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1 2	Influence of ultra-low ethylene partial pressure on microstructural and compositional evolution of sputter-deposited Zr-C thin films
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15	
16	Abstract
17	Zr-C thin films are grown on single-crystalline MgO(001) substrates via ultra-high vacuum dc
18	magnetron sputtering of Zr target in 10 mTorr Ar-C ₂ H ₄ gas mixtures with ethylene partial
19	pressures ($p_{C_2H_4}$) between 2 × 10 ⁻⁷ Torr and 2 × 10 ⁻⁴ Torr at substrate temperature T_s = 923 K and
20	using $p_{C_2H_4} = 2 \times 10^{-6}$ Torr at 723 K $\leq T_s \leq 1123$ K. The as-deposited layer microstructure and
21	composition are determined using X-ray diffraction, transmission electron microscopy, and X-ray
22	photoelectron spectroscopy. We find that the layers sputter-deposited at $T_s = 923$ K using the
23	lowest $p_{C_2H_4} = 2 \times 10^{-7}$ Torr are polycrystalline, close-packed hexagonal structured Zr:C solid
24	solutions. At higher $p_{C_2H_4} = 2 \times 10^{-6}$ Torr and 2×10^{-5} Torr, we obtain films composed of free-
25	carbon (C) and NaCl-structured ZrC_x , $x \le 1$. The amount of C increases 104% with ten-fold
26	increase in $p_{C_2H_4}$ from 2 × 10 ⁻⁶ Torr to 2 × 10 ⁻⁵ Torr. At the highest $p_{C_2H_4} = 2 \times 10^{-4}$ Torr, the
27	layers are X-ray amorphous with ~ 49 at.% C. Films grown at 723 K $\leq T_s \leq 1123$ K using
28	constant $p_{C_2H_4} = 2 \times 10^{-6}$ Torr exhibit qualitatively similar microstructures, irrespective of T_s ,
29	composed of dense columnar ZrC_x grains surrounded by C and corrugated surfaces. Our results
30	suggest that the compositional and microstructural evolution of Zr-C films during reactive

- 31 sputter-deposition of Zr is highly sensitive to ethylene partial pressure, with as little as 0.02% of
- 32 the total pressure sufficient at $T_s \ge 723$ K to obtain ZrC_x films.
- 33 Keywords: transition-metal carbides, reactive magnetron sputtering, Zr-C thin films

1. Introduction

35	Group 4 to 6 transition-metal carbides (TMCs) are highly refractory compounds with
36	excellent thermomechanical and thermochemical properties due to a mixture of ionic, covalent,
37	and metallic bonds between the metal cations and carbon anions. Among the TMCs, ZrC
38	crystallizes in B1 (rock salt) structure (Fm $\overline{3}$ m; space group 225) with a bulk lattice parameter $a_0 =$
39	0.4693 nm at room temperature [1]. ZrC is a hard (> 25 GPa), high elastic modulus (> 350 GPa),
40	and high melting point (> 3673 K) solid with good thermal (20.5 W/m.K at 293 K) and electrical
41	conductivities (2326 S/m at 293 K) and excellent resistance to wear, corrosion, and oxidation [2].
42	ZrC is used as hard protective coatings on cutting tools [3–7], as structural components in
43	aerospace vehicles, as coating material for nuclear fuel in nuclear reactors [2,3,8–11], and as
44	field-emission cathodes in electronic devices [12].
45	ZrC thin films have been grown via reactive sputtering of elemental Zr in hydrocarbon/Ar
46	gas mixtures [3,13], sputtering of compound ZrC [14,15] and Zr and C targets [16] in pure Ar
47	discharges, sol-gel synthesis [17], chemical vapor deposition [18-20], and pulsed laser deposition
48	[21,22]. Among all these techniques, reactive sputter-deposition has been the most commonly
49	used method to grow ZrC and other TMC thin films [3,13,16,23–28]. In this approach, one can
50	control both the thin film composition and the growth rate by appropriate choice of the reactive
51	gas and its flux [29]. The TMC coatings deposited via this technique typically result in two-phase
52	mixtures, composed of TMC crystallites and free-carbon (C) [3,24,27], with reactive gas
53	pressure-dependent TMC and C phase fractions, crystallinity, and mechanical properties
54	[3,24,26,27,30]. Recently, Tanaka et al. [31] have demonstrated tunability of Ta-C phase
55	composition in thin films sputter-deposited with ultra-low amounts of ethylene partial pressures,
56	$p_{C_2H_4}$ (0.0025 ~ 2.5% of total pressure) using a compound TaC target. Here, we focus on the

microstructural and compositional evolutions of thin films deposited by sputtering elemental Zr target using similarly low $p_{C_2H_4}$ between 0.002 and 2% of the total pressure. 58

