

Properties of Va metal-B films prepared by r.f.-sputtering

Part 1 *Characterization and properties of films in the system Ta-B*

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Ta_{100-x}B_x alloy films were prepared by r.f.-sputtering in the chemical composition range $45 \leq x \leq 77$. Ta_{100-x}B_x ($45 \leq x \leq 58$) films consist of the amorphous phase, while the TaB₂ crystal phase was observed in Ta_{100-x}B_x ($66 \leq x \leq 77$) films. A remarkable preferred orientation with the (001) plane of TaB₂ parallel to the film surface was observed in Ta₃₄B₆₆. The d.c. electrical conductivity of Ta_{100-x}B_x ($45 \leq x \leq 77$) films decreases with increasing boron content in the range 6.7×10^3 to $1.3 \times 10^3 \Omega^{-1} \text{cm}^{-1}$. The micro-Vickers hardness of Ta_{100-x}B_x ($45 \leq x \leq 77$) films was in the range 2200 to 2600 kg mm⁻².

1. Introduction

The borides are a highly refractory group of ceramic materials characterized by extreme hardness and high electrical conductivity at high temperatures. There are more than 30 binary borides with melting points higher than 2000°C. The most interesting borides as regards usefulness are the diborides of zirconium (ZrB₂), titanium (TiB₂), tantalum (TaB₂), niobium (NbB₂) and so on [1, 2].

Recently, it has been noted that these diborides are superior refractory materials compared to refractory oxides, and much effort has been devoted to the development of better structural materials. Furthermore, these borides are favourable for use as coating materials, being characterized not only by hardness and high electrical conductivity, but also by chemical durability. TaB₂ is one of the diborides with such favourable characteristics.

There are many methods of fabricating coating films. The r.f.-sputtering technique is particularly useful in fabricating coating films because it has the capability of lowering the substrate temperature, evaporating starting materials with high melting points, and can be used on many kinds of substrates.

In this paper, the authors applied the r.f.-sputtering technique to the fabrication of Ta-B films in order to develop the application of borides as coating materials. Characterization based on chemical analysis, X-ray diffractometry, electron probe microanalysis (EPMA), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) observations were carried out on the films. The d.c. electrical conductivity and micro-Vickers hardness, being

characteristic properties of the films, were also measured.

2. Experimental details

Ta-B films were prepared by the use of an Ulvac SBR-1104 type r.f.-sputtering apparatus. A co-sputtering technique was employed to control the composition of the Ta-B films. A target was placed on the lower electrode and a substrate was attached in the centre of the upper electrode. As shown in Fig. 1, the target used for co-sputtering was composed of a boron powder disk (99%, 100 mm diam.) and 69 geometrically arranged tantalum metal chips (99.96%, 4 to 8 mm square).

Glass slides and polyimide films were used as substrates. Ta-B films for X-ray diffraction, SEM observation, d.c. electrical conductivity, and micro-Vickers hardness testing were sputtered onto glass slide substrates. Ta-B film samples for TEM observation were sputtered onto polyimide film substrates, and were stripped from the polyimide substrate with HF solution. Sputtering conditions are shown in Table I.

The chemical composition of the Ta-B films was determined by absorption spectroscopy with pyrogallol for tantalum and methylene-blue for boron, respectively. The uniformity of the film composition was determined by EPMA. Film thickness was measured using a stylus-type surface analyser. D.c. electrical conductivity was measured by the four terminals method in the temperature range -150 to 150°C.

Micro-Vickers hardness was measured at room temperature by the use of a Matsuzawaseiki Co., Ltd,

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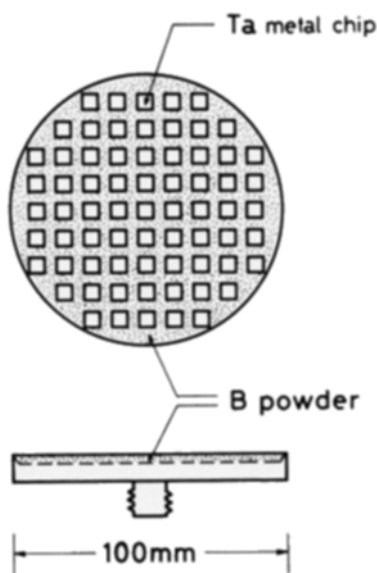


Figure 1 Typical assembly of the target for co-sputtering.

