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Stoichiometric, epitaxial ZrB₂ thin films with low oxygen-content deposited by magnetron sputtering from a compound target: Effects of deposition temperature and sputtering power

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Abstract

Zirconium diboride (ZrB₂) thin films have been deposited on 4H-SiC(0001) substrates by direct current magnetron sputtering from a compound target. The effect of deposition temperature (500-900 °C) and sputtering power (100-400 W) on the composition and structure of the films have been investigated. Electron microscopy and X-ray diffraction reveal that high sputtering power values and high deposition temperatures are favorable to enhance the crystalline order of the epitaxial 0001-oriented films. X-ray photoelectron spectroscopy shows that the composition of the films is near-stoichiometric for all deposition temperatures and for high sputtering power

values of 300 W and 400 W, whereas understoichiometric films are obtained when applying 100 W or 200 W. Decreasing the deposition temperature, or in particular the sputtering power, result in higher C and O impurity levels. The resistivity of the films was evaluated by four-point-probe measurements and found to scale with the amount of O impurities in the films. The lowest resistivity value obtained is 130 $\mu\Omega\text{cm}$, which makes the ZrB_2 films interesting as an electrical contact material.

Keywords

A1. X-ray diffraction; A1. X-ray photoelectron spectroscopy; A3. Physical vapor deposition processes; B1. Borides

1. Introduction

Zirconium diboride (ZrB_2) exhibits a number of attractive properties including high melting point, high hardness, and low resistivity [1, 2]. In addition, the compound is chemically inert and shows good wear and corrosion resistance, even at elevated temperatures. These properties make epitaxial ZrB_2 thin films grown on closely lattice matched semiconductor substrates, such as 4H-SiC(0001), interesting as an electrical contact material in demanding environments [3-6].

ZrB_2 thin films can be synthesized by sputtering from a compound or composite target [7-15]. This is the predominant synthesis route, given the lack of a suitable boron precursor for reactive sputtering. However, the literature shows that the resulting films usually exhibit a high level of contaminants [4, 7, 11, 12, 16], with O levels of up to 30 % due to the reactive nature of B under the applied process conditions [7]. In many cases the films are also non-stoichiometric [11, 16], which is problematic for maintaining the crystal structure of ZrB_2 since thermodynamics predicts ZrB_2 to be a line phase with a narrow homogeneity range ($<1\%$) [17]. Excess atoms of Zr or B are

thus not accommodated in the ZrB_2 lattice, but nucleate as different phases. This means that the composition of the films can only deviate very little to avoid undesired phase separation. The occurrence of these separate phases will disrupt sought epitaxial growth conditions. Thus, it is necessary to have a stoichiometric growth flux during deposition of ZrB_2 films. In addition, the presence of a foreign element such as O during nucleation of ZrB_2 is likely to cause unwanted chemical reactions between the film constituents and the contaminant. Such conditions will affect the properties, including the electrical resistivity [16], of the films. Thus, the resistivity is an important parameter for evaluating the quality of ZrB_2 thin films.

Recently, we demonstrated that stoichiometric ZrB_2 thin films with a low fraction of contaminants can be deposited from a ZrB_2 compound target in an industrial coating system [14]. For growth of such films, we applied a combination of a relatively short target-to-substrate distance of 7 cm, high sputtering power on the target of 11.36 Wcm^{-2} , a short deposition time of 100 s, and in a geometry where the sputtered material arrives nearly perpendicular to the substrate.

Previous studies on the structure of ZrB_2 thin films grown using sputtering techniques have mostly concentrated on low temperature growth [9, 10, 12-14, 18, 19] with 550°C being the highest deposition temperature used. Some of these studies [12, 13, 19] report on films with an amorphous structure. Takeyama et al. [12] states that their films are amorphous regardless of deposition temperature between RT and 500°C and that annealing the films at temperatures up to 700°C for 1 h only results in a slight increase of the intensity of the diffraction peaks, meaning that this temperature is not enough to completely crystallize the films. Lee et al. [19] and Brandstetter et al. [13] also report on amorphous film growth at low temperatures, but state that there is a transition from amorphous growth to crystalline growth at $400\text{-}450^\circ\text{C}$ and $200\text{-}300^\circ\text{C}$, respectively. In contrast, we [14] and others [9, 10, 18] have shown that it is possible to grow crystalline films also

at temperatures below 200 °C. Characteristic for these studies are a short target-to-substrate distance (5.5 cm or 7 cm) and high sputtering powers applied to the targets ranging from 2.8 Wcm⁻² to 11.32 Wcm⁻². Films grown on 4H-SiC(0001) substrates without external heating are 0001-oriented and fiber textured [14]. When the deposition temperature is increased up to 550 °C the films exhibit a more random growth behavior with an increasing contribution from 10 $\bar{1}$ 1-oriented grains [14]. Following those experiences, we demonstrated that it is possible to grow epitaxial films of ZrB₂ on 4H-SiC(0001) substrates, with the epitaxial relationship of ZrB₂(0001) || 4H-SiC(0001) and ZrB₂[1 $\bar{1}$ 00] || 4H-SiC[1 $\bar{1}$ 00], in a laboratory scale ultra-high vacuum (UHV) system at 900 °C [15]. However, the growth behavior on 4H-SiC(0001) at temperatures between 550 °C and 900 °C remains to be investigated.

Given some substrate materials' tendencies to react with the film at high temperatures [15], such as for Si and GaN, it is desirable to find a synthesis route to increase the crystal ordering in the film without increasing temperature. One parameter that is likely to affect the structure of the film is the amount of power applied to the cathode, where a higher sputtering power results in a denser flux of precursors arriving at the substrate. As mention above, we note that all studies reporting on crystalline, and not amorphous, growth at low deposition temperatures, have applied high sputtering powers [9, 10, 14, 18]. Given the issues discussed above, the aim of our work is to grow stoichiometric, dense, highly ordered crystalline ZrB₂ thin films with low oxygen-content, preferably at lower deposition temperature than we have demonstrated previously [15].

In this study, we investigated the influence of growth temperature and sputtering power on the structure of ZrB₂ thin films on 4H-SiC(0001) by using direct current magnetron sputtering (DCMS) of a ZrB₂ compound target in an UHV deposition system. The deposited films were characterized

with respect to their chemical composition including oxygen-content, structural properties, and resistivity.

2. Experimental details

The ZrB₂ thin film growth was conducted in an UHV system with the same set-up and conditions as described elsewhere [15]. The substrates were outgassed in the growth chamber at 900 °C for 1 h. The temperature was then changed to a deposition temperature of either 500 °C, 600 °C, 700 °C, 820 °C or left at 900 °C. The ZrB₂ deposition was carried out by DCMS of a circular 3 inch ZrB₂ compound target of 99.5 % purity (excluding Hf) from Kurt J. Lesker Company Ltd. Before the coating process was initiated the ZrB₂ target was pre-sputtered by slowly increasing the power from 50 to 400 W. This was followed by decreasing the power to 200 W, where the target was run in during several hours. Prior to each deposition, the target was pre-sputtered behind a shutter for at least 2 minutes following a slow increase from 50 W to the applied sputtering power. Films were deposited using a magnetron power of 100 W, 200 W, 300 W, and 400 W. In order to achieve roughly the same film thickness (~ 425 nm) for all films the product of the sputtering current and deposition time values was kept constant, resulting in applied deposition times of 1080 s, 600 s, 450 s, and 300 s, respectively. The Ar (99.9997 %) plasma was held at 0.53 Pa and a substrate bias of -80 V was applied. The substrates were 4H-SiC(0001) that had been degreased with trichloroethylene, acetone, and ethanol, followed by cleaning with a modified RCA process, as described elsewhere [14], and finally dipped in 10 % HF before loading into the UHV system.

Transmission electron microscopy (TEM) imaging was 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.

The cross-sectional TEM specimens were prepared by gluing two pieces of samples face to face together, polishing from both sides of the specimen down to 60 μm in thickness, and finally ion milling to electron transparency.

X-ray diffraction (XRD) was used to evaluate the structural properties of the films. A Philips PW 1820 system, equipped with a Cu anode X-ray tube operated at 40 kV and 40 mA, was employed to record θ -2 θ scans. The growth mode (random, textured or epitaxial) was assessed from XRD pole figures recorded in a PANalytical EMPYREAN system and a Philips MRD diffractometer (for complementary measurements presented in supplementary information), both equipped with Cu anode X-ray tubes operated at 45 kV and 40 mA.

The chemical bonding structure, elemental composition and level of contaminants of the films were investigated by X-ray photoelectron spectroscopy (XPS), using an AXIS Ultra DLD instrument from Kratos Analytical, at a base pressure of 1.5×10^{-7} Pa, with monochromatic Al K α radiation ($h\nu = 1486.6$ eV) and the x-ray anode operated at 225 W. The binding energy scale was previously calibrated by setting the position of the Fermi edge of a sputter-cleaned Ag sample to 0.0 eV [20] resulting in the position of the Ag 3d $_{5/2}$ core-level peak of 368.30 eV [21]. The samples were analyzed both in the as-deposited state and after sputter-cleaning for 180 s with 4 keV Ar-ions incident at an angle of 70° with respect to the surface normal, in order to remove adsorbed contaminants following air exposure. Quantification was performed using Casa XPS software (version 2.3.16), based upon peak areas from narrow energy range scans and elemental sensitivity factors supplied by Kratos Analytical Ltd [22]. The confidence level of XPS is typically around ± 5 %.

Four point probe measurements were performed at room temperature conditions using an Auto map system Model 280C from Four Dimensions, Inc. The attained sheet resistance was multiplied with the film thickness, measured by TEM, to obtain the in-plane resistivity.

3. Results and discussion

3.1 Influence of deposition temperature on film structure

Electron microscopy investigation shows that the films exhibit a dense columnar microstructure, regardless of deposition temperature for a fixed power of 400 W applied to the target, see Fig 1 for a film deposited at 900 °C. The low-magnification image shows the start of the columns on the substrate surface and in the high-resolution image it can be seen that the columns extend throughout the film.

In Fig 2, all peaks seen in the θ -2 θ diffractograms can be assigned to the single-crystal 4H-SiC-substrate or ZrB₂ [23] and demonstrate that the phase has been deposited and that the films are crystalline regardless of deposition temperature. The diffractograms reveal that the $10\bar{1}1$ peak is the strongest for films grown at temperatures up to 600 °C, which is consistent with our previous findings [14]. At higher deposition temperatures the films become 0001 oriented. The transition towards a 0001 texture is gradual, but the intensity relationship of the ZrB₂(0001)/4H-SiC(0004) peaks are 40 times higher for the film grown at 820 °C compared to the film grown at 700 °C and 60 times higher for the film grown at 900 °C compared to the film grown at 820 °C. The high intensity of the ZrB₂ 0001-peak in the films grown at higher temperatures indicates that the films are well-ordered. In addition to the 0001 peak, the $10\bar{1}1$ peak is present in all films and for films deposited at temperatures below 900 °C there are also low-intensity peaks from $10\bar{1}0$ and $11\bar{2}0$ present, revealing a mixture of growth directions. To deduce whether the films grow fiber

textured or epitaxial, pole figure measurements were conducted for the temperature series of films.

Fig 3 a) shows the 0001 pole of the film grown at 600 °C. A ring of uniform intensity is seen meaning that the majority of the grains grow in the same direction out-of-plane, but that they are rotated in all directions in-plane, i.e. the film is fiber textured. The position of the ring at $\psi \approx 55^\circ$ is in accordance with the calculated value for the angle between the 0001 and the $10\bar{1}1$ planes in ZrB_2 (52°), indicating that the film is mainly $10\bar{1}1$ oriented. However, the high intensity point in the middle shows that there are also some grains oriented in the 0001 direction. The 0001 pole figure for the film grown at 500 °C (not shown) is similar to the one for 600 °C, but the ring is of slightly lower intensity. The pole figures seen in Fig 3 b) and c) for the films grown at 700 °C and 820 °C, respectively, shows the $10\bar{1}1$ pole. The intense points in the middle show that there are still $10\bar{1}1$ -oriented grains in the films grown at these temperatures. At $\psi \approx 55^\circ$ a pattern of six high intensity points separated by 60° in ϕ starts to appear, becoming stronger for the film grown at 820 °C. This pattern is a consequence of the six-fold symmetry present in the ZrB_2 crystal structure and suggests that one specific in-plane direction is becoming more favorable than the rest, i.e. the growth is transitioning from fiber textured to epitaxial. However, the film grown at 820 °C is not fully epitaxial. For comparison, Fig 3 d) shows the $10\bar{1}1$ pole for an epitaxial film grown at 900 °C where the six points are very distinct and high in intensity and the point in the middle is almost gone, meaning that there is a very small fraction of $10\bar{1}1$ -oriented grains in this film. This is supported by the low intensity ratio of 0.02 % for the $10\bar{1}1/0001$ peaks in the θ -2 θ diffractogram.

To summarize thus far, our results show that the deposition temperature, i.e. the mobility of the condensed atoms is, as expected, crucial for the structural properties of the resulting films and

that the epitaxial growth of ZrB_2 thin films on 4H-SiC(0001) requires a growth temperature higher than 820 °C under the deposition conditions used in this study. It should be investigated if 900 °C is the optimal deposition temperature or if even higher temperatures would increase the quality of the grown films further. However, limitations of our deposition system prevent us from investigating higher temperatures at present.

3.2 Influence of sputtering power on film structure

Following the results from the temperature study, we investigated ZrB_2 thin film growth at sputtering powers of 100 W, 200 W, 300 W, and 400 W, all at a deposition temperature of 900 °C. In the θ -2 θ diffractograms in Fig 4 it can be seen that although all films are 0001-oriented there is, in the films grown at lower power, a larger component of grains oriented in other directions as well. For instance, the $10\bar{1}1$, $10\bar{1}2$, $10\bar{1}3$, and $11\bar{2}0$ peaks are present in the film grown at 100 W and they get weaker with increased power. Also, the intensity of the 0001 peak is lower for films deposited applying lower sputtering power. In addition, the FWHM value of the 0001 peak is increased from 0.13 to 0.19 when the sputtering power is decreased from 400 W to 100 W, where the peak broadening indicate less ordered growth of the columns for films deposited applying a lower sputtering power.

TEM images in Fig 5, of a film grown at 100 W, reveal that part of the film is growing columnar, although with the columns tilted somewhat in respect to the substrate surface normal, but there are also other features in the film. Some grains grow in other directions and grow out of the film, making the surface uneven. This rough surface structure and the trenches and hollow spaces in between these grains create voids where it is easy for oxygen and other impurities from the atmosphere to dissolve when the film is taken out of the vacuum chamber, which is supported by

XPS results presented in section 3.3. We believe that the microstructure of this film is due to the low flux of sputtered material at such low (100 W) sputtering power, most likely resulting in a larger uptake of contaminants.

From the pole figures in Fig 6 it is seen that the six distinct points of high intensity at $\psi \approx 55^\circ$, revealing epitaxial growth in the 0001 direction, is present for all films regardless of applied sputtering power. However, in the films grown at lower power the intensity of the points is lower and there are also other features present, indicating a mixture of growth directions, which is in agreement with what is observed in the TEM images in Fig 5. The high-intensity points in the middle of the pole figures recorded for the films grown between 100 W and 300 W confirm that there are grains oriented in the $10\bar{1}l$ directions, as already seen in the θ - 2θ diffractograms (Fig 4). The largest differences in structure can be seen between the films grown at 200 W and 300 W, indicating that the growth behavior changes in this region of sputtering power. In Fig 6 a)-c) there are also six points visible at $\psi \approx 25^\circ$. In order to deduce the origin of these diffraction points, additional pole figure measurements were conducted (see supplementary material online). These revealed 5 groups of crystals with the c-axis being inclined with respect to the sample surface normal. Every group exhibits 6-fold rotation around the sample surface normal. Those 5 groups are the origin of the additional peaks in Fig 6, see supplementary material for a more detailed investigation.

We have ruled out that the change in structure seen at different applied powers is due to differences in deposition time by depositing control films using 400 W for 450 s and 600 s. Neither of these films showed signs of deteriorated crystal quality.

From these results it is evident that a higher power is desirable in order to grow high quality crystalline films. We believe that this is due to the mobility improvement of adatoms sputtered on the surface, which is required to form dense and highly crystalline films.

This study could not determine the minimum deposition temperature for growing epitaxial films. In order to do that, even higher sputtering power values should be investigated. We are, however, unable to investigate this at present due to the fact that using very high sputtering powers is hinged on the performance of the sintered targets, the bonding of the targets and effective cooling of the cathode in order to prevent the target from cracking.

