

# Low temperature deposition of TiB<sub>2</sub> by inductively coupled plasma assisted CVD

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Available online 7 September 2006

## Abstract

Inductively coupled plasma (ICP) chemical vapor deposition (CVD) was used to deposit titanium diboride (TiB<sub>2</sub>) films on H13 steel and (100) Si wafer substrate using a gas mixture of TiCl<sub>4</sub>, BCl<sub>3</sub>, H<sub>2</sub> and Ar. The effects of the ICP on the TiB<sub>2</sub> film properties were investigated. TiB<sub>2</sub> films with high hardness (>40 GPa) could be prepared at relatively low temperatures (400–250 °C) using ICP. The hardness increased with the ICP power and gas flow ratio of TiCl<sub>4</sub>/BCl<sub>3</sub>. The film structure also changed from a (100) preferred orientation to a random orientation with increasing rf power. It is believed that the high hardness of the TiB<sub>2</sub> films resulted from the strong chemical bonding of the stoichiometric TiB<sub>2</sub> films, the nano-sized small grains of TiB<sub>2</sub>.

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PACS: 52.80Yr; 81.15Gh

Keywords: Titanium diboride (TiB<sub>2</sub>); Inductively coupled plasma; CVD

## 1. Introduction

There is increasing interest in the titanium diboride (TiB<sub>2</sub>) films on account of its high hardness, high corrosion and wear resistances as well as its low electrical resistivity. Moreover, the low solubility of TiB<sub>2</sub> in aluminum enables TiB<sub>2</sub> to be used as a coating material for die-casting or dry cutting of aluminum alloys [1,2]. Recently, it has been suggested to be an interesting candidate for a diffusion barrier of LSI [3] and its high electrical conductivity and anti-corrosion property means that it can be used as a protective coating of separate plates (bipolar plate) in polymer electrolyte membrane fuel cells (PEMFC) [4].

The high hardness (>40 GPa) of the TiB<sub>2</sub> films could be obtained using conventional plasma enhanced chemical vapor deposition (PECVD) only at high deposition temperatures (>~500 °C) (Fig. 1), which restricts the selection of the substrate material. An attempt was made to substitute BCl<sub>3</sub> with diborane (B<sub>2</sub>H<sub>6</sub>) to lower the deposition temperature [5]. Although the thermodynamics for this reaction is favorable,

the reaction rate was too low at a low temperature. As a result, films deposited at temperatures lower than 700 °C were soft and non-cohesive, and contained too much boron.

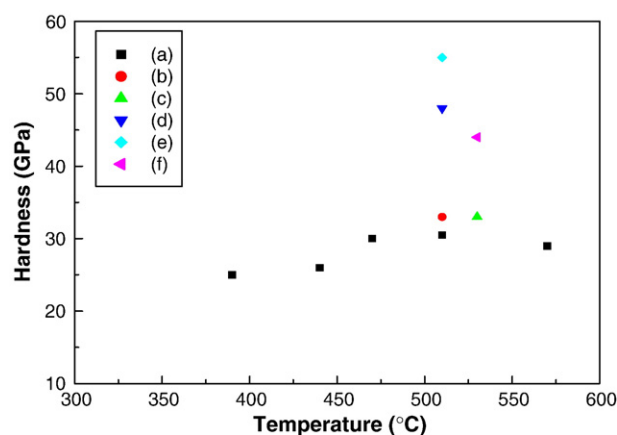


Fig. 1. The reported micro-hardness of TiB<sub>2</sub> films deposited by PECVD technique at various deposition temperature. ((a) H. Karner et al. [6], (b)–(c) K.-T. Rie et al. [1,7], (d) K. H. Kim et al. [8], (e) C. Mitterer et al. [9], (f) J.W. Lim et al. [10]).

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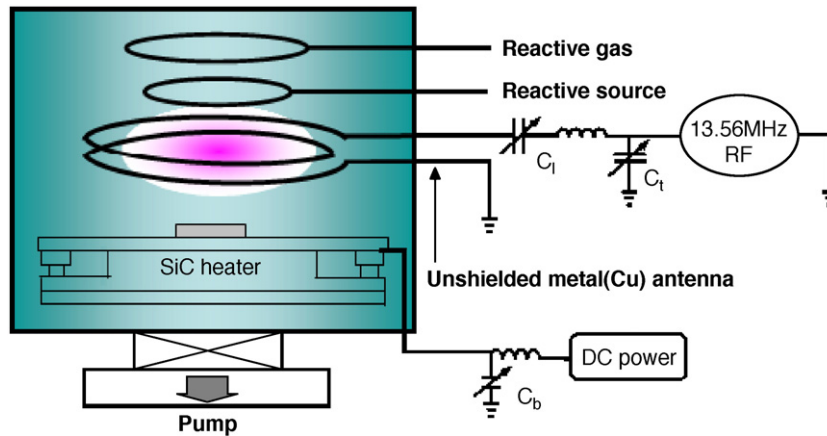


Fig. 2. Schematic diagram of ICP-assisted CVD system.

In this study, an attempt was made to lower the deposition temperature using high-density plasma and the structure and properties of the  $\text{TiB}_2$  films were investigated.

## 2. Experimental

$\text{TiB}_2$  films were deposited on H14 steel and (100) silicon wafers by internal ICP-assisted CVD using a gas mixture of  $\text{TiCl}_4$ ,  $\text{BCl}_3$ ,  $\text{H}_2$  and Ar. Ar was used as the carrier gas for the  $\text{TiCl}_4$ . The gas lines were heated with heating tape to avoid the condensation of the source gases on the way. ICP was generated by applying rf power of 13.56 MHz through a tuning network to a two-turn coil (RFI coil) water-cooled copper tube. The RFI coil had a main diameter of approximately 100 mm. It was located inside the vacuum chamber between the substrate and the gas distributor. The  $\text{TiCl}_4$  and  $\text{BCl}_3$  gases were injected into the hot spot where the electron temperature is highest. It was reported that the precursor could be efficiently dissociated by direct injection into the hot spot of an internal type ICP [11]. The location of the hot spot was determined by measuring the plasma density ( $N_p$ ) and electron temperature ( $T_e$ ) by a Single Langmuir probe. Fig. 2 is a schematic diagram of the CVD system.

The base pressure was  $<2 \times 10^{-6}$  mTorr, while deposition was carried out at 70 mTorr. The deposition temperature and ICP power ranged from 250 to 550 °C and from 200 to 500 W, respectively. The substrate was pre-cleaned using an Ar and  $\text{H}_2$

gas mixture and deposition was carried out on a grounded substrate. Table 1 summarizes deposition conditions.

The microhardness and elastic modulus were evaluated from the loading/unloading curves measured using a computer

