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Preferred orientation of TiB_2 plates prepared by CVD of the $TiCl_4 + B_2H_6$ system

M. MUKAIDA, T. GOTO, T. HIRAI
Institute for Materials Research, Tohoku University, Sendai 980, Japan

Titanium diboride (TiB_2) plates (about 1 mm maximum thickness) were prepared by chemical vapour deposition (CVD) using a $TiCl_4$, B_2H_6 and H_2 system at deposition temperatures, T_{dep} of 1323–1773 K. The B/Ti atomic ratio in the deposits was 2, and the composition is strictly stoichiometric. Chlorine was not detected. The measured lattice parameters were $a = 0.3029$ nm and $c = 0.3229$ nm. Density is in close agreement with the theoretical value (4.50 g cm^{-3}). Preferred orientation of the CVD TiB_2 plates varies mainly with total gas pressures, P_{tot}. At $P_{tot} = 4$ kPa the (1 0 0) plane and at $P_{tot} = 40$ kPa the (1 1 0) plane is preferably oriented parallel to the substrates. The effect of P_{tot} on the preferred orientation is discussed thermodynamically, and explained by supersaturation in the gas phase.

1. Introduction

Titanium diboride (TiB_2) is a promising material as a cathode of electrolysis in fused salt [1], or as various structural ceramics [2], because of its high electrical conductivity [3] and corrosion/erosion resistances [4–6]. The TiB_2 bodies are usually fabricated via sintering techniques such as hot-press processing; however, the properties of the sintered TiB_2 bodies are often inferior due to the existence of pores or impurities such as additives or free B [7]. Therefore, it is highly desirable to be able to prepare high-density and high-purity TiB_2 plates maintaining the intrinsic properties. Furthermore, the properties of TiB_2 may be anisotropic due to its hexagonal structure, and change depending on preferred orientation [7].

Chemical vapour deposition (CVD) is the most suitable technique known for preparing highly dense, pure and oriented materials [7]. In the past, thin TiB_2 films (about 0.01–0.1 mm thick) were prepared by CVD using $TiCl_4 + BCl_3$ [2, 5, 7–12] and $TiCl_4 + B_2H_6$ [13] systems; however, thick TiB_2 plates (thickness 1 mm) have never been prepared. We have successfully prepared dense and pure TiB_2 plates of about 1 mm thickness at the maximum rate of 0.5 mm h^{-1} by CVD using the $TiCl_4 + B_2H_6$ system [14]. Some papers have dealt with the preferred orientation of the CVD TiB_2 films, and the existence of (1 0 0) [13], (1 1 0) [8] and (1 0 1) [10] orientations has been reported. However, the relationship between CVD conditions and the preferred orientation has not yet been fully explained.

In the present work, the effect of CVD conditions on density, purity, composition and preferred orientation was investigated by preparing thick TiB_2 plates by CVD using the $TiCl_4 + B_2H_6$ system.

2. Experimental procedure

The thick TiB_2 plates were prepared using $TiCl_4$ vapour, B_2H_6(5 vol %) + H_2(95 vol %) mixture gas and H_2 gas on graphite substrates heated by an electric current. The experimental apparatus and the detailed preparation procedure have been reported elsewhere [14]. The CVD conditions are summarized in Table I.

The surface morphology of the prepared samples was observed by scanning electron microscopy (SEM) (Akashi ALPHA-30 W). The preferred orientation and lattice parameters were evaluated by X-ray diffractometry (Rigaku: RAD-2B, Ni-filtered, CuK_α). The density was measured by Archimedean method by immersing in toluene. The Ti and B contents were determined by inductively coupled plasma analysis (ICP; Seiko, SPS 1200A) and chemical analyses. The electron probe microanalysis (EPMA) was used to identify Cl.

The supersaturation of Ti and B in the gas phase during the reaction process was calculated by the code SOLGASMIX-PV [15] using the JANAF thermochemical data [16].

3. Results and discussion

Figs 1 and 2 show the effect of the deposition temperature, T_{dep} on the lattice parameters and density, respectively, at $P_{tot} = 4$ kPa and $m_{B/Ti} = 0.6$. Both lattice parameters and densities are constant and independent of T_{dep}. The same tendency was found at all other P_{tot} and $m_{B/Ti}$.

TABLE I Deposition conditions for the preparation of TiB_2 plate

Deposition temperature, T_{dep} (K)		1323–1773
Total gas pressure, P_{tot} (kPa)		4–40
Gas flow rate (m^3 s^{-1})	$TiCl_4$	2.33×10^{-7}–5.62×10^{-7}
	B_2H_6	1.68×10^{-7}–4.34×10^{-7}
	H_2	2.0×10^{-5}
$2B_2H_6/TiCl_4$ ($m_{B/Ti}$)		0.6, 2, 4
Deposition time (ks (h))		7.2 (4)

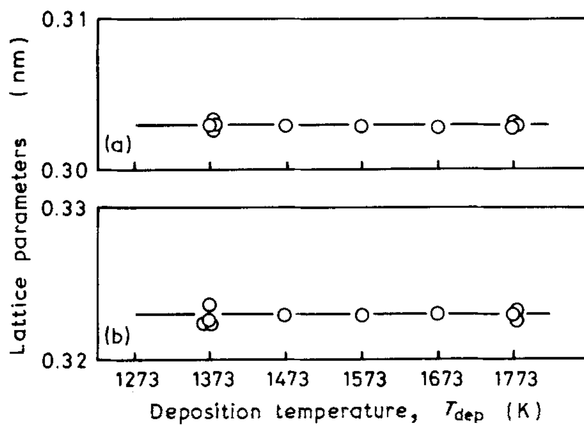


Figure 1 Effect of deposition temperature, T_{dep}, on lattice parameters of CVD TiB_2; $m_{B/Ti} = 0.6$, $P_{tot} = 4$ kPa. (a) *a*-axis, (b) *c*-axis.

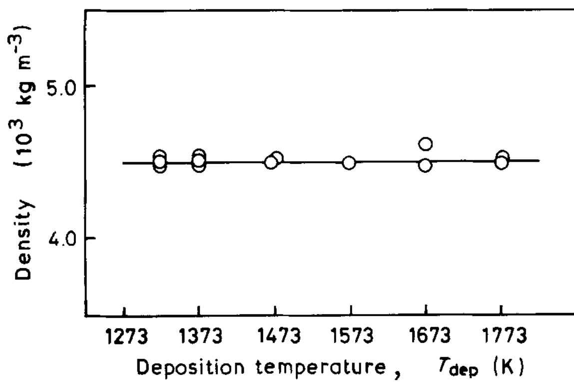


Figure 2 Effect of deposition temperature on density of CVD TiB_2; $m_{B/Ti} = 0.6$, $P_{tot} = 4$ kPa.

The lattice parameters of the CVD TiB_2 plates were $a = 0.3029$ nm and $c = 0.3229$ nm. These values are closely in agreement with those of the JCPDS card ($a = 0.3030$ nm, $c = 0.3230$ nm) [17].

The measured density was 4.5×10^3 kg m^{-3}, and this value is in agreement with a theoretical value calculated from the lattice parameters (4.49×10^3 kg m^{-3}).

The Ti and B contents of the CVD TiB_2 plates were 69 and 31 wt %, respectively. These values agree well with the stoichiometric compositions (68.9 wt % Ti, 31.1 wt % B). No Cl was identified within the sensitivity (about 0.04 wt %) of the EPMA.

Previously reported values of composition, lattice parameters and density of CVD TiB_2 films are summarized in Table II. Excess free B is easily codeposited whatever the gas systems used, while the lattice parameters are independent of the free B content. The density of TiB_2 film containing free B is explained well by a rule of mixtures for TiB_2 (4.50×10^3 kg m^{-3}) and B (2.33×10^3 kg m^{-3} [19]) [7]. It is widely believed that TiB_2 is strictly stoichiometric, and excess B is present as a dispersed second phase in amorphous or crystalline states [7]. In the $TiCl_4 + BCl_3$ system, a large amount of excess $TiCl_4$ and H_2 compared to BCl_3 is necessary in order to prepare CVD TiB_2 films containing no free B at temperatures above 1000 K [7]. The reason for this need is that the formation of free B from BCl_3 is much easier than the formation of TiB_2 at the high temperatures in the $TiCl_4 + BCl_3$ system [7]. In the $TiCl_4 + B_2H_6$ system, a large amount of free B forms even at a temperature below 1000 K [20] because the decomposition of B_2H_6 gas to free B is easy [20], while the reduction of $TiCl_4$ is difficult at low temperatures. In the present work, no free B is detected in the CVD TiB_2 plates; however, a large amount of B powder was formed inside the cold-wall type CVD furnace. Therefore, it is suspected that the source gas contains excess Ti near the substrate surface.

