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Epitaxial semimetallic $Hf_xZr_{1-x}B_2$ templates for optoelectronic integration on silicon

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High quality heteroepitaxial $Hf_xZr_{1-x}B_2$ (x=0-1) buffers were grown directly on Si(111). The compositional dependence of the film structure and *ab initio* elastic constants were used to show that hexagonal $Hf_xZr_{1-x}B_2$ possess tensile in-plane strain (0.5%) as grown. High quality HfB_2 films were also grown on strain compensating ZrB_2 -buffered Si(111). Initial reflectivity measurements of thick ZrB_2 films agree with first principles calculations which predict that the reflectivity of HfB_2 increases by 20% relative to ZrB_2 in the 2–8 eV range. These tunable structural, thermoelastic, and optical properties suggest that $Hf_xZr_{1-x}B_2$ templates should be suitable for broad integration of III nitrides with Si. © 2006 American Institute of Physics. [DOI: 10.1063/1.2403189]

With increasing device integration and miniaturization, it is highly desirable to grow Al-Ga-N optoelectronic devices directly on Si wafers. These are inexpensive, widely available, and can be produced in large diameters suitable for commercial scale integration. The main complication of this approach is the difference in crystal structures (hexagonal wurtzite versus diamond cubic). Even so, it is well known that the hexagonal symmetry of the Si(111) surface promotes growth of hexagonal nitrides¹ in spite of the significant mismatch between the Si-Si distance (3.84 Å) and the hexagonal basal parameters of GaN (a_0 =3.19 Å) and AlN (a_0 = 3.099 Å). A large mismatch also exists between the thermal expansion coefficients of Si $(2.6 \times 10^{-6} \text{ K}^{-1})$ and GaN (5.6 $\times 10^{-6}$ K⁻¹). To circumvent these difficulties, we have recently developed a hybrid substrate technology based on intermediate thin ZrB₂ buffer layers.^{2,3} Perfectly epitaxial ZrB₂ films with defect-free microstructures and atomically smooth surfaces were deposited on Si(111) via a coincidence-misfit mechanism in which the strain is accommodated by edge dislocations along the interface. This approach has several important advantages: (a) the semimetallic character of ZrB_2 provides technologically useful buffer layers that are reflective and possess low resistivity;⁴ (b) the thermal expansion coefficient of ZrB_2 (5.9×10⁻⁶ K⁻¹) is similar to that of GaN $(5.6 \times 10^{-6} \text{ K}^{-1})$, and its thermal conductivity is comparable to single-crystal Si; and (c) the reported in-plane lattice parameter has a small mismatch with GaN (+0.7%) and AlN (-2.1%), accommodating close lattice matching.

In our previous reports, we demonstrated the use of thin $(20-30 \text{ nm}) \text{ ZrB}_2$ layers on Si(111) to grow GaN by molecular beam epitaxy (MBE) and Al_{0.2}Ga_{0.8}N by metal organic chemical vapor deposition³ [note that ZrB₂ growth on Si(100) produced a two-domain surface structure precluding subsequent nitride growth]. We found that these samples exhibit intense band edge photoluminescence at 10 K. In this context ZrB₂ virtually matches the lattice constant of

Al_{0.2}Ga_{0.8}N, reducing strain and leading to high quality optical properties.

While these studies showed that thin buffer layers are suitable for subsequent heteroepitaxy, the desirable properties, including high conductivity, reflectivity, and thermal matching, are only optimized in thicker layers (>100 nm). An objective of this study is therefore to develop a practical rapid growth process to obtain large-area, large thickness films suitable for device development.

The thin ZrB₂ films were typically grown by gas source molecular beam epitaxy (GS-MBE) of Zr(BH₄)₄ at 900 °C and 10⁻⁷ Torr. Our initial rapid growth rate studies were conducted at higher pressures which led to poisoning of the surface with B-rich fragments [due to gas phase reactions of the Zr(BH₄)₄] and high surface roughness of ~20 nm. We circumvented these problems by mixing Zr(BH₄)₄ (1%–2% by volume) with high purity H₂ to obtain thick films of up to ~0.5 μ m and surface roughness of ~2 nm. These films were characterized by Rutherford backscattering (RBS), high resolution cross sectional transmission electron microscopy (XTEM), Z-contrast imaging, and high resolution x-ray diffraction (HR-XRD) as discussed below.