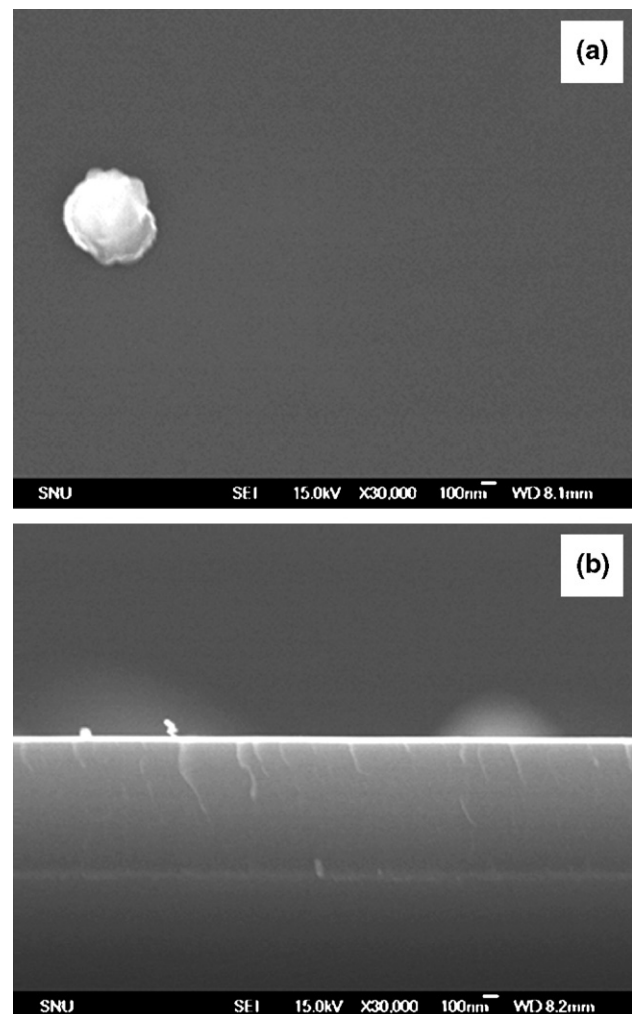


Fig. 3. FESEM images of a typical  $\text{TiB}_2$  deposited at 70 mT, 400 °C, rf 400 W. (a) surface and (b) cross-sectional image.

Table 1  
Deposition condition of  $\text{TiB}_2$  coatings by ICP-CVD

Substrate	H13 steel
Deposition temperature	250, 400, 550 °C
Deposition pressure	70 mTorr
Flow rate of $\text{TiCl}_4$	0.5–2.5 sccm
Flow rate of $\text{BCl}_3$	0.5–2.5 sccm
Flow rate of $\text{H}_2$	20 sccm
Flow rate of Ar	20 sccm
Rf power	200–500 W

(Pre-cleaning of substrate : RF 300 W, 40 mTorr (Ar+ $\text{H}_2$ ), dc bias-50 V, 10 min).

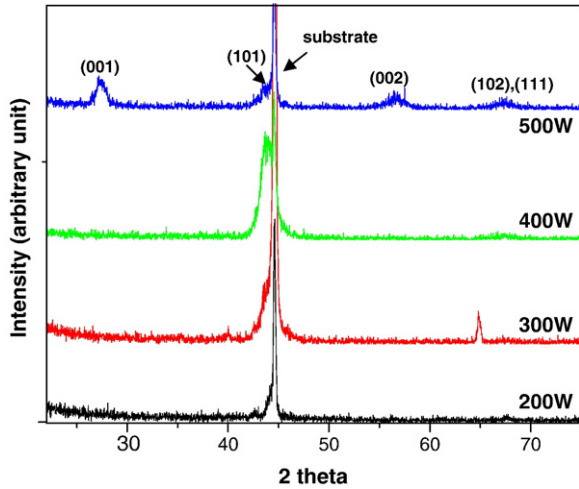


Fig. 4. XRD patterns of  $\text{TiB}_2$  deposited at 70 mT, 400 °C and  $\text{TiCl}_4/\text{BCl}_3 = 1/2$ .

controlled microhardness tester (Fischerscope H100). The structure of the films was examined by X-ray diffraction (XRD) (M18XHF-SRA) with Cu  $K\alpha$  ( $\lambda = 1.54050 \text{ \AA}$ ) and by field emission scanning electron microscopy (FESEM) (JEOL JSM-6330F). The chemical composition of the films was determined by wavelength dispersive electron-probe X-ray micro-analysis (EPMA) (JXA-8900R) and was calibrated using standard samples of each component.

### 3. Results and discussion

Fig. 3 shows FESEM images of the  $\text{TiB}_2$  films. A very smooth surface could be observed in all coatings irrespective of deposition temperature and rf power. The cross-sectional view shows a very compact and dense structure without any columns. The surface and cross-sectional images of the  $\text{TiB}_2$  films show similar morphologies to the  $\text{TiB}_2$  films prepared by conventional PECVD.

