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Crystalline texture in hafnium diboride thin films grown by chemical vapor deposition

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Abstract

The texture evolution of hafnium diboride (HfB_2) thin films grown by chemical vapor deposition from the single source precursor $Hf(BH_4)_4$ was studied. Films grown on amorphous substrates show a (0 0 0 1) orientation at growth temperatures $\leqslant 700\,^{\circ}C$, but a $(1\,0\,\underline{1}\,0)$ orientation at 800 °C and above. Single-crystal substrates greatly influence the preferred orientation and in-plane texture of the films: $(1\,0\,\underline{1}\,0)$ orientation is favored on Si (0 0 1), whereas there is a strong tendency to grow in a (0 0 0 1) orientation on Si (1 1 1). At a growth temperature of 950 °C, HfB_2 can be epitaxially grown on Si (1 1 1) substrates.

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Keywords: A3. Chemical vapor deposition processes; A3. Crystalline texture; B1. Metal diborides

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1. Introduction

Hafnium diboride (HfB_2), a metallic ceramic material, has a high melting point (3250 °C), excellent chemical resistance, high hardness (bulk value 29 GPa), and high electrical conductivity (bulk value 15 $\mu\Omega$ cm). These properties make it potentially useful for microelectronics and hard coating applications [1–5]. However, when a material is deposited as a thin film, the crystallographic texture plays an important role in determining the properties [6]. A prominent example is the transition metal nitrides, especially TiN, for which the dependence of texture on growth parameters and the underlying mechanisms responsible for texture development have been studied in detail [7–11]. In contrast, the textures of transition metal diboride thin films have received much less attention [12,13]. We recently reported that stoichiometric and impurity-free HfB_2 thin films can be grown by thermal chemical vapor deposition (CVD) from the single-source precursor $Hf(BH_4)_4$, which is halogen-, oxygen-, and carbon-free [14]. From temperature programmed reaction studies, we found that the apparent activation energy of the deposition process is only 0.43 eV (41 kJ/mol) and that the growth transits from reaction-limited to flux-limited at ~350 °C. Films grown at low temperatures (200–300 °C) are dense and X-ray amorphous, whereas at $T > 400\,^{\circ}C$ the films become columnar and crystalline.

The growth of nearly single-crystal HfB_2 has great scientific and technological importance: the (0 0 0 1) plane of HfB_2 has a −1.5% lattice mismatch with the (1 1 1) plane of GaN, thus making HfB_2 a potential substrate for the heteroepitaxial overgrowth of III–V semiconductor

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materials. Previously, Belyansky et al. [15,16] demonstrated that HfB_2 can be synthesized epitaxially on single-crystal hafnium substrates by reacting the surface with B_2H_6 gas. However, this method is not suitable for practical applications because of the small size of available Hf single crystals and the limited HfB_2 thickness that can be formed by such boriding reactions.

In this paper, we describe the crystallographic texture of HfB_2 films grown by thermal CVD from $Hf(BH_4)_4$ at temperatures between 400 and 900 °C, and discuss the probable mechanisms of texture development. We also report the heteroepitaxial growth of HfB_2 on Si (1 1 1) substrates, which appears to be a simple and practical means to synthesize large areas of nearly single-crystal HfB_2.

2. Experiment

HfB_2 films were deposited in a turbo-pumped chamber of ultra-high vacuum construction. The deposition system and the growth procedure are described in detail elsewhere [14]. Unless specified, films were grown with a fixed precursor feed rate of 3.2×10^{16} molecules/s, for which the precursor partial pressure is estimated to be 10^{-5}–10^{-6} Torr inside the chamber; films were grown to ~300 nm thick by controlling the growth time. Five types of substrates were used in this study: Si (1 1 1), Si (0 0 1), Si (0 0 1) covered with 100 nm of thermal SiO_2, free-standing SiO_x membranes on copper TEM grids, and Si (0 0 1) covered with 90 nm of plasma-deposited a-C:H film. Before being loaded into the chamber, the substrates were degreased by washing successively in acetone, isopropyl alcohol, and deionized water for 10 min each in an ultrasonic bath. The Si (0 0 1) and Si (1 1 1) substrates were then dipped in a 10% HF solution to remove the native oxide. Heating of the substrate was achieved by passing direct current through the silicon. The substrate temperature was measured by means of an infrared pyrometer.