3.3 Chemical bonding structure and elemental composition

The chemical bonding structure and elemental composition of the films was evaluated by XPS. Fig 7 displays XPS spectra of the Zr 3d and B 1s photoelectron region obtained from a ZrB₂ film grown on 4H-SiC(0001) at 900 °C and with 400 W. The dotted line is the spectrum acquired from the as-deposited film and the solid line is the spectrum obtained after sputter cleaning. The sputter-cleaned surface exhibits peaks at 179.0 eV, 181.3 eV, and 188.0 eV assigned to Zr 3d_{5/2}, Zr 3d_{3/2}, and B 1s core levels of ZrB₂, respectively. These values fit well with the reported peak positions for ZrB₂ single crystals of 178.9 eV (Zr 3d_{5/2}), 181.3 eV (Zr 3d_{3/2}), and 187.9 eV (B 1s) [24] as well as 179.0 eV (Zr 3d_{5/2}), 181.4 eV (Zr 3d_{3/2}), and 188.0 eV (B 1s) [25]. In addition, the symmetrical shape of the B 1s peak indicates that there is only one chemical state of B present in the film, in agreement with what has been reported for ZrB₂ [24]. Thus, we conclude that all peaks present in this spectrum originate from bonds between Zr and B.

The dotted curve recorded from the as-deposited film exhibits, apart from contributions described above, additional peaks at 183.4 eV, 185.8 eV, and 193.0 eV. The first two peaks are assigned to

Zr 3d_{5/2} and Zr 3d_{3/2} core levels from zirconium oxide while the third peak is identified as B 1s contribution due to B-O bonds. The fact that these peaks are not seen after the sample has been sputter-cleaned shows that the O signal mainly originates from a thin surface oxide layer on the as-deposited film. This is also supported by high-resolution O 1s spectra (not shown), revealing substantially decreased intensity of the O peak after sputtering.

Fig 8 displays an XPS spectrum of a ZrB₂ film grown on 4H-SiC(0001) at 900 °C and with 100 W. In contrast to the corresponding spectrum obtained from the film grown at 400 W (see Fig 7), the signal contributions due to Zr-O and B-O bonds persist even in the spectrum of the sputter-cleaned film (solid line). Given the UHV growth conditions, these O signals are most likely due to the high film porosity, seen in the TEM images in Fig 5, causing significant amounts of O to dissolve in the voids, following air exposure [26].

XPS spectra recorded for films deposited using 200 W and 300 W sputtering power (not shown) look similar to those shown in Fig 8 and Fig 7, respectively. This supports the change in growth behavior, between 200 W and 300 W, seen in the pole figures in section 3.2.

In Table 1 the XPS-derived compositions and contamination levels for films grown at 400 W, 300 W, 200 W, and 100 W are summarized. For the films deposited using power levels of 400 W and 300 W, the B/Zr ratio is 2.07 and 2.12, respectively, i.e. close to the stoichiometric composition of B/Zr = 2, but with some excess of B. However, when a lower power is applied to the cathode (200 W and 100 W), the B/Zr ratio is significantly reduced to only 1.54 and 1.51, respectively. It should be noted that in the case of oxygen-rich films the B/Zr ratio estimates are rather challenging due to significant overlap between the Zr 3d_{3/2} peak from Zr-O bonds and the B 1s peak from B-Zr bonds, which has a negative effect on confidence levels. The contamination

levels in these films following air exposure are also extremely high with an O level of almost 27 at% and a C content of 8 at% in the film grown at 100 W. This shows that sputtering at 300 W and 400 W yields stoichiometric films whereas sputtering at 100 W and 200 W results in understoichiometric films. The negative effect of low power on the density of the films is clearly seen from the TEM results as well as from the high O content in films deposited at 100 W and 200 W and is in agreement with the XRD results on the structure of the films, showing decreased crystalline quality at lower sputtering powers.

XPS spectra recorded from films deposited at other temperatures (not shown) look similar to those in Fig 7 revealing that the chemical bonding structure is not substantially influenced by the deposition temperature. Our results show that we have developed robust deposition processes and are able to deposit the ZrB_2 phase over a wide temperature range.

Table 2 shows the variation of composition and level of contaminants for films deposited at temperatures between 500 °C and 900 °C. The films are close to stoichiometric with B/Zr ratios between 2.06 and 2.12. Thus, the deposition temperature does not considerably affect the composition. Our results are seemingly in contrast to the results of Mitterer et al. [9] showing an increasing B/Zr ratio from 2.5 to 2.9 when raising the deposition temperature from 100 °C to 400 °C. We note the use of an increased pressure $\times$ target-to-substrate distance product in their study ($1.1 \text{ Pa} \times 5.5 \text{ cm} = 6.05 \text{ Pacm}$) compared to ours ($0.53 \text{ Pa} \times 7 \text{ cm} = 3.71 \text{ Pacm}$), which cause the much larger atom Zr to scatter more and therefore arrive in smaller quantities at the substrate.