In this paper, we report on the effects of $p_{C_2H_4}$ (between 2×10^{-7} Torr and 2×10^{-4} Torr) and 59 substrate temperature (723 K $\leq T_s \leq 1123$ K) on the composition and crystallinity of Zr-60 61 C/MgO(001) thin films sputter-deposited in 10 mTorr Ar-C₂H₄ gas mixtures. (Here, and in the following sections, we use Zr-C to refer to both Zr:C solid solutions and ZrC_x , $x \le 1$, 62 63 compounds.) Using X-ray diffraction (XRD), transmission electron microscopy (TEM), and Xray photoelectron spectroscopy (XPS), we characterized the as-deposited layer microstructure and 64 composition. We find that the films sputter-deposited at $T_s = 923$ K using $p_{C_2H_4} = 2 \times 10^{-7}$ Torr 65 are polycrystalline with primarily hexagonal close-packed (hcp) Zr:C solid solutions. At $p_{C_2H_4}$ = 66 2×10^{-6} Torr and 2×10^{-5} Torr, the films are composed of a two-phase mixture of B1-structured 67 ZrC_x and C with an increasing phase fraction of C with increasing $p_{C_2H_4}$. At $p_{C_2H_4} = 2 \times 10^{-4}$ Torr, 68 the film is X-ray amorphous and with a high C content. The Zr-C layers sputter-deposited with 69 $p_{C_{2}H_{4}} = 2 \times 10^{-6}$ Torr at T_{s} between 723 K and 1123 K are all two-phase mixtures of B1-ZrC_x and 70 C with little changes in the C content with increasing T_s . Our experiments reveal that the carbon 71 72 content in reactively sputter-deposited Zr-C thin films is highly sensitive to the reactive gas 73 pressure.

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2. Experimental details

All the Zr-C films are grown on single-side polished $0.5 \times 2 \times 10$ mm³ rectangular strips of 76 MgO(001) substrates in a custom-designed ultra-high vacuum (UHV, base pressure $< 5.3 \times 10^{-9}$ 77 Torr) deposition system following the procedure described in Ref. [32]. Briefly, the MgO(001) 78 substrates are cut from $0.5 \times 10 \times 10$ mm³, 99.95% pure crystals (purchased from MTI), cleaned 79

80	via sonication sequentially in acetone, isopropyl alcohol, and deionized water, and oven-baked in
81	air at 523 K for one hour. The samples are mounted on a pyrolytic boron nitride heating stage
82	[33], where they are held by Mo clips, transferred to the main chamber, and degassed by
83	resistively heating to and holding at 1273 K until the chamber pressure is below 6×10^{-9} Torr.
84	The sample temperature T_s is then set to the desired value. In our experiments, we estimate that
85	the maximum variation in T_s across the substrate is \pm 100 K. The magnetron sputter-deposition is
86	carried out using a 3.2-mm-thick \times 50.8 mm diameter Zr target (99.91 wt.% pure with 0.08 wt.%
87	Hf from ACI Alloys, Inc.), located at about 30 cm directly above the substrate. The chamber is
88	first filled with ethylene (99.999% purity) gas up to the desired pressure $p_{C_2H_4}$ between 2×10^{-7}
89	Torr and 2×10^{-4} Torr set using a UHV leak valve. Subsequently, Ar (99.999% purity) gas is let
90	in and the total pressure is adjusted to 10 mTorr. Zr-C thin films are deposited using Zr target
91	power maintained constant at 50 W for 30 minutes. The target voltage increases with increasing
92	$p_{\rm C_2H_4}$ from 225 V (2 × 10 ⁻⁷ Torr) to 227 V (2 × 10 ⁻⁶ Torr and 2 × 10 ⁻⁵ Torr), and 234 V (2 × 10 ⁻⁴)
93	Torr). Prior to deposition, the Zr target is sputter-cleaned using the same Ar/C ₂ H ₄ composition as
94	that used for the film growth for 2 minutes with the sample rotated out-of-sight from the target.
95	After deposition, the ethylene and Ar gas supplies are shut off and the chamber is evacuated
96	while the sample is passively cooled to room temperature by switching off the current supplied to
97	the substrate heater.
98	XRD 2 θ - ω data are obtained following the procedure described in Ref. [34] using a Jordan