The film texture was determined from X-ray 2θ–ω scans obtained on a Rigaku D-Max system. Pole figures were obtained on a Philips X'pert system. The latter instrument was also used to measure the rocking curve (ω scans) of the epitaxial sample. The instrumental resolution was 0.05° and Cu K_α radiation ($\lambda = 1.5418$ Å) was used. In the 2θ–ω scans, the diffraction from the crystal planes parallel to the substrate surface was collected; the resulting data therefore provide information about the film texture only in the substrate normal direction. Pole figures, on the other hand, yield information about film texture both in and out of the plane parallel to the substrate (ϕ–ψ scans) [17]. Note that the (1 0 1 0) diffraction peak of HfB_2 has the same 2θ value (32.9°) as the (0 0 2) diffraction peak of Si. Although the latter reflection should be absent by symmetry, multiple diffraction effects give it significant intensity [18]. To avoid the interference from the substrate peak in the 2θ–ω scans, a ω value of 0.5° off substrate normal was used for all the films grown on Si (0 0 1) substrates. The sharp Si (0 0 2) peak vanishes for this offset, but the HfB_2 $(1\,0\,\underline{1}\,0)$ intensity persists due to the much broader ω distribution of this reflection, which in turn is a result of the polycrystalline nature of the film. Plan-view TEM was used for selective-area diffraction studies of a few films deposited directly on SiO_x membrane substrates. The morphology and microstructure of the films were investigated by scanning electron microscopy (SEM).

3. Results

3.1. Texture of HfB_2 films grown on amorphous substrates

To determine the dependence of the HfB_2 texture on deposition parameters in the absence of substrate crystallography, we investigated growth on an amorphous substrate: thermal silicon dioxide on silicon. Because the $Hf(BH_4)_4$ precursor reacts with SiO_2 above 800 °C, we used a different amorphous substrate at these higher temperatures: Si covered with PECVD amorphous carbon.

Fig. 1(a) shows the 2θ–ω X-ray diffraction (XRD) patterns from ~300 nm-thick HfB_2 films grown at various temperatures. At the bottom of the same figure is the powder diffraction pattern for HfB_2 taken from the ICDD file (no. 381398). All the HfB_2 films showed a strong (0 0 0 1) or $(1\,0\,\underline{1}\,0)$ preferred orientation. Because contributions from the other orientations are small, we can use the (0 0 0 1) and $(1\,0\,\underline{1}\,0)$ peak intensities to quantify the film texture by calculating a texture coefficient (TC), for which the (0 0 0 1) peak is defined as follows:

$$\mathrm{TC}_{0001} = \frac{I_{0001}/I^0_{0001}}{I_{0001}/I^0_{0001} + I_{10\underline{1}0}\big/I^0_{10\underline{1}0}},$$

where I_{hkil} is the integrated intensity of the *hkil* peak from the measured diffraction pattern, and ${I_{hkil}}^0$ is the integrated intensity from the reference ICDD file. The TC_{0001} values for the films grown on amorphous and single-crystal substrates at various temperatures are listed in Table 1.

At growth temperatures between 400 and 700 °C, the preferred orientation of the HfB_2 films is (0 0 0 1), i.e. the basal plane of the hexagonal structure is parallel to the substrate surface. The peak intensity and sharpness both increase with increasing growth temperature. At growth temperatures above 800 °C, the preferred orientation switches to (1 0 1 0), the prismatic plane of the hexagonal structure. No in-plane texture is observed in the corresponding pole figures for these samples, as expected due to the use of amorphous substrates.

To determine whether the texture evolves with film thickness, films were grown under the same conditions but to only $\frac{1}{10}$ the thickness (~40 nm). All the thinner films showed the same preferred orientation as the thick films of Fig. 1(b). However, the texture of the films grown at 700 and 800 °C is weaker than for the corresponding thick films; this result indicates that competitive growth may be occurring after the nucleation stage. To investigate this

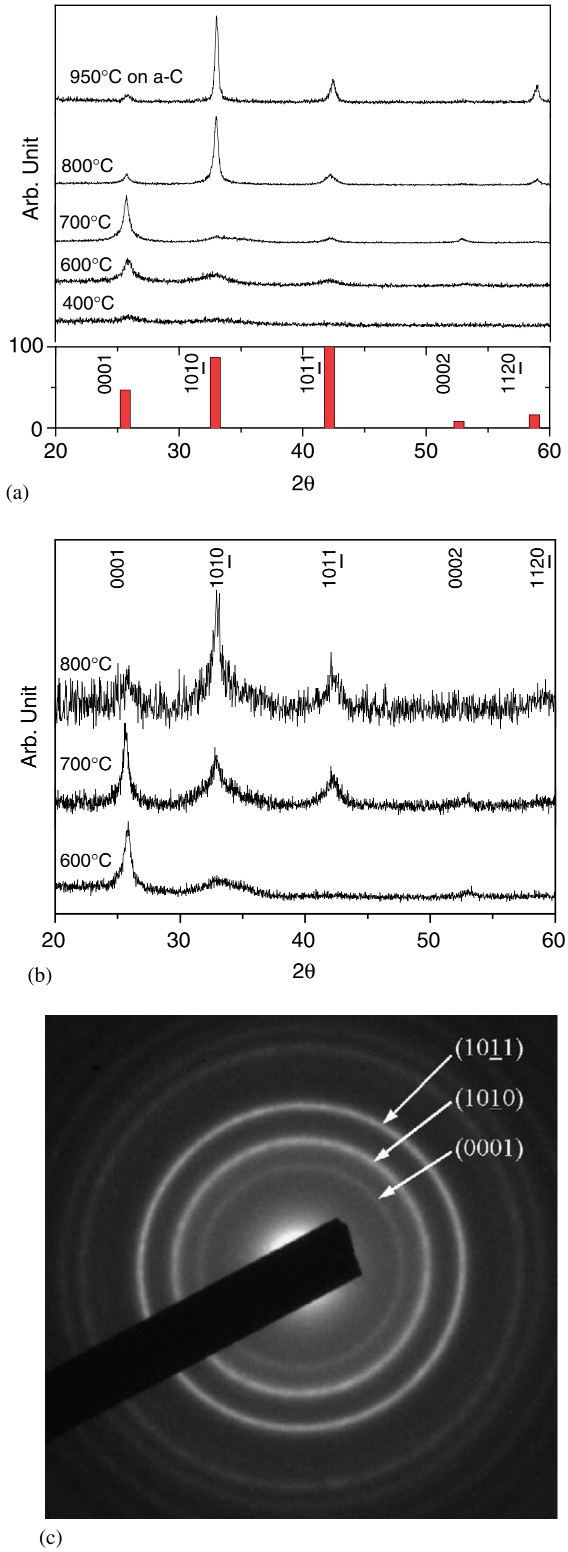

Fig. 1. (a) X-ray diffraction patterns of ~300 nm thick HfB_2 films grown from the single-source precursor $Hf(BH_4)_4$ on amorphous substrates at different substrate temperatures. The default substrate is SiO_2. The film grown on amorphous carbon substrate is marked as "a-C." The bottom of the figure is a histogram of the X-ray powder diffraction pattern of HfB_2 taken from the ICCD file. (b) X-ray diffraction pattern of HfB_2 films with thickness of ~40 nm. (c) TEM diffraction pattern of a 20 nm HfB_2 film grown at 600 °C.

possibility further, even thinner films (~20 nm) were grown, then analyzed by XRD using very long scans. Again, the data (not shown) have essentially the same peak height ratios as those for the 40 nm films in Fig. 1(b). We also carried out plan-view TEM studies of ~20 nm-thick HfB_2 films grown on SiO_2 membrane TEM grids at 600–800 °C. The electron diffraction patterns contain rings of all allowed reflections (Fig. 1(c)), suggesting that the films are, at most, weakly textured. Thus, the competitive development of texture must occur slowly, over a film thickness of many tens of nm.

3.2. *Texture of HfB_2 films grown on single-crystal substrates*

Fig. 2 shows the XRD patterns of HfB_2 films grown on bare Si (0 0 1) and (1 1 1) substrates. On Si (0 0 1), the film texture shows the same temperature dependence as on amorphous substrates: the preferred orientation is (0 0 0 1) at temperatures below 800 °C and changes to (1 0 $\underline{1}$ 0) at and above 800 °C. On Si (1 1 1) substrates, however,

Table 1
The (0 0 0 1) texture coefficients of the HfB_2 films grown on various substrates

T_s	600 °C	700 °C	800 °C	950 °C
SiO_2	0.70	0.85	0.28	0.09[a]
Si (0 0 1)	0.68	0.71	0.00	
Si (1 1 1)	0.96	1.00	0.94	

[a] On amorphous-carbon-covered Si (0 0 1) substrate.