DMH-2 type micro-Vickers tester. The load was 10 g and the loading time was 15 sec during the micro-Vickers hardness measurement, conditions were chosen by considering the film thickness and measurement precision.

3. Results and discussion

3.1. Characterization of the films

All the Ta-B films have a metallic lustre. The deposition rate is 4.0 to 5.5 nm min⁻¹ under the sputtering conditions given above, and Ta-B films of thickness 1 to 3 μm are obtained after 4 to 8 h sputtering. The results of the chemical analysis of the Ta-B films are summarized in Table II.

A plot of the concentration of boron in the film against the area ratio of boron in the target is shown in Fig. 2. It is found that the concentration in the film increases in a concave manner with increasing area ratio in the target (see Fig. 2). Ta-B films are obtained in the composition range from 45 to 77 at % B.

A representative result of the EPMA analysis of the Ta-B film is shown in Fig. 3. It is apparent that the Ta-B film composition is fairly uniform. The above results suggest that the co-sputtering technique in the present work is also useful in controlling film composition, as noted by Mimura *et al.* [3].

X-ray diffraction patterns of Ta-B films sputtered onto glass slide for 8 h are shown in Fig. 4. Ta-B-1 (45 at % B) exhibits very broad diffraction line around $3\theta = 35^\circ$, corresponding to d_{110} of bcc-tantalum metal. Similar X-ray diffraction patterns are observed on Ta-B-2 (53 at % B) and Ta-B-3 (58 at % B). The

TABLE I Sputtering conditions

Target	Ta-B
Substrate	Glass slide, polyimide film
Gas	Ar
Pressure	2×10^{-2} mm Hg
Sputtering power	100 W
Substrate temperature	160°C

TABLE II Target constitution as surface area ratio Ta/B and film composition of Ta-B co-sputtered films

Sample no.	Area ratio S_{Ta}/S_B	Film composition (at % B)
Ta-B-1	56/44	45
Ta-B-2	43/57	53
Ta-B-3	32/68	58
Ta-B-4	22/78	66
Ta-B-5	14/86	77

X-ray diffraction lines of Ta-B-4 (66 at % B) are identified as those of the TaB₂ crystal phase, which corresponds stoichiometrically to the composition of the film. Additionally, a remarkable preferred orientation with the (00 1) plane of TaB₂ parallel to the film surface is observed in Ta-B-4 (66 at % B). It can be assumed that the preferred orientation of the TaB₂ crystals is due to the growth rate of the *c*-plane being faster than that of other planes under the present sputtering conditions. Similar results have been observed on BaFe₁₂O₁₉ sputtered onto glass substrate [4] and AlN sputtered onto sapphire substrate [5]. Beyond 66 at % B, the preferred orientation of TaB₂ crystals is not observed. The X-ray diffraction pattern of Ta-B-5 (77 at % B) shows the superposition of an X-ray amorphous pattern and weak diffraction lines due to randomly oriented TaB₂ crystals.

In order to investigate the solid state nature of the X-ray amorphous film, TEM observations were carried out for as-sputtered Ta-B-1 (45 at % B) film (Fig. 5). It was found that the film consists of an amorphous phase since the electron diffraction pattern showed a typical amorphous pattern (Fig. 5b).

In Fig. 6, the above results from both X-ray diffraction analysis and electron diffraction are illustrated schematically in relation to the phase diagram for the system Ta-B as determined by Nowotny *et al.* [6]. Rawson pointed out that the region of glass formation for the binary oxide system was often found to be in a region of eutectic composition where the liquidus temperature was low [7]. In the system Ta-B, a low eutectic point (E₁) at 20 at % B (e.t. = 1780°C) exists between tantalum (m.p. = 3060°C) and TaB₂

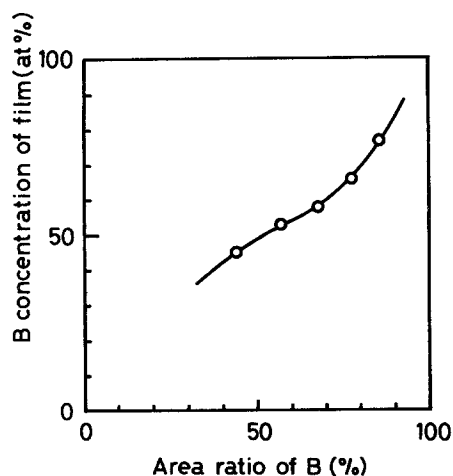


Figure 2 Plot of boron concentration in film against area ratio of boron in target.

