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Magnetron sputtering of epitaxial ZrB₂ thin films on 4H-SiC(0001) and Si(111)

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Epitaxial ZrB₂ thin films were deposited at a temperature of 900 °C on 4H-SiC(0001) and Si(111) substrates by magnetron sputtering from a ZrB₂ source at high rate

~80 nm/min. The films were analyzed by thin film X-ray diffraction including pole figure measurements and reciprocal space mapping as well as high resolution electron microscopy.

1. Introduction Zirconium diboride (ZrB₂) films on closely lattice matched semiconductor substrates GaN(0001) and 4H-SiC(0001) are interesting as electrical contact material for application in demanding environments [1-4]. This is due to a favorable property envelope, shown by this diboride with an AlB₂ type structure [5] that includes high hardness of 23 GPa, high melting point of 3245 °C and high electrical conductivity, as seen from a resistivity of ~10 μΩcm for the bulk material [6,7]. In addition, epitaxial ZrB₂ thin films can be applied as an active diffusion layer for growth of epitaxial silicene, the silicon counterpart to graphene, on Si(111) [8] or as a buffer layer on Si(111) to enable epitaxial growth of GaN(0001) thereby integrating III-V materials with Si technology [9]. Thus, many of the envisioned applications for ZrB₂ thin films depend on the ability to grow epitaxial films.

The literature shows that epitaxial ZrB₂ films have been deposited by chemical vapor deposition (CVD) on Si(111) [9,10], Si(100), [11] and Al₂O₃(0001) [12] substrates by thermal decomposition of the precursor zirconium borohydride Zr(BH₄)₄ or by pulsed laser deposition from a ZrB₂ target [4] whereas sputtering of epitaxial films remains to be demonstrated. Common features for the CVD processes are that they are initiated by a high-temperature substrate pre-treatment that is performed *in-vacuo* at ultra-high-vacuum (UHV) conditions, including flashing steps to 1100-1200 °C and in some cases outgassing of the

substrates at 500 °C for 10 hours [9,11-13]. Furthermore, the ZrB₂ synthesis by both techniques is characterized by very low deposition rates (~0.3–1.2 nm/min) and long deposition

times to produce films with thicknesses of ~20 nm at a temperature of 900-950 °C. The low deposition rate in combination with long deposition times limits the use of CVD for growth of thicker ZrB₂ films above 100 nm, which is necessary for, e.g., electrical contact applications. This restriction calls for process development of CVD processes or the use of alternative thin film synthesis techniques.

In this article, we demonstrate that direct current magnetron sputtering (DCMS) of a ZrB₂ compound target can be applied to deposit epitaxial ZrB₂ films on 4H-SiC(0001) and Si(111) substrates with 70 to 280 times higher growth rates than those reported for CVD films to enable growth of epitaxial films with thicknesses of ~400 nm during 300 s.

2. Experimental details The ZrB₂ thin film growth was conducted in a UHV system held at a base pressure of ~5 x 10⁻⁷ Pa, previously described elsewhere [14]. Our process, as inspired by those developed for CVD, was initiated by outgassing of the 3 substrates in each run (on-axis 4H-SiC(0001), epitaxial GaN(0001) deposited on 4H-SiC(0001) [15], and Si(111) cut with a vicinal angle of ~2-3 °) in the system's load-lock at ~300 °C for 1 hour at a pressure of ~1 x 10⁻⁴ Pa. The 4H-SiC(0001) substrates had previously been degreased with trichloroethylene, acetone and ethanol, cleaned with a modified RCA process and dipped in 10 % HF. The Si(111) substrates and the GaN(0001) epi layers were degreased and dipped in 4 % HF. The outgassing was followed by a heat treatment in the growth chamber, which was conducted for 1 hour at the deposition temperature of 900 °C. The ZrB₂ growth was carried out by DCMS of a circular 3 inch ZrB₂ compound

source of 99.5 % purity (excluding Hf) from Kurt J. Lesker Company Ltd. The target with its dedicated shutter was placed directly below the substrates at a distance of 7 cm. Sputter cleaning of the target behind the shutter was conducted for at least 60 s before initiating the 300 s long coating process that was performed using a magnetron power of 400 W in an Ar (99.9997 %) plasma kept at 0.53 Pa, using a substrate bias of -80 V and with no substrate rotation. These conditions resulted in a growth rate of ~ 80 nm/min calculated from a corresponding film thickness of ~ 400 nm determined by high resolution transmission electron microscopy (HRTEM).

The structural properties of the films were assessed by X-ray diffraction (XRD) $\theta/2\theta$ scans as well as ω scans of the ZrB_2 0001-reflection in a Philips PW 1820 system equipped with a Cu $K\alpha$ source operated at 40 kV and 40 mA. The measured ω scan full width at half maximum (FWHM) values were obtained by correcting the measured data for the instrumental broadening (0.03°) by quadratic subtraction. Epitaxial growth was determined from XRD pole figures recorded in a PANalytical EMPYREAN system at 45 kV and 40 mA. The lattice parameters of the films were determined from high and low resolution reciprocal space mapping (RSM) of the symmetrical 0002 and the asymmetrical $10\bar{1}3$ ZrB_2 peaks, using a Philips X'Pert MRD system operated at 45 kV and 40 mA. The maps were recorded as consecutive coupled $\omega/2\theta$ scans, each separated by an ω offset. For a more detailed description of the RSM method the reader is referred to [16,17]. HRTEM imaging and collection of selected area diffraction patterns (SAED) as well as Energy Dispersive Spectroscopy (EDS) were carried out by using a FEI Tecnai G2 TF20 UT HRTEM with a field emission gun operated at 200 kV and with a point resolution of 1.9 Å.

3. Results and discussion The diffractogram in Fig. 1 was obtained from a ZrB_2 film deposited on 4H-SiC(0001). As can be seen, the pattern contains 4 peaks that are located at the approximate 2θ angles: 25, 52, 82, and 122° . These are the 000 l peaks of ZrB_2 and the initial 0001 peak has about $\frac{1}{4}$ intensity of the main substrate 0004 peak at $2\theta \approx 35.7^\circ$. In addition to the unmarked and needle-shaped peaks originating from the substrate, there is also a peak from ZrB_2 $10\bar{1}1$ at $2\theta \approx 41.7^\circ$ visible, albeit with only

Figure 1 X-ray diffractogram of an ZrB_2 film deposited on 4H-SiC(0001) at 900°C and using a substrate bias of -80 V.

a fraction of intensity $\sim 2.4 \times 10^{-4}$ compared to the 0001 peak, given the logarithmic scale. The ensemble of peaks from ZrB_2 in the $\theta/2\theta$ diffractogram shows that the film is epitaxial or highly textured.

The pole figure measurement of the $10\bar{1}1$ pole in Fig. 2a reveals, by the presence of six elliptically-shaped points of high intensities that are separated by 60° in ϕ , that the film deposited on 4H-SiC(0001) is epitaxial.

Figure 2 XRD pole figures from a) the $10\bar{1}1$ pole of a ZrB_2 film deposited on 4H-SiC(0001) and b) $10\bar{1}1$ pole of the 4H-SiC(0001)

substrate, c) the $10\bar{1}1$ pole of a ZrB_2 film deposited on Si(111), and d) 220 pole of the Si(111) substrate.

This pattern is a consequence of the 6-fold symmetry present in the AlB_2 type structure and the location of the spots at a ψ -angle of $\sim 50^\circ$ is close to the interplanar angle between the 0001 and $10\bar{1}1$ planes in ZrB_2 of 52.14° , keeping in mind the inherent low resolution in ψ characteristic in pole figure measurements. The $10\bar{1}1$ pole obtained from the substrate in Fig. 2b also display six sharp points at a ψ -angle of $\sim 75^\circ$, which are positioned at ϕ angles that coincide with those recorded for the film. The ψ -angle corresponds to that between 0001 and $10\bar{1}1$ planes in 4H-SiC and the match in ϕ angles shows that the orientation of the film unit cell coincides with that of the substrate. This gives the epitaxial relationship to $\text{ZrB}_2(0001)//4\text{H-SiC}(0001)$ and an in-plane orientation of $\text{ZrB}_2[1\bar{1}00]//4\text{H-SiC}[1\bar{1}00]$. The SAED pattern shown as an inset in Fig. 3a confirms the results from the $10\bar{1}1$ pole figure measurements. Note that the $\text{ZrB}_2(1\bar{1}00)$ and the $4\text{H-SiC}(1\bar{1}00)$ reflections are very close together and should not be mistaken for one reflection.

The crystalline quality of the film deposited on $4\text{H-SiC}(0001)$ was determined by an ω scan of the ZrB_2 0001-reflection. The diffractogram (not shown) displayed a sharp peak with a broad base similar to that found for growth on $\text{Al}_2\text{O}_3(0001)$ [12]. The determined FWHM value was 0.07° , to compare with 160 arc seconds corresponding to 0.04° for the bulk [18] and 0.01° for films deposited on $\text{Al}_2\text{O}_3(0001)$ [12].

The HRTEM images show that the ZrB_2 film grown on $4\text{H-SiC}(0001)$ is epitaxial from the film-substrate interface all the way to the film-vacuum interface and that the thickness of the film is ~ 400 nm. From the low-resolution image in Fig. 3a, visualized from the zone axis $[11\bar{2}0]$,

Figure 3 TEM micrographs of an epitaxial ZrB_2 film deposited on $4\text{H-SiC}(0001)$ at 900°C with a substrate bias of -80 V showing a) low- and high-resolution images and SAED pattern along the zone

axis $[11\bar{2}0]$ and b) high-resolution image and SAED pattern along $[1\bar{1}00]$.

It can be discerned that the film grows columnar with only slight misorientation, and from plan-view images (not shown) the size of the columns was determined to ~ 5 nm and with slight tilting and rotation between the individual columns. In Fig. 3b a diffraction pattern and HRTEM image observed from the other major zone axis $[1\bar{1}00]$ is shown and there it can be seen that the steps on the 4H-SiC surface cause the ZrB_2 film columns to be shifted half a unit cell to constitute stacking mismatch boundaries.

Figure 4 TEM micrographs of an epitaxial ZrB_2 film deposited on Si(111) at 900°C with a substrate bias of -80 V showing a) low-magnification image and SAED pattern along the zone axis $[110]$ and b) high-resolution image of the substrate-film interface along $[11\bar{2}]$.

The $\theta/2\theta$ diffractogram recorded from a film deposited on Si(111) (not shown) also displays 000 ℓ and 10 $\bar{1}$ 1 peaks from ZrB₂, but with a factor of 10 lower intensity for the 0001 peak compared to the film deposited on 4H-SiC(0001) as well as double the intensity for the 10 $\bar{1}$ 1 peak. For ZrB₂ films grown on Si(111), we first note the large mismatch between the in-plane distance of the Si atoms on Si(111) of 3.84 Å and the *a*-axis of the ZrB₂ of 3.169 Å that results in epitaxial growth conditions where six lattice planes for the film coincides with five lattice planes for the substrate [9,10]. Here we find a lower crystalline quality as evidenced by a considerable broader 0001 peak in the ω scan (not shown). The determined ω FWHM was 3.2°. This can be compared to 3.5 arc minutes corresponding to 0.06° obtained from CVD-grown films [9] and indicates a lower crystalline quality for our sputtered films compared to those grown by CVD. The low-magnification cross-sectional TEM image with corresponding SAED pattern and the HRTEM image in Fig. 4 a and b, respectively, further support this inferior film quality by revealing growth of epitaxial ZrB₂ columns on Si(111), but including areas where the epitaxy is locally disrupted. This growth behavior is different from our present results on 4H-SiC(0001) and those reported for films deposited by CVD [9,10]. From the low-magnification image it is evident that the interface between the film and the substrate surface is uneven, suggesting either a film/substrate reaction or excessive etching. This indicates that additional heating from the plasma or the ions in the plasma present during a sputtering process affect the Si(111) substrate at the applied deposition conditions. The actual mechanism will be the subject of further investigation. In addition, there is amorphous material present at the interface, which is not seen by Tolle et al or Hu et al [9,10]. EDS shows that the amorphous phase consists of Si and O, where the latter element is likely picked up by the material during *ex-situ* handling. The thickness of this amorphous layer varies across the substrate surface as it is preferentially located in the valleys of the wavy interface. From our images, we see no clear correlation between the thickness of this layer and the growth of either epitaxial columns or poly crystalline areas. The reason for this growth behavior is unknown, but here we note that curvature-driven interface diffusion processes together with mismatch strain effects and very high deposition rate may be at play to cause the observed microstructure evolution.