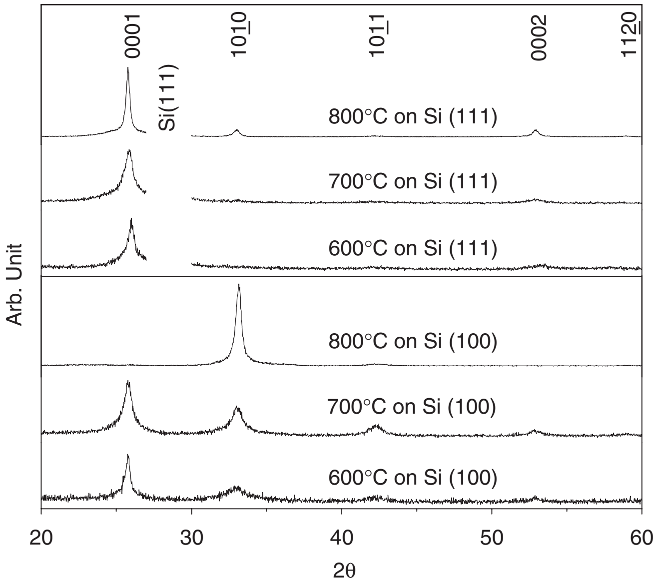

Fig. 2. X-ray diffraction patterns of HfB_2 films grown from the single-source precursor $Hf(BH_4)_4$ on single-crystal substrates at various substrate temperatures.

(0 0 0 1) is the dominant orientation at all growth temperatures. At all temperatures between 600 and 800 °C, films grown on Si (1 1 1) show a higher TC_{0001} than films grown on Si (0 0 1).

The influence of substrate symmetry on the film texture can be further determined from the $(1\,0\,\underline{1}\,1)$ pole figures of the HfB_2 films grown on Si (0 0 1) and Si (1 1 1) at 600 and 800 °C, respectively (Fig. 3). On Si (0 0 1), no in-plane texture is observed at 600 °C. However, films grown at 800 °C show sharp diffraction spots at $\psi = 38.1^\circ$ and 66.8° (Fig. 3(b)), corresponding to HfB_2 grains with their (1 0 1 0) planes parallel to the substrate and with a specific in-plane orientation, Si [1 1 0]//HfB_2 $[2\,\underline{1}\,\underline{1}\,0]$, as determined by a comparison with the (1 1 1) pole figure of the silicon substrate. Because there are two equivalent [1 1 0] directions on Si (0 0 1), the HfB_2 diffraction spots show two different in-plane orientations, labeled A and B in Fig. 3(b). These observations are very similar to the results of Roucka et al. [19] for ZrB_2 films deposited on Si (0 0 1). On Si (1 1 1) substrates, similar pole figures are observed at both 600 and 800 °C, except that the HfB_2 films grown at the higher temperature show more intense and sharper diffraction peaks (Fig. 3(d)). Because both the (1 1 1) plane of Si and the (0 0 0 1) plane of HfB_2 have hexagonal symmetry, the only in-plane orientation relationship observed is Si [1 1 0]//HfB_2 $[2\underline{1}\underline{1}0]$.

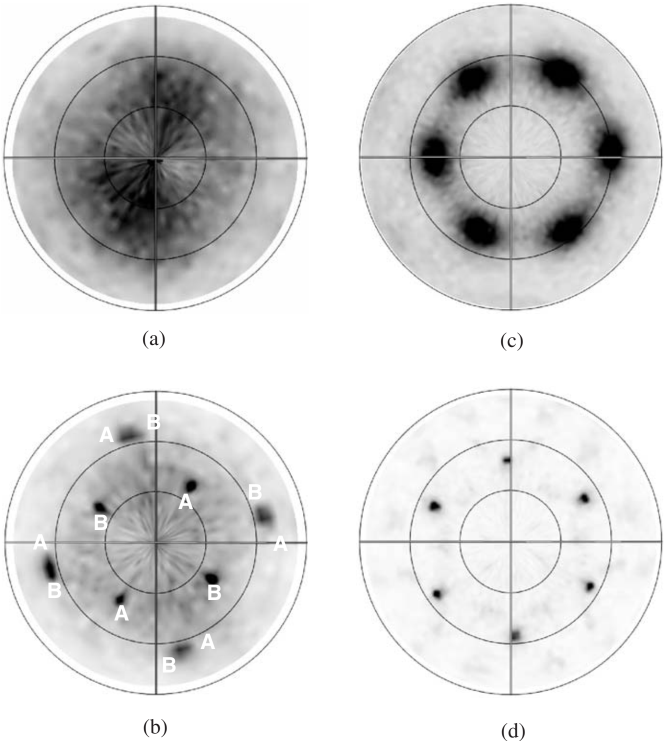
(a)
(c)
(b)
(d)

Fig. 3. $(1\,0\,\underline{1}\,1)$ pole figures of HfB_2 films grown from the single-source precursor $Hf(BH_4)_4$ on: (a) Si(0 0 1) at 600 °C; (b) Si(0 0 1) at 800 °C; (c) Si(1 1 1) at 600 °C; (d) Si(1 1 1) at 800 °C. In (c), the letters A and B designate the two different in-plane orientations; see text for details. The off-center nature of the diffraction pattern in (c) and (d) results from the 3° miscut of the Si (1 1 1) substrates employed.