The thick ZrB_2 layers synthesized here allowed us to obtain reliable film reflectivities across the entire spectrum. The dielectric functions in the 0.2–0.8 and 0.7–8.8 ranges were determined at 22 °C using an infrared variable angle spectroscopic ellipsometer and a variable angle ellipsometer, respectively. The air reflectivity of pure ZrB_2 grown on Si(111) is plotted as a function of incident photon energy in Fig. 1 where it is compared with the reflectivity of bulk Si. The sample exhibits metallic behavior with a reflectivity increasing sharply from values near 0.5 to unity at low photon energy (IR region). However, in the region from 2 to 6 eV (620–200 nm) relevant to AlGaN applications, the reflectivity of ZrB_2 is lower than that of Si.

To elucidate these differences, we calculated the reflectivities of ZrB_2 and Si from first principles using density functional theory (DFT). We also simulated the reflectivity of the isostructural HfB₂ analog to explore whether the ZrB_2 -HfB₂ system can be used to tune the optical properties of buffer layers on Si. All calculations were performed using

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FIG. 1. (Color online) Measured (symbols, 22 °C) and calculated (lines) reflectivities for ZrB₂ (red), HfB₂ (blue), and Si (gray) showing metallic character ($R \sim 1$ in the IR region). A scissors correction of ΔE_{scis} =0.65 eV was applied to the Silicon band structure.

the full-potential linearized augmented plane wave method as implemented in the EXCITING DFT code³ (details will be presented elsewhere). Due to the semimetallic character of the compounds, the complex dielectric function was calculated as the sum of interband and intraband contributions.⁶ For the latter we use a Drude model $\varepsilon = 1 - \omega_p^2 / (\omega^2 + i\omega\Gamma)$, where ω_p is the free-electron plasma frequency (calculated values are $\hbar \omega_p = 4.56$ and 4.81 eV for ZrB_2 and HfB_2 , respectively), and a lifetime broadening of Γ =50 meV was found to reproduce the observed low energy behavior. The steep rise observed in IR reflectivities of both HfB_2 and ZrB_2 is due to the Drude term. The close agreement between the observed and simulated spectra for Si and ZrB₂ suggests that the reflectivity of pure HfB2 films should be about 20% larger than that of ZrB_2 in the 2–8 eV range. Hf–Zr– B_2 materials grown on Si may therefore offer tunable reflectivities across the entire spectral range. This behavior is expected to be of particular significance for the design of nitride based interband (near-IR) and intersubband (IR) devices grown on $Zr_{1-x}Hf_xB_2$ -buffered Si.

Alloys of ZrB₂, with bulk hexagonal lattice constants $a_0=3.169$ Å and $c_0=3.525$ Å, and HfB₂ ($a_0=3.142$ Å and $c_0=3.48$ Å) are expected to have lattice constants smaller than those of ZrB₂ and should therefore make it possible to grow higher Al content Al_xGa_{1-x}N layers with less strain, paving the way towards full integration of these materials with Si. Accordingly, we synthesized Zr_{1-x}Hf_xB₂ materials across the entire compositional range and explored their usefulness for simultaneous thermal and lattice matching applications. We develop a strain analysis for hexagonal films on Si(111) based on compositional interpolation of the elastic constants of ZrB₂ and HfB₂.

Films of $Zr_{1-x}Hf_xB_2$ solid solutions were grown by GS-MBE using the Hf(BH₄)₄ and Zr(BH₄)₄ precursors mixed with H₂ at 2% by volume. The composition in the film was tuned by varying the ratio of Hf(BH₄)₄/Zr(BH₄)₄ in the stock mixture. The Si(111) substrates were outgassed in the MBE chamber at 650 °C and the native oxide was removed by flashing at 1200 °C. The gases were then allow to react on the substrate surface at 900 °C and $10^{-5}-10^{-6}$ Torr (base pressure of 10^{-10} Torr) for 30–120 min depending on film thickness. Under these conditions both precursors thermally

decomposed to form films according to



FIG. 2. (Color online) (a) RBS spectra of 40 nm thick $Zr_{0.70}Hf_{0.30}B_2$ film. (b) XRD (<u>1</u>13) reciprocal space map from $Zr_{0.70}Hf_{0.30}B_2/Si(111)$ yielding a=3.176 Å and c=3.505 Å [reciprocal lattice units (rlu) are employed in which $Q_x = \lambda a \sqrt{3}$ ($\lambda = 1.54$ Å) and $Q_y = 3\lambda/2c$]. (c) Diffraction contrast micrograph of the entire layer showing defect-free microstructure and smooth surface. Inset: high resolution image of the perfectly epitaxial interface.

$$(1-x)\operatorname{Zr}(\operatorname{BH}_4)_4 + x\operatorname{Hf}(\operatorname{BH}_4)_4 \to \operatorname{Zr}_{1-x}\operatorname{Hf}_x\operatorname{B}_2 + \operatorname{B}_2\operatorname{H}_6$$
$$+ 5\operatorname{H}_2.$$

Figure 2(a) shows the RBS spectrum of a $Zr_{0.70}Hf_{0.30}B_2$ sample with a nominal thickness of 50 nm. The ratio of the aligned versus the random peak heights (χ_{\min}) is 6% for both Hf and Zr, indicating their full substitutionality in the alloy and the high degree of epitaxial alignment of the film with respect to the Si substrate. XTEM indicates that the layers are perfectly monocrystalline, highly coherent, and atomically flat [Figs. 2(b) and 2(c)]. The lattice misfit is taken up by pure edge-type dislocations via insertion of extra {1100} planes along the [1120] direction.² Diffraction contrast micrographs reveal that no threading dislocation cores propagate to the surface within the field of view of $\sim 3 \ \mu m$. Electron energy loss spectroscopy (EELS) with a nanometersized electron probe shows that the constituent Zr and Hf elements appear together at every nanometer scale region probed without any segregation of the individual alloy components. Atomic force microscopy (AFM) revealed a smooth surface with a roughness of $\sim 2 \text{ nm}$ for a 5×5 μm^2 area which is highly suitable for buffer layer applications. The surface morphology further improves by *ex situ* annealing of the films at 900 °C and 10^{-9} Torr for 8 h. This yields a roughness below 1.5 nm and a surface consisting of large atomically flat areas connected by steps.

For all Zr_{1-r}Hf_rB₂ films, HR-XRD on-axis scans show only the (001) and (002) peaks of the AlB₂ structure, oriented with (0001) parallel to the Si(111). The (002) peaks, which are more sensitive to the compositional changes of the alloys, were significantly shifted from those of pure ZrB₂. The absence of splitting or broadening in these peaks corroborates the full substitutionality of both Hf and Zr atoms in the lattice. We have also observed thickness fringes in the vicinity of the (001) and (002) reflections, confirming the high quality of the interface and the uniformity and smoothness of the layers. Accurate a and c lattice parameters were extracted from the asymmetric (113) reciprocal space maps of the AlB₂ structure and are provided in Table I for samples with thicknesses of \sim 50±5 nm. Due to strain, these measured lattice parameters do not correspond to the relaxed hexagonal lattice parameters a_0 and c_0 .

TABLE I. Lattice parameters of $Zr_{1-x}Hf_xB_2$ films obtained from HR-XRD analysis (bold font). The relaxed lattice parameters (a_0 and c_0) and calculated strains (ε_a and ε_c) are obtained from a compositional interpolation of the elastic ratio $\xi(x)$ and bulk c/a ratio $\eta(x)$.

x	0	15	30	60	100
а	3.187	3.183	3.176	3.167	3.160
$\boldsymbol{\varepsilon}_{a}$	+0.52	+0.54	+0.50	+0.48	+0.66
с	3.521	3.513	3.505	3.491	3.467
$\boldsymbol{\varepsilon}_{c}$	-0.30	-0.32	-0.28	-0.27	-0.36
$\xi(x)$	-0.584	-0.580	-0.574	-0.565	-0.552
$\eta(x)$	1.114	1.113	1.112	1.111	1.108
a_0	3.170	3.166	3.160	3.152	3.140
c_0	3.531	3.524	3.515	3.501	3.480