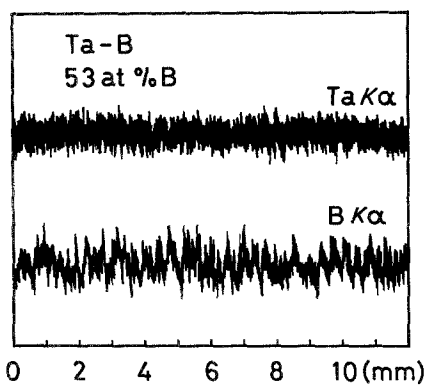


Figure 3 Line profile of EPMA analysis for tantalum and boron of Ta-B-2 (53 at % B) film.

(m.p. = 3100°C), and another eutectic point (E_2) exists at 98 at % B, as seen in Fig. 6. The liquidus temperature falls radically from the melting point of TaB_2 toward both eutectic compositions. Consequently, by considering the phase diagram for the system Ta-B and the rapid quenching conditions produced by the sputtering process, the formation region of the amorphous phase for the Ta-B films shows a similar trend to that found in the oxide system. Similar results have been observed in the case of Fe-B films prepared by the r.f.-sputtering technique [8]. Therefore, it is confirmed that Rawson's criterion for oxide glass formation is also applicable for non-oxide systems such as Fe-B and Ta-B.

SEM observations were made on Ta-B-1 (45 at % B) and Ta-B-4 (66 at % B). Scanning electron

microphotographs of fracture surfaces and film surfaces of as-sputtered Ta-B films are shown in Fig. 7. No cracks are observed and fairly dense film is obtained by the r.f.-sputtering technique.

3.2. Properties of the films

The relationship between $1/T$ and the d.c. conductivity of Ta-B films in the temperature range -150 to 150°C is shown in Fig. 8. All the samples exhibit metallic conductivity, and the conductivity is almost independent of temperature. The d.c. conductivity of Ta-B films decreases with increasing boron content. However, Ta-B-4 (66 at % B) film gives a lower d.c. conductivity value of $3.4 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ than that of TaB_2 bulk ($1.5 \times 10^4 \Omega^{-1} \text{cm}^{-1}$). HJuttemann *et al.* [9] prepared β -Ta film by d.c. diode sputtering which produced a relatively low conductivity value of $5.4 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ [10], which is of the same order as that of Ta-B-3 (58 at % B). Therefore, it is found that the Ta-B films obtained show relatively high conductivity even with a high content of boron. It may be considered that the lower conductivity is due to the very small amount of impurity oxygen in the film rather than the mismatching between Ta-B film and substrate, because such apparent cracks are not observed on the Ta-B films.

Fig. 9 shows the relationship between Ta-B film composition and micro-Vickers hardness at room temperature. For measurement of hardness the film is sputtered onto glass slide substrate and the thickness is 2.0 to 2.7 μm . The glass slide substrate has a low hardness value of 530 kg mm^{-2} . All Ta-B film samples