At a growth temperature of 950 °C, HfB_2 (0 0 0 1) can be grown epitaxially on Si (1 1 1) substrates if the precursor feed rate is kept low (e.g., 8.0×10^{15} molecules/s). The XRD pattern and the rocking curve for such epitaxial films are presented in Fig. 4. Tolle et al. have reported the epitaxial growth of ZrB_2 (0 0 0 1) on Si (1 1 1) at 900 °C, and attributed the alignment to the 6:5 coincidence site lattice match. Because ZrB_2 is also lattice matched to GaN, Tolle et al. [20,21] have proposed that ZrB_2 films may be useful as buffer layers to grow GaN epitaxially on Si (1 1 1). HfB_2 has the same crystal structure and its lattice constants are very close to those of ZrB_2 ($a_{HfB_2} = 3.143$ Å vs. $a_{ZrB_2} = 3.189$ Å), and thus it too may serve as a useful buffer layer. For the 6:5 coincidence relationship, the lattice mismatch between HfB_2 (0 0 0 1) and Si (1 1 1) is 1.5%. The lattice parameters of the HfB_2 epitaxial films, determined by high-resolution XRD, are $a = 3.1523$ Å and $c = 3.4755$ Å. These values are very close to those for the bulk, 3.1425 and 3.4760 Å, respectively, indicating that the epitaxial films are essentially relaxed. Epitaxial growth of HfB_2 (950 °C) requires slightly higher temperatures than for epitaxial growth of ZrB_2 (900 °C), a difference we attribute to the higher Hf–B bond strength, which is also manifested in the relative melting temperatures (3250 °C for HfB_2 vs. 2950 °C for ZrB_2).

At temperatures above 900 °C, the growth of HfB_2 on silicon substrates is very slow. A film grown at 950 °C with a precursor feed rate of 4×10^{16} molecule/min has a growth rate of ~0.5 nm/min, which is significantly smaller than the growth rate at lower temperatures (>10 nm/min at 600 °C). By contrast, no suppression of the growth rate is observed on high melting point substrates such as molybdenum and sapphire. XPS studies of the films deposited on silicon at temperatures greater than 800 °C reveal significant amounts of silicon on the surface of the HfB_2 films (Fig. 5), which is due to the high diffusivity of silicon

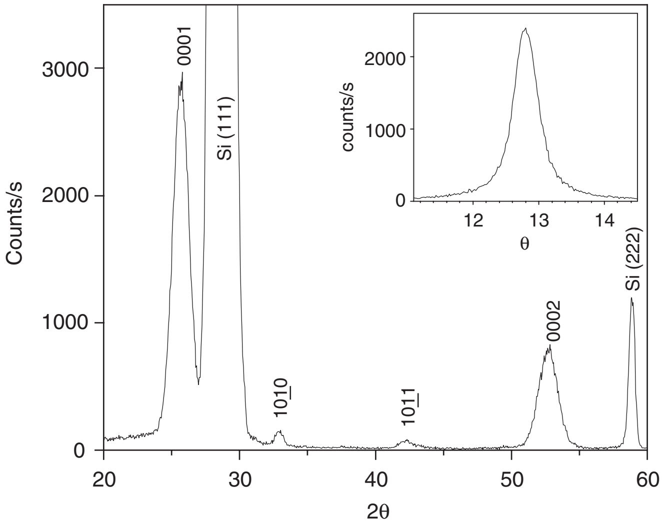

Fig. 4. X-ray 2θ–ω scans of a HfB_2 film grown from the single-source precursor $Hf(BH_4)_4$ epitaxially on a Si (1 1 1) substrate at 950 °C. The insert is the rocking curve of the (0 0 0 1) peak; the FWHM is 0.4°.

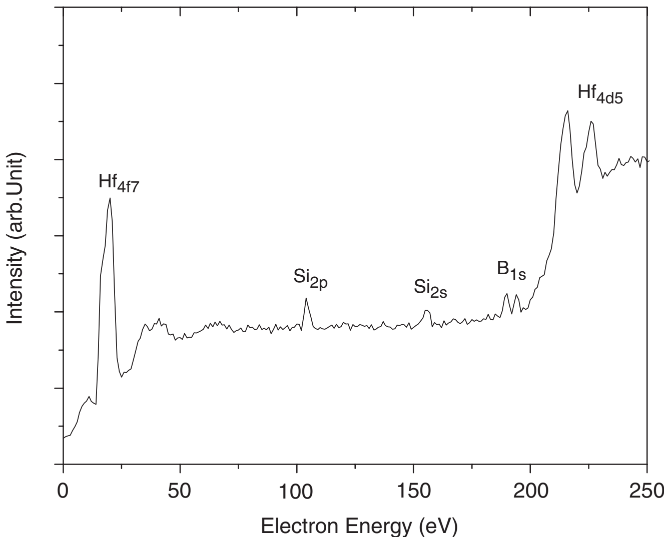

Fig. 5. Surface XPS spectrum of a HfB_2 film grown from the single-source precursor $Hf(BH_4)_4$ on a Si (0 0 1) substrate at 800 °C.

through HfB_2 films at such temperatures. It is known that metallic hafnium reacts with silicon at high temperatures (>550 °C) [22], but we saw no evidence of silicide formation from XRD. Hu et al. [21] observed the presence of Si on the top of epitaxial ZrB_2 films grown at similar temperatures. We previously demonstrated that there is a reaction barrier for the precursor $Hf(BH_4)_4$ to react with a fresh silicon surface [14]; here, we interpret that Si diffuses to the film surface at high growth temperatures and reduces the precursor reaction probability or otherwise interferes with HfB_2 growth. The low growth rate and the high silicon diffusivity are potential problems for using MB_2 films as buffer layers for growing GaN epitaxially on Si, especially because Si is a dopant in GaN [23].

3.3. Growth temperature modulation

To further investigate the mechanism responsible for texture development, we modulated the substrate temperature during growth on amorphous substrates. In our experiments, the first layer was grown to a thickness of 30–40 nm and the second layer, grown at different temperature, was much thicker; under these conditions, the X-ray signature of the final film was dominated by the second layer. XRD from the first layer was readily obtained from samples grown at a single temperature.

The growth conditions of these bilayer films and the TCs of each layer are summarized in Table 2; the XRD patterns are shown in Fig. 6. For comparison, the last column of Table 2 repeats the TCs of the films grown without temperature modulation. For a bilayer in which a thin film grown at 700 °C was then covered with a thick film grown at 800 °C (entry (a)), both layers had a preferred orientation of (0 0 0 1). This is the preferred orientation seen for growth of HfB_2 films at lower temperatures. If the temperatures were switched (first 800 °C and then 700 °C; entry (b)), both layers still have the same orientation, but now it is $(1 0 \underline{1} 0)$. This result suggests that the preferred orientation of the films follows the orientation adopted during the initial stages of growth. In entry (c), a thicker first layer (80 nm) was deposited at 800 °C to produce a stronger $(1 0 \underline{1} 0)$ texture, and the overlayer was grown at a lower temperature of 600 °C. Under these conditions, the overlayer reverts to the (0 0 0 1) orientation seen at lower temperatures. This result suggests that at 600 °C, the (0 0 0 1) texture of the film is substrate independent.

Table 2
The (0 0 0 1) texture coefficients of the HfB_2 films grown with and without temperature modulations

	Initial layer		Second layer		Unmodulated growth	
a	700 °C	0.60	800 °C	0.92	800 °C	0.28
b	800 °C (40 nm)	0.39	700 °C	0.30	700 °C	0.85
c	800 °C (80 nm)	0.28	600 °C	0.88	600 °C	0.70

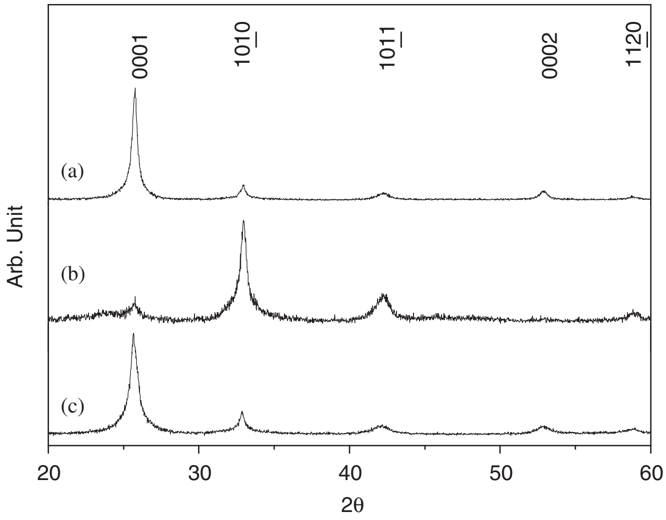

Fig. 6. X-ray diffraction patterns of the HfB_2 films from the single-source precursor $Hf(BH_4)_4$ with substrate temperature modulated (a) from 700 to 800 °C; (b) from 800 to 700 °C; (a) from 600 to 800 °C during growth. See Table 2 for details.

