Epitaxial Growth of Magnetron-Sputtered ZrB₂ Films on Si(100) Substrates

Claudia Schnitter, Johanna Rosen, and Hans Högberg*

Epitaxial growth of ZrB₂ films on Si(100) substrates at 900 °C is demonstrated using direct-current magnetron sputter deposition from sintered ZrB₂ targets. This case of epitaxial growth is structurally more challenging than on Si(111), 4H-SiC(001), and Al₂O₃(001). From pole figure measurements, two epitaxial relationships are determined: A) in-plane: ZrB₂[001]||Si[110] and ZrB₂[110]||Si[110], out-of-plane: ZrB₂[100]||Si[100], and B) in-plane: ZrB₂[11̅2]||Si[110] and the same multiply rotated 90° around the 102 axis, out of plane: ZrB₂[102]||Si[100]. From full width at half maximum (FWHM) values from rocking curve measurements (ω-scans) of the 100 and 102 peaks, a measure of epitaxial quality for these two preferred orientations is obtained. Both ω-scans and θ/2θ diffractograms show higher quality for the A-type with a FWHM value of 2.00° compared with 4.97° for the B-type. The film composition is found to be ZrB₂,3 from time-of-flight elastic recoil detection analysis. The B-type crystallographic relationship ZrB₂[102]||Si[100] and ZrB₂[120]||Si[110] has not been previously reported.

1. Introduction

The interest for transition metal diboride (B₂) films, where is a group 4 to 6 transition metal, deposited on semiconductor substrates such as silicon, arose in the 1980s. They were initially considered as diffusion barriers and for interconnect metallization. [1,2] Their property envelope is characterized by high electrical conductivities, higher than the parent, in combination with high hardness, chemical resistance, and high melting point. Therefore, B₂ films were suggested as replacement to the transition metal silicides used in the semiconductor industry. [1]

In 1983, Shappirio and Finnegan applied radio frequency (RF) diode sputtering without external substrate heating to study the growth of ZrB₂ films for interconnect metallization on silicon substrates. [3] The resulting ZrB₂ films were polycrystalline and B deficient with 6 wt% O in the film. Chakrabarti et al. [4] deposited understoichiometric ZrB₂ films from a hot-pressed ZrB₂ target (89% of theoretical bulk density) with a direct current (DC) triode sputtering process. Annealing results in improved crystallinity, but these early studies indicated the challenge of growing ZrB₂ epitaxially and with low impurity levels. [3-5]

While TMBC₂ films were not implemented as diffusion barriers and interconnects in the semiconductor industry, they attract attention as refractory or protective coatings, conductive functional ceramics, and as superconductors. [7-9] In particular, ZrB₂ can be made superconducting by doping, [10-13] stressing the need for being able to grow well-defined epitaxial ZrB₂ films. Today, the quality of diboride compound targets is greatly improved, and it has been possible to obtain films with high crystal quality on certain substrates, in particular using DC magnetron sputtering (DCMS) as seen, for example, in a study comparing the chemical bonding in a sputter target and in the ZrB₂ film on Al₂O₃ sputtered from it. [14] For example, stoichiometric and 001 fiber-textured ZrB₂ films with approximately O could be deposited on Si(100) substrates by DCMS of a ZrB₂ compound target without external heating. [15] However, epitaxial growth was not obtained, neither without heating nor at 550 °C. Thus, enhanced adatom mobility, which comes with elevated substrate temperature, is of key importance for epitaxial growth of ZrB₂, as for most ceramics.

To date, epitaxial growth of ZrB₂ films by DCMS has been reported for 4H-SiC(001) and Si(111) substrates [16] as well as Al₂O₃(001) substrates [17] kept at 900 °C.

For Si(100), using chemical vapor deposition (CVD) using thermal decomposition of the single-source precursor zirconium tetraborohydride Zr(BH₄)₄, at a substrate temperature of 900 °C, Roucka et al. [18] demonstrated epitaxial growth of ZrB₂ films on Si(100). Here we note that the out-of-plane orientation of epitaxial ZrB₂ films deposited on Si(100) is ZrB₂[100]||Si[100] and thus orthogonal to that of ZrB₂ films previously deposited on 4H-SiC(001), Al₂O₃(001), and Si(111). [16,17] Chemically vapor deposited films grow at thermodynamic equilibrium, and it is interesting to study the growth of ZrB₂ films on Si(100) deposited by DCMS, a technique that provides far-from-equilibrium conditions. Epitaxial growth on the most widely used and least expensive Si substrate, Si(100), remains to be demonstrated by DCMS of a ZrB₂ compound target, which could potentially be important for ease of processing.

In this study, we deposit ZrB₂ by DCMS from a ZrB₂ compound target on Si(100) substrates at 900 °C to investigate...
epitaxial growth at an out-of-plane orientation of ZrB$_2$[100], orthogonal to the commonly studied ZrB$_2$[001]. Thin-film X-ray diffraction shows that the ZrB$_2$ films exhibit two epitaxial relationships, one of which was not reported in the CVD case.\(^{18}\) Time-of-flight elastic recoil detection analysis (ToF-ERDA) shows a boron-rich composition as seen from B:Zr ratio of 2.3. We further describe the epitaxial growth of ZrB$_2$ on Si(100) and note that it is more challenging than on Si(111).

## 2. Results

Quantitative analysis by ToF-ERDA of the as-deposited ZrB$_2$ film showed 68.3 at% B, 30.0 at% Zr, 0.1 at% O, and 1.5 at% C corresponding to a B:Zr ratio of 2.3. Figure 1 shows the X-ray $\theta$/2$\theta$ diffractogram of a ZrB$_2$ film deposited on Si(100). The $n00$ peaks ($n = 1,2,3...$), marked by red solid lines in the PDF card inset at the bottom of the figure, show highest intensities among all film peaks and the corresponding 200 peak overlaps with the Si substrate’s 400 peak, marked by a gray broken line in the inset. In addition, ZrB$_2$ peaks of lower intensities are present in the diffractograms, corresponding to other orientations. These peaks are marked by black solid lines in the inset. Among these minority orientations, especially the 102 peak, but also the 00$n$ peaks, are relatively strong, when comparing with the other minority orientations and considering their intensity distribution according to the PDF card shown in the inset of the figure.

The 001, 101, and 111 pole figures of the ZrB$_2$ film presented in Figure 2 show distinct but broad peaks. In the ZrB$_2$ 001 pole figure, four peaks are positioned in the range $\psi = 29$ to 35° and with 90° apart in $\varphi$. A weak peak originating from 001-oriented grains is visible in the center.

The ZrB$_2$ 101 pole figure shows three (four when including those at $\psi > 85°$) series of four peaks that are at the same $\psi$-angle, each, $\psi \approx 20°; 40°; 65°$. The four peaks in each series are 90° apart in $\varphi$ and the $\psi \approx 20°$ and $40°$ series are aligned in $\varphi$, while the $\psi \approx 65°$ series is rotated in $\varphi$ by 45° relative to them. In the center of the ZrB$_2$ 101 pole figure a weak peak from 101-oriented grains is visible. It can be noted that the peaks of the $\psi \approx 20°$ series are the sharpest, while the peaks from the other series are broader. The peaks from the $\psi \approx 40°$ series are broader in $\psi$ than in $\varphi$, while the peaks from the $\psi \approx 65°$ series are very wide in $\varphi$, broader than in $\psi$.

The ZrB$_2$ 111 pole figure shows four peaks at $\psi \approx 37.5°$ and 90° apart in $\varphi$. They are narrow in $\psi$ but $\approx 6°$ broad in $\varphi$.

---

**Figure 1.** $\theta$/2$\theta$ X-ray diffractogram measured from ZrB$_2$ films deposited at 900 °C onto Si(100). The inset at the bottom marks the position of the ZrB$_2$ peaks and their intensity distribution according to another study.\(^{19}\)

**Figure 2.** Pole figures of 001, 101, and 111 from a ZrB$_2$ film sputter deposited on Si(100) substrate at 900 °C. The color scales indicate logarithmic intensities.
Table 1. $\phi$ and $\psi$ values for the peaks in the ZrB$_2$ 001, 101, and 111 pole figures.

<table>
<thead>
<tr>
<th>001 pole figure</th>
<th>101 pole figure</th>
<th>111 pole figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi$ [°]</td>
<td>$\psi$ [°]</td>
<td>$\psi$ [°]</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>31</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>33.5</td>
<td>92</td>
<td>20</td>
</tr>
<tr>
<td>35</td>
<td>180</td>
<td>20</td>
</tr>
<tr>
<td>33</td>
<td>270</td>
<td>20</td>
</tr>
<tr>
<td>$\psi$ [°]</td>
<td>$\psi$ [°]</td>
<td>$\psi$ [°]</td>
</tr>
<tr>
<td>$\approx 33^\circ$</td>
<td>$\approx 20^\circ$</td>
<td>$\approx 38^\circ$</td>
</tr>
<tr>
<td>$\approx 39^\circ$</td>
<td>90</td>
<td>180</td>
</tr>
<tr>
<td>38–40</td>
<td>38</td>
<td>38</td>
</tr>
<tr>
<td>37.5–41</td>
<td>37.5</td>
<td>37.5</td>
</tr>
<tr>
<td>38–41</td>
<td>38</td>
<td>38</td>
</tr>
<tr>
<td>66–69</td>
<td>41–44</td>
<td>41–44</td>
</tr>
<tr>
<td>65–69</td>
<td>131–140</td>
<td>131–140</td>
</tr>
<tr>
<td>66–69</td>
<td>220–238</td>
<td>220–238</td>
</tr>
<tr>
<td>66–69</td>
<td>311–320</td>
<td>311–320</td>
</tr>
</tbody>
</table>

The rocking curve, $\omega$-scans, of the 100 and 102 peaks from the ZrB$_2$, and for reference, the Si substrate 400 peak are presented in Figure 3. It is evident that, of the film peaks, the 100 peak has the lowest full width at half maximum value (FWHM) with 2.00°, while the FWHM of 102 is 4.97°, where the substrate peak is shown and its FWHM value (0.01°) given as reference for the peak broadening caused by the optics.

3. Discussion

The strongest peaks in the $\theta$/2$\theta$ diffractogram are from diffraction with the n00 plane family. This results from the fact that most of the film is oriented $(\text{ZrB}_2(100)||\text{Si}(100)$, i.e., c-axis parallel to the surface). In addition, the relatively high intensity of the 102 peak (compared with the peak height distribution of the PDF card) shows that a significant diffraction volume of the film is oriented this way $(\text{ZrB}_2(102)||\text{Si}(100))$, which means that the c-axis is neither parallel, nor perpendicular to the substrate surface, but tilted by 32.75° relative to the surface normal.

From the pole figure measurements, based on the appearance of distinct peaks, but no rings, it can be concluded that the film is epitaxial. The $\psi$-angle of the four strongest peaks in the 001 pole figure at around 32° matches well with the expected appearance of the 001 reflex from 102-oriented grains, at $\psi = 31.3^\circ$, whose existence was indicated already in the $\theta$/2$\theta$ diffractograms. We can further retrieve the information that these 102-oriented crystallites exist four times, 90° apart in $\phi$, and together with the Si (220) pole figure (see Figure S1, Supporting Information) this yields ZrB$_2[1\overline{1}00]||\text{Si}(110)$. This is to be expected, given the four-fold symmetry of the Si(100) substrate surface. The $\theta$/2$\theta$ diffractograms showed strong peaks of the n00 family, but in the 001 pole figure, 001 reflexes of this orientation cannot be observed. This is also to be expected, as these reflexes would appear at $\psi = 90^\circ$ and the pole figure measurement ends at $\psi = 85^\circ$. If epitaxial n00 grains exist in the film, peaks from these should be observable in the 101 and 111 pole figures.

This is in fact observed in both those pole figures: a n00-oriented ZrB$_2$ crystal shows six peaks in the 101 pole figure, three in each half ($\phi = 0$ to 179° and 180 to 359°), where the pattern of one half is repeated 180° rotated in $\phi$. From the peak pattern in the 101 pole figure, we can conclude that these six peaks exist (see the black diamonds in Figure 4). More so, there are two times these six peaks, rotated by 90° in $\phi$, originating from two types of n00-oriented grains that are rotated by 90° in the film plane. The four double peaks at $\psi \approx 65^\circ$ stem from differently in-plane-oriented n00 grains. This finding is similar to those previously reported in CVD studies: by Roucka et al.[18] for a ZrB$_2$ film deposited on Si(100), and for the group 4 neighboring HfB$_2$, having similar lattice parameters to ZrB$_2$, by Yang et al.[21] on Si(100). Together with the Si (220) pole figure (see Figure S1, Supporting Information) this gives: ZrB$_2[1\overline{1}00]||\text{Si}[110]$ and ZrB$_2[001]||\text{Si}[110]$.

The epitaxial 102-oriented grains previously identified in the 001 pole figure appear in the 101 pole figure with a distorted hexagon of peaks for each of the four orientations (see blue stars in Figure 4), where the peaks at $\psi \approx 40^\circ$ result from two of the 102-oriented grain types that are rotated 90° in the film plane and are actually double peaks at similar $\psi$ and $\phi$. Knowing the in-plane orientation of the Si(100) substrate from the Si 220 pole figure (Figure S1, Supporting Information), we conclude the following: ZrB$_2[1\overline{2}00]||\text{Si}[110]$. We are not aware of any previous reports describing this type of epitaxial relationship for ZrB$_2$ or HfB$_2$ films deposited on Si(100) substrates.

Figure 3. Rocking curve of the ZrB$_2$ film’s 100 (black) and 102 (blue) peaks, and the Si substrate 400 peak (inset). Peak positions according to other studies[19,20] are marked by the dashed lines in the figure. FWHM values are denoted in the figure.
In the 111 pole figure, peaks show up where they would be expected from the two orientations of the n00-oriented crystal grains described earlier. The strong peak in the center results mainly from the strong 400 peak of the substrate as the 2θ angle of this pole figure (64.4°) is close to the 2θ angle of the Si 400 peak (69.1°). The 111 pole figure also shows peaks from the above-described 102-oriented grain types, yet at very low intensity.

The weak intensity from the 102-oriented grains can be understood when considering the relative intensities for ZrB$_2$ given in another study$^{[19]}$. 111 peaks have only 16% intensity relative to the highest intensity peaks, that is, 101 peaks, at 100%, and 001 peaks have 30% intensity. These intensities match well with the intensities of the peaks originating from 102-oriented grains in the three pole figures. In the 101 and 111 pole figures, where peaks from the n00-oriented grains are visible, those peaks are much higher in intensity than peaks originating from 102-oriented grains, which match well with the peak intensity distribution of the θ/20 diffractograms, where n00 peaks show much higher intensity than 102 peaks.

The lower FWHM of the 100 peak in the rocking curve measurement of 2.0° supports that the crystallites with this orientation have a higher crystalline quality than those from the 102 orientation (who show larger FWHM values, 4.97°, in the rocking curve measurement). For the 00n peak, no FWHM value could be determined. Our FWHM value for the 100 peak is almost one order of magnitude higher than 0.285° reported by Roucka et al.$^{[18]}$ for their ZrB$_2$ films deposited on Si(100) by CVD, indicating a lower crystalline quality. The broadening of the present rocking curve peak could be from excess B in our deposited ZrB$_2$ films, seen from a B:Zr ratio of 2.3, with likely pending segregation of B to grain boundaries,$^{[23,24]}$ together with the formation of domain boundaries to 102-oriented grains, both disturbing the lattice. Sputtering of boron-rich TMB$_2$ films is frequently reported in the literature$^{[60]}$ and shows a strong tendency for B to segregate to the grain boundaries. For the closely related TiB$_2$, we note that the B:Ti ratio depends on the pressure-distance product$^{[25]}$ and has been tuned to 2.0 through an increase of the Ar pressure from 5 to 20 mTorr at a substrate-to-target distance of 65 mm (requiring strong external magnets to maintain dense films).$^{[26]}$ Further reported methods to reach stoichiometric TiB$_2$ films are the increase of the plasma density near the substrate by use of a coil in a highly unbalanced magnetron sputter process$^{[27]}$ or altering the sputtering process from DCMS to HiPIMS and adjusting the pulse length, while keeping average power and pulse frequency constant.$^{[28]}$ Epitaxial growth of ZrB$_2$ films on Si(100) would benefit from similar strategies.

The lattice mismatch for the 102-oriented grains is in one direction of the previously reported coincidental 6:5 mismatch,$^{[18]}$ where 6 Zr–Zr $(a_{ZrB_2} = 3.1687 \text{ Å})$ distances match 5 Si–Si $(\sqrt{2} a_{Si} = 3.84021 \text{ Å})$ distances with only 0.98% deviation and in the other in-plane direction a 4:5 mismatch occurs where 4 Zr–Zr $(\sqrt{(a_{ZrB_2} \sqrt{3})^2 + c_{ZrB_2}}) = 6.5256 \text{ Å})$ distances match 5 Si–Si $(2 \sqrt{2} a_{Si} = 3.84021 \text{ Å})$ distances with 1.18% deviation.

For the 100-oriented grains, the same 6:5 mismatch holds for one direction, whereas the other has a 12:11 mismatch where 12 ZrB$_2$ c-plane distances $(3.53002 \text{ Å})$ match 11 Si–Si distances $(\sqrt{2} a_{Si} = 3.84021 \text{ Å})$ with 0.28% deviation. These mismatch calculations show that the mismatch for the 100-oriented grains is smaller than that for the 102-oriented grains, which helps explain why the latter is not observed when ZrB$_2$ is deposited by CVD, a process conducted close to thermodynamic equilibrium.

4. Conclusion

Epitaxial growth of ZrB$_2$ films is possible to achieve using DCMS from ZrB$_2$ targets onto Si(100) substrates kept at 900 °C. The films exhibit two types of epitaxial relationships to the substrate; one exists as 2 domains, rotated by 90° around the surface normal, consistent with previous observations for ZrB$_2$ and HfB$_2$: out-of-plane: ZrB$_2$(100)||Si(100) and in-plane: ZrB$_2$(110)||Si(110) and ZrB$_2$(001)||Si(110). The other, previously not known, is constituted by 4 domains, mutually rotated by 90° degree around the surface normal with out-of-plane: ZrB$_2$(102)||Si(100) and in-plane: ZrB$_2$(110)||Si(110).

5. Experimental Section

The ZrB$_2$ films were deposited at 900 °C using DCMS from a 3” compound target made from sintered ZrB$_2$ powder (99.5% purity from Kurt J. Lesker Company Ltd, Hastings, UK) in a vacuum chamber at a base pressure of $\approx 1 \times 10^{-5}$ Pa. During deposition, a working pressure of 0.53 Pa was maintained by introducing Ar sputter gas (99.9997%) into the chamber. The sputtering target was held at a constant sputtering power at 400 W, resulting in a sputtering current of 880 mA. The rotating substrates were placed in the holder 7 cm above the type-II unbalanced 3° magnetron and 3 cm radially outward from the target-holder axis. After 5 min of presputtering, during which the power was gradually increased from 50 to 400 W to avoid cracking of the ZrB$_2$ compound target, the shutter that covers the magnetron and prevents stray coating of the substrates was opened for a deposition time of 300 s. The process resulted in a deposition rate of 1 nm s$^{-1}$ and thus a film thickness of 300 nm (measured by cross-sectional secondary electron microscopy imaging). During
deposition, the substrates were kept at floating potential and were rotated at 4 revolutions min−1. The substrates were 1 × 1 cm² pieces cut from a 10 cm-circular p-doped Si(100) wafer from University Wafers, Boston, MA, USA (resistivity: 0-100 Ωcm). The substrates were degreased in trichloroethylene, then acetone, and finally isopropanol for 5 min each, in an ultrasonic bath followed by removal of the native surface oxide by etching in 4% HF solution for 4 s. Afterward, the samples were transported in H₂O to be introduced into the vacuum chamber.

To assess the composition of the deposited film, ToF-ERDA was carried out in a 5-MV NEC-SSDH-2 pelletron tandem accelerator using TiN, CaF₂, and Au reference samples. The 36 MeV ¹³⁷Cs beam was directed at an incident angle of 22.5° to the sample surface and recoils were measured at an angle of 45° with respect to the incident beam. To evaluate the acquired raw data, the software version 2.0 was applied.[28]

Measurements of the θ/2θ diffractograms were conducted in a PANalytical X’Pert PRO diffractometer with Cu Kα source (1.54 Å) and were operated at 45 kV and 40 mA and covered a range from 5° to 126.5°. The optics were a 0.5° divergence slit in front of a Bragg–Brentano optical module, and a 0.5° antiscatter slit on the primary side, while a 5° antiscatter slit, 0.04 rad soller slits, and Ni Kα filter were used on the secondary side. The X’Celerator detector scanned in continuous mode with a step size of 0.0167° and a counting time of 26.670 s.

The XRD pole figures and ω-diffraction patterns (rocking curve measurements) were recorded in a PANalytical Empyrean diffractometer containing a Cu Kα source (1.54 Å) that was operated at 45 kV and 40 mA, in point focus and line focus for pole figures and ω-diffraction patterns, respectively. The optics for the pole figures were on the incoming-beam an X-ray lens with crossed slits at 2 mm width, each, and on the secondary side, a parallel plate collimator with a 0.27° opening in front of an area detector in receiving slit mode. The step width in ω and ψ was 2° and 2.5°, respectively.

For the recording of the ω-diffraction patterns, primary optics were a 1/4° divergence slit and a hybrid monochromator (2-bounce Ge(220)) and secondary optics were a parallel plate collimator with 0.27° opening in front of an area detector in receiving slit mode. The step width was 0.5° for the ZrB₂ 100 peak, 0.3° for the ZrB₂ 102 peak, and 0.004° for the Si 400 peak. FWHM values were obtained using the peak parameters tool in the software PANalytical Data Viewer version 1.3b (1.3.2.6).

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

bortides, epitaxial growth, Si(100), sputter deposition, thin-film X-ray diffraction

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors acknowledge financial support from The Knut and Alice Wallenberg Foundation, Project Grant (The Boride Frontier, KA 2015:0043), and from Åfors Foundation, grant no. 16-430. J.R. and H.H. acknowledge the Swedish Government Strategic Research Area in Materials Science on Advanced Functional Materials at Linköping University (Faculty Grant SFO-Mat-LIU No. 2009-00971). Support from the Swedish research council VR-RFI (#2017-00646_9) for the Accelerator-based ion-technological center, and from the Swedish Foundation for Strategic Research (contract RIF14-0053) for the tandem accelerator laboratory in Uppsala, is gratefully acknowledged. The authors acknowledge Lars Hultman for reviewing the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

[19] JCPDS - International Centre for Diffraction Data ZrB₂, Ref ID: 00-0423.
[20] JCPDS - International Centre for Diffraction Data Si, Ref ID: 00-27-1402.