Fig. 3 shows the relationship between the orientation factor, *F*, and the deposition temperature at $m_{B/Ti} = 0.6$. The orientation factor, F_{hkl}, of a $(h\,k\,l)$ face is calculated from Lotgering's equation [21].

$$F_{hkl} = (P - P_0)/(1 - P_0) \quad (1)$$

$$P = I_{hkl}/\Sigma I_{hkl} \quad (2)$$

TABLE II Compositions, lattice parameters and density of CVD TiB_2

System	Deposition temperature (K)	Composition (wt %)			Lattice parameters (nm)		Density (10^3 kg m^{-3})	Reference
		Ti	B	Cl	*a*	*c*		
$TiCl_4 + BCl_3$	–	–	–	–	0.3028	0.3228	4.52	[18]
	1173–1873	–	–	–	0.3028	0.3232	–	[4]
	1123–1373	68.2	31.8	–	0.30283	0.32292	–	[2]
	1473–1688	35.82	64.18[a]	–	0.3038	0.3232	3.104	[7]
		59.93	40.07[a]	–	0.3038	0.3234	3.980	
		68.89	31.11	–	0.3034	0.3233	4.500	
	1123	65.61	34.22[a]	0.17	0.30405	0.31537	–	[12]
	1173	62.91	36.93[a]	0.16	0.30456	0.31664	–	
	1273	65.22	34.75[a]	0.03	0.30294	0.32289	–	
$TiCl_4 + B_2H_6$	873	62.45	35.66[a]	1.89	–	–	–	[13]
	973	66.72	29.98	3.30	–	–	–	
	1173	68.00	31.48	0.52	–	–	–	
	1323–1773	69	31	–	0.3029	0.3229	4.50	Present work
Theoretical		68.9	31.1		0.303034[b]	0.322953[b]	4.4935	

[a] Free-B is present.
[b] JCPDS [17].

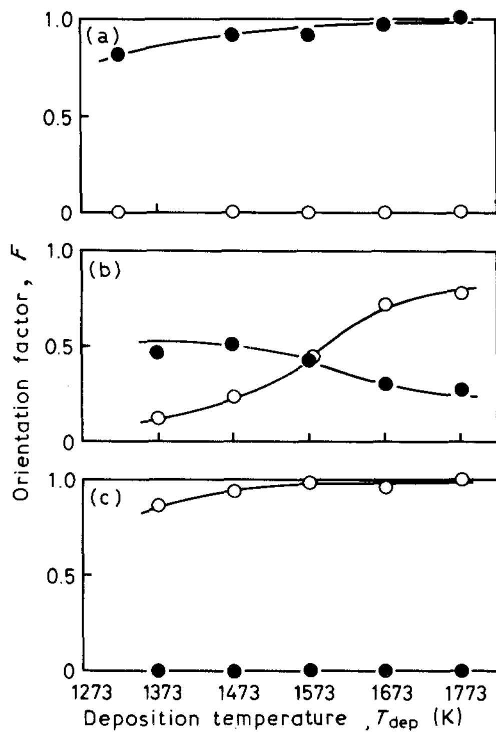


Figure 3 Relationship between the orientation factor and deposition conditions of CVD TiB_2 prepared at $m_{B/Ti} = 0.6$; (a) $P_{tot} = 4$ kPa, (b) $P_{tot} = 13$ kPa, (c) $P_{tot} = 40$ kPa. (●) F_{100}, (○) F_{110}.

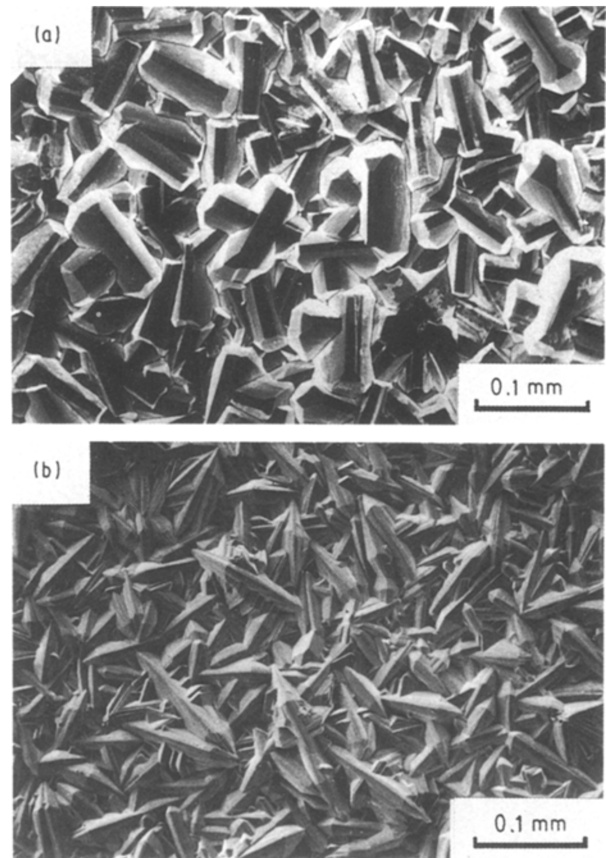


Figure 4 Typical surface textures of the (a) (1 0 0) and (b) (1 1 0) orientation CVD TiB_2 plates prepared at $m_{B/Ti} = 0.6$ and $T_{dep} = 1773$ K; (a) $P_{tot} = 4$ kPa, (b) $P_{tot} = 40$ kPa.

here I_{hkl} is the X-ray diffraction intensity from an (hkl) face, ΣI_{hkl} is the sum of all X-ray diffraction intensities over the whole measurement range, and P and P_0 are the X-ray intensity ratios for plate and powder samples.

The (1 0 0) and (1 1 0) planes are preferably oriented parallel to the substrate at $P_{tot} = 4$ kPa and at $P_{tot} = 40$ kPa as shown in Fig. 3a and c, respectively. When $P_{tot} = 13$ kPa, the preferred orientation changes from the (1 0 0) to the (1 1 0) orientation with increasing temperature.

Fig. 4 shows the typical surface texture of the (1 0 0) and (1 1 0) orientation samples observed by SEM. The (1 0 0) orientation sample shows that many flat facets are parallel to the substrate, whereas in the case of the (1 1 0) orientation sample, flat facets are inclined to the substrate. These surface morphologies may correspond to the crystal habit of TiB_2 as shown in Fig. 5.

The preferred orientation of CVD TiB_2 films, their CVD conditions and some properties reported previously are summarized in Table III. Previously, three kinds of preferred orientation (i.e. (1 0 0), (1 1 0) and (1 0 1) orientation) have been reported. No one, except Takahashi and Itoh [10], mentioned the effects of CVD conditions on the preferred orientation of CVD TiB_2. Takahashi and Itoh [10] examined the effect of CVD conditions in the temperature range 1123–1323 K and at a fixed $P_{tot} = 0.1$ MPa using a $TiCl_4 + BCl_3$ system. They reported that when $T_{dep} = 1123$ K, the (1 0 0) orientation was dominant at $m_{B/Ti} = 0.03$–0.3 and the (1 0 1) orientation was dominant at $m_{B/Ti} = 0.3$–1.0. When $T_{dep} = 1323$ K, no preferred orientation at $m_{B/Ti} = 0.03$–0.07 while the (1 1 0) orientation is seen at $m_{B/Ti} = 0.07$–1.0. On the other hand, the effect of $m_{B/Ti}$ on the orientation was not observed in the present work. This discrepancy may be caused by the difference in CVD conditions. Takahashi and Itoh [10] used a $TiCl_4 + BCl_3$ system, and their experiments were carried out mostly under Ti-excess conditions from $m_{B/Ti} = 0.03$–1. However, in the present work, the $TiCl_4 + B_2H_6$ system is used and the experiments were under relatively B-excess conditions from $m_{B/Ti} = 0.6$–4. However, in the $m_{B/Ti}$ range from 0.1–0.2, Takahashi and Itoh [10] showed that the oriented plane varied from (1 0 0) to (1 1 0) plane with an increase in T_{dep} from 1123–1323 K. This result is very similar to the tendency obtained in the present work at $P_{tot} = 13$ kPa as shown in Fig. 3b.