3.4. Microstructure

The crystalline HfB_2 films on SiO_2 substrates have characteristic microstructures: Fig. 7(a) and (b) are typical plan- and cross-sectional SEM images of films with (0 0 0 1) and $(1 0 \underline{1} 0)$ preferred orientation, respectively. The faceted microstructure in Fig. 7(a) reflects the hexagonal symmetry of the HfB_2 basal plane. The films are characterized by a columnar microstructure with a large void volume. The $(1 0 \underline{1} 0)$-oriented film shows a plate-like morphology in which the faces of these plates are the HfB_2 basal plane. The in-plane orientation of the plates is random when the film is deposited on an amorphous substrate, but has an orthogonal reticular pattern when the film is deposited on

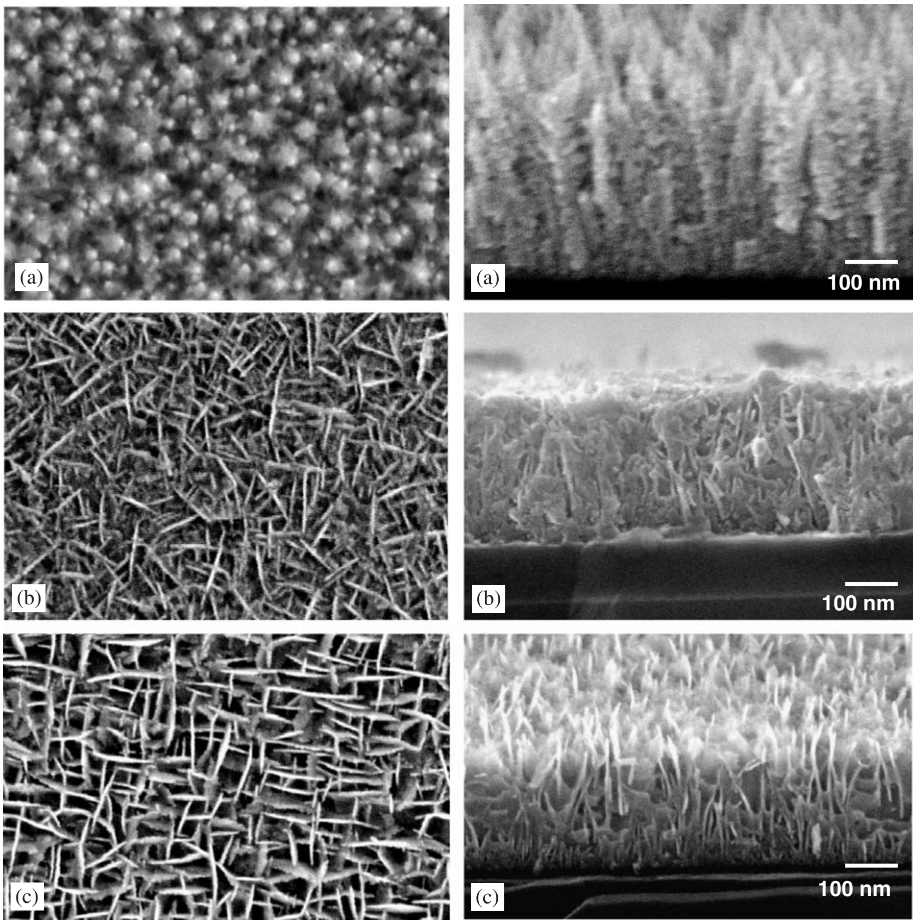

Fig. 7. SEM plan-view and cross-sectional images of HfB_2 films grown from the single-source precursor $Hf(BH_4)_4$ (a) on SiO_2 at 600 °C, where the preferred orientation is (0 0 0 1); (b) on SiO_2 at 800 °C, where the preferred orientation is $(1\,0\,\underline{1}\,0)$; and (c) on Si (0 0 1) at 800 °C, where the preferred orientation is $(1\,0\,\underline{1}\,0)$.

