Conformal growth of low friction HfB$_x$C$_y$ hard coatings

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ARTICLE INFO

ABSTRACT

Thin films of HfB$_x$C$_y$ are deposited in a cold wall CVD apparatus using Hf(BH$_4$)$_4$ precursor and 3,3-dimethyl-1-butene, (CH$_3$)$_3$CCH=CH$_2$, as a controllable source of carbon, at substrate temperatures of 250–600 °C. As-deposited films grown at 250 °C are highly conformal (e.g., in a very deep trench, the step coverage is above 90% at a depth/width of 30:1), exhibit dense microstructure, and appear amorphous in X-ray diffraction. Increasing the carbon content from 5 to 21 at.% decreases the hardness from 21 to 9 GPa and the reduced modulus from 207 to 114 GPa. Films grown at 600 °C with carbon contents of 28 and 35 at.% exhibit enhanced hardness of 25 and 23 GPa, and reduced modulus of 211 and 202 GPa, respectively. Annealing the 300 °C grown films at 700 °C affords a nanocrystalline structure with improved mechanical properties. For films with the highest and lowest carbon contents, respectively: the coefficient of sliding friction is in the range of 0.05–0.08 and the H/E and H^3/E^2 ratios range from 0.08–0.11 and 0.15–0.40. These values indicate that C-containing films should exhibit improved wear performance in tribological applications.

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1. Introduction

Conformal coatings with high hardness, low wear rates and low coefficient of friction are desirable for applications such as machines with relative motion of parts [1] and tools with re-entrant shapes [2]. Transition metal diborides and their C- or N-alloyed counterparts offer a combination of favorable tribo-mechanical properties, high chemical stability and thermal conductivity [3–10]. These films are deposited using a variety of techniques such as sputtering [6–8], chemical vapor deposition [3,11] and pulsed laser ablation [12,13]. A significant challenge is that physical vapor deposition methods lack the ability to deposit a conformal coating.

We previously reported the chemical vapor deposition (CVD) of stoichiometric, pure, and smooth HfB$_2$ hard coatings at substrate temperatures ≥200 °C using the halogen-free, single source precursor Hf(BH$_4$)$_4$. We showed that the films are extremely conformal in very high aspect ratio features, and explained this effect using a model of surface-saturated growth rate in combination with precursor transport down the depth of the feature by molecular diffusion [14,15]. We also reported the growth of Hf–B–N films by directing plasma-generated atomic nitrogen [14] or molecular ammonia to the growth surface [16].

These materials have attractive properties for tribological applications. As-deposited HfB$_2$ has a modulus of 340 GPa and nanoindentation hardness of 20 GPa; annealing at 700 °C transforms the structure from amorphous to nanocrystalline and raises the hardness to 40 GPa. As-deposited Hf–B–N films have somewhat reduced elastic modulus (200 GPa) and hardness (16 GPa), compared with HfB$_2$, and they do not crystallize upon annealing. Varying the N content or growing multi-layer (HfB$_2$/Hf–B–N) films provides a means to tailor the overall hardness and modulus [14].

The average coefficient of friction of as deposited and annealed HfB$_2$ is 0.10 and 0.08, respectively, and increases to 0.18 and 0.14 after 50 passes [17]. Pin on disc experiments at high contact pressure, ~700 MPa, against AISI 440C martensitic steel showed high wear resistance of HfB$_2$ films. All noticeable wear was localized on the steel side and as a highly sought-after tribological quality, HfB$_2$ did not exhibit any measurable surface damage at all [18].

In this work, we alloy C into HfB$_2$ in order to enhance the tribomechanical properties of the coating expressed through a reduced coefficient of sliding friction and enhanced nanoindentation hardness, while maintaining high wear resistance. This approach is inspired and motivated by two main materials engineering and tribology considerations: firstly, aside from entirely carbon or carbon-based thin films and tribological coatings such as a-C (amorphous carbon), a-C:H (hydrogenated amorphous carbon), ta-C (tetrahedral amorphous carbon) and DLC (diamond-like carbon), introduction of elemental C into the surface of many metallic, ceramic and cermet thin film material systems has been shown to impart beneficial friction and wear properties in general [19]. Secondly, in the particular case of transition metal diborides, previous attempts to alloy C into TiB$_2$ coatings produced very high (or super-) hardness and improved wear properties [7]. However, Ti–B–C is typically deposited using unbalanced DC magnetron co-sputtering [6,7], a highly directional coating technique [20].

Using CVD, we report the growth of highly conformal, low friction and wear resistant HfB_xC_y films using a halogen free process at low substrate temperature. The highly conformal nature of the process is suitable for coating complex micro- or nano-mechanical devices, vias or the interfaces of miniaturized systems that have high aspect ratio components, as well as for coating traditional tribological surfaces or parts subject to lubrication-free wear conditions at elevated temperatures.

In many CVD studies, methane (CH_4) is used as the carbon source to deposit transition metal carbide or ternary films such as HfC [11,21], TiC [22,23], and TiBC [3]. However, methane does not crack easily, which necessitates growth temperatures >800 °C [3,23] or the use of plasma decomposition [5]. In addition, the majority of metal source precursors are halogenated molecules that also require high temperature in order to react. Here, we remove these restrictions by using non-halogenated molecules — the precursor $Hf(BH_4)_4$ in combination with the olefinic carbon source 3,3-dimethyl-1-butene (DMB), $(CH_3)_3CCH{=}CH_2$. These molecules have exceptionally high vapor pressures at room temperature, 15 and 417 Torr, respectively, react at temperatures as low as 200 °C, and have efficient chemical pathways to eliminate excess atoms from the ligand groups in the form of volatile byproducts.