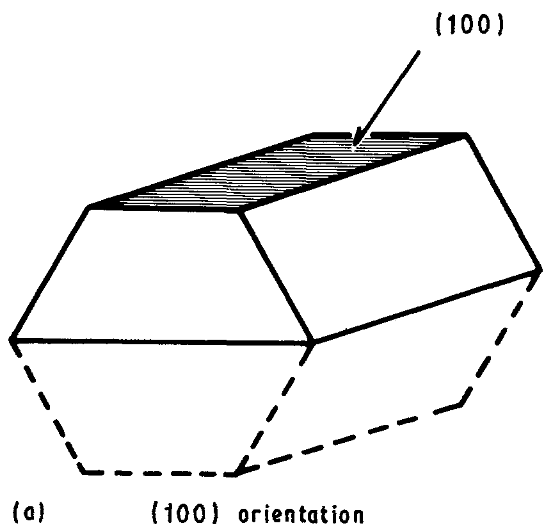
It is known that the growth mechanism of preferred orientation of the deposited materials can be explained by the Pangarov's model [22]. According to this model, the preferred orientation plane is the crystal face where a two-dimensional nucleus can form at the lowest energy (W_{hkl}). Pangarov also revealed the relationship between the W_{hkl} and supersaturation for various crystalline systems. Using this model, the preferred orientation of CVD Al_2O_3 films and CVD AlN plates was explained, by the changing of supersaturation, by Park *et al.* [23] and Goto *et al.* [24].

The supersaturation values, S, in the CVD process are defined by Equation 3 [23]

$$S_i = nP^{in}(i) \Big/ \sum_j n_j P_j^{eq}(i) \qquad (3)$$

TABLE III Preferred orientation of CVD TiB_2

System	Preferred orientation	Deposition temperature (K)	Substrate	Film thickness (mm)	Deposition rate ($mm\,h^{-1}$)	Reference
$TiCl_4 + BCl_3$	(1 1 0)	1473–2073	Graphite	0.24	–	[8]
	(1 0 0), (1 1 0)	473–1688	Graphite	0.3	0.3	[7]
	(1 0 0), (1 1 0)	873–1373	Graphite	0.05	–	[9]
	(1 0 1), (1 0 0), (1 1 0)	823–1373	Steel	0.1	0.1	[10]
$TiCl_4 + B_2H_6$	(1 0 0)	873–1173	Graphite	< 0.1	< 0.1	[13]
	(1 0 0), (1 1 0)	1323–1773	Graphite	1	0.5	Present work



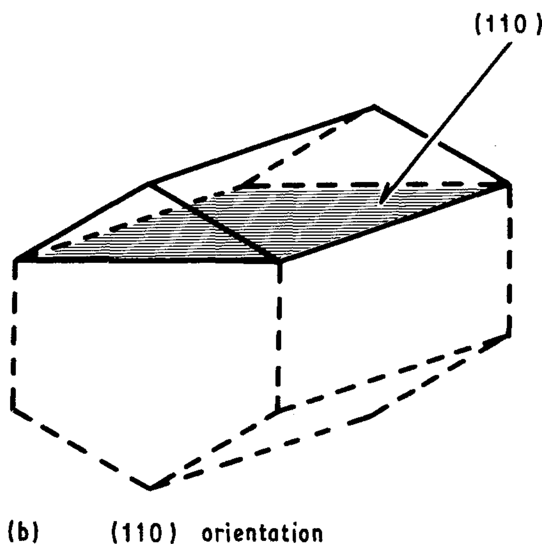


Figure 5 Crystal habits of TiB_2.

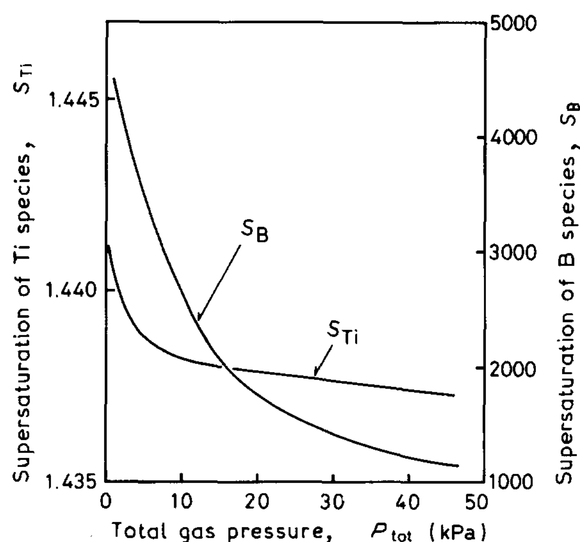


Figure 6 Effect of total gas pressure, P_{tot}, on the supersaturation of Ti and B species; $T_{dep} = 1573$ K, $m_{B/Ti} = 0.6$.

where S_i is the supersaturation of the i atom (Ti or B), $P^{in}(i)$ is the partial pressure of a source gas containing an i atom, and $P_j^{eq}(i)$ is the equilibrium partial pressure of a gas containing an i atom. n and n_j are the stoichiometric number of the gases containing an i atom in input and equilibrium, respectively.

Figure 6 shows the effect of total gas pressure on the S_{Ti} and S_B at $T_{dep} = 1573$ K and $m_{B/Ti} = 0.6$. S_{Ti} and S_B decrease with increasing P_{tot}, as indicated in Fig. 6.

The preferred orientation of hexagonal close packed (h c p) system materials changes from (1 0 0) to (1 1 0) to (0 0 1) orientation with decreasing supersaturation, according to Pangarov's calculations [21]. In the present work, the (0 0 1) orientation was not observed. However, the (1 0 0) orientation changed to the (1 1 0) orientation with increasing P_{tot}, as shown in Fig. 3. This change is explained well by the decrease in the supersaturation of Ti and B atoms in the gas phase. It is known that the supersaturation decreases at a higher T_{dep}, due to powder formation by homogeneous reactions in the gas phase [4, 12, 13]. At $P_{tot} = 13$ kPa, as shown in Fig. 3b, the preferred orientation changes from (1 0 0) to (1 1 0) orientation. This result may also be caused by the decrease in the supersaturation in the gas phase.

4. Conclusions

High-purity and high-density TiB_2 plates (about 1 mm thick) were prepared by CVD at $T_{dep} = 1323$–1773 K, $P_{tot} = 4$–40 kPa and $m_{B/Ti} = 0.6$–4. The following results were obtained:

1. The composition of the CVD TiB_2 plates is nearly stoichiometric. No Cl and free B were identified. The lattice parameters were $a = 0.3029$ nm and $c = 0.3229$ nm, and the density was $4.50 \times 10^3\ kg\,m^{-3}$. These values agree well with the literature values, and are independent of CVD conditions.

2. The preferred orientation of the CVD TiB_2 plates mainly depends on P_{tot}. The (1 0 0) orientation is dominant at $P_{tot} = 4$ kPa, and the (1 1 0) orientation is dominant at $P_{tot} = 40$ kPa. When $P_{tot} = 13$ kPa, the (1 0 0) orientation changes to the (1 1 0) orientation with increasing T_{dep}. This P_{tot} dependence of the preferred orientation was explained by the supersaturation of the source gases.

3. The surface morphologies of the oriented CVD TiB_2 plates correspond to the crystal habits of TiB_2. The (1 0 0) oriented CVD TiB_2 plates have flat crystal facets, the surface of which is parallel to the substrate, and the facets of the (1 1 0) oriented ones are inclined to the substrate.

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