However, pole figure measurements of the 10 $\bar{1}$ 1 pole on films deposited on Si(111) results in a pattern with six more intensive spots and six less intensive spots (located 30° from the more intensive spots in ϕ) showing that there are two competing epitaxial growth orientations for ZrB₂ on Si(111), see Fig. 2c. It can also be seen that the ψ -positions

of the spots are shifted ~2-3° from the value of 52°, which is due to the vicinal cut of the substrate. The 220 pole figure recorded from the Si(111) substrate in Fig. 2d displays 3 distinct points with a 120° spacing in ϕ that are located at a ψ -angle of ~35°, where the ϕ spacing reflects the 3-fold symmetry of the (220) plane and ψ is the interplanar angle between (110) and (111) planes in a cubic crystal system. From these measurements it was possible to determine the epitaxial relationship to be ZrB₂(0001)//Si(111) out-of-plane and ZrB₂[11 $\bar{2}$ 0]/Si[10 $\bar{1}$] in-plane for the majority orientation and ZrB₂[11 $\bar{2}$ 0]/Si[112] in-plane for the minority orientation. Epitaxial growth of ZrB₂ was also attempted on epitaxial GaN(0001) deposited on 4H-SiC(0001). However, the films were not epitaxial, but 0001 textured (pole figure measurements not shown). The reason for this difference in growth behavior should be investigated further.

From the RSM of the 0002 and 10 $\bar{1}$ 3 lattice points in Fig. 5 a-d, it was possible to determine the lattice parameters for the films deposited on 4H-SiC(0001) and Si(111). The film grown on 4H-SiC(0001) exhibits an *a*-axis of 3.174 Å and a *c*-axis of 3.518 Å, while the film deposited on Si(111) shows an *a*-axis of 3.151 Å and a *c*-axis of 3.529 Å. These values deviates somewhat from the literature values with an *a*-axis of 3.1687 Å and a *c*-axis of 3.53 Å [5], which can be explained from thermal expansion mismatch strain, isotropic stress component due to point defects, and epitaxial mismatch strain. However, the prevailing mechanism(s) are outside the scope of this article.

Figure 5 RSM of the ZrB₂ 0002 and 10 $\bar{1}$ 3 lattice point from a) and c) a film deposited on 4H-SiC(0001), and b) and d) a film grown on Si(111). In d) the Si 313 lattice point is also visible. Note the different magnitudes in Q-scale for the two substrates.

Furthermore, the broadening visible in the Q_x direction for the symmetrical 0002 maps support the difference in crystalline qualities between the films grown on 4H-SiC(0001) and Si(111), see Fig. 5 a-b. In addition, the $10\bar{1}3$ lattice point for the film deposited on Si(111) show a broadening in the ω direction indicative of a relaxed film with mosaicity. The $10\bar{1}3$ lattice point originating from the film grown on 4H-SiC(0001) also exhibits a significant broadening in the ω direction, albeit with an additional component along the lateral direction. This reflects a limited coherence length for the diffracted beam in the plane, suggesting that this film consists of epitaxial columns of limited lateral size, such as the stacking mismatch domains observed in the HRTEM.

4. Conclusions We have applied DCMS from a ZrB_2 target to grow ~ 400 nm thick epitaxial ZrB_2 films on 4H-SiC(0001) and Si(111) substrates at 900°C . The epitaxial relationships are $ZrB_2(0001)//4H\text{-SiC}(0001)$ and $ZrB_2[1\bar{1}00]//4H\text{-SiC}[1\bar{1}00]$. For Si(111) substrates, the much larger lattice mismatch and deterioration of the substrate surface during processing yielded a dual epitaxial relationship for the film of $ZrB_2(0001)//\text{Si}(111)$ and $ZrB_2[1\bar{1}\bar{2}0]//\text{Si}[10\bar{1}]$ for the majority and $ZrB_2[1\bar{1}\bar{2}0]//\text{Si}[112]$ for the minority of domains as well as textured columns. The achieved deposition rate of ~ 80 nm/min is considerably faster than those reported for other processes including chemical vapor deposition and pulse laser ablation.

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