 χ XRD 20- ω data are obtained following the procedure described in Ref. [34] using a Jordan Valley D1 diffractometer with a sealed copper X-ray tube source, a MaxFlux specular mirror to produce a parallel beam, a two bounce channel-cut (2 2 0) Si collimator crystal to select the Cu $K_{\alpha 1}$ wavelength ($\lambda = 0.154056$ nm) for the incident beam, and a two bounce channel-cut (2 2 0) Si analyzer crystal for the third axis optics. The sample and stage are calibrated with respect to ω , ϕ (out-of-plane rotation perpendicular to ω), and χ (in-plane rotation) about the MgO(004) peak, 2θ = 94.0496°. 2θ-ω scans for 2θ values between 20° and 100° are acquired using double-axis diffraction with a step size of 0.02° and a dwell time of 1 s.

106 Cross-sectional TEM (XTEM) samples are prepared using 30 kV Ga⁺ ions in an FEI Nova 107 600 NanoLab DualBeamTM scanning electron microscope equipped with a focused ion beam 108 (FIB) source. Prior to milling, the film surface is protected by ~ 150 nm and ~ 1 μ m thick Pt 109 layers deposited sequentially, first using electron beams to minimize any damage that may incur 110 during the subsequent ion-beam-assisted deposition of the thicker layers. TEM images of the film 111 and the film-substrate interface are acquired in an FEI Titan 80-300 kV scanning TEM (S/TEM) 112 operated at 300 kV for imaging.

113 XPS data are obtained using a Kratos Analytical AXIS Ultra DLD at binding energies 114 between 0 and 1200 eV with a pass energy of 160 eV, step size of 1.0 eV, and dwell time of 0.1 s. 115 High-resolution Zr 3d and C 1s spectra are acquired using a pass energy of 20 eV and a step size 116 of 0.1 eV over the energy ranges 160 - 215 eV and 264 - 300 eV, respectively, with dwell times 117 of 0.5 s and 2 s. In order to accurately determine the bulk composition and minimize the 118 contribution to the XPS signal from surface contamination, the XPS data are obtained after Ar⁺ ion etching of all but one samples for 1 h and the other sample (grown using $p_{C_2H_4} = 2 \times 10^{-7}$ Torr 119 120 and $T_s = 923$ K) for 2.5 h. The relative concentrations of Zr and C in the films are determined 121 from the ratios of the high-resolution Zr 3d and C 1s spectral peak areas, measured using 122 CasaXPS software and defined with a Shirley background type [35], corrected by their respective 123 relative sensitivity factors, 2.58 and 0.278. In order to assess the accuracy of our quantification procedure, we acquired both XPS and Rutherford backscattering spectrometry (RBS) data (details 124 125 below) from the same ZrC_x film (sputter-deposited on Al₂O₃(0001) using a ZrC target [36]. From

the XPS measurements, following the procedure described above, we determined the film
composition as C/Zr = 1.44, while the RBS analysis yielded C/Zr = 2.04. The apparent
discrepancy in the carbon contents measured using these two techniques could be due to
preferential removal of C from the surface during sputter-etching of the samples prior to XPS
measurements coupled with the fact that XPS is a surface-sensitive technique while RBS probes
the entire cross-section of the film.