2. Experimental

HfB_xC_y coatings are deposited in a cold wall, high vacuum CVD chamber reported elsewhere [15,24]. Partial pressures of 0.10–0.20 mTorr for the $Hf(BH_4)_4$ precursor and 0.01–0.40 mTorr for the DMB carbon source yield different compositions of HfB_xC_y films. The substrate temperature for planar substrates is either 300 or 600 °C, and 250 °C for macrotrench and microtrench samples. Selected films are post-annealed in a tube furnace at 700 °C for 3 h in Ar gas to induce crystallization.

Si (100) is used as substrate material; it is cleaned in an ultrasonic bath for 10 min each in acetone and isopropyl alcohol, rinsed with DI water, then blown dry with nitrogen prior to loading in the chamber. The coating conformality under different growth conditions is measured using macrotrench substrates [25,26], which consist of silicon slices, 1.2 cm wide, separated by a 25 μm thick spacer on three sides. Gas transport within the macrotrench occurs in the molecular flow regime, as is the case within lithographically defined microtrench substrates, hence the kinetics that lead to conformal coating are identical. (However, the actual thickness profile is a function of the aspect ratio because the bottom of the trench introduces a boundary condition, and because microtrenches may be subject to pinch off at the opening.) The macrotrench is disassembled after film growth; precise measurements of coating thickness, composition, roughness, etc., are made as a function of depth in the trench. The conformality results are further confirmed using microtrench samples of nm-sized features.

Film microstructure and thickness are determined using cross-sectional scanning electron microscopy (SEM). Average growth rate is derived from the cross sectional SEM thickness of each film divided by the growth time. Composition and bonding are determined using X-ray photoelectron spectroscopy (XPS; PHI 5400, pass energy of 35.75 eV). ω-2θ X-ray diffraction (XRD) is used to measure the crystallinity. The adsorption of DMB and the onset of film growth are detected using in situ spectroscopic ellipsometry (SE) with photon energies in the range of 0.75–5.0 eV. Rutherford Backscattering Spectrometry (RBS) is used to calculate the atomic density of hafnium atoms by dividing the areal density obtained from RBS, by the film thickness measured from cross-sectional SEM.

The nanoindentation hardness and reduced modulus of the films are measured using a very sharp diamond indenter with tip radius of <40 nm following the Oliver–Pharr procedure [27,28]. In each loading profile, multiple loading-partial unloading (PUL) cycles are employed with increasing loads up to a maximum of 1 mN [29]. Indentation measurements are performed on films in the thickness range 150–300 nm and the maximum penetration depth of the indenter is kept to less than 10% of the film thickness to avoid substrate effects. The elastic

Table 1
Deposition conditions and composition for HfB_xC_y films A–F.

Sample	C (at.%)	B (at.%)	Hf (at.%)	T_{sub} (°C)	$P_{Hf(BH4)4}$ (mTorr)	P_{DMB} (mTorr)	Thick. (nm)
A	5	62	33	300	0.2	0.01	200
B	8	59	33	300	0.2	0.05	180
C	15	49	36	300	0.2	0.13	180
D	21	46	33	300	0.2	0.20	150
E	28	38	34	600	0.2	0.20	200
F	35	33	32	600	0.2	0.40	260

modulus of the film E_f is calculated using the experimentally measured reduced modulus as follows:

$$\frac{1}{E_r} = \frac{1 - \nu_d^2}{E_d} + \frac{1 - \nu_f^2}{E_f}. \tag{1}$$

Eq. 1 assumes isotropic linearly elastic mechanical behavior for the film and indenter tip, where Poisson's ratios for diamond (ν_d) and film (ν_f) are taken as 0.07 and 0.25, respectively. The elastic modulus for the diamond tip (E_d) is 1141 GPa.

Nanoscratch experiments are performed using a conospherical diamond tip of 1 μm radius. Constant normal loads of 100, 200, 350 and 500 μN are used at a constant scratch length of 6 μm. For each film, the number of passes is continually incremented from 1 to 50 at constant 0.64 μm/s lateral tip velocity by applying successive trace and retrace motions. The coefficient of sliding friction is determined as the ratio of the measured lateral force to the applied normal load during the scratch test.

3. Results and discussion

3.1. HfB_xC_y film deposition

A series of growth conditions is used to prepare HfB_xC_y films of different compositions, denoted as films A to F (5–35 at.% C) (Table 1). At a $Hf(BH_4)_4$ pressure of 0.20 mTorr, substrate temperature of 300 °C, and DMB pressures of 0.01–0.2 mTorr, the film carbon content increases from 5 to 21 at.% with increasing DMB pressure. Growth ceases altogether at higher DMB pressures (discussed below), but at higher temperatures growth resumes and the films have carbon concentrations up to 35 at.%.

3.2. Growth inhibition and conformal coating

A coating will be highly conformal within a deep or complex structure, when the growth rate is kinetically limited by the reaction at the film
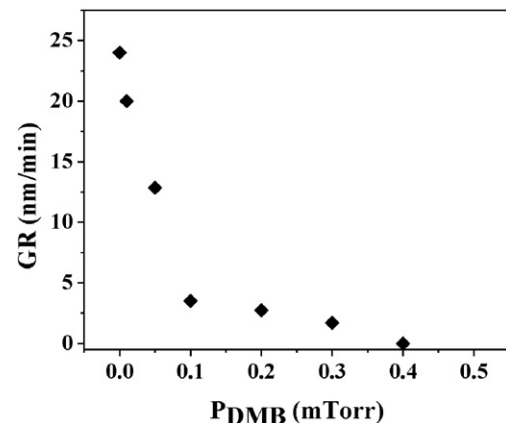

Fig. 1. Growth rate data vs. DMB pressure for HfB_xC_y samples.