For hexagonal films with the [0001] plane oriented normal to the substrate, the perpendicular (ε_c) and parallel (ε_a) strains are given by $\varepsilon_c = -2C_{13}\varepsilon_a/C_{33}$, where $\varepsilon_c = (c-c_0)/c_0$ and $\varepsilon_a = (a - a_0)/a_0$. For bulk ZrB₂ and HfB₂ the known c/aratios (denoted by η below) are only slightly different (1.114 and 1.108, respectively). Therefore, in order to determine the strain state, we make the following approximations: (i) η for the relaxed epitaxial film is identical to that of the equilibrium bulk crystals and (ii) the c/a ratio (η) and elastic ratio $\xi = -2C_{13}/C_{33}$ are both linear functions of composition; $\eta(x) = x \eta^{\text{HfB}_2} + (1-x) \eta^{\text{ZrB}_2}$ and $\xi(x) = x \xi^{\text{HfB}_2} + (1-x) \xi^{\text{ZrB}_2}$, respectively. Since the elastic constants of both ZrB₂ and HfB₂ are generally not well known, we used the VASP DFT code to calculated them using finite strain deformations of the equilibrated systems.⁸ From inversion of the strain relation, the relaxed lattice constants are then given by $a_0(x)$ $= \{c(x) / \eta(x) - \xi(x)a(x)\} / \{1 - \xi(x)\}$ and $c_0(x) = \eta(x) a_0(x)$, and these are listed in Table I. We note that the relaxed film lattice constant of the end members match the known values for the bulk phases. This provides additional justification for the approximations discussed above. We also note that the relaxed lattice constants for the alloys follow Vegard's law quite closely. Our analysis shows that ZrB₂ and the alloy films exhibit a slight tensile strain ($\varepsilon_a \sim +0.50\%$, $\varepsilon_c \sim$ -0.29%), while the HfB₂ film is strained even more ($\varepsilon_a \sim$ +0.66%, $\varepsilon_c \sim -0.36\%$). The tensile state of these films (including ZrB₂) has significant implications for lattice engineering, since this provides better matching with Ga-rich alloys. In particular, the measured value of a for the ZrB₂ films is essentially identical to that of GaN.

As noted above, the in-plane strain systematically increases in the Hf-rich compositional regime with a concomitant reduction in growth rate (~ 0.5 nm/min, for pure HfB₂). The increase in strain reduces the reactivity and surface mobility. In fact, for HfB_2 , the growth on Si(111) eventually produces almost exclusively rough films with large surface undulations (AFM roughness >15 nm). The growth, in this case, was conducted at 900 °C via decomposition of pure $Hf(BH_4)_4$ under conditions similar to those described above for the alloys. The RBS and XTEM data confirmed the presence of predominately rough layers dominated by ensembles of large islands. Nevertheless, and in spite of the slightly larger film strain (see Table I), the data also showed stoichiometric and aligned materials with sharp and commensurate interfaces. XRD off-axis measurements gave a=3.160 Å and c=3.467 Å which are larger/smaller than a=3.142 Å and



FIG. 3. (Color online) (a) Z-contrast image of $HfB_2/ZrB_2/Si(111)$ heterostructure. (b) High resolution XTEM of the perfectly epitaxial HfB_2/ZrB_2 interface and corresponding EELS composition profile of Hf (*M* edge) and Zr (*L* edge).

c=3.48 Å of bulk HfB₂, due to strain imposed by the Si substrate. These results motivated us to pursue growth of HfB₂ films on isostructural ZrB₂ buffers [rather than directly on the Si(111) surface to promote formation of smooth films suitable for nitride integration. These HfB₂ films grow much more readily ($\sim 2 \text{ nm/min}$) and exhibit exceptional morphological and structural properties, including flat surfaces (AFM roughness ~ 2 nm), highly coherent interfaces, and virtually defect-free microstructures. The XRD measurements show that the layers are partially strained and the lattice parameters are close to those of HfB₂ films grown on Si (Table I). We note that growth of thin HfB₂ layers has been reported on oxidized Si via decomposition of Hf(BH₄)₄, but no evidence of epitaxy was given.⁹ The XTEM data in Fig. 3(a) indicate that our ZrB_2 buffers bridge the strain differential between HfB2 and Si, allowing the formation of perfectly epitaxial HfB₂ films that cannot be obtained directly on Si. XTEM Z-contrast images and EELS profiles of Zr and Hf across the interface showed an abrupt transition of the elements from ZrB_2 to HfB_2 with no evidence of intermixing between the two materials at the nanometer scale (Fig. 3).

In summary, we have shown that heteroepitaxial semimetallic $Hf_xZr_{1-x}B_2$ templates with tunable structural and optical properties represent a potentially very useful practical system for optoelectronic integration applications on Si.

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