132 RBS-Nuclear Reaction Analysis (RBS-NRA) data, used to determine the film stoichiometry of one sample apart from the set of samples presented in this article, are obtained using 1.2 MeV 133 134 deuteron beam generated by the nuclear microprobe of CEA Saclay, France. The incident deuteron beam size is $4 \times 3 \ \mu m^2$. Backscattered particles produced from nuclear reactions are 135 136 detected with an annular surface barrier particle detector (detection angle 170°). C concentrations are measured from the peak of the nuclear reaction ${}^{12}C(d,p_0){}^{13}C$ and Zr concentration from that of 137 138 backscattered deuterons. The film composition is deduced by fitting experimental data with 139 simulated spectra using SIMNRA code [37], which takes into account experimental beam 140 conditions and related cross-sections of scattering and deuteron induced nuclear reactions.

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142 **3. Results and discussion**

Figure 1a shows XRD 2 θ - ω scans acquired from Zr-C/MgO(001) samples (open circles) grown at $T_s = 923$ K using Ar/C₂H₄ gas mixtures with $p_{C_2H_4}$ between 2 × 10⁻⁷ Torr and 2 × 10⁻⁴ Torr. In Fig. 1a, the solid line is an experimental XRD 2 θ - ω scan of a bare MgO(001) substrate, provided as a reference. The higher intensity peaks at 2 θ = 42.9° and 41.0° labeled with asterisks (*) correspond to 002 reflections of the MgO single-crystal substrate due to Cu K_{a1} (λ = 0.154056 nm) and unintentional W L_a (λ = 0.147635 nm) radiations from the X-ray source, respectively.

XRD data obtained from the layers deposited using the lowest $p_{C_2H_4}$ (= 2 × 10⁻⁷ Torr) do not 149 150 show any peaks due to B1-ZrC but reveal reflections at 20 values corresponding to hcp Zr 0002 151 and $10\overline{1}1$. The lattice constants (a_{Zr} , c_{Zr}) determined from the XRD data are (0.325 ± 0.003 nm, 152 0.517 ± 0.003 nm), which are within the measurement uncertainties the same as (0.323 nm, 0.515 nm) of pure Zr [38]. In the same XRD pattern, we also note the presence of seemingly high 153 background intensity at $2\theta \approx 35^{\circ}$, highlighted by a dotted circle, between the Zr 0002 and Zr $10\overline{1}1$ 154 peaks. We suggest and provide supporting evidence in the following section that this result is 155 156 likely due to the formation of hexagonal-structured carbides, e.g., Zr₃C₂ (P3₁21, space group 152; $a_1 = 0.306$ nm and $c_1 = 1.491$ nm), whose $10\overline{1}2$ and 0006 reflections are at $2\theta = 35.9^{\circ}$ and 36.1° , 157 respectively. At higher $p_{C_2H_4}$ (= 2 × 10⁻⁶ Torr and 2 × 10⁻⁵ Torr), the XRD data reveal peaks 158 159 corresponding to 002 and 111 reflections of B1-structured ZrC_x . We observe a shift in ZrC_x 111 reflection peak position to lower 20 values, i.e., 111 interplanar spacing d_{111} increases, with 160 increasing $p_{C_{2}H_{4}}$ from $2\theta = 33.12^{\circ}$ ($d_{111} = 0.270$ nm) at 2×10^{-6} Torr to $2\theta = 32.84^{\circ}$ ($d_{111} = 0.273$ 161 nm) at 2×10^{-5} Torr. (The 002 reflections are too broad to accurately measure any variations in 162 their peak positions and therefore we are unable to determine the existence, if any, of 163 inhomogeneous distortions in the ZrC lattice.) From the measured d_{111} values at each $p_{C_2H_4}$, we 164 determine $a = 0.468 \pm 0.004$ nm at 2×10^{-6} Torr and 0.472 ± 0.004 nm at 2×10^{-5} Torr. The 165 166 former is, within the measurements uncertainties, the same as $a_0 = 0.4693$ nm of the bulk stoichiometric ZrC [1], while the latter is ~0.6 % larger than *a*₀, likely due to distortion of the ZrC 167 168 lattice due to increased incorporation of C in the films [6,13,26,27]. Similar shifts in XRD peak 169 positions have been previously observed with increasing carbon contents in sputter-deposited ZrC 170 [13], HfC [26], and NbC [27] thin films. The XRD scan from the sample grown with the highest $p_{C_2H_4}$ (= 2 × 10⁻⁴ Torr) does not show any peaks, suggesting that the film is X-ray amorphous. 171

Based on the data in Fig. 1a, we identify $p_{C_2H_4} = 2 \times 10^{-6}$ Torr as the optimal ethylene partial 172 173 pressure for the growth of B1-ZrC at $T_s = 923$ K in our deposition system. 174 We investigated the effect of T_s , another key parameter that can influence the crystallinity of sputter-deposited films [13,39]. Fig. 1b shows XRD data obtained from Zr-C layers sputter-175 deposited at 723 K $\leq T_{s} \leq 1123$ K using Ar/C₂H₄ gas mixtures with $p_{C_{2}H_{4}} = 2 \times 10^{-6}$ Torr. At all 176 177 $T_{\rm s} \le 1023$ K, we observe two sets of peaks corresponding to B1-structured ZrC_x 111 reflection at 20 values between 32.92° and 33.14°, and 002 reflection at around 38.52°. The lattice parameters 178 179 extracted from the 002 reflection are ~0.5% smaller compared to a_o of stoichiometric ZrC [1], while those determined from the 111 reflections are ~0.3% larger (for $2\theta = 32.92^{\circ}$) and ~0.3% 180 181 smaller (for $2\theta = 33.14^{\circ}$) than a_o . The peaks are however too broad and weak in intensity to 182 accurately determine the temperature-dependent variations, if any, in the carbon content x, grain 183 size, and strain. Interestingly, the XRD data obtained from the ZrC_x film grown at the highest $T_s =$ 1123 K showed only one peak corresponding to 002 reflection, indicating that 002 texture is 184 185 preferred at higher T_s . These results suggest that, in our experiments, 111 texture is promoted in sputter-deposited ZrC_x at lower T_s , a likely consequence of kinetic limitations inherent to the 186 187 deposition process. Similar T_s -dependent 111 texture evolution has been reported in a variety of 188 sputter-deposited TMC thin films [13,28,39–41]. We now present the microstructures of Zr-C layers sputter-deposited as a function of $p_{C_2H_4}$ 189 190 and T_s . Figs. 2a-d are typical XTEM images obtained from the Zr-C thin films grown at $T_s = 923$ K using $p_{C_2H_4}$ = a) 2 × 10⁻⁷ Torr, b) 2 × 10⁻⁶ Torr, c) 2 × 10⁻⁵ Torr, and d) 2 × 10⁻⁴ Torr. We find 191

192 that the film thickness increases with increasing $p_{C_2H_4}$ from 87 ± 4 nm at $p_{C_2H_4} = 2 \times 10^{-7}$ Torr to

193 245 \pm 20 nm at $p_{C_{2}H_{4}} = 2 \times 10^{-4}$ Torr. (This is in contrast with the results reported in Ref. [13],

194 where the deposition rate decreases with increasing reactive gas (methane) partial pressure.) We 195 attribute this result to the increase in the carbon content (supporting evidence provided in the following section) within the films with increasing $p_{C_2H_4}$ during sputter-deposition. The TEM 196 images of Zr-C sample deposited using $p_{C_2H_4} = 2 \times 10^{-7}$ Torr reveal that the film is dense with 197 smooth surface and compositionally-abrupt film-substrate interface (see Fig. 2a); these results are 198 199 in striking contrast with the interfacial reactions observed during sputter-deposition of pure Zr 200 films on Al₂O₃(0001) [33]. Lattice-resolved TEM image (for example, Fig. 2a') and 201 corresponding Fourier transform (FT) (inset in Fig. 2a') show that the Zr-C layers deposited with the lowest $p_{C_2H_4} = 2 \times 10^{-7}$ Torr are crystalline and that the layer is primarily composed of hcp-202 structured Zr. We have also observed additional reflections that we attribute to trigonal-Zr₃C₂ 203 204 $000\overline{3}$, the presence of which could explain the observed high background XRD intensity at $2\theta \approx$ 35° in Fig. 1a. This result suggests the coexistence of hcp-Zr and trigonal Zr₃C₂. Increasing $p_{C_2H_4}$ 205 to 2×10^{-6} Torr and 2×10^{-5} Torr leads to porous films with dendritic columns and facetted 206 207 surfaces (Figs. 2b and c). The corresponding higher resolution XTEM images in Figs. 2b' and c' 208 reveal regions with diffraction contrast indicative of crystallinity; surrounding regions without 209 such contrast are likely composed of amorphous C. FTs in Figs. 2b' and c' reveal reflections 210 corresponding to B1-structured 002 and 111 grains in the films, consistent with the XRD results. 211 FTs (not shown here) of the XTEM images acquired from the regions near the film-substrate 212 interfaces in these two samples reveal two sets of identical reflections, indicative of cube-on-cube epitaxial growth of 002-oriented ZrC layers on the MgO(001) substrate. At the highest $p_{C_2H_4} = 2$ 213 $\times 10^{-4}$ Torr used in our experiments, the layers appear to be dense (see Fig. 2d). The XTEM 214 image in Fig. 2d' lacks any diffraction contrast and the corresponding FT shows a broad diffuse 215 216 ring, commonly associated with amorphous samples. These observations suggest that the Zr-C

films deposited using 2×10^{-4} Torr ethylene are amorphous and are consistent with the XRD data (Fig. 1a).

219 Figs. 3a-d and 3a'-d' are series of low-magnification and higher-resolution XTEM images, 220 respectively, obtained from near the substrate-film interfaces in the ZrC_x/MgO(001) samples grown using $p_{C_2H_4} = 2 \times 10^{-6}$ Torr at different T_s . All the TEM images reveal fully dense layers 221 with columnar grains and corrugated surfaces, indicating that the growth morphologies and 222 223 microstructures are qualitatively similar in all the samples grown at different T_s . XTEM images 224 (not shown here) obtained along the growth direction also reveal the presence of amorphous 225 regions throughout the films. These results are qualitatively similar to those reported in previous 226 studies [3]. Diffraction spots corresponding to both ZrC_x 002 and 111 reflections are observed in 227 the FTs in Figs. 3a'-c', indicating that the films are polycrystalline. The FT in Fig. 3d' shows only 228 002 reflections due to B1-ZrC_x, consistent with the XRD data in Fig. 1b. From the ZrC 002 229 reflections, we extract a values (= 0.47 ± 0.01 nm), ~ 0.5% smaller compared to a_o , and are 230 consistent with the value determined from the XRD data. High-resolution TEM images along 231 with their corresponding FTs (not shown here) of all samples show the presence of only 002-232 oriented ZrC grains at the interface with a cube-on-cube relation with respect to the MgO(001) 233 substrate, indicative of heteroepitaxial growth during the early stages of deposition. 234 In order to quantify the free and the bonded carbon contents in ZrC_x in the films, we used 235 XPS. Fig. 4a shows representative high-resolution C 1s and Zr 3d XPS data acquired from the bulk of Zr-C samples grown using different $p_{C_2H_4}$. Within these spectra, we identify peaks 236 237 associated with carbon at binding energies: 284.0 ~ 284.2 eV as C-C bonds in free-carbon; 281.2 ~ 282 eV as C-Zr bonds; and 282 ~ 284 eV as C-Zr* bonds [3,5,42,43]. The XPS peak due to C-238 C bond in carbides is often attributed to the presence of disordered, sp^2 (graphite), and/or sp^3 239

240 (diamond) hybridized carbon, whose exact contributions to the XPS signal are not resolvable in 241 our measurements [6,44]. The peaks observed at binding energies between 178.1 and 180.5 eV 242 correspond to Zr $3d_{5/2}$ and Zr $3d_{3/2}$, respectively. We find that the Zr peaks are better defined at lower $p_{C_2H_4}$ than at higher values, presumably due to the decrease in free-C content. With 243 increasing $p_{C_2H_4}$, we observe a shift (compared to the dashed vertical lines in the plot, which 244 correspond to binding energies in stoichiometric ZrC) in the C-Zr and Zr 3d peak positions to 245 246 higher binding energies. Based on the increase in C-C, and concomitant decrease in the C-Zr, peak intensities with increasing $p_{C_2H_4}$, we suggest that the observed peak shifts are due to the 247 increase in free-C content in the films. 248

From the measurements of the Zr 3d, C-C, C-Zr, and C-Zr* peak areas from Fig. 4a, we 249 quantify the concentrations of total carbon, free-C, and bonded-carbon x in ZrC_x , plotted as 250 magenta, black, and green curves, respectively, as a function of $p_{C_2H_4}$ in Fig. 4b. The label free-C 251 252 in the plot refers to the elemental carbon that is not bonded to Zr and corresponds to C-C peaks in Fig. 4a. We find that the amount of total C and free-C increase while the fraction of carbon 253 bonded to Zr, i.e. the carbide phase, decreases with increasing $p_{C_2H_4}$ during sputter-deposition. 254 255 These results are consistent with the observation of increasing fraction of amorphous phase with increasing $p_{C_2H_4}$ in the TEM images in Fig. 2 and are commonly observed in sputter-deposited 256 257 Zr-C films [3]. Interestingly, the fraction of free-C relative to the amount of carbon in the carbide 258 phase is higher in our films than in the films deposited using three orders of magnitude higher 259 reactive gas (methane) partial pressure [3]. Possible reasons for this behavior include: differences 260 in the rates of dissociative chemisorption of carbon due to precursor composition (relatively more 261 stable methane with one C atom/molecule vs. ethylene with two C atoms/molecule), Zr 262 deposition rates, T_s , total gas pressure, plasma characteristics, and residual gas composition and

concentration. Among all these samples, based on the XPS data, we note that the films deposited using $p_{C_2H_4} = 2 \times 10^{-6}$ Torr yield the highest fraction of Zr-C phase with the least amount of free-C. In the following section, we present the effect of T_s on the composition of Zr-C films deposited with $p_{C_2H_4} = 2 \times 10^{-6}$ Torr.

267 Fig. 4c shows representative C 1s and Zr 3d spectra obtained from the Zr-C samples grown at different $T_{\rm s}$ using $p_{\rm C_2H_4} = 2 \times 10^{-6}$ Torr. From the spectra, we identify the two characteristic Zr 268 269 $3d_{5/2}$ and $3d_{3/2}$ peaks. In the C 1s spectra, we observe one high intensity peak at ~ 281 eV, which 270 we attribute to C-Zr bonds, and one relatively broader peak around 284 eV due to C-C bonds. 271 With increasing T_s , we observe shifts (~ 0.3 eV) in both the Zr 3d and C-Zr peaks to higher 272 binding energies, suggestive of stronger bonding presumably due to decrease in the C-content 273 within the carbide; the magnitude of shift is more pronounced at higher $T_s (\ge 923 \text{ K})$. In all the 274 samples grown at different T_s , C-C peaks are broad, shallow, and changes (if any) in the peak 275 positions are not detectable. The T_s -dependent changes in total C, free-C, and bonded-carbon 276 concentrations are plotted in Fig. 4d. We find that the amounts of total C (magenta curve) and 277 free-C (black curve) increase marginally with increasing T_s , indicating that substrate temperatures 278 over 723 K have little influence on the total C and free-C contents in the Zr-C films sputterdeposited using $p_{C_2H_4} = 2 \times 10^{-6}$ Torr. (These results are opposite to those reported for Zr-C films 279 sputter-deposited using methane gas [13], which as mentioned earlier could be not only due to the 280 281 use of ethylene vs. methane but also system-specific deposition parameters.) Based on these 282 results, we suggest that during reactive sputter-deposition of Zr using low ethylene partial pressures, such as $p_{C_2H_4} = 2 \times 10^{-6}$ Torr, incorporation of C from C₂H₄ into the growing films 283 occurs readily at all $T_s \ge 723$ K. 284

4. Conclusions

This report presents the effects of ethylene partial pressure $(p_{C_2H_4})$ and substrate temperature 287 (T_s) on the microstructural and compositional evolution of reactively sputter-deposited Zr-C thin 288 289 films on MgO(001) substrates using ultra-high vacuum dc magnetron sputtering of Zr target in Ar/C₂H₄ gas mixtures with fairly low $p_{C_2H_4} \le 2\%$ of the total pressure. We find that all the Zr-C 290 films, irrespective of the $p_{C_2H_4}$ and T_s , are polycrystalline two-phase mixtures composed of 291 hexagonal close-packed Zr:C solid solutions (at ultra-low $p_{C_2H_4} = 0.002\%$) or B1-ZrC_x (at higher 292 $p_{C_2H_4}$) and free-C. The amount of free-C incorporated into the films depends sensitively on $p_{C_2H_4}$ 293 at $T_s = 923$ K. Increasing the T_s above 723 K (with $p_{C_2H_4} = 2 \times 10^{-6}$ Torr) has little effect on the 294 295 carbon incorporation rate. Our results indicate that relatively small amount of ethylene gas 296 (0.02% of the total pressure in our experiments) is sufficient to deposit two-phase mixtures of 297 ZrC and free-carbon. Given that pure, single-phase carbide films are often desirable, we suggest 298 that reactive sputter-deposition of ZrC (and other TMC) films is probably best carried out using 299 ultra-low partial pressures of carbon containing precursors; the exact pressure however depends 300 on the deposition system, substrate temperature, deposition rate, and the precursor.

301

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453	Fig. 1. 20-w X-ray diffraction (XRD) data obtained from Zr-C/MgO(001) samples sputter-
454	deposited in 10 mTorr Ar/C ₂ H ₄ gas mixtures at (a) $T_s = 923$ K with 2×10^{-7} Torr $\leq p_{C_2H_4} \leq 2 \times$
455	10 ⁻⁴ Torr and (b) 723 K $\leq T_{\rm s} \leq 1123$ K using $p_{\rm C_2H_4} = 2 \times 10^{-6}$ Torr. An XRD scan of MgO(001)
456	substrate (solid line) is plotted as a reference. The peaks labeled with * denote MgO 002
457	reflections due to Cu K α at 2 θ = 42.9° and W L α at 2 θ = 40.94°. The vertical dashed lines
458	identify the 111 and 002 reflections in stoichiometric B1-ZrC and 0002 and $10\overline{1}1$ reflections in
459	hcp-Zr. The dotted circle highlights the high background intensity at $2\theta \sim 35^{\circ}$.
460	
461	Fig. 2. Typical bright-field cross-sectional transmission electron microscopy (XTEM) images of
462	Zr-C/MgO(001) samples grown at $T_s = 923$ K with $p_{C_2H_4} = (a) 2 \times 10^{-7}$ Torr, (b) 2×10^{-6} Torr, (c)
463	2×10^{-5} Torr, and (d) 2×10^{-4} Torr. (a'-d') Higher resolution XTEM images of the samples in (a-
464	d), respectively. The insets are the Fourier transforms (FTs) of the images in a'-d'. Cyan, purple,
465	red, and green circles highlight Zr 0002, Zr_3C_2 0003, ZrC 002, and ZrC 111 reflections,
466	respectively. The absence of any spots in the Fig. 2d' FT implies that the region within the field of
467	view is likely amorphous.
468	
469	Fig. 3. Bright-field XTEM images of Zr-C/MgO(001) samples sputter-deposited using $p_{C_2H_4} = 2$

470 × 10⁻⁶ Torr at T_s = (a) 723 K, (b) 823 K, (c) 1023 K, and (d) 1123 K. All the samples appear

471 dense with columnar microstructures and smoother surfaces. (a'-d') Representative higher-

472 resolution XTEM images with corresponding FTs as insets of the samples in (a-d), respectively.

All the TEM images show crystalline and amorphous regions. ZrC 002 and 111 reflections are
highlighted using red and green circles in the FTs, respectively.

475 **Fig. 4.** (a) X-ray photoelectron spectroscopy (XPS) data acquired around Zr 3*d* (175 – 190 eV)

476 and C 1s (279 – 288 eV) from sputter-etched Zr-C samples deposited as a function of $p_{C_2H_4}$. (b)

477 Total, free, and bonded carbon concentrations extracted from the XPS data plotted as a function

478 of $p_{C_{2}H_{4}}$. (c) XPS data of sputter-etched Zr-C samples deposited as a function of T_{s} . (d) Plot of

- total, free, and bonded carbon concentrations vs. T_s . In both (a) and (c), the dashed vertical lines
- 480 correspond to binding energies in stoichiometric ZrC; black, purple, and light magenta curves
- 481 correspond to C-C, C-Zr, and C-Zr* components, respectively. In the plots (b) and (d), magenta,
- 482 black, and green curves represent the total C, free-C, and bonded carbon (labeled 'C in Zr-C')

483 contents in the Zr-C samples, respectively.



Figure 1



Figure 2



Figure 3