The XRD patterns of the  $\text{TiB}_2$  films in Fig. 4 show three different crystal structures according to the rf power (1) Amorphous structure with an excessive boron content at a low rf power, (2) a (101) preferred orientation at a medium rf power (300–400 W), and (3) a random orientation at a high rf power (>500 W). It is believed that the change in the film structure resulted from the increase in the ion and electron density as well as the atomic mobility with rf power. The large full width values at half maximum (FWHM) of the diffraction peaks for all the crystallized films indicate nanometer grain sizes, irrespective of the crystalline orientation. The grain size calculation using Scherrer formula and image analysis by high resolution transmission electron microscope (HRTEM) show that the grain size of as-deposited  $\text{TiB}_2$  films is 3–5 nm.

Compositional analysis by EPMA revealed an excess of boron (B) and chlorine (Cl) in the films deposited at a low rf power (Fig. 5(a)–(b)). As the rf power was increased, the B and Cl contents decreased and the B/Ti ratio approached to the stoichiometric value of 2. Soft and boron rich  $\text{TiB}_x$  ( $X > 2$ ) films were deposited at a low temperature and rf power, because

insufficient energy was supplied for the reaction. The enhanced ion density and ion mobility at high rf power and temperature produced stoichiometric  $\text{TiB}_2$  films. The B/Ti ratio also decreased with increasing  $\text{TiCl}_4/\text{BCl}_3$  gas flow ratio (Fig. 5 (c)). Randich and Gerlach [12] calculated the CVD phase diagram of

