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Optical properties and electronic band lineup on Si of amorphous zirconium modified $Bi_2Zn_{2/3}Nb_{4/3}O_7$ thin films

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ABSTRACT

We have investigated optical and band alignment properties of pulsed laser deposited amorphous thin films of bismuth based monoclinic pyrochlore $Bi_2Zn_{2/3-x/3}Nb_{4/3-2x/3}Zr_xO_7$ (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 ($\varepsilon' - j\varepsilon''$), 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–DiDomenico 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.

1. Introduction

Transparent electronic materials have gained considerable research interest for future technological developments, such as electronic sheets and flexible displays [1–3]. 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 μA/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

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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 [16–18]. 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 [19–22]. 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 (∼2 Å/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 Kα1 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 ∼0.1–1 Ω 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 ∼3 nm and ∼70 nm, respectively. Al Kα (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. Fig. 1(b) –(d) demonstrates 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 $2\theta = 33.2°$ and 45.5° appearing in thinner films of thicknesses 500 nm and 350 nm and the intense peak present at $2\theta = 50.7°$ 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 ($XY = 5\ \mu m \times 5\ \mu m$ and $Z = 15$ 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