator wavelength, etc. were investigated. The conduction band (ΔE_C) and the valence band discontinuity (ΔE_V) on Si and the optical bandgap E_g were estimated to be ~ 2.46 eV, ~ -0.1 eV, and ~ 3.46 eV, respectively and the Zr-BZN/Si heterojunction was found to be in a type II staggered configuration. The above experimental results are crucial to provide key insight for the integration of Zr-BZN high-k dielectric in electronic and optical technologies.

Acknowledgements

This work was supported by DOE Grant# DE-FG02-08ER46526. S. K. acknowledges UGC for a Raman fellowship under Indo-US 21st century knowledge initiatives [No:5-53/2013(I.C)]. S. P. P. is grateful to NSF for financial assistance under Grant No: NSF-EFRI RESTOR # 1038272.

Table 1. The energy bandgap (E_g) determined from Tauc's plots, Urbach tail energy (E_u) derived by modelling subgap absorption data with Urbach formula, and integrated subgap state absorption (α_{int}) as a qualitative measure of defect density, for the three samples under study.

Film thickness (nm)	Optical gap (E_g) eV	Urbach energy (E_u) (meV)	α_{int} (meV/cm) $\times 10^3$
650	3.40	224	10580
500	3.48	256	11027
350	3.51	282	13677

Table 2. Dispersion parameters of the index of refraction of amorphous Zr-BZN thin films computed by fitting experimental data with Sellmeier expression.

Dispersion Parameters	Film Thickness (nm)		
	650	500	350
n @ (550 nm)	2.133	2.158	2.251
$S_0 (\times 10^{14} \text{ m}^{-2})$	0.759	0.651	0.665
λ_0 (nm)	201.62	217.99	225.65
E_0 (eV)	6.15	5.69	5.50
$E_0/S_0 (\times 10^{-14} \text{ eV m}^2)$	8.11	8.74	8.26
E_d (eV)	18.98	17.62	18.63
$A (\times 10^{-16} \text{ m}^2)$	131.80	153.5	150.3
n_∞	2.021	2.024	2.095
ϵ_∞	4.084	4.096	4.388
S	0.512	0.511	0.466

Figure Captions

Fig. 1. The *in situ* evolution of structure less RHEED patterns during Zr-BZN film growth (a) Quartz (0001) substrate, after deposition by (b) one (~ 2 Å/shot growth rate), (c) two (d) three laser ablation shots and (e) after completion of deposition (~ 500 nm).

Fig. 2. XRD spectra of amorphous Zr-BZN thin films of thicknesses (a) 650 nm (b) 500 nm, and (c) 350 nm on quartz substrates (d) quartz (0001), and (e) Zr-BZN target.

Fig. 3. AFM plane view images ($XY = 5 \mu\text{m} \times 5 \mu\text{m}$ and $Z = 15$ nm) of Zr-BZN thin films deposited at 300°C on Quartz substrates; (a) 650 nm, (b) 500 nm and (c) 350 nm.

Fig. 4. UV-Visible transmittance spectra of amorphous Zr-substituted BZN thin films of various thicknesses on quartz substrates (a) 650 nm, (b) 500 nm and (c) 300 nm and the corresponding spectra of an uncoated quartz substrate (d). Inset shows the optical model for a weakly absorbing Zr-BZN thin film, bounded by two non-absorbing media; air and quartz (0001) substrate. The complex refractive indices of air, Zr-BZN thin layer and quartz substrate are represented by n_{air} , n_{Zr-BZN} and n_{quartz} , respectively. d_{Zr-BZN} and d_{quartz} denote the thicknesses of the dielectric film and the substrate, respectively.

Fig. 5. Tauc plots for the Zr-substituted amorphous BZN samples of thicknesses (a) 650 nm (b) 500 nm, and (c) 350 nm on quartz substrates for the direct bandgap estimation.

Fig. 6. Optical absorption coefficient, α , as a function of excitation energy and the corresponding Urbach simulation using Eq. (5) for the Zr-BZN thin films of thicknesses (a) 650 nm (b) 500 nm, and (c) 350 nm on quartz substrates. Regions I, II, and III represent the various optical transitions happening within the amorphous dielectric material. The integral over the range 1.37 eV to E_g gives a qualitative estimate of the defect density in the samples according to Jackson-Amer postulate.

Fig. 7. Optical constants (complex refractive indices and dielectric functions) that embody the linear optical property of the pulsed laser deposited Zr-BZN thin films of various thicknesses, estimated using envelope method.

Fig. 8. Simulation of the refractive index dispersion behavior of Zr-BZN thin films by applying Sellmeier single electronic oscillator model; the Sellmeier expression fits well to a straight line in the 1.5–3.4 μm^2 sub-bandgap range illustrating the applicability of the DiDomenico-Wemple model.

Fig. 9. The real and imaginary (σ' and σ'') parts of complex optical conductivity as a function of wavelength for the pulsed laser deposited Zr-BZN thin films.

Fig. 10. XPS spectra of shallow core levels in (a) HF wet etched p-Si (100), (b) ~70nm Zr-BZN/Si and (c) ~3nm Zr-BZN/Si. Valence band spectrum of Si and Zr-BZN are given in insets of Fig. 10 (a) and (b), respectively.

Fig. 11. Relative alignment of energy bands at a Zr-BZN (gate oxide)/Si (semiconductor channel) interface, showing the type II staggered band discontinuity where a straight forward spatial separation of electrons and holes is allowed at the interface.

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Highlights

- ✓ In-depth optical analysis of Zr-BZN ultra high-k thin films
- ✓ A variety of optical parameters are estimated from spectrophotometric data
- ✓ Refractive index dispersion confirmed the Wemple–Di Domenico oscillator model
- ✓ A complete TypeII band lineup of Zr-BZN/Si heterostructure has been determined
- ✓ Results are crucial for integration of Zr-BZN in electronic & optical technologies

Figure 1

FIG. 1

Figure 2

FIG. 2

Figure 3

FIG. 3

Figure 4

FIG. 4

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FIG. 5

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Figure 10

Figure 11