In contrast to the stoichiometry stability, our results show that decreasing the deposition temperature causes increased O concentration. The effect, however, is not nearly as large as when

decreasing the applied power. The O level dependence on deposition temperature can be explained by the known physical fact that desorption of O, or rather OH, from surfaces is favored by higher temperatures. This is in agreement with Oder et al. [27] who reported that the O concentration in ZrB₂ films decreased when the deposition temperature was increased from 20 °C to 600 °C.

Since XPS is a surface sensitive technique, the O levels recorded by this technique are expected to be higher than what is actually present in the bulk of the films due to the presence of a thin surface oxide. Also, it is known that O is hard to remove by sputter-cleaning, due to high reactivity of O towards Zr, and this will affect the results. This is supported by our previous finding of O levels of around 1 at% by using elastic recoil detection analysis (ERDA), which is a bulk technique, while XPS on the same samples show O levels of around 5-6 at% for films deposited at both room temperature (RT) and 550 °C in an industrial deposition system [14]. The same is true for the C content, which is < 0.5 % in these films according to ERDA. We therefore conclude that the level of impurities inside our present films, grown at high sputtering powers and at high deposition temperatures, is low.

Several sources of the O in the films have been discussed in the literature. Oder et al. [27] suggest that the O originates from oxides on the substrate surface and that the reason for the decreased O content in films deposited at higher temperature is that the O at the film surface is removed by the formation of B₂O₃ and H₃BO₃, which are volatile at 300 °C. Chakrabarti et al. [16] discuss that O could become dissolved in microvoids in the film after deposition, but also states that it is unlikely that this can be the whole reason and that most of the O probably originates from the incorporation of residual gases such as H₂O and CO₂ during deposition. Takeyama et al. [12] infers that O could originate partly from the residual gas, but that it could also stem from

impurities in the target. Since we have previously shown that films with a low level of O can be deposited using a high vacuum deposition system [14] and that an increased deposition time employed by Samuelsson et al. [18] does not result in higher O levels, we proposed that at least part of the O originates from the compound targets. To confirm this we analyzed a piece of the target with XPS and found considerable amounts of both C (~8 at%) and O (~19 at%) even after 25 min of sputter-cleaning. As the properties of ZrB_2 films are compromised when grown at high loads of contaminants, this suggests that a target material with a lower amount of contaminants would enable us to further increase the quality of our films, potentially at lower deposition temperatures.

3.4 Resistivity

The resistivity of the films deposited in this study varies between $130\ \mu\Omega\text{cm}$ (best value) and $500\ \mu\Omega\text{cm}$. This is in the same region as for other as-deposited magnetron sputtered films from compound targets ranging between 100 and $440\ \mu\Omega\text{cm}$ [11, 12, 14, 16, 18, 19, 28].

Fig 9 shows that the resistivity decreases almost linearly with increased sputtering power. The trend for deposition temperature, seen in Fig 9 as well, is also that the resistivity decreases when the temperature is increased, but the difference is not as prominent. The resistivity follows the same trends as the O level in the films determined by XPS, which we described in section 3.3 above. These results are consistent with other reports stating that the resistivity is affected by the deposition temperature [19, 27] or changes in the O level due to low deposition rates or higher process pressure [16].

Since the resistivity of the films is clearly influenced by the O level and we believe that at least part of the O originates from the target, this shows the need of further process development to

lower the amount of O in the films, particular at sputtering power values below 300 W, and where targets with lower amounts of contaminants are an important factor for increasing the quality of the films.

4 Conclusions

Our investigation of the growth behavior of ZrB_2 thin films on 4H-SiC(0001) at temperatures between 550 °C and 900 °C shows that the structural properties of ZrB_2 thin films are affected substantially by deposition temperature. Pole figure measurements show that the structure changes gradually from a $10\bar{1}1$ fiber texture to a 0001 epitaxial growth when increasing the temperature from 500 °C to 900 °C. Our results show that the temperature needs to exceed 820 °C in order for the surface mobility of the condensed atoms to be sufficiently high to achieve epitaxial growth.

The sputtering power, i.e. the flux of the sputtered material, also has a further positive impact on the quality of the thin films deposited at 900 °C. A significant change in growth behavior is observed between 200 W and 300 W, where the lower sputtering powers result in understoichiometric porous films with high levels of contaminants, and with grains growing in multiple directions, whereas the higher sputtering powers result in stoichiometric films with low level of impurities and high crystalline ordering.

