

High-Power Impulse Magnetron Sputter Deposition of Boron Carbide with Full- Face Erosion Magnetron and Mixed Ar- Ne Plasma

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High-power impulse magnetron sputter deposition of boron carbide with full-face erosion magnetron and mixed Ar-Ne plasma --Manuscript Draft--

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Abstract:	<p>Boron carbide (B4C) is an attractive inertial confinement fusion ablator material. The fabrication of B4C ablators by magnetron sputtering requires process optimization. To increase process flexibility, here, we explore high-power impulse magnetron sputter (HiPIMS) deposition of B4C in pure Ar and mixed Ar-Ne plasmas. Results show that higher plasma discharge currents can be reached with a mixed Ar-Ne plasma in the entire working pressure range studied (5 – 50 mTorr). At 45 mTorr with 10% of Ne in the Ar-Ne mix, high peak target current densities of ~ 1 A cm⁻² are demonstrated. Films deposited with such a mixed Ar-Ne plasma with a full-face erosion magnetron source on substrates biased at -25 V exhibit higher density and improved mechanical properties albeit with higher compressive residual stresses compared to the case of HiPIMS deposition in a pure Ar plasma. This work demonstrates additional process flexibility of the HiPIMS discharge mode for the deposition of B4C coatings.</p>
Author Comments:	Thank you for your consideration.

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High-power impulse magnetron sputter deposition of boron carbide with full-face erosion magnetron and mixed Ar-Ne plasma
by Gregory Taylor et al.

Point-by-point response to reviewers' comments

We thank the reviewers for appreciating our work and providing constructive feedback aimed at improving the clarity and quality of this manuscript. Below is our detailed, point-by-point response, indicating where changes have been made in the revised manuscript. A marked version of the manuscript highlighting the changes is also included in this resubmission.

Response to comments of Reviewer 1

--- Reviewer 1, comment 1

Authors indicated ultimate goal is to coat on spherical mandrels. What is the implication the data presented will have on the coating on spheres.

--- Response to Reviewer 1, comment 1

Deposition on spheres is inherently an oblique angle deposition process, meaning that the growth processes are not only determined by particle energies, adatom mobility, and absorption probabilities, but also by “shadowing effects” and ballistic momentum transfer effects. Shadowing involves the prevention of incident particles from arriving at areas shadowed in the line of sight of depositing species flux. The custom-designed faceted substrate holder used in the present study enables us to systemically observe and measure effects of oblique angle deposition on microstructure major film properties at various substrate tilt angles.

This study demonstrates that the reduction in mechanical properties and densities of coatings deposited at oblique angles can be mitigated via HiPIMS with a mixed Ar/Ne plasma. For ICF ablator coatings on spheres, these improvements at oblique angles have major implications because having a dense and mechanically robust capsule increases its chance of survivability during various handling and processing steps that the capsule undergoes during target fabrication.

We have clarified some of these points on P. 3 of the revised manuscript.

--- Reviewer 1, comment 2

It is noted that under heated substrate the base pressure achieved is 4×10^{-6} torr. With this elevated background pressure, what is the impact to the coating quality, stress and density etc.

--- Response to Reviewer 1, comment 2

While the effect of base pressure during B4C sputter deposition has not been studied systemically as of yet, our recent study (Ref. 14 of the revised manuscript) has explored a wider set of base pressure conditions of $(5-200) \times 10^{-7}$ Torr to shine some light on effects of residual chamber gas. In this previous study (Ref. 14), it was observed that O-content in resultant films was low (< 1 at.%), below the amount detected in the starting B4C sputtering target itself (~ 2.5 at.% O). These observations of low levels of oxygen incorporation have been attributed to the volatility of oxygen-containing species that could form from B, C, H, and O interactions in vacuum during the deposition process. In other words, this previous study (Ref. 14) suggests negligible effects of the elevated pressure of residual gases in the chamber (in the range studied) on the deposition process.

We clarify these points on P. 3 of the revised manuscript.

--- Reviewer 1, comment 3

Very high gas pressure is used for HiPIMS coating, e.g. 45mTorr. What is the high pressure contribution to coating stress, density etc.

--- Response to Reviewer 1, comment 3

Elevated working pressure is expected to increase vapor phase scattering of sputtered particles, leading to the thermalization of depositing species flux and to a broadening of the distribution of particle impact angles. As a result, films deposited at higher working gas pressures are expected to have lower residual compressive stress and reduced adhesion. We clarify it on P. 4 of the revised manuscript.

--- Reviewer 1, comment 4

Since Ar ionization energy is 15.7eV and Ne ionization energy is 21.5eV. Ne is harder to ionize than Ar. Can authors explain why mixing Ne will enhance ionization.

--- Response to Reviewer 1, comment 4

The addition of Ne to a predominantly Ar plasma modifies plasma properties in non-trivial ways. The ionization potential of Ne is indeed significantly larger than that of Ar. However, Ne also has much higher electron impact ionization cross section, and Ne ion bombardment of the B4C target

emits more secondary electrons that act as the main “fuel” for the magnetron discharge. Several previous studies (see, for example, Refs. 22-23 of the revised manuscript) have clearly demonstrated that the addition of Ne to the predominantly Ar plasma leads to an increased electron temperature and, hence, a higher fraction of the ionized atoms in depositing species flux. We clarify these points on P. 3 of the revised manuscript and add Refs. 22-23.

Response to comments of Reviewer 3

--- Reviewer 3, comment 1

The x-axis in figure 3 is inconsistent between a-d and e, leaving a-d unlabeled. The axis should be adjusted for consistency across all graphs a-e.

--- Response to Reviewer 3, comment 1

The plot has been corrected. Thank you.

--- Reviewer 3, comment 2

Dep. Rate and density data are missing in Figure 3 for high tilt angle depositions, though other film properties are included. This should be addressed in the discussion, particularly as the stress, hardness, and Young's Modulus change significantly for tilt angle = 90.

--- Response to Reviewer 3, comment 2

The missing deposition rate data has been included for the 90° substrate tilt angles.

--- Reviewer 3, comment 3

The authors should consider adding discussion of the relationship between the deposition rate and the film density. Typically, one might expect the normalized deposition rate to decrease as film density increases. That this is not observed in this work suggests the sputter rate may be increasing significantly upon adding Ne.

--- Response to Reviewer 3, comment 3

In Fig. 3(e) of the revised manuscript, we have added the missing data point at 80°. With the measurement method of this study (i.e., RBS), density could be measured only for films deposited

on substrates with a tantalum marker layer. In the revised manuscript, we clarify that Ta-coated substrates could only be placed on 0-80 degree facets.

On P. 7 of the revised manuscript, we discuss the relationship between deposition rate and film density. The fact that the deposition rate does not decrease with increasing film density indeed suggests that the addition of Ne results in an increase in the sputter rate of the target.

--- Reviewer 3, comment 4

Previous studies of B₄C deposition by DCMS and HiPIMS (e.g. <https://doi.org/10.1007/s10853-016-0262-4>) found the film composition was sensitive to process pressure. The changes in film properties observed by the authors may be attributable to a change in the stoichiometry of the deposited films. The authors should consider adding discussion of their expected film composition and how it might be impacted by introducing Ne and by the change in substrate angle.

--- Response to Reviewer 3, comment 4

In the present study, we did not measure the stoichiometry of B₄C films since these films were too thin for RBS measurements so that the signal from the Si substrate was interfering with signals from B, C and O. Film stoichiometry, however, was measured in several of our previous studies of sputter deposited B₄C (Refs. 12-18 of the revised manuscript). These previous studies have revealed that the B/C ratio in films was the same as the B/C ratio in the starting sputtering target, as expected from negligible volatility of B and C at these temperatures and similar masses and, hence, angular emission profiles of sputtered B and C atoms.

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4 **1 High-power impulse magnetron sputter deposition of boron carbide with full-face**
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6 **2 erosion magnetron and mixed Ar-Ne plasma**

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8 3 G. V. Taylor, S. Graiser, L. B. Bayu Aji, S. J. Shin, D. C. Goodelman, X. Lepro Chavez,
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16 7 (Dated: 2 August 2025)

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18 8 Boron carbide (B_4C) is an attractive inertial confinement fusion ablator material. The
19 9 fabrication of B_4C ablators by magnetron sputtering requires process optimization.
20 10 To increase process flexibility, here, we explore high-power impulse magnetron sputter
21 11 (HiPIMS) deposition of B_4C in pure Ar and mixed Ar-Ne plasmas. Results show that
22 12 higher plasma discharge currents can be reached with a mixed Ar-Ne plasma in the
23 13 entire working pressure range studied (5 – 50 mTorr). At 45 mTorr with 10% of Ne in
24 14 the Ar-Ne mix, high peak target current densities of $\sim 1 \text{ A cm}^{-2}$ are demonstrated.
25 15 Films deposited with such a mixed Ar-Ne plasma with a full face erosion magnetron
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27 17 properties albeit with higher compressive residual stresses compared to the case of
28 18 HiPIMS deposition in a pure Ar plasma. This work demonstrates additional process
29 19 flexibility of the HiPIMS discharge mode for the deposition of B_4C coatings.
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I. INTRODUCTION