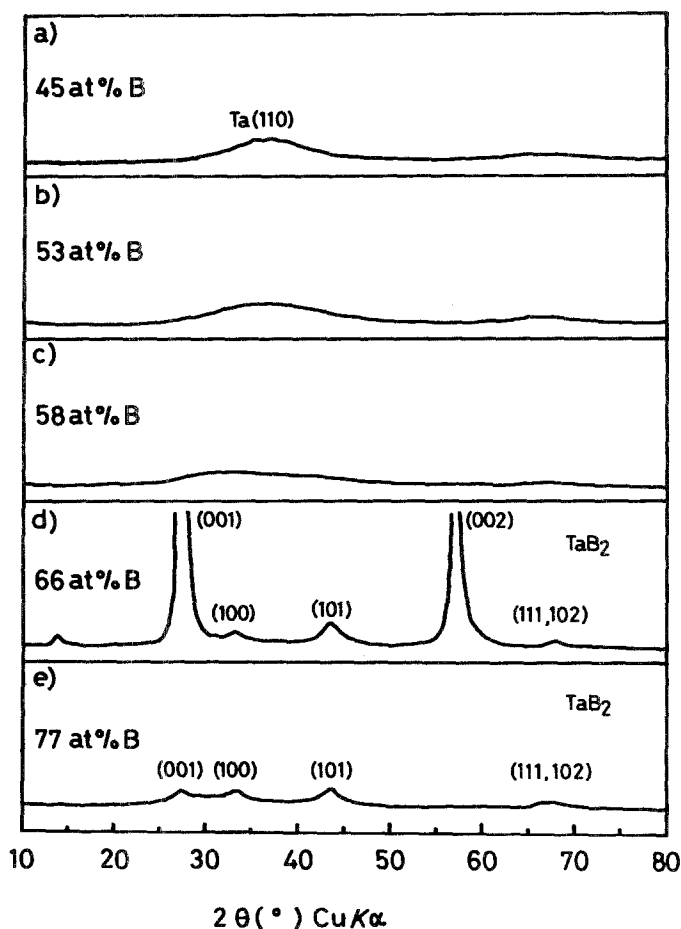


Figure 4 X-ray diffraction patterns of Ta-B films.

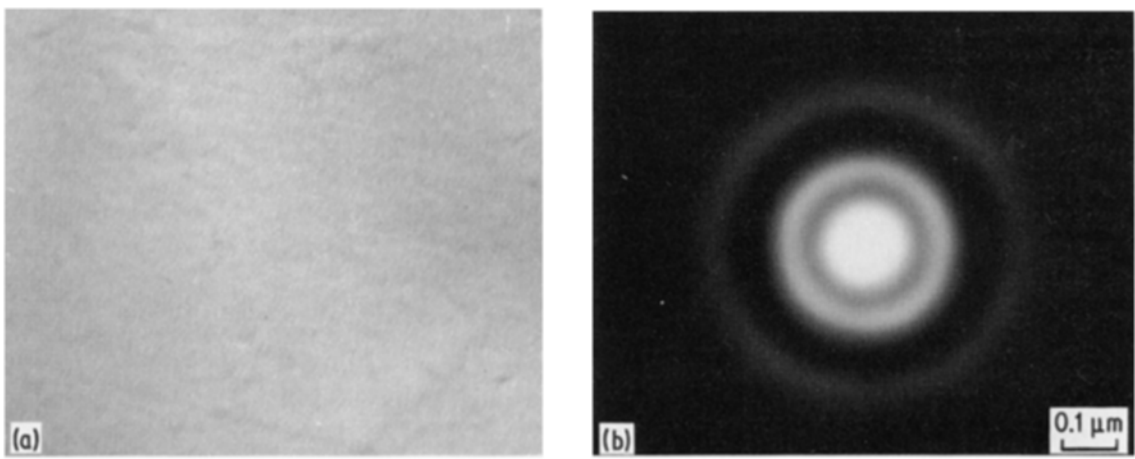


Figure 5 Transmission electron microscope observation of Ta-B-1 (45 at % B) film. (a) Transmission electron microphotograph. (b) Electron diffraction.

exhibit very high hardness in the range 2200 to 2600 kg mm⁻², and the hardness reaches a maximum value around the composition 58 at % B. Vahldiek and Mersol reported that the Knoop hardness of TaB₂ single crystal had a value of 2755 kg mm⁻² for the (0001) plane [11]. The r.f.-sputtered TaB₂ film in the present work shows high hardness of the same order as that of TaB₂ prepared by chemical vapour deposition ($H_v = 2700 \text{ kg mm}^{-2}$) [12]. Moreover, the hardness of the film maintains a fairly high value over the wide composition range in which the amorphous state exists. It may be supposed that the hardness of

the amorphous state with composition close to TaB₂ crystal is superior to that of the crystalline phase (TaB₂) because the amorphous state has neither grain boundary nor slip face of TaB₂.

4. Conclusions

1. The r.f.-sputtering method is applied to the preparation of coating film in the Ta-B system using a co-sputtering technique. Ta_{100-x}B_x alloy films with the composition range of 45 ≤ x ≤ 77 are obtained. Ta-B films consist of the amorphous phase in the composition range 45 ≤ x ≤ 58 and the TaB₂ crystal

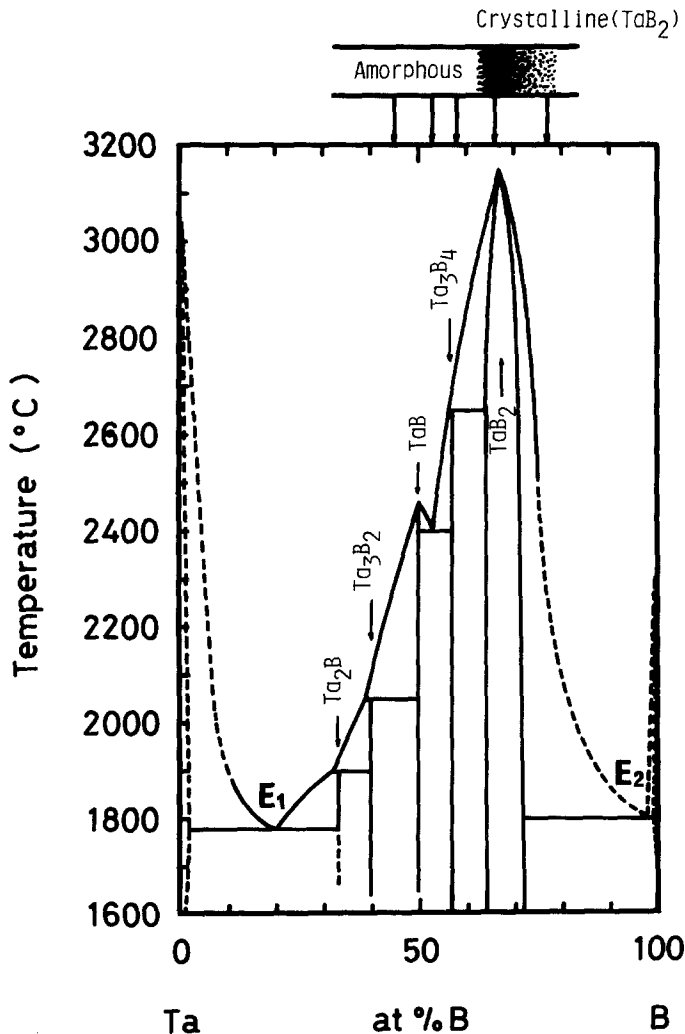


Figure 6 Phase diagram of the system Ta-B [6].

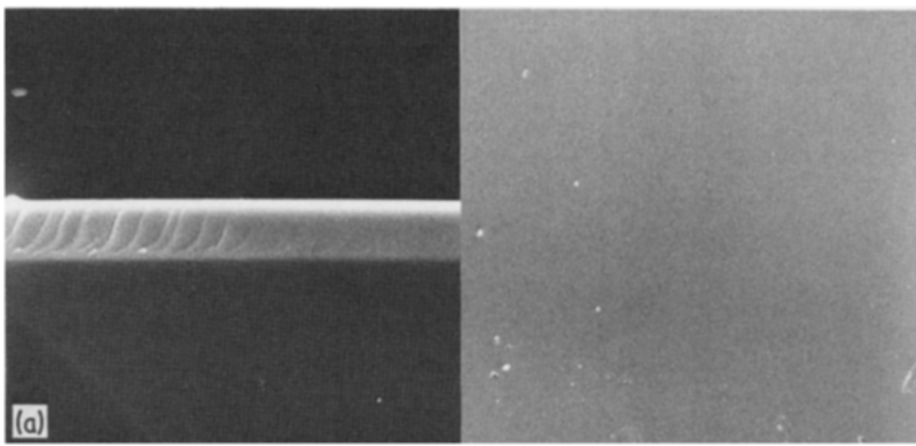
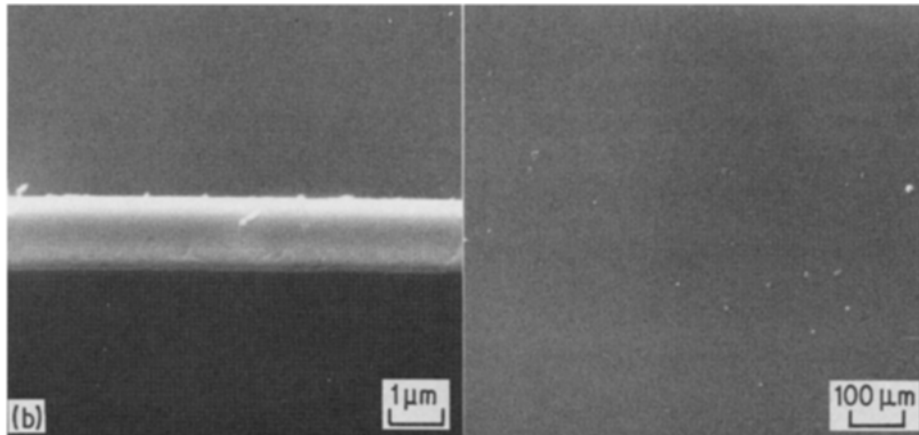


Figure 7 Scanning electron microscope observation of fracture surfaces and film surfaces of Ta-B films. (a) Ta-B-1 (45 at % B); (b) Ta-B-4 (66 at % B).



phase is observed in the composition range $66 \leq x \leq 77$.

2. A remarkable preferred orientation is observed on $Ta_{34}B_{66}$ film, which consists of TaB_2 crystals with the (001) plane parallel to the film surface.

3. Observed phases can be explained by considering the phase diagram of Ta-B and the rapid quenching produced by the r.f.-sputtering process.

4. D.c. electrical conductivity of Ta-B films is

metallic and almost independent of temperature in the range -150 to $150^\circ C$, and decreases with increasing boron content in the range 6.7×10^3 to $1.3 \times 10^3 \Omega^{-1} cm^{-1}$. D.c. electrical conductivity of Ta-B films is of the order of that of β -Ta d.c. diode-sputtered film.

5. Micro-Vickers hardness of Ta-B films is in the range 2200 to $2600 kg mm^{-2}$, comparable to that of TaB_2 film prepared by chemical vapour deposition.

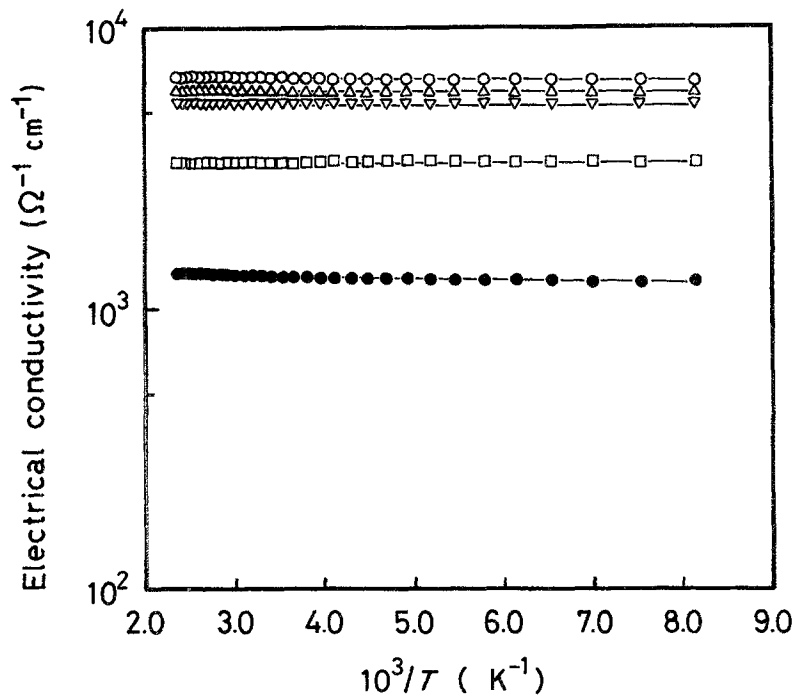


Figure 8 Temperature dependence of electrical conductivity of Ta-B films, of various compositions, (○) 45 at % B, (△) 53 at % B, (▽) 58 at % B, (□) 66 at % B and (●) 77 at % B.

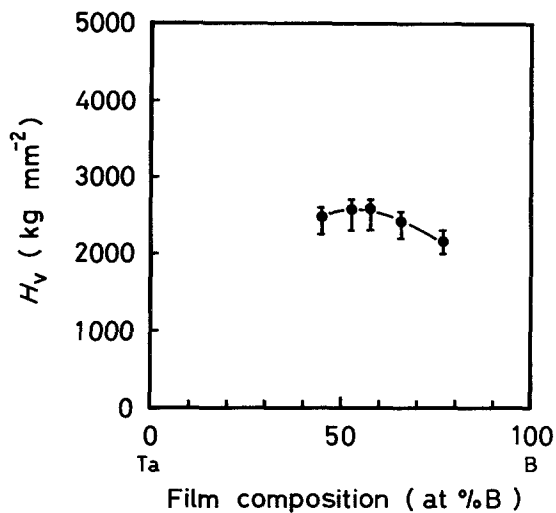


Figure 9 Micro-Vickers hardness of Ta-B films sputtered onto glass slide substrate for 8 h (glass slide substrate: $H_v = 530 \text{ kg mm}^{-2}$). Film thickness 2 to $3 \mu\text{m}$, load 10 g.

Ta₄₂B₅₈ film shows the maximum value of H_v , which may be due to the presence of the amorphous state, because no grain boundary exists and its composition is close to TaB₂.

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