The level of contaminations in the films is increased when either the deposition temperature or the sputtering power is decreased. The film resistivity varies between 130 $\mu\Omega\text{cm}$ and 500 $\mu\Omega\text{cm}$ and follows the same trends as the O concentration in the films. Thus, in order to grow films with even lower resistivity, the O concentration needs to be further reduced. Our results suggest that applying high deposition temperatures, high sputtering powers and using target materials with a low amount of contaminants are important factors to achieve this goal.

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List of captions

Table 1 Composition and level of contaminants determined by XPS, following 180 s of sputter-cleaning, for ZrB_2 films deposited at 900 °C with different amount of power applied to the target.

Table 2 Composition and level of contaminants determined by XPS, following 180 s of sputter-cleaning, for ZrB_2 films deposited with 400 W applied to the target at different deposition temperatures.

Fig 1 TEM images of a film deposited at 900 °C and with 400 W applied to the target. a) High-magnification image of the film near the surface and b) low-magnification image of the film-substrate interface.

Fig 2 X-ray θ -2 θ scans from ZrB_2 films deposited with 400 W applied to the target. Deposition temperatures from the bottom of the stack: 500 °C, 600 °C, 700 °C, 820 °C and 900 °C.

Fig 3 XRD pole figures from ZrB_2 films deposited with 400 W applied to the target showing (a) the 0001 pole of a film deposited at 600 °C, (b) the $10\bar{1}1$ pole of a film deposited at 700 °C, (c) the $10\bar{1}1$ pole of a film deposited at 820 °C, and (d) the $10\bar{1}1$ pole of a film deposited at 900 °C. Color online.

Fig 4 X-ray θ -2 θ scans from ZrB_2 films deposited at 900 °C. Power applied to the cathode from the bottom of the stack: 100 W, 200 W, 300 W, and 400 W.

Fig 5 TEM images of a film deposited at 900 °C and with 100 W applied to the target. a) Low-magnification overview image of the film b) High-magnification image of part of the film

Fig 6 XRD pole figures from ZrB_2 films deposited at 900 °C showing the $10\bar{1}1$ pole of (a) a film deposited at 100 W, (b) a film deposited at 200 W, (c) a film deposited at 300 W, and (d) a film deposited at 400 W. Color online.

Fig 7 High-resolution XPS spectra of the Zr 3d and B 1s photoelectron region from a ZrB_2 film deposited at 900 °C and with 400 W applied to the target. The dotted line represents the as-deposited film and the solid line is after 180 s of sputter-cleaning.

Fig 8 High-resolution XPS spectra of the Zr 3d and B 1s photoelectron region from a ZrB_2 film deposited at 900 °C and with 100 W applied to the target. The dotted line represents the as-deposited film and the solid line is after 180 s of sputter-cleaning.

Fig 9 Resistivity values for films grown at 400 W sputtering power and five temperatures (solid squares) as well as resistivity values for films grown at 900 °C and four values of sputtering power (hollow circles).

ESM 1 Supplementary material available online describing the detailed structural properties of a film deposited at 100 W sputtering power. Includes additional pole figures.

Power [W]	B [at%]	Zr [at%]	B/Zr	O [at%]	C [at%]
400	63.92	30.89	2.07	2.99	2.20
300	64.79	30.49	2.12	3.30	1.42
200	46.81	30.47	1.54	18.90	3.82
100	39.53	26.13	1.51	26.46	7.88

Temp [°C]	B [at%]	Zr [at%]	B/Zr	O [at%]	C [at%]
900	63.92	30.89	2.07	2.99	2.20
820	64.43	31.16	2.07	2.82	1.59
700	64.56	30.49	2.12	3.53	1.42
600	64.25	31.16	2.06	3.56	1.03
500	63.72	30.90	2.06	4.17	1.21

Electronic Supplementary Material

Stoichiometric, Epitaxial ZrB₂ Thin Films with Low Oxygen Content Deposited by Magnetron Sputtering from a Compound Target; Effects of Deposition Temperature and Sputtering Power

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XRD investigation of a film deposited at 100 W

To study the orientation of the minority phases present in the film deposited with 100 W sputtering power, we investigated the 0001, $10\bar{1}1$ and $10\bar{1}0$ poles, see Suppl. Fig 1 a)-c), respectively. The Suppl. Fig 1 a) displays a high intensity peak in the center, while the features located outside the central point are extremely low. This observation supports a film with a majority of (0001) oriented grains and where other orientations are in minority, which was already established from the $10\bar{1}1$ pole figure in Fig 6 a) as well as from an additional measurement of the $10\bar{1}1$ pole seen in Suppl. Fig 1 b). Furthermore, in Suppl. Fig 1 a) there are 6 lines separated by 60° in ϕ -angle and where clear peaks are visible at ψ -angles of $\sim 40^\circ$, $\sim 50^\circ$ and $\sim 75^\circ$. These correspond to the $10\bar{1}l$ minority orientations that are supported by the presence of $10\bar{1}1$, $10\bar{1}2$ and $10\bar{1}3$ peaks in the θ - 2θ scans in Fig 4, which may suggest polycrystalline growth for these orientations. However, by monitoring {0001}, $\{10\bar{1}1\}$ and $\{10\bar{1}0\}$ planes in pole figure measurements it was observed that only discrete c-axis inclinations are present. In addition, the inclined c-axis is found to exhibit 6-fold rotational symmetry around the surface normal (Suppl. Fig 1 a)). Rotation of these crystals around the

surface normal is limited to the conditions that $\{1\bar{1}00\} \text{ ZrB}_2 \parallel \{1\bar{1}00\} 4\text{H-SiC}$, which results in the 6-fold symmetry of the minority grains observed in the pole figures.

The peaks in the pole figures of $\{10\bar{1}1\}$ and $\{10\bar{1}0\}$ planes (Suppl. Fig 1 b) and c)) can be accounted for by the following 5 minor crystal orientation groups:

a) $\angle(\mathbf{c}, \mathbf{n}) = 90^\circ$; b) $\angle(\mathbf{c}, \mathbf{n}) = 74^\circ$; c) $\angle(\mathbf{c}, \mathbf{n}) = 52^\circ$; d) $\angle(\mathbf{c}, \mathbf{n}) = 33^\circ$; and e) $\angle(\mathbf{c}, \mathbf{n}) = 23^\circ$, where $\mathbf{c}$ is the c-axis of the crystal ($[0001]$) and $\mathbf{n}$ is the sample surface normal.

In the $10\bar{1}1$ pole figures (Suppl. Fig 1 b) and Fig 6 b)) inclination a) results in poles at $\psi = 37^\circ$ and 66° b) – pole at $\psi = 22^\circ$; c) – pole at $\psi = 0^\circ$ and ring at $\psi = 46^\circ$; d) – pole at $\psi = 19^\circ$, and e) – pole at $\psi = 28^\circ$. Thus, cases a, b, d, and e result in a broad feature visible in Suppl. Fig 1 b) and Fig 6 b) centered at $\psi = 25^\circ$. Case a) also results in the “Mickey Mouse ears”-like features around poles at $\psi = 54.5^\circ$ that are discernible at $\psi = 66^\circ$ and rotated 10° in both directions from the pole at $\psi = 54.5^\circ$.

In the $10\bar{1}0$ pole figure (Suppl. Fig 1 c)) inclination a) results in poles at $\psi = 0^\circ$ and 60° ; b) – poles at $\psi = 15^\circ$ and 61° ; c) – poles at $\psi = 39^\circ$ and 67° ; d) – poles at $\psi = 57^\circ$ and 74° ; and e) – poles at $\psi = 67^\circ$ and 78° . Thus, features characteristic for cases c and e, and a, b and d result in the broadening of the poles at around $\psi = 67^\circ$ and $\psi = 60^\circ$, respectively.

To summarize, the inclinations a), b), c), and d) correspond to the observation of $10\bar{1}0$, $10\bar{1}1$, $10\bar{1}2$ and $10\bar{1}3$ peaks, respectively. An additional minority orientation of the ZrB_2 phase of our films was also observed in the recorded θ - 2θ scans, where a peak originating from $\{11\bar{2}0\}$ planes is visible (Fig 6). This condition would lead to the observation of the $10\bar{1}0$ pole at $\psi = 30^\circ$ and 30° rotated from the poles observed around $\psi = 15^\circ$ in Suppl. Fig 1 c), but no such features were observed in the pole figures, probably due to the low intensity of the peak or no in-plane ordering of the corresponding grains.

Suppl. Fig 1

Pole figures recorded for the a) 0001, b) $10\bar{1}1$, and c) $10\bar{1}0$ poles of a ZrB_2 film deposited at 100 W of sputtering power.