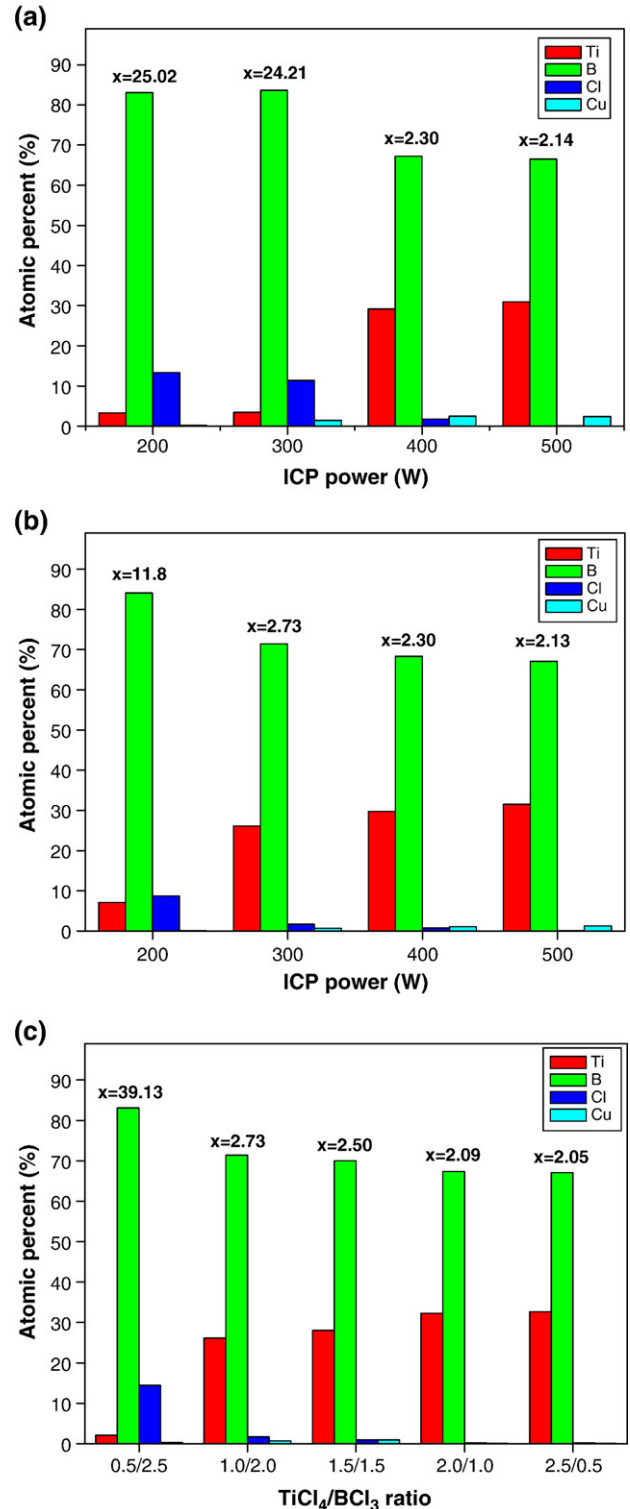


Fig. 5. Atomic composition of  $\text{TiB}_2$  films determined by EPMA deposited at (a) 250 °C and  $\text{TiCl}_4/\text{BCl}_3 = 1/2$ , (b) 400 °C and  $\text{TiCl}_4/\text{BCl}_3 = 1/2$ , (c) 400 °C and rf 300 W.

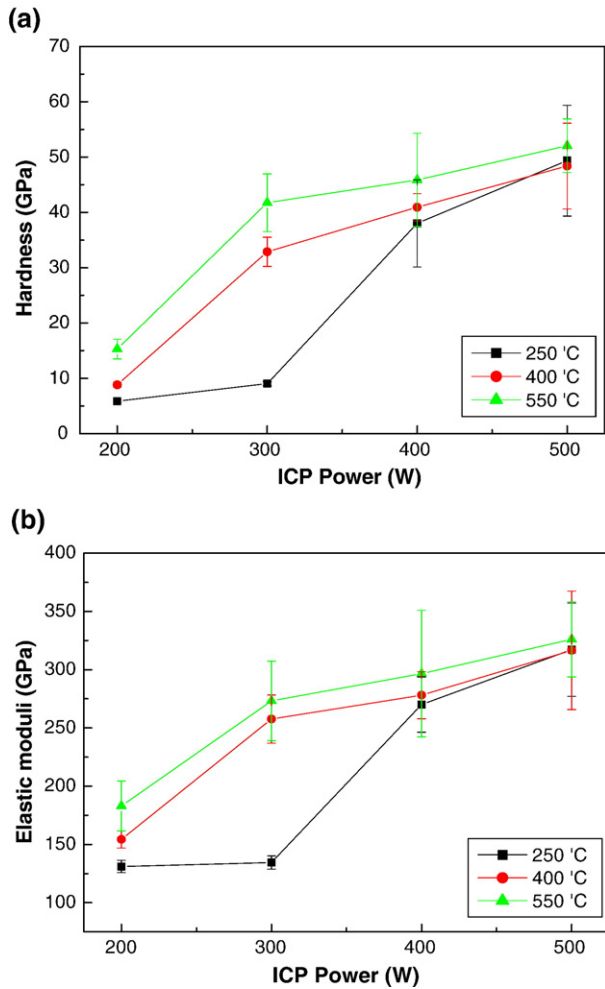


Fig. 6. Hardness (a) and elastic modulus (b) of TiB<sub>2</sub> films deposited at the various ICP power. (TiCl<sub>4</sub>/BCl<sub>3</sub> = 1/2).

the Ti–B–H–Cl system. According to the phase diagram, the formability of TiB<sub>2</sub> depends on the distance between the process tie line and the phase boundary of the (TiB<sub>2</sub>+gas) and the gas phases. When the BCl<sub>3</sub> concentration was low, a boron rich TiB<sub>x</sub>

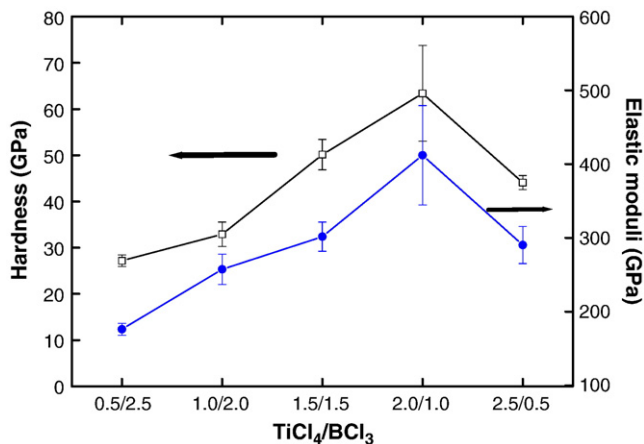


Fig. 7. Hardness and elastic modulus of TiB<sub>2</sub> films deposited at the various TiCl<sub>4</sub>/BCl<sub>3</sub> gas flow ratio (rf 300 W and 400 °C).

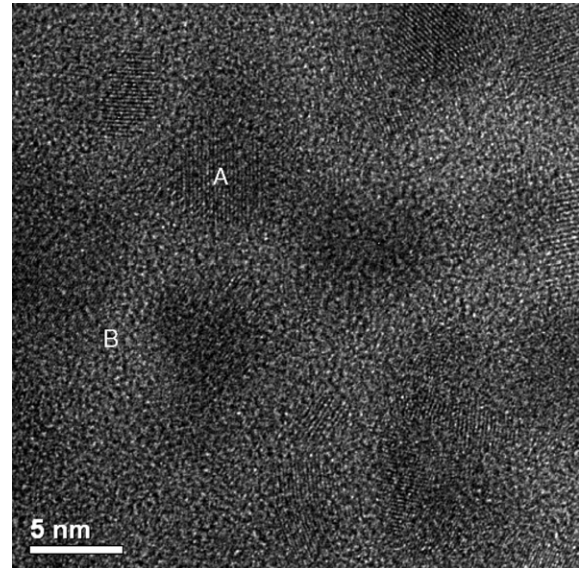


Fig. 8. HRTEM image of TiB<sub>x</sub> (x=3) films. (A — crystallized TiB<sub>2</sub> phase, B — amorphous boron phase).

film was deposited, because the process tie line went through the region of the (B+TiB<sub>2</sub>+Gas) phase. Therefore, soft and boron rich TiB<sub>x</sub> films were formed instead of TiB<sub>2</sub> at a low TiCl<sub>4</sub>/BCl<sub>3</sub> gas ratio.

Cu contamination from RFI coil was less than 2 at.% in all coatings. Figs. 6 and 7 show that the micro-hardness and elastic modulus of the TiB<sub>2</sub> films increased with increasing deposition temperature, rf power and a TiCl<sub>4</sub>/BCl<sub>3</sub> gas ratio.

The bulk TiB<sub>2</sub> has a high hardness (>25 GPa) because of a strong bonding between graphitic B-layers along the *c*-axis [13]. Therefore, the high hardness of stoichiometric TiB<sub>2</sub> films, which is obtained at high rf power and a high TiCl<sub>4</sub>/BCl<sub>3</sub> gas ratio, is the result of intrinsic high hardness of TiB<sub>2</sub> and nano grain size effect of the films. However, the B-rich TiB<sub>x</sub> films show low hardness because of the high proportion of the soft and amorphous B-phase (Fig. 8).

#### 4. Conclusion

TiB<sub>2</sub> films with superior mechanical properties could be formed at low temperatures (250–400 °C) using ICP for conventional CVD. The film hardness was determined by the rf power, deposition temperature and the gas flow ratio of TiCl<sub>4</sub>/BCl<sub>3</sub>. TiB<sub>2</sub> films with a very high hardness could be formed when the film had a stoichiometric composition and a nano-sized grain structure, which could be obtained using a suitable TiCl<sub>4</sub>/BCl<sub>3</sub> gas flow ratio and high ion density ICP.

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