The widespread use of boron carbide (B_4C) for nuclear, defense, aerospace, and tribological applications is owed to its distinct set of properties.¹ Low density in combination with high mechanical strength, hardness, and chemical stability make B_4C an excellent material for ballistic armor plating² and various wear-resistant coatings.³ In addition, the high neutron absorption cross-section and excellent thermal and mechanical properties make B_4C attractive for nuclear reactor applications, including reaction control rods, neutron detectors, and radiation shielding.^{4,5} Moreover, B_4C is an attractive next-generation ablator material for inertial confinement fusion (ICF) and inertial fusion energy (IFE) applications.^{6,7} For ICF and IFE, B_4C is required in the form of hollow spherical shells with a diameter of $\sim 0.5 - 5.0$ mm and a wall thickness of $\sim 20 - 200$ μm .⁸

Magnetron sputtering⁹ is currently the leading method for the fabrication of such spherical B_4C shells for ICF and IFE.^{8,10,11} It is a highly repeatable and scalable physical vapor deposition technique with a large and tunable parameter space.⁹ It is used in many industries to deposit both metals and ceramics. Recent developments in magnetron sputtering of B_4C include systematic studies of working gas pressure,^{12,13} substrate temperature,^{8,14} substrate tilt angles,^{8,13,15-17} and plasma composition^{15,18} on film properties. A significant reduction in the density of nodular defects has been demonstrated for B_4C films deposited with a full face erosion (FFE) magnetron source.¹⁷ A follow up work¹¹ has explored the FFE source deposition of B_4C onto rolling spherical substrates, as required for ICF ablator capsule fabrication. All these previous studies^{8,11-18} have used either the direct current magnetron sputtering (DCMS) or radio-frequency magnetron sputtering (RFMS) plasma discharge mode.

High-power impulse magnetron sputtering (HiPIMS)^{19,20} is another plasma discharge mode offering expanded process flexibility compared to conventional DCMS and RFMS modes. Schmidt *et al.*²¹ have evaluated HiPIMS deposition of B_4C , with the focus on effects of Ar working gas pressure at two substrate temperatures of 100 and 400 $^{\circ}\text{C}$. They have compared films deposited by DCMS and HiPIMS discharge modes, with relatively low peak target current densities of ~ 0.16 A cm^{-2} . They found a negligible difference in properties of films deposited onto electrically floating substrates by DCMS or HiPIMS. Their results suggest that, for such low peak target current densities and their specific

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4 experimental conditions, HiPIMS adds process complexity but offers no advantage over
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6 conventional DCMS.

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8 Here, we explore the capabilities of HiPIMS deposition of B₄C by capitalizing on our
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10 recent findings of reduced nodular defect densities in films deposited with FFE magnetrons¹⁷
11 and higher discharge current densities for Ne-containing plasmas.¹⁸ The addition of Ne to a
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13 predominantly Ar plasma has also been demonstrated to increase electron temperature and,
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15 hence, the degree of ionization of of depositing species flux.^{22,23} We use an FFE magnetron
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17 source operated in the HiPIMS mode and compare properties of films deposited on negatively
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19 biased substrates with different tilt angles in pure Ar and mixed Ar-Ne plasmas with peak
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21 target current densities of $\sim 1 \text{ A cm}^{-2}$. The understanding of oblique angle deposition effects
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23 is directly relevant to ICF and IFE ablator fabrication since it involves the deposition onto
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25 non-planar (spherical) substrates.⁸ Our results demonstrate that HiPIMS offers additional
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27 process flexibility for B₄C deposition and warrants further systematic studies.
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31 II. METHODS

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34 Table I summarizes deposition conditions for the two coating runs of the present study.
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36 Coatings were deposited in a cylindrical high-vacuum chamber with a diameter and height of
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38 44 and 36 cm, respectively. Prior to admitting working gases into the chamber, the substrate
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40 holder was heated to 450 °C, corresponding to a substrate temperature of 330 °C, and the
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42 chamber pressure was $\sim 5 \times 10^{-6}$ Torr. Our previous study¹⁴ has found negligible effects
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44 of the residual chamber pressure, in the range of $(5 - 200) \times 10^{-7}$ Torr, on the elemental
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46 composition of sputter deposited B₄C films. Depositions were performed with a 75-mm
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48 diameter circular FFE magnetron source (Gencoa Ltd, model FFE-75, UK) modified for
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50 direct target cooling. The source axis was positioned horizontally. Disk-shaped B₄C targets
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52 (Feldco International, USA) had a diameter of 71 mm, an initial thickness of 3 mm, a density
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54 of 2.4 g cm³ and an electrical resistivity of $\sim 2 \times 10^4 \Omega \text{ cm}$. Disks of B₄C were bonded with
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56 In to 2-mm-thick Mo backing plates. The total thickness of the bonded target assembly
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58 at the thinnest point of the racetrack before and after each deposition experiment was in
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60 the range of 4.84 – 4.91 mm. The DC plasma was driven with an Advanced Energy MDX
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62 1K power supply unit. The HiPIMS plasma was driven with an Advanced Energy MDX
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64 1K power supply unit, which was coupled to a high-voltage pulser unit (Ionautics, model
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4 81 HiSPTER 1, Sweden). The two deposition runs described here were done in the constant
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6 82 peak target voltage mode.

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8 83 Depositions were performed with high purity Ar (99.998 %) and Ne (99.998 %) gases.
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10 84 Following a survey of various partial pressures of Ne, we used an Ar-Ne mix with 10% of Ne
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12 85 and a long pulse duration as it resulted in a stable plasma discharge at 45 mTorr. Such a
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14 86 relatively high working gas pressure of 45 mTorr was also chosen to minimize compressive
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16 87 residual stress in films, based on our previous study.¹² The total working gas flow rate was
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18 88 55 standard cubic centimeters per minute. Prior to each run, a 30-minute pre-conditioning
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20 89 of the target was performed at the set point parameters with the substrates shielded from
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22 90 the target by an electrically grounded shutter.

23 91 Substrates were mounted on a custom-designed faceted substrate holder machined from
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25 92 a solid Mo block, which was described previously.¹⁶ Heating of the substrate holder was
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27 93 achieved with an electrically grounded resistive heater (HeatWave Labs Inc., model 112868,
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29 94 USA). Substrates were mechanically clamped to the holder with Mo screws and washers.
30
31 95 In this configuration, the normal of substrate holder facets were at the following angles (α)
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33 96 to the magnetron source axis: 0°, 20°, 40°, 60°, 80°, and 90°. The two substrate types
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35 97 used were (i) 10 × 10 mm² Si (100) chips with a 200-nm-thick Ta metal layer deposited on
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37 98 top in a separate DCMS run used for density measurements and (ii) 3 × 12 mm², 280 μm
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39 99 thick Si (100) cantilevers used for residual stress, mechanical properties, and deposition rate
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41 100 measurements. Due to design restrictions of the faceted substrate holder, chips were only
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43 101 included on facets with $\alpha = 0 - 80^\circ$, while cantilevers were placed on all six facets. To ensure
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45 102 consistent initial substrate cleanliness, we used the following three-step substrate cleaning
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47 103 procedure in an ultrasonic bath (with 15 minutes for each step): (i) acetone, (ii) ethanol,
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49 104 and (iii) a water-based detergent solution. This was followed by a final rinse in de-ionized
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51 105 water and blow drying with dry nitrogen.

52 106 Film thickness was measured by stylus profilometry (Bruker, model Dektak XT, USA).
53
54 107 Residual stress in films was calculated with the Stoney equation based on the change in
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56 108 cantilever curvature measured by profilometry before and after deposition. The thermal
57
58 109 stress component originating from the difference in coefficients of thermal expansion be-
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60 110 tween the B₄C film and Si substrate was estimated to be 100 MPa (tensile), as in our
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62 111 previous studies.^{16,17} The Ta layer on Si chips was used as a marker in the areal density
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64 112 measurements by Rutherford backscattering spectrometry (RBS) with a 2 MeV ¹H⁺ ion
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113 beam. The presence of this Ta marker layer has a negligible effect on the properties and
114 morphology of B₄C films deposited as substrate temperatures of the present study.⁸

115 Mechanical properties were evaluated by nanoindentation (MTS, model XP, USA) in the
116 load-controlled mode with a Berkovich diamond tip. Meyer’s hardness (H_M) was defined as
117 average contact pressure, and Young’s Modulus (E_Y) was calculated based on the conven-
118 tional Oliver-Pharr method.²⁴ In Oliver-Pharr calculations, we assumed Poisson’s ratios of
119 diamond and B₄C films of 0.07 and 0.17, respectively, and Young’s modulus of diamond of
120 1141 GPa.²⁵ Values of H_M and E_Y were averaged over the indenter penetration depth range
121 of $\sim 10 - 20\%$ of film thickness.

122 III. RESULTS AND DISCUSSION

123 A. Discharge characteristics

124 Figure 1 shows dependencies of DCMS plasma discharge target current (I_t) versus target
125 voltage (V_t) for Ar-Ne mixes with 0 and 10% of Ne, collected at three representative working
126 pressures. In the entire pressure range studied of 5 – 50 mTorr, for both gas mixes, the
127 discharge behavior is qualitatively similar. All $I_t(V_t)$ curves are superlinear, as commonly
128 observed for Ar magnetron discharges⁹ and different from the abnormal $I_t(V_t)$ dependence
129 characteristic of the discharge with a pure Ne plasma.¹⁸

130 As working pressure is increased, Fig. 1 shows that I_t at any given V_t increases. Hence,
131 higher I_t values at lower voltages can be achieved at larger working pressures. While this
132 general trend is the same for Ar-Ne mixes with 0 and 10% of Ne, the effect of pressure on
133 the $I_t(V_t)$ dependence is significantly larger for the 10% Ne case. This could be attributed
134 to a combination of (i) a reduction in rarefaction²⁶ near the target surface due to the higher
135 thermal conductivity and smaller collisional cross section of Ne compared to Ar and (ii) a
136 higher secondary ion-electron emission coefficient of Ne.^{18,27} It is seen from Fig. 1 that, for
137 a given V_t , larger I_t is achieved for higher pressure with 10% of Ne in the mix. Hence, we
138 chose these conditions for HiPIMS film deposition runs of the present study (Table I).

139 Figure 2 shows waveforms of I_t [Fig. 2(a)] and substrate current [I_s , Fig. 2(b)] for Ar-Ne
140 mixtures with 0 and 10% of Ne with at 45 mTorr. For both working gas configurations, the
141 HiPIMS waveforms have peak target currents that are two-orders of magnitude greater than

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4 142 their DCMS counterparts at similar average discharge power (Fig. 1). It is also seen from
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6 143 Fig. 2(a) that the admix of Ne to the plasma helps achieve higher peak currents. The peak
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8 144 I_t and I_s for the 10% of Ne mix are ~ 2 times those for the 0% Ne case, leading to a higher
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10 145 plasma density and larger flux of ions bombarding the film surface during growth with the
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12 146 Ne-containing plasma.

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14 147 The shape of V_t and V_s waveforms in Figs. 2(a) and 2(b) are qualitatively the same.
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16 148 They exhibit a gradual increase to a peak at $\sim 150 \mu\text{s}$ from the pulse start, followed by a
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18 149 decrease and saturation for $\gtrsim 400 \mu\text{s}$. This waveform shape is qualitatively similar to those
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20 150 revealed in our recent systematic study of HiPIMS deposition of Au-Ta alloys with 2-inch
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22 151 MAK-model magnetron sources.²⁸ However, the time scales are ~ 4 times slower for the
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24 152 B_4C discharge. This is an interesting observation with practical implications for deposition
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26 153 process optimization, and more work is clearly needed to better understand B_4C HiPIMS
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28 154 plasma and deposition processes.

31 155 B. Film properties

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34 156 Figure 3(a) shows the substrate tilt angle (α) dependence of the deposition rate. The
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36 157 rate has been normalized by the average discharge power in order to compare results for
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38 158 two runs with 0 and 10% of Ne in the Ar-Ne mix performed at constant peak target voltage
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40 159 and different peak I_t and average discharge power values (Table I). It is seen from Fig. 3(a)
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42 160 that, for both cases of 0 and 10% of Ne, the deposition rates are essentially identical.
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44 161 Interestingly, the rapid decrease in the deposition rate with increasing α observed in several
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46 162 previous investigations^{13,16–18} of DCMS and RFMS deposition of B_4C is not seen in Fig. 3(a).
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48 163 Instead, a decrease in the deposition rate occurs between $\alpha = 0^\circ$ and 20° , followed by a nearly
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50 164 constant rate for α in the range of $20 - 60^\circ$, and then another decrease for strongly oblique
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52 165 angles of $\alpha = 80$ and 90° . This observation may result from a combination of high working
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54 166 pressure of 45 mTorr, resulting in efficient scattering of depositing species flux, and ion
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56 167 extraction through the substrate plasma sheath due to the electric field generated from the
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58 168 negative substrate bias. A follow up systematic investigation of depositing species flux as
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60 169 well their energy and angular distributions could help better understand this unexpected
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62 170 behavior.

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64 171 Figure 3(b) shows the α dependence of residual stress (σ), revealing that, compared to
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4 172 the case of pure Ar plasma deposition, films deposited with a 10% Ne mix have higher
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6 173 compressive σ for low α cases of 0 and 20°. For example, for untilted films, compressive σ
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8 174 increases from 1.4 to 2.2 GPa with the addition of Ne to the plasma. This can be attributed
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10 175 to a corresponding increase in ion flux [Fig. 2(b)]. For both plasma conditions, σ is close to
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12 176 zero for α of 40° and above. This suggests that the growth of films at such oblique angles
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14 177 is dominated by oblique angle atomic impacts resulting in a columnar microstructure with
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16 178 low residual stress.¹⁶

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18 179 As shown in Fig. 3(c), high hardness values ($H_M = 38$ GPa) are measured in coatings
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20 180 from both runs for the $\alpha = 0^\circ$ tilt angle. For larger α films, H_M values for 0 and 10% of
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22 181 Ne cases diverge. Films deposited with 10% of Ne have consistently higher H_M values. The
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24 182 same trend is replicated by the α dependence of E_Y shown in Fig. 3(d). Films deposited with
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26 183 a 10% of Ne are stiffer. This trend could be explained by examining the evolution of film
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28 184 density shown in Fig. 3(e). It reveals that films deposited with the Ne-containing plasma
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30 185 have higher density although their their normalized deposition rates are largely the same
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32 186 [Fig. 3(a)]. This suggests that the deposition with a Ne-containing plasma is characterized
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34 187 by an increased target sputtering rate. Films deposited with a 100% Ar plasma have a
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36 188 density of 2.4 g/cm³ at $\alpha = 0^\circ$, ~ 2.0 g/cm³ for α in the range of 0 – 60°, and 1.8 g/cm⁻³
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38 189 for $\alpha = 80^\circ$. Films deposited with a 10% Ne mix exhibit a similar trend but with overall
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40 190 higher density values. Overall, the density in films is shown to be weakly dependent on
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42 191 substrate tilt angle, and this is especially the case for the 10% Ne samples. This behavior
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44 192 could be attributed to a larger ion-to-atom fraction and more efficient ion bombardment of
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46 193 the growing film surface for the case of Ne-containing plasma although additional systematic
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48 194 studies involving plasma diagnostics are currently needed to better understand film growth
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50 195 mechanisms and optimize the deposition process.

51 196 **IV. SUMMARY**

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54 197 We have used magnetron sputtering to deposit B₄C films with an FFE source modified
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56 198 for direct cooling with the HiPIMS plasma discharge mode with two different working gases
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58 199 (pure Ar and an Ar-Ne mix with 10% of Ne) and substrates biased at -25 V. Higher
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60 200 plasma densities, as indicated by larger target and substrate currents, can be achieved by
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62 201 using larger process pressure and adding Ne to the working gas mixture. This work has
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demonstrated that the density and mechanical properties of B_4C films can be improved with the deposition in the HiPIMS mode in an Ar-Ne working gas mix. Our results demonstrate that the HiPIMS discharge mode coupled with Ar-Ne gas mixture expands the flexibility of magnetron sputter deposition of B_4C and offers additional process control. However, it also increases process complexity, and more work is currently needed to better understand the physics of the HiPIMS B_4C mixed plasma discharge with an FFE magnetron source.

V. ACKNOWLEDGMENTS

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VI. DATA AVAILABILITY STATEMENT

The data that supports the findings of this study is available within the article.

VII. AUTHOR DECLARATIONS

A. Conflict of Interest

The authors have no conflicts to disclose.

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5 TABLE I. Conditions and resulting film thicknesses of the two deposition runs of the present study.
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7 The substrate tilt angle (α) is defined in the text.
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9 Parameter	Run 1	Run 2
10 Ne content in Ar-Ne mix (%)	0	10
11 Peak voltage (V)	680	680
12 Average power (W)	210	370
13 Peak target current (A)	25	46
14 Pulse frequency (Hz)	50	50
15 Pulse width (μ s)	500	500
16 Substrate bias (V)	-25	-25
17 Pressure (mTorr)	45	45
18 Deposition time (h)	3	3
19 Target-to-substrate distance (mm)	50	50
20 Film thickness for $\alpha = 0^\circ$ (μ m)	2.8	4.6

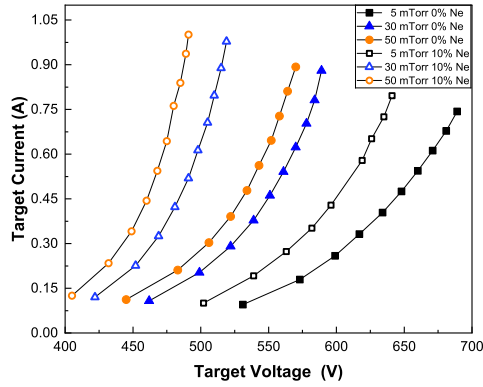


FIG. 1. Dependence of target current on the absolute value of (negative) target voltage for the DCMS discharge in Ar-Ne mixtures with 0 and 10% of Ne at 5, 30, and 50 mTorr, as indicated in the legend.

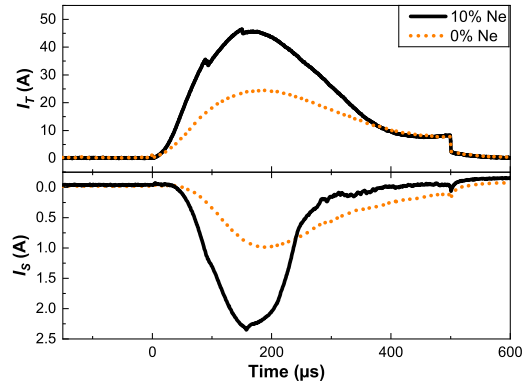


FIG. 2. Waveforms of (a) target current (I_t) and (b) substrate current (I_s) for Ar-Ne mixtures with 0 and 10% of Ne at 45 mTorr, a peak target voltage of 680 V, and a substrate bias of -25 V. Current of ions from the plasma is shown as positive in both panels. The legend in (a) applies to both panels.

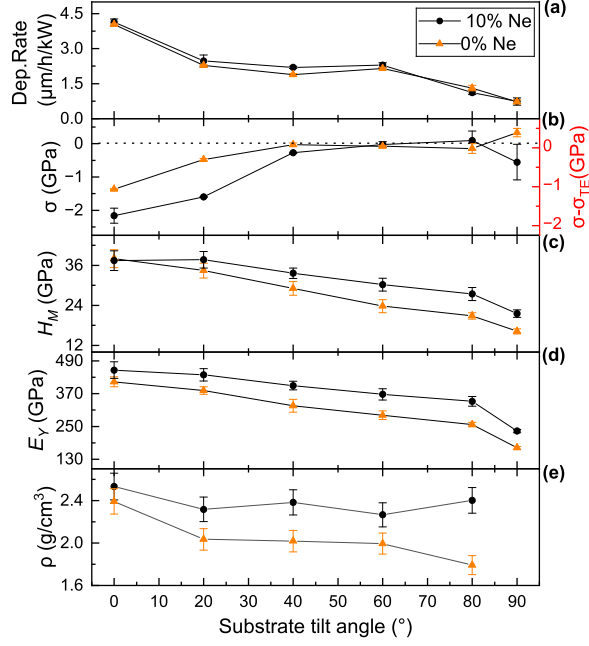


FIG. 3. Substrate tilt dependencies of (a) the deposition rate normalized to the average discharge power, (b) residual stress (σ , where σ_{TE} is the stress contribution due to the thermal expansion mismatch between the substrate and the film), (c) Meyer's Hardness (H_M), (d) Young's Modulus (E_Y), and (e) mass density (ρ) of B_4C films deposited at 45 mTorr in Ar-Ne mixtures with 0 and 10% of Ne, as indicated in the legend in (b), which applies to all five panels.

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4 **1 High-power impulse magnetron sputter deposition of boron carbide with full-face**
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6 **2 erosion magnetron and mixed Ar-Ne plasma**

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8 3 G. V. Taylor, S. Graiser, L. B. Bayu Aji, S. J. Shin, D. C. Goodelman, X. Lepro Chavez,
9 and S. O. Kucheyev

10 4
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16 7 (Dated: 2 August 2025)

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18 8 Boron carbide (B_4C) is an attractive inertial confinement fusion ablator material. The
19 9 fabrication of B_4C ablators by magnetron sputtering requires process optimization.
20 10 To increase process flexibility, here, we explore high-power impulse magnetron sputter
21 11 (HiPIMS) deposition of B_4C in pure Ar and mixed Ar-Ne plasmas. Results show that
22 12 higher plasma discharge currents can be reached with a mixed Ar-Ne plasma in the
23 13 entire working pressure range studied (5 – 50 mTorr). At 45 mTorr with 10% of Ne in
24 14 the Ar-Ne mix, high peak target current densities of $\sim 1 \text{ A cm}^{-2}$ are demonstrated.
25 15 Films deposited with such a mixed Ar-Ne plasma with a full face erosion magnetron
26 16 source on substrates biased at -25 V exhibit higher density and improved mechanical
27 17 properties albeit with higher compressive residual stresses compared to the case of
28 18 HiPIMS deposition in a pure Ar plasma. This work demonstrates additional process
29 19 flexibility of the HiPIMS discharge mode for the deposition of B_4C coatings.
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20 **I. INTRODUCTION**

21 The widespread use of boron carbide (B_4C) for nuclear, defense, aerospace, and tribolog-
22 ical applications is owed to its distinct set of properties.[?] Low density in combination with
23 high mechanical strength, hardness, and chemical stability make B_4C an excellent mate-
24 rial for ballistic armor plating[?] and various wear-resistant coatings.[?] In addition, the high
25 neutron absorption cross-section and excellent thermal and mechanical properties make B_4C
26 attractive for nuclear reactor applications, including reaction control rods, neutron detectors,
27 and radiation shielding.[?] [?] Moreover, B_4C is an attractive next-generation ablator material
28 for inertial confinement fusion (ICF) and inertial fusion energy (IFE) applications.[?] [?] For
29 ICF and IFE, B_4C is required in the form of hollow spherical shells with a diameter of
30 $\sim 0.5 - 5.0$ mm and a wall thickness of $\sim 20 - 200$ μm .[?]

31 Magnetron sputtering[?] is currently the leading method for the fabrication of such spher-
32 ical B_4C shells for ICF and IFE.[?] [?] [?] It is a highly repeatable and scalable physical vapor
33 deposition technique with a large and tunable parameter space.[?] It is used in many indus-
34 tries to deposit both metals and ceramics. Recent developments in magnetron sputtering
35 of B_4C include systematic studies of working gas pressure,[?] [?] substrate temperature,[?] [?]
36 substrate tilt angles,[?] [?] [?] [?] [?] and plasma composition[?] [?] on film properties. A significant
37 reduction in the density of nodular defects has been demonstrated for B_4C films deposited
38 with a full face erosion (FFE) magnetron source.[?] A follow up work[?] has explored the
39 FFE source deposition of B_4C onto rolling spherical substrates, as required for ICF ablator
40 capsule fabrication. All these previous studies[?] [?] [?] [?] [?] [?] [?] [?] have used either the direct
41 current magnetron sputtering (DCMS) or radio-frequency magnetron sputtering (RFMS)
42 plasma discharge mode.

43 High-power impulse magnetron sputtering (HiPIMS)[?] [?] is another plasma discharge
44 mode offering expanded process flexibility compared to conventional DCMS and RFMS
45 modes. Schmidt *et al.*[?] have evaluated HiPIMS deposition of B_4C , with the focus on effects
46 of Ar working gas pressure at two substrate temperatures of 100 and 400 $^{\circ}\text{C}$. They have
47 compared films deposited by DCMS and HiPIMS discharge modes, with relatively low peak
48 target current densities of ~ 0.16 A cm^{-2} . They found a negligible difference in properties
49 of films deposited onto electrically floating substrates by DCMS or HiPIMS. Their results
50 suggest that, for such low peak target current densities and their specific experimental con-
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ditions, HiPIMS adds process complexity but offers no advantage over conventional DCMS.

Here, we explore the capabilities of HiPIMS deposition of B_4C by capitalizing on our recent findings of reduced nodular defect densities in films deposited with FFE magnetrons[?] and higher discharge current densities for Ne-containing plasmas.[?] The addition of Ne to a predominantly Ar plasma has also been demonstrated to increase electron temperature and, hence, the degree of ionization of depositing species flux.[?] We use an FFE magnetron source operated in the HiPIMS mode and compare properties of films deposited on negatively biased substrates with different tilt angles in pure Ar and mixed Ar-Ne plasmas with peak target current densities of $\sim 1 \text{ A cm}^{-2}$. The understanding of oblique angle deposition effects is directly relevant to ICF and IFE ablator fabrication since it involves the deposition onto non-planar (spherical) substrates.[?] Our results demonstrate that HiPIMS offers additional process flexibility for B_4C deposition and warrants further systematic studies.

II. METHODS

Table ?? summarizes deposition conditions for the two coating runs of the present study. Coatings were deposited in a cylindrical high-vacuum chamber with a diameter and height of 44 and 36 cm, respectively. Prior to admitting working gases into the chamber, the substrate holder was heated to 450 °C, corresponding to a substrate temperature of 330 °C, and the chamber pressure was $\sim 5 \times 10^{-6}$ Torr. Our previous study[?] has found negligible effects of the residual chamber pressure, in the range of $(5 - 200) \times 10^{-7}$ Torr, on the elemental composition of sputter deposited B_4C films. Depositions were performed with a 75-mm diameter circular FFE magnetron source (Gencoa Ltd, model FFE-75, UK) modified for direct target cooling. The source axis was positioned horizontally. Disk-shaped B_4C targets (Feldco International, USA) had a diameter of 71 mm, an initial thickness of 3 mm, a density of 2.4 g cm^3 and an electrical resistivity of $\sim 2 \times 10^4 \Omega \text{ cm}$. Disks of B_4C were bonded with In to 2-mm-thick Mo backing plates. The total thickness of the bonded target assembly at the thinnest point of the racetrack before and after each deposition experiment was in the range of 4.84 – 4.91 mm. The DC plasma was driven with an Advanced Energy MDX 1K power supply unit. The HiPIMS plasma was driven with an Advanced Energy MDX 1K power supply unit, which was coupled to a high-voltage pulser unit (Ionautics, model HiSPTR 1, Sweden). The two deposition runs described here were done in the constant

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81 peak target voltage mode.

82 Depositions were performed with high purity Ar (99.998 %) and Ne (99.998 %) gases.
83 Following a survey of various partial pressures of Ne, we used an Ar-Ne mix with 10% of Ne
84 and a long pulse duration as it resulted in a stable plasma discharge at 45 mTorr. Such a
85 relatively high working gas pressure of 45 mTorr was also chosen to minimize compressive
86 residual stress in films, based on our previous study.[?] The total working gas flow rate was
87 55 standard cubic centimeters per minute. Prior to each run, a 30-minute pre-conditioning
88 of the target was performed at the set point parameters with the substrates shielded from
89 the target by an electrically grounded shutter.

90 Substrates were mounted on a custom-designed faceted substrate holder machined from
91 a solid Mo block, which was described previously.[?] Heating of the substrate holder was
92 achieved with an electrically grounded resistive heater (HeatWave Labs Inc., model 112868,
93 USA). Substrates were mechanically clamped to the holder with Mo screws and washers.
94 In this configuration, the normal of substrate holder facets were at the following angles (α)
95 to the magnetron source axis: 0° , 20° , 40° , 60° , 80° , and 90° . The two substrate types
96 used were (i) $10 \times 10 \text{ mm}^2$ Si (100) chips with a 200-nm-thick Ta metal layer deposited on
97 top in a separate DCMS run used for density measurements and (ii) $3 \times 12 \text{ mm}^2$, $280 \mu\text{m}$
98 thick Si (100) cantilevers used for residual stress, mechanical properties, and deposition rate
99 measurements. Due to design restrictions of the faceted substrate holder, chips were only
100 included on facets with $\alpha = 0 - 80^\circ$, while cantilevers were placed on all six facets. To ensure
101 consistent initial substrate cleanliness, we used the following three-step substrate cleaning
102 procedure in an ultrasonic bath (with 15 minutes for each step): (i) acetone, (ii) ethanol,
103 and (iii) a water-based detergent solution. This was followed by a final rinse in de-ionized
104 water and blow drying with dry nitrogen.

105 Film thickness was measured by stylus profilometry (Bruker, model Dektak XT, USA).
106 Residual stress in films was calculated with the Stoney equation based on the change in
107 cantilever curvature measured by profilometry before and after deposition. The thermal
108 stress component originating from the difference in coefficients of thermal expansion be-
109 tween the B_4C film and Si substrate was estimated to be 100 MPa (tensile), as in our
110 previous studies.[?] ? The Ta layer on Si chips was used as a marker in the areal density
111 measurements by Rutherford backscattering spectrometry (RBS) with a 2 MeV $^1\text{H}^+$ ion
112 beam. The presence of this Ta marker layer has a negligible effect on the properties and

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4 morphology of B₄C films deposited as substrate temperatures of the present study.[?]
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6 Mechanical properties were evaluated by nanoindentation (MTS, model XP, USA) in the
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8 load-controlled mode with a Berkovich diamond tip. Meyer's hardness (H_M) was defined as
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10 average contact pressure, and Young's Modulus (E_Y) was calculated based on the conven-
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12 tional Oliver-Pharr method.[?] In Oliver-Pharr calculations, we assumed Poisson's ratios of
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14 diamond and B₄C films of 0.07 and 0.17, respectively, and Young's modulus of diamond of
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16 1141 GPa.[?] Values of H_M and E_Y were averaged over the indenter penetration depth range
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18 of $\sim 10 - 20\%$ of film thickness.
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22 III. RESULTS AND DISCUSSION

23 24 25 A. Discharge characteristics

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28 Figure ?? shows dependencies of DCMS plasma discharge target current (I_t) versus target
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30 voltage (V_t) for Ar-Ne mixes with 0 and 10% of Ne, collected at three representative working
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32 pressures. In the entire pressure range studied of 5 – 50 mTorr, for both gas mixes, the
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34 discharge behavior is qualitatively similar. All $I_t(V_t)$ curves are superlinear, as commonly
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36 observed for Ar magnetron discharges[?] and different from the abnormal $I_t(V_t)$ dependence
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38 characteristic of the discharge with a pure Ne plasma.[?]

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40 As working pressure is increased, Fig. ?? shows that I_t at any given V_t increases. Hence,
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42 higher I_t values at lower voltages can be achieved at larger working pressures. While this
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44 general trend is the same for Ar-Ne mixes with 0 and 10% of Ne, the effect of pressure on
45
46 the $I_t(V_t)$ dependence is significantly larger for the 10% Ne case. This could be attributed
47
48 to a combination of (i) a reduction in rarefaction[?] near the target surface due to the higher
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50 thermal conductivity and smaller collisional cross section of Ne compared to Ar and (ii) a
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52 higher secondary ion-electron emission coefficient of Ne.[?] It is seen from Fig. ?? that, for
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54 a given V_t , larger I_t is achieved for higher pressure with 10% of Ne in the mix. Hence, we
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56 chose these conditions for HiPIMS film deposition runs of the present study (Table ??).

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58 Figure ?? shows waveforms of I_t [Fig. ??(a)] and substrate current [I_s , Fig. ??(b)] for Ar-
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60 Ne mixtures with 0 and 10% of Ne with at 45 mTorr. For both working gas configurations,
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62 the HiPIMS waveforms have peak target currents that are two-orders of magnitude greater
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64 than their DCMS counterparts at similar average discharge power (Fig. ??). It is also seen
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4 from Fig. ??(a) that the admix of Ne to the plasma helps achieve higher peak currents. The
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6 peak I_t and I_s for the 10% of Ne mix are ~ 2 times those for the 0% Ne case, leading to
7
8 a higher plasma density and larger flux of ions bombarding the film surface during growth
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10 with the Ne-containing plasma.

11 The shape of V_t and V_s waveforms in Figs. ??(a) and ??(b) are qualitatively the same.
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13 They exhibit a gradual increase to a peak at $\sim 150 \mu\text{s}$ from the pulse start, followed by a
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15 decrease and saturation for $\gtrsim 400 \mu\text{s}$. This waveform shape is qualitatively similar to those
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17 revealed in our recent systematic study of HiPIMS deposition of Au-Ta alloys with 2-inch
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19 MAK-model magnetron sources.[?] However, the time scales are ~ 4 times slower for the
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21 B_4C discharge. This is an interesting observation with practical implications for deposition
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23 process optimization, and more work is clearly needed to better understand B_4C HiPIMS
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25 plasma and deposition processes.

154 B. Film properties

155 Figure ??(a) shows the substrate tilt angle (α) dependence of the deposition rate. The
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157 rate has been normalized by the average discharge power in order to compare results for
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159 two runs with 0 and 10% of Ne in the Ar-Ne mix performed at constant peak target volt-
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161 age and different peak I_t and average discharge power values (Table ??). It is seen from
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163 Fig. ??(a) that, for both cases of 0 and 10% of Ne, the deposition rates are essentially iden-
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165 tical. Interestingly, the rapid decrease in the deposition rate with increasing α observed in
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167 several previous investigations^{???} of DCMS and RFMS deposition of B_4C is not seen in
168
169 Fig. ??(a). Instead, a decrease in the deposition rate occurs between $\alpha = 0^\circ$ and 20° , fol-
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171 lowed by a nearly constant rate for α in the range of $20 - 60^\circ$, and then another decrease for
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173 strongly oblique angles of $\alpha = 80$ and 90° . This observation may result from a combination
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175 of high working pressure of 45 mTorr, resulting in efficient scattering of depositing species
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177 flux, and ion extraction through the substrate plasma sheath due to the electric field gen-
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179 erated from the negative substrate bias. A follow up systematic investigation of depositing
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181 species flux as well their energy and angular distributions could help better understand this
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183 unexpected behavior.

184 Figure ??(b) shows the α dependence of residual stress (σ), revealing that, compared
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186 to the case of pure Ar plasma deposition, films deposited with a 10% Ne mix have higher
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4 172 compressive σ for low α cases of 0 and 20°. For example, for untilted films, compressive σ
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6 173 increases from 1.4 to 2.2 GPa with the addition of Ne to the plasma. This can be attributed
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8 174 to a corresponding increase in ion flux [Fig. ??(b)]. For both plasma conditions, σ is close
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10 175 to zero for α of 40° and above. This suggests that the growth of films at such oblique angles
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12 176 is dominated by oblique angle atomic impacts resulting in a columnar microstructure with
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14 177 low residual stress.?

15 178 As shown in Fig. ??(c), high hardness values ($H_M = 38$ GPa) are measured in coatings
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17 179 from both runs for the $\alpha = 0^\circ$ tilt angle. For larger α films, H_M values for 0 and 10% of
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19 180 Ne cases diverge. Films deposited with 10% of Ne have consistently higher H_M values. The
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21 181 same trend is replicated by the α dependence of E_Y shown in Fig. ??(d). Films deposited
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23 182 with a 10% of Ne are stiffer. This trend could be explained by examining the evolution of film
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25 183 density shown in Fig. ??(e). It reveals that films deposited with the Ne-containing plasma
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27 184 have higher density although their their normalized deposition rates are largely the same
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29 185 [Fig. ??(a)]. This suggests that the deposition with a Ne-containing plasma is characterized
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31 186 by an increased target sputtering rate. Films deposited with a 100% Ar plasma have a
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33 187 density of 2.4 g/cm³ at $\alpha = 0^\circ$, ~ 2.0 g/cm³ for α in the range of 0 – 60°, and 1.8 g/cm⁻³
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35 188 for $\alpha = 80^\circ$. Films deposited with a 10% Ne mix exhibit a similar trend but with overall
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37 189 higher density values. Overall, the density in films is shown to be weakly dependent on
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39 190 substrate tilt angle, and this is especially the case for the 10% Ne samples. This behavior
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41 191 could be attributed to a larger ion-to-atom fraction and more efficient ion bombardment of
42
43 192 the growing film surface for the case of Ne-containing plasma although additional systematic
44
45 193 studies involving plasma diagnostics are currently needed to better understand film growth
46
47 194 mechanisms and optimize the deposition process.

48 49 195 IV. SUMMARY

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52 196 We have used magnetron sputtering to deposit B₄C films with an FFE source modified
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54 197 for direct cooling with the HiPIMS plasma discharge mode with two different working gases
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56 198 (pure Ar and an Ar-Ne mix with 10% of Ne) and substrates biased at -25 V. Higher
57
58 199 plasma densities, as indicated by larger target and substrate currents, can be achieved by
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60 200 using larger process pressure and adding Ne to the working gas mixture. This work has
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62 201 demonstrated that the density and mechanical properties of B₄C films can be improved with
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202 the deposition in the HiPIMS mode in an Ar-Ne working gas mix. Our results demonstrate
203 that the HiPIMS discharge mode coupled with Ar-Ne gas mixture expands the flexibility of
204 magnetron sputter deposition of B₄C and offers additional process control. However, it also
205 increases process complexity, and more work is currently needed to better understand the
206 physics of the HiPIMS B₄C mixed plasma discharge with an FFE magnetron source.

207 **V. ACKNOWLEDGMENTS**

208 This work was performed under the auspices of the U.S. DOE by LLNL under Contract
209 DE-AC52-07NA27344.

210 **VI. DATA AVAILABILITY STATEMENT**

211 The data that supports the findings of this study is available within the article.

212 **VII. AUTHOR DECLARATIONS**

213 **A. Conflict of Interest**

214 The authors have no conflicts to disclose.

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TABLE I. Conditions and resulting film thicknesses of the two deposition runs of the present study. The substrate tilt angle (α) is defined in the text.

Parameter	Run 1	Run 2
Ne content in Ar-Ne mix (%)	0	10
Peak voltage (V)	680	680
Average power (W)	210	370
Peak target current (A)	25	46
Pulse frequency (Hz)	50	50
Pulse width (μ s)	500	500
Substrate bias (V)	-25	-25
Pressure (mTorr)	45	45
Deposition time (h)	3	3
Target-to-substrate distance (mm)	50	50
Film thickness for $\alpha = 0^\circ$ (μ m)	2.8	4.6

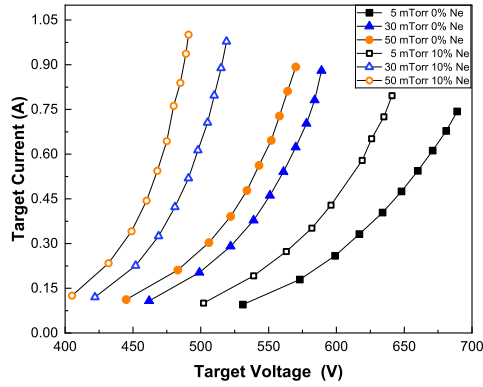


FIG. 1. Dependence of target current on the absolute value of (negative) target voltage for the DCMS discharge in Ar-Ne mixtures with 0 and 10% of Ne at 5, 30, and 50 mTorr, as indicated in the legend.

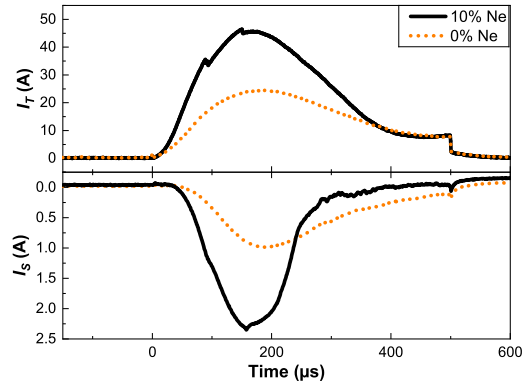


FIG. 2. Waveforms of (a) target current (I_t) and (b) substrate current (I_s) for Ar-Ne mixtures with 0 and 10% of Ne at 45 mTorr, a peak target voltage of 680 V, and a substrate bias of -25 V. Current of ions from the plasma is shown as positive in both panels. The legend in (a) applies to both panels.

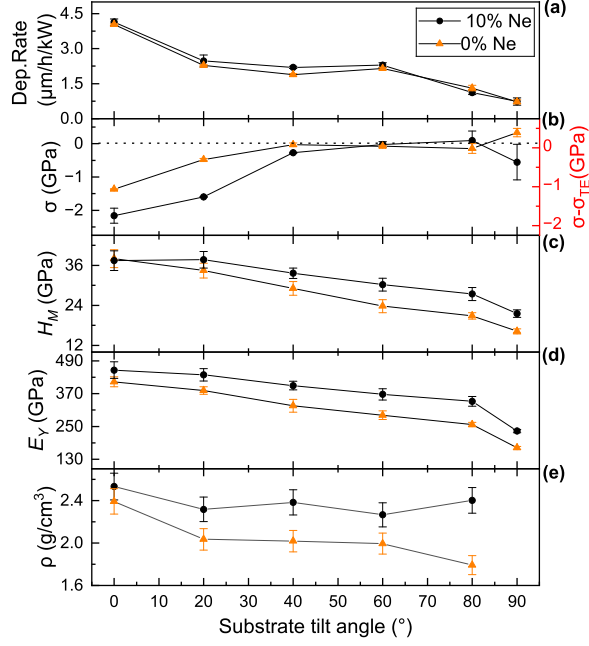


FIG. 3. Substrate tilt dependencies of (a) the deposition rate normalized to the average discharge power, (b) residual stress (σ , where σ_{TE} is the stress contribution due to the thermal expansion mismatch between the substrate and the film), (c) Meyer's Hardness (H_M), (d) Young's Modulus (E_Y), and (e) mass density (ρ) of B_4C films deposited at 45 mTorr in Ar-Ne mixtures with 0 and 10% of Ne, as indicated in the legend in (b), which applies to all five panels.

1 **High-power impulse magnetron sputter deposition of boron carbide with full-face**
2 **erosion magnetron and mixed Ar-Ne plasma**

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7 (Dated: 1 August 2025)

8 Boron carbide (B_4C) is an attractive inertial confinement fusion ablator material. The
9 fabrication of B_4C ablators by magnetron sputtering requires process optimization.
10 To increase process flexibility, here, we explore high-power impulse magnetron sputter
11 (HiPIMS) deposition of B_4C in pure Ar and mixed Ar-Ne plasmas. Results show that
12 higher plasma discharge currents can be reached with a mixed Ar-Ne plasma in the
13 entire working pressure range studied (5 – 50 mTorr). At 45 mTorr with 10% of Ne in
14 the Ar-Ne mix, high peak target current densities of $\sim 1 \text{ A cm}^{-2}$ are demonstrated.
15 Films deposited with such a mixed Ar-Ne plasma with a full face erosion magnetron
16 source on substrates biased at -25 V exhibit higher density and improved mechanical
17 properties albeit with higher compressive residual stresses compared to the case of
18 HiPIMS deposition in a pure Ar plasma. This work demonstrates additional process
19 flexibility of the HiPIMS discharge mode for the deposition of B_4C coatings.

20 I. INTRODUCTION

21 The widespread use of boron carbide (B_4C) for nuclear, defense, aerospace, and tribo-
22 logical applications is owed to its distinct set of properties.¹ Low density in combination
23 with high mechanical strength, hardness, and chemical stability make B_4C an excellent ma-
24 terial for ballistic armor plating² and various wear-resistant coatings.³ In addition, the high
25 neutron absorption cross-section and excellent thermal and mechanical properties make B_4C
26 attractive for nuclear reactor applications, including reaction control rods, neutron detectors,
27 and radiation shielding.^{4,5} Moreover, B_4C is an attractive next-generation ablator material
28 for inertial confinement fusion (ICF) and inertial fusion energy (IFE) applications.^{6,7} For
29 ICF and IFE, B_4C is required in the form of hollow spherical shells with a diameter of
30 $\sim 0.5 - 5.0$ mm and a wall thickness of $\sim 20 - 200$ μm .⁸

31 Magnetron sputtering⁹ is currently the leading method for the fabrication of such spher-
32 ical B_4C shells for ICF and IFE.^{8,10,11} It is a highly repeatable and scalable physical vapor
33 deposition technique with a large and tunable parameter space.⁹ It is used in many indus-
34 tries to deposit both metals and ceramics. Recent developments in magnetron sputtering
35 of B_4C include systematic studies of working gas pressure,^{12,13} substrate temperature,^{8,14}
36 substrate tilt angles,^{8,13,15-17} and plasma composition^{15,18} on film properties. A significant
37 reduction in the density of nodular defects has been demonstrated for B_4C films deposited
38 with a full face erosion (FFE) magnetron source.¹⁷ A follow up work¹¹ has explored the
39 FFE source deposition of B_4C onto rolling spherical substrates, as required for ICF abla-
40 tor capsule fabrication. All these previous studies^{8,11-18} have used either the direct current
41 magnetron sputtering (DCMS) or radio-frequency magnetron sputtering (RFMS) plasma
42 discharge mode.

43 High-power impulse magnetron sputtering (HiPIMS)^{19,20} is another plasma discharge
44 mode offering expanded process flexibility compared to conventional DCMS and RFMS
45 modes. Schmidt *et al.*²¹ have evaluated HiPIMS deposition of B_4C , with the focus on
46 effects of Ar working gas pressure at two substrate temperatures of 100 and 400 $^\circ\text{C}$. They
47 have compared films deposited by DCMS and HiPIMS discharge modes, with relatively
48 low peak target current densities of ~ 0.16 A cm^{-2} . They found a negligible difference in
49 properties of films deposited onto electrically floating substrates by DCMS or HiPIMS. Their
50 results suggest that, for such low peak target current densities and their specific experimental

51 conditions, HiPIMS ~~add~~adds process complexity but offers no advantage over conventional
52 DCMS.

53 Here, we explore the capabilities of HiPIMS deposition of B₄C by capitalizing on our
54 recent findings of reduced nodular defect densities in films deposited with FFE magnetrons¹⁷
55 and higher discharge current densities for Ne-containing plasmas.¹⁸ The addition of Ne to a
56 predominantly Ar plasma has also been demonstrated to increase electron temperature and,
57 hence, the degree of ionization of of depositing species flux. ^{22,23} We use an FFE magnetron
58 source operated in the HiPIMS mode and compare properties of films deposited on negatively
59 biased substrates with different tilt angles in pure Ar and mixed Ar-Ne plasmas with peak
60 target current densities of $\sim 1 \text{ A cm}^{-2}$. The understanding of oblique angle deposition effects
61 is directly relevant to ICF and IFE ablator fabrication since it involves the deposition onto
62 non-planar (spherical) substrates. ⁸ Our results demonstrate that HiPIMS offers additional
63 process flexibility for B₄C deposition and warrants further systematic studies.

64 II. METHODS

65 Table I summarizes deposition conditions for the two coating runs of the present study.
66 Coatings were deposited in a cylindrical high-vacuum chamber with a diameter and height of
67 44 and 36 cm, respectively. Prior to admitting working gases into the chamber, the substrate
68 holder was heated to 450 °C, corresponding to a substrate temperature of 330 °C, and the
69 chamber pressure was $\sim 5 \times 10^{-6}$ Torr. Our previous study ¹⁴ has found negligible effects
70 of the residual chamber pressure, in the range of $(5 - 200) \times 10^{-7}$ Torr, on the elemental
71 composition of sputter deposited B₄C films. Depositions were performed with a 75-mm
72 diameter circular FFE magnetron source (Gencoa Ltd, model FFE-75, UK) modified for
73 direct target cooling. The source axis was positioned horizontally. Disk-shaped B₄C targets
74 (Feldco International, USA) had a diameter of 71 mm, an initial thickness of 3 mm, a density
75 of 2.4 g cm³ and an electrical resistivity of $\sim 2 \times 10^4 \Omega \text{ cm}$. Disks of B₄C were bonded with
76 In to 2-mm-thick Mo backing plates. The total thickness of the bonded target assembly
77 at the thinnest point of the racetrack before and after each deposition experiment was in
78 the range of 4.84 – 4.91 mm. The DC plasma was driven with an Advanced Energy MDX
79 1K power supply unit. The HiPIMS plasma was driven with an Advanced Energy MDX
80 1K power supply unit, which was coupled to a high-voltage pulser unit (Ionautics, model

81 HiSPTER 1, Sweden). The two deposition runs described here were done in [the](#) constant
82 peak target voltage mode.

83 Depositions were performed with high purity Ar (99.998 %) and Ne (99.998 %) gases.
84 Following a survey of various partial pressures of Ne, we used an Ar-Ne mix with 10% of Ne
85 and a long pulse duration as it resulted in a stable plasma discharge ~~at 45 mTorr.~~ [Such a](#)
86 [relatively high working gas pressure of 45 mTorr was also chosen to minimize compressive](#)
87 [residual stress in films, based on our previous study.](#)¹² The total working gas flow rate was
88 55 standard cubic centimeters per minute. Prior to each run, a 30-minute pre-conditioning
89 of the target was performed at the set point parameters with the substrates shielded from
90 the target by an electrically grounded shutter.

91 Substrates were mounted on a custom-designed faceted substrate holder machined from
92 a solid Mo block, which was described previously.¹⁶ Heating of the substrate holder was
93 achieved with an electrically grounded resistive heater (HeatWave Labs Inc., model 112868,
94 USA). Substrates were mechanically clamped to the holder with Mo screws and washers.
95 In this configuration, the normal of substrate holder facets were at the following angles (α)
96 to the magnetron source axis: 0°, 20°, 40°, 60°, 80°, and 90°. The two substrate types
97 used were (i) 10 × 10 mm² Si (100) chips with a 200-nm-thick Ta metal layer deposited on
98 top in a separate DCMS run [used for density measurements](#) and (ii) 3 × 12 mm², 280 μm
99 thick Si (100) cantilevers ~~used for residual stress measurements.~~ [mechanical properties, and](#)
100 [deposition rate measurements. Due to design restrictions of the faceted substrate holder,](#)
101 [chips were only included on facets with \$\alpha = 0 - 80^\circ\$, while cantilevers were placed on all](#)
102 [six facets.](#) To ensure consistent initial substrate cleanliness, we used the following three-
103 step substrate cleaning procedure in an ultrasonic bath (with 15 minutes for each step): (i)
104 acetone, (ii) ethanol, and (iii) a water-based detergent solution. This was followed by a final
105 rinse in [de-ionized](#) water and blow drying with dry nitrogen.

106 Film thickness was measured by stylus profilometry (Bruker, model Dektak XT, USA).
107 Residual stress in films was calculated with the Stoney equation based on the change in
108 cantilever curvature measured by profilometry before and after deposition. The thermal
109 stress component originating from the difference in coefficients of thermal expansion be-
110 tween the B₄C film and Si substrate was estimated to be 100 MPa (tensile), as in our
111 previous studies.^{16,17} The Ta layer on Si chips was used as a marker in the areal density
112 measurements by Rutherford backscattering spectrometry (RBS) with a 2 MeV ¹H⁺ ion

113 beam. The presence of this Ta marker layer has a negligible effect on the properties and
114 morphology of B₄C films deposited as substrate temperatures of the present study.⁸

115 Mechanical properties were evaluated by nanoindentation (MTS, model XP, USA) in the
116 load-controlled mode with a Berkovich diamond tip. Meyer’s hardness (H_M) was defined as
117 average contact pressure, and Young’s Modulus (E_Y) was calculated based on the conven-
118 tional Oliver-Pharr method.²⁴ In Oliver-Pharr calculations, we assumed Poisson’s ratios of
119 diamond and B₄C films of 0.07 and 0.17, respectively, and Young’s modulus of diamond of
120 1141 GPa.²⁵ Values of H_M and E_Y were averaged over the indenter penetration depth range
121 of $\sim 10 - 20\%$ of film thickness.

122 III. RESULTS AND DISCUSSION

123 A. Discharge characteristics

124 Figure 1 shows dependencies of DCMS plasma discharge target current (I_t) versus target
125 voltage (V_t) for Ar-Ne mixes with 0 and 10% of Ne, collected at three representative working
126 pressures. In the entire pressure range studied of 5 – 50 mTorr, for both gas mixes, the
127 discharge behavior is qualitatively similar. All $I_t(V_t)$ curves are superlinear, as commonly
128 observed for Ar magnetron discharges⁹ and different from the abnormal $I_t(V_t)$ dependence
129 characteristic of the discharge with a pure Ne plasma.¹⁸

130 As working pressure is increased, Fig. 1 shows that I_t at any given V_t increases. Hence,
131 higher I_t values at lower voltages can be achieved at larger working pressures. While this
132 general trend is the same for Ar-Ne mixes with 0 and 10% of Ne, the effect of pressure on
133 the $I_t(V_t)$ dependence is significantly larger for the 10% Ne case. This could be attributed
134 to a combination of (i) a reduction in rarefaction²⁶ near the target surface due to the higher
135 thermal conductivity and smaller collisional cross section of Ne compared to Ar and (ii) a
136 higher secondary ion-electron emission coefficient of Ne.^{18,27} It is seen from Fig. 1 that, for
137 a given V_t , larger I_t is achieved for higher pressure with 10% of Ne in the mix. Hence, we
138 chose these conditions for HiPIMS film deposition runs of the present study (Table I).

139 Figure 2 shows waveforms of I_t [Fig. 2(a)] and substrate current [I_s , Fig. 2(b)] for Ar-Ne
140 mixtures with 0 and 10% of Ne with at 45 mTorr. For both working gas configurations, the
141 [HiPIMS](#) waveforms have peak target currents [that](#) are two-orders of magnitude greater than

142 their DCMS counterparts at similar average discharge power (Fig. 1). It is also seen from
143 Fig. 2(a) that the admix of Ne to the plasma helps achieve higher peak currents. The peak
144 I_t and I_s for the 10% of Ne mix are ~ 2 times those for the 0% Ne case, leading to a higher
145 plasma density and larger flux of ions bombarding the film surface during growth with the
146 Ne-containing plasma.

147 The shape of V_t and V_s waveforms in Figs. 2(a) and 2(b) are qualitatively the same.
148 They exhibit a gradual increase to a peak at $\sim 150 \mu\text{s}$ from the pulse start, followed by a
149 decrease and saturation for $\gtrsim 400 \mu\text{s}$. This waveform shape is qualitatively similar to those
150 revealed in our recent systematic study of HiPIMS deposition of Au-Ta alloys with 2-inch
151 MAK-model magnetron sources.²⁸ However, the time scales are ~ 4 times slower for the
152 B_4C discharge. This is an interesting observation with practical implications for deposition
153 process optimization, and more work is clearly needed to better understand B_4C HiPIMS
154 plasma and deposition processes.

155 B. Film properties

156 Figure 3(a) shows the substrate tilt angle (α) dependence of the deposition rate. The
157 rate has been normalized by the average discharge power in order to compare results for
158 two runs with 0 and 10% of Ne in the Ar-Ne mix performed at constant peak target voltage
159 and different peak I_t and average discharge power values (Table I). It is seen from Fig. 3(a)
160 that, for both cases of 0 and 10% of Ne, the deposition rates are essentially identical.
161 Interestingly, the rapid decrease in the deposition rate with increasing α observed in several
162 previous investigations^{13,16–18} of DCMS and RFMS deposition of B_4C is not seen in Fig. 3(a).
163 Instead, a decrease in the deposition rate occurs between $\alpha = 0^\circ$ and 20° , followed by a nearly
164 constant rate for α in the range of $20 - 60^\circ$, and then another decrease for ~~a strongly oblique~~
165 ~~angle of $\alpha = 80^\circ$~~ strongly oblique angles of $\alpha = 80$ and 90° . This observation may result
166 from a combination of high working pressure of 45 mTorr, resulting in efficient scattering of
167 depositing species flux, and ion extraction through the substrate plasma sheath due to the
168 electric field generated from the negative substrate bias. A follow up systematic investigation
169 of depositing species flux as well their energy and angular distributions could help better
170 understand this unexpected behavior.

171 Figure 3(b) shows the α dependence of residual stress (σ), revealing that, compared to

172 the case of pure Ar plasma deposition, films deposited with a 10% Ne mix have higher
173 compressive σ for low α cases of 0 and 20°. For example, for untilted films, compressive σ
174 increases from 1.4 to 2.2 GPa with the addition of Ne to the plasma. This can be attributed
175 to a corresponding increase in ion flux [Fig. 2(b)]. For both plasma conditions, σ is close to
176 zero for α of 40° and above. This suggests that the growth of films at such oblique angles
177 is dominated by oblique angle atomic impacts resulting in a columnar microstructure with
178 low residual stress.¹⁶

179 As shown in Fig. 3(c), high hardness values ($H_M = 38$ GPa) are measured in coatings
180 from both runs for the $\alpha = 0^\circ$ tilt angle. For larger α films, H_M values for 0 and 10% of
181 Ne cases diverge. Films deposited with 10% of Ne have consistently higher H_M values. The
182 same trend is replicated by the α dependence of E_Y shown in Fig. 3(d). Films deposited with
183 a 10% of Ne are stiffer. This trend could be explained by examining the evolution of film
184 density shown in Fig. 3(e). It reveals that films deposited with the Ne-containing plasma
185 have higher density ~~—although their their normalized deposition rates are largely the same~~
186 [Fig. 3(a)]. This suggests that the deposition with a Ne-containing plasma is characterized
187 by an increased target sputtering rate. Films deposited with a 100% Ar plasma have a
188 density of 2.4 g/cm³ at $\alpha = 0^\circ$, ~ 2.0 g/cm³ for α in the range of 0 – 60°, and 1.8 g/cm⁻³
189 for $\alpha = 80^\circ$. Films deposited with a 10% Ne mix exhibit a similar trend but with overall
190 higher density values. Overall, the density in films is shown to be weakly dependent on
191 substrate tilt angle, and this is especially the case for the 10% Ne samples. This behavior
192 could be attributed to a larger ion-to-atom fraction and more efficient ion bombardment of
193 the growing film surface for the case of Ne-containing plasma although additional systematic
194 studies involving plasma diagnostics are currently needed to better understand film growth
195 mechanisms and optimize the deposition process.

196 IV. SUMMARY

197 We have used magnetron sputtering to deposit B₄C films with an FFE source modified
198 for direct cooling with the HiPIMS plasma discharge mode with two different working gases
199 (pure Ar and an Ar-Ne mix with 10% of Ne) and substrates biased at -25 V. Higher
200 plasma densities, as indicated by larger target and substrate currents, can be achieved by
201 using larger process pressure and adding Ne to the working gas mixture. This work has

202 demonstrated that the density and mechanical properties of B₄C films can be improved with
203 the deposition in the HiPIMS mode in an Ar-Ne working gas mix. Our results demonstrate
204 that the HiPIMS discharge mode [coupled with Ar-Ne gas mixture](#) expands the flexibility of
205 magnetron sputter deposition of B₄C and offers additional process control. However, it also
206 increases process complexity, and more work is currently needed to better understand the
207 physics of the HiPIMS B₄C [mixed](#) plasma discharge with an FFE magnetron source.

208 **V. ACKNOWLEDGMENTS**

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211 **VI. DATA AVAILABILITY STATEMENT**

212 The data that supports the findings of this study is available within the article.

213 **VII. AUTHOR DECLARATIONS**

214 **A. Conflict of Interest**

215 The authors have no conflicts to disclose.

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TABLE I. Conditions and resulting film thicknesses of the two deposition runs of the present study. The substrate tilt angle (α) is defined in the text.

Parameter	Run 1	Run 2
Ne content in Ar-Ne mix (%)	0	10
Peak voltage (V)	680	680
Average power (W)	210	370
Peak target current (A)	25	46
Pulse frequency (Hz)	50	50
Pulse width (μ s)	500	500
Substrate bias (V)	-25	-25
Pressure (mTorr)	45	45
Deposition time (h)	3	3
Target-to-substrate distance (mm)	50	50
Film thickness for $\alpha = 0^\circ$ (μ m)	2.8	4.6

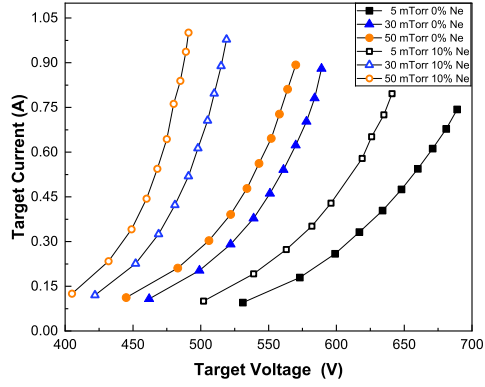


FIG. 1. Dependence of target current on the absolute value of (negative) target voltage for the DCMS discharge in Ar-Ne mixtures with 0 and 10% of Ne at 5, 30, and 50 mTorr, as indicated in the legend.

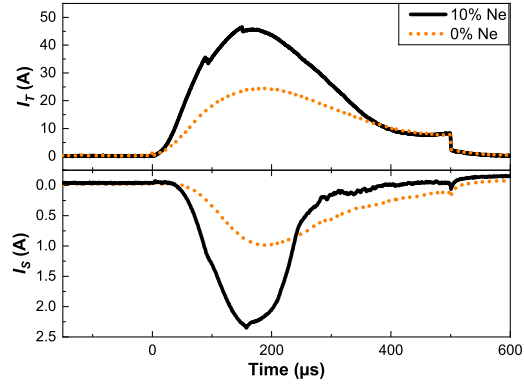


FIG. 2. Waveforms of (a) target current (I_t) and (b) substrate current (I_s) for Ar-Ne mixtures with 0 and 10% of Ne at 45 mTorr, a peak target voltage of 680 V, and a substrate bias of -25 V. Current of ions from the plasma is shown as positive in both panels. The legend in (a) applies to both panels.

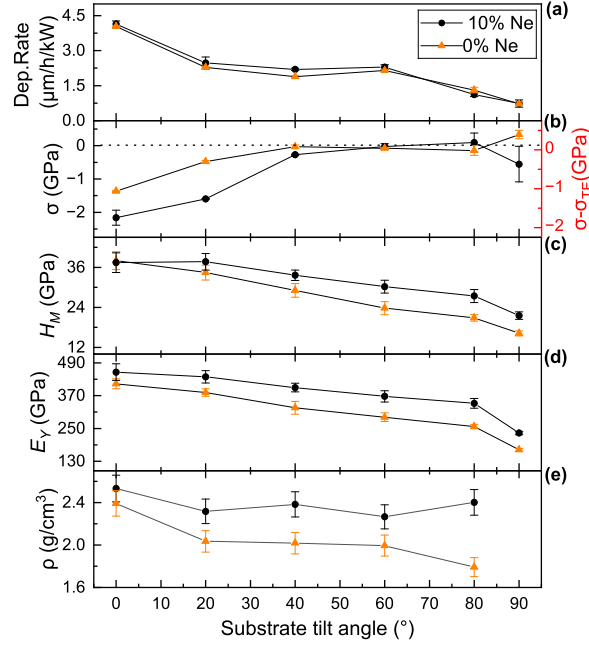


FIG. 3. Substrate tilt dependencies of (a) the deposition rate normalized to the average discharge power, (b) residual stress (σ , where σ_{TE} is the stress contribution due to the thermal expansion mismatch between the substrate and the film), (c) Meyer's Hardness (H_M), (d) Young's Modulus (E_Y), and (e) mass density (ρ) of B_4C films deposited at 45 mTorr in Ar-Ne mixtures with 0 and 10% of Ne, as indicated in the legend in (b), which applies to all five panels.