Si (0 0 1), Fig. 7(c). The orthogonal arrangement of the plates is consistent with the two in-plane orientations observed in the pole figure, Fig. 3(b).

4. Discussion

The formation of crystallographic texture during thin film growth is a complex phenomenon that results from the competition between several kinetic processes. For physical vapor deposition, the effects of the most important mechanisms such as surface and bulk diffusion have been reviewed [24–26]. In CVD, the gas phase or surface reactions introduce mechanisms that are specific to the growth chemistry and are significantly different from system to system [27,28]. The present data are insufficient to provide a complete understanding of the texture development in HfB_2 films grown by CVD from the single-source precursor $Hf(BH_4)_4$, but some general conclusions about the mechanisms can be drawn from the data.

The HfB_2 films grown at 600 °C have a (0 0 0 1) preferred orientation that is independent of the substrate crystallography, as shown in Figs. 1(a), 2 and 6. On amorphous substrates, the texture of the film is unchanged as the film thickens. The structure appears to be nanocrystalline, as indicated by the broad XRD peaks; the SEM images (Fig. 7(a)) reveal a dendritic microstructure. Because 600 °C corresponds to a low homologous temperature, $T_s/T_m = 0.25$, we expect that surface diffusion of growth adspecies is too slow to sustain epitaxial grain growth [29], and re-nucleation continuously takes place as the film thickens. The results imply that (0 0 0 1)-oriented grains dominate the continuous re-nucleation process at 600 °C, which could be a result of preferential nucleation, and that this preference leads to an overall (0 0 0 1) texture of the film that is independent of substrate and film thickness.

At HfB_2 growth temperatures of 700 and 800 °C, the sharp XRD peaks and the faceted microstructures strongly suggest that epitaxial grain growth dominates the film thickening process; this conclusion is plausible because the higher T_s permits greater surface diffusion of adspecies. The importance of grain growth as the dominant film thickening process is further supported by the temperature modulation experiments, in which the texture of the initial layer determines the texture of the entire film. The homologous temperature $T_s/T_m = 0.33$ is, however, not high enough to promote bulk or grain boundary diffusion; therefore grain boundaries will be immobile at these temperatures and the columnar morphology must be a direct result of the growth kinetics. The texture selection under these growth conditions is well described by the van der Drift model, in which the fastest growing crystal planes envelop the slower growing ones and produce elongated grain growth with a strong preferred orientation [9,30]. At 800 °C, the HfB_2 films grown on amorphous substrates are $(10\underline{1}0)$ oriented, implying that $(10\underline{1}0)$ is the fastest growing plane. The microstructure of the thin films is plate-like (Fig. 7(b) and (c)), therefore the $(10\underline{1}0)$ and (0001) planes correspond to the thin edge and the broad side of the plates, respectively. As inferred from the heights and widths of the plates, the ratio of $(10\underline{1}0)$ to (0001) growth rates is more than 10:1. It appears qualitatively reasonable that adatoms can attach more rapidly to the edges, rather than to the faces, of this hexagonal-layered structure. However, the (0001) preferred orientation seen for films grown on amorphous substrates at 700 °C suggests that preferential nucleation still controls the early stage of growth at this temperature, and that the resulting (0001) texture is preserved during the subsequent film growth.

The crystallographic face of the Si substrate also affects the film texture; this effect is weak at 600 °C but strong at or above 700 °C (Fig. 3). Our data indicate the epitaxial relationships HfB_2 (0001)//Si (111) and HfB_2 $(10\underline{1}0)$//Si (001); both are consistent with a preference for a coincidence–site relationship at the film/substrate interface. The combination of the out-of-plane TCs listed in Table 1 and the in-plane orientations shown in Fig. 3 suggest that Si (111) strongly favors the HfB_2 (0001) orientation and Si (001) weakly favors the HfB_2 $(10\underline{1}0)$ orientation.

5. Conclusions

We report the texture of HfB_2 thin films grown by chemical vapor deposition from the single-source precursor $Hf(BH_4)_4$ as a function of the growth temperature and substrate (c-Si vs. SiO_2). At low temperatures ($\leqslant$600 °C), films grow with their (0001) plane parallel to the substrate surface regardless of the underlying substrate crystallography. At high temperatures ($\geqslant$800 °C), grain growth occurs along the substrate normal direction. On amorphous substrates, a $(10\underline{1}0)$ texture is observed, consistent with a Van der Drift competitive grain growth mechanism assuming that HfB_2 $(10\underline{1}0)$ is the fastest growing plane.

Acknowledgments

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