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Role of Carbon Vacancies on Mechanical Properties of Transition-Metal Carbide Thin Films

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We developed a reactive sputter-deposition procedure, wherein one can precisely vary the reactive gas partial pressure from ultra-high vacuum (UHV) levels up to a few milliTorr. Through a series of experiments, we demonstrate control over the Ta-C phase (Ta2C to Ta3C2 to TaC) and C concentration by varying the deposition parameters (substrate temperature and reactive gas pressure). In addition, we have carried out detailed mechanical and compositional characterization of refractory high-entropy alloy, VNbTaMoW, developed new insights into the growth kinetics of 2D layered graphene and hBN, and demonstrated the growth of selforganized nanostructures of (VNbTaMoW)N.

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Abstract

This project aims to determine the role of carbon vacancies on the mechanical behavior of B1-structured transition-metal carbide (TMC) thin films with the ultimate goal of developing thin TMC films with superior hardness and enhanced ductility for aerospace and other advanced structural applications. In order to achieve this goal, proposed research efforts include: varying the TMC composition (e.g., through cation substitution and carbon vacancies), crystal orientation, and thickness of epitaxially grown films and derive a mechanistic understanding of relationship between these parameters and the mechanical behavior. Through a series of thin film synthesis followed by structural and *in situ* nanomechanical characterization experiments, the factors influencing mechanical properties of TMCs will be determined. As part of the project, over the past 3 years (Nov. 2017 – Oct. 2020), we have published 12 peer-reviewed journal articles. A few highlights of our work include but not limited to:

- **two invited papers** [*Thin Solid Films* **688**, 137440 (2019); *Surface and Coatings Technology* **398**, 126053 (2020)] and
- **one cover page article** [*Nano Letters* **21**, 577-582 (2021)]
- **graduation of two doctoral students** [Drs. Pedro Arias and Koichi Tanaka] with one of them [Dr. Koichi Tanaka] awarded the **outstanding PhD award**.

Our accomplishments include:
1) Development of a reactive sputter-deposition procedure, wherein one can precisely vary the reactive gas partial pressure from ultra-high vacuum (UHV) levels up to a few milliTorr.
2) Demonstrate control over the Ta-C phase (Ta_2C to Ta_3C_2 to TaC) and C concentration by varying the deposition parameters (substrate temperature and reactive gas pressure).
3) Mechanical and compositional characterization of refractory high-entropy alloy, VNbTaMoW.
4) New insights into the growth kinetics of 2D layered graphene and hBN.
5) Growth of self-organized nanostructures of (VNbTaMoW)N.
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Brief summaries of key accomplishments directly related to the proposed research:

1) *Effects of ultra-low ethylene partial pressure on microstructure and composition of reactively sputter-deposited Ta-C thin films*

In this work, Ta-C films are reactively sputter-deposited at 1123 K using Ar/C_2H_4 gas mixtures with different C_2H_4 partial pressures, P_c.

Highlights of this work include:

* the use of ultra-low reactive gas pressures during reactive sputter deposition;
* demonstration of Ta-C thin film compositional and microstructural tunability;
* observation of trigonal Ta_2C phase in thin films deposited using TaC target; and
* observation of multiply twinned 111-oriented TaC grains.

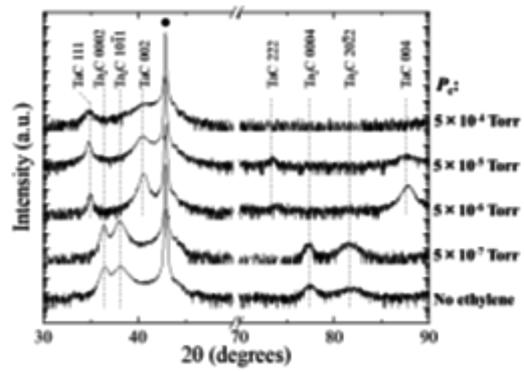

Figure 1. Representative X-ray diffraction (XRD) ω-2θ scans obtained from Ta-C thin films sputter-deposited on MgO(001). Solid circle denotes 002 reflection of the substrate. Dotted lines indicate the expected peak positions of stoichiometric B1-TaC and trigonal-Ta_2C phases.

2) *Effects of ultra-low ethylene partial pressure on microstructure and composition of reactively sputter-deposited Ta-C thin films*

In this work, we investigated the effects of substrate temperature (1073 K ≤ T_s ≤ 1373 K) and deposition time on microstructural evolution of $Ta_2C/Al_2O_3(0001)$ thin films grown *via* UHV dc magnetron sputtering of TaC target in pure Ar atmospheres. We obtain 0001-oriented, trigonal-structured α-Ta_2C films that are increasingly smoother and thinner with increasing T_s. The 0001-texture improves with increasing T_s up to 1273 K. At T_s = 1373 K, we observe highly coherent 0001-oriented growth with the following orientation relationship: $(0001)_{Ta_2C} \parallel (0001)_{Al_2O_3}$ and $[10\bar{1}0]_{Ta_2C} \parallel [11\bar{2}0]_{Al_2O_3}$ during the early stages of deposition followed by the formation of anti-phase domains and misoriented grains at the later times yielding polycrystalline layers with reduced 0001-texture.

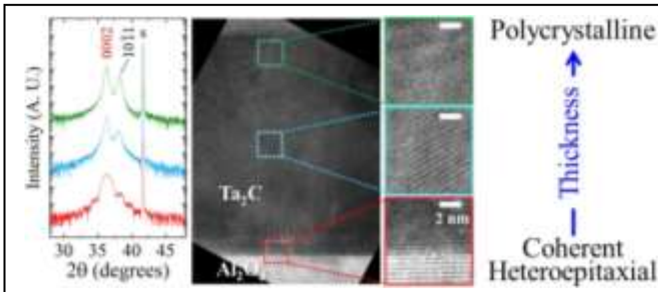

Figure 2. Representative XRD ω-2θ scans and TEM images showing thickness-dependent changes in crystallinity of trigonal-Ta_2C thin films on $Al_2O_3(0001)$.

3) *Growth of heterolayered [cubic-TaC(111) + rhombohedral-Ta_3C_2(0001)] nanocomposite thin films on Al_2O_3(0001)*

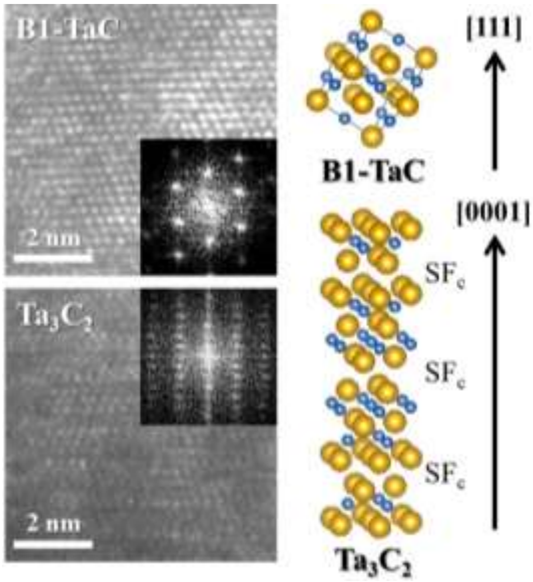

Figure 3. Cross-sectional TEM images and associated schematics of the B1-TaC and rhombohedral Ta_3C_2 phases obtained during reactive sputter-deposition of Ta-C films on Al_2O_3(0001) substrates.

We report the formation of highly-oriented B1-TaC(111) and rhombohedral-Ta_3C_2(0001) phases on Al_2O_3(0001) substrate during UHV dc magnetron sputtering of a TaC target in 5 mTorr Ar/C_2H_4 gas mixtures with p_c = 0.1% and 1% and at T_s = 1123 K and 1273 K. We find that the films deposited using higher p_c show primarily B1-TaC 111 reflections. Layers grown at the lower T_s (= 1123 K) and lower p_c exhibit highly-oriented two-phase mixture of rhombohedral-Ta_3C_2(0001) and B1-TaC(111) twins, oriented with respect to Al_2O_3(0001) as: $(111)_{TaC} \parallel (0001)_{Ta_3C_2}$, $[\bar{2}11]_{TaC} \parallel [11\bar{2}0]_{Ta_3C_2}$ and $(111)_{TaC} \parallel (0001)_{Ta_3C_2}$, $[\bar{1}\bar{1}2]_{TaC} \parallel [11\bar{2}0]_{Ta_3C_2}$ and $(0001)_{Ta_3C_2} \parallel (0001)_{Al_2O_3}$, $[10\bar{1}0]_{Ta_3C_2} \parallel [11\bar{2}0]_{Al_2O_3}$. Interestingly, we observe the Ta_3C_2 phase near the film/substrate interfaces and TaC phase on top of the Ta_3C_2 layers.

Tasks that were proposed but not achieved: We proposed to investigate the mechanical behavior of TMC thin films as a function of composition and microstructure. While we have some preliminary data on *in situ* nanomechanical testing (beam bending tests) of Ta-C thin films, we have not carried out a systematic investigation.
A second aspect of the proposed research was to investigate the growth and mechanical behavior of TMC alloys. We are yet to carry out such growth and mechanical test experiments.

Unexpected outcomes: We (re)discovered that using a 2D layered material such as hexagonal boron nitride (hBN) as the buffer layer can enhance crystallinity of Ta_2C thin films sputter-deposited on single-crystalline Al_2O_3(0001) substrates. Our results indicate that the heteroepitaxial and homoepitaxial growths of Ta_2C on hBN-covered Al_2O_3(0001) and Ta_2C, respectively yield higher crystalline quality than those grown on bare Al_2O_3(0001) and Ta_2C. We have also tested the generality of these findings for the growth of other materials: face-centered (fcc) cubic Pd, body-centered cubic (bcc) Mo, and (VNbTaMoW), a bcc-structured high-entropy alloy. Our results indicate the possibility of enhancing heteroepitaxy and homoepitaxy using 2D crystals as buffer layers. These results are yet to be published.
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Archival Publications (published) during the course of this project:

1. K. Tanaka, M. E. Liao, A. Aleman, H. Zaid, M. S. Goorsky, and S. Kodambaka. Growth of heterolayered [cubic-TaC(111) + rhombohedral-Ta3C2(0001)] nanocomposite thin films on Al2O3(0001). ***Acta Materialia* 204**, 116499 (2021).
2. (***cover page***) H. Zaid, K. Tanaka, M. Liao, M. S. Goorsky, S. Kodambaka, and H. Kindlund. Self-Organized Growth of 111-Oriented (VNbTaMoW)N Nanorods on MgO(001). ***Nano Letters* 21**, 577-582 (2021).
3. H. Zaid, A. Aleman, and S. Kodambaka. Size-dependent yielding and strain-hardening of compositionally-enriched body-centered cubic VNbTaMoW alloy. ***Scripta Materialia* 178**, 518-521 (2020).
4. P. Arias, J. Tesař, A. Kavner, T. Šikola, and S. Kodambaka. In Situ Variable-Temperature Scanning Tunneling Microscopy Studies of Graphene Growth Using Benzene on Pd(111). ***ACS Nano* 14**, 1141-1147 (2020).
5. P. Arias, A. Ebnonnasir, C. V. Ciobanu, and S. Kodambaka. Growth Kinetics of Two-Dimensional Hexagonal Boron Nitride Layers on Pd(111). ***Nano Letters* 20**, 2886-2891 (2020).
6. H. Zaid, J. W. Stremfel, K. Tanaka, M. Liao, M. S. Goorsky, J.-M. Yang, and S. Kodambaka. Mechanical properties of compositionally-rich body-centered cubic VNbTaMoW alloy. ***Materialia* 12**, 100746 (2020).
7. (***invited paper***) H. Zaid, A. Aleman, K. Tanaka, C. Li, P. Berger, T. Back, J. Fankhauser, M. S. Goorsky, and S. Kodambaka. Influence of ultra-low ethylene partial pressure on microstructural and compositional evolution of sputter-deposited Zr-C thin films. ***Surface and Coatings Technology* 398**, 126053 (2020).
8. K. Tanaka, A. Aleman, H. Zaid, M. E. Liao, K. Hojo, Y. Wang, M. S. Goorsky, and S. Kodambaka. Ultra-high vacuum dc magnetron sputter-deposition of 0001-textured trigonal α-Ta2C/Al2O3(0001) thin films. ***Materialia* 13**, 100838 (2020).
9. T. Glechner, R. Hahn, T. Wojcik, D. Holec, S. Kolozsvári, H. Zaid, S. Kodambaka, P. H. Mayrhofer, and H. Riedl. Assessment of ductile character in superhard Ta-C-N thin films. ***Acta Materialia* 179**, 17-25 (2019).
10. (*invited paper*) K. Tanaka, A. Aleman, M. E. Liao, Y. Wang, M. S. Goorsky, and S. Kodambaka. Effects of ultra-low ethylene partial pressure on microstructure and composition of reactively sputter-deposited Ta–C thin films. ***Thin Solid Films* 688**, 137440 (2019).
11. P. Arias, A. Abdulslam, A. Ebnonnasir, C. V. Ciobanu, and S. Kodambaka. Bifurcation and orientation-dependence of corrugation of 2D hexagonal boron nitride on palladium. ***2D Materials* 5**, 045001 (2018).
12. K. Tanaka, J. Fankhauser, H. Zaid, A. Aleman, M. Sato, D. Yu, A. Ebnonnasir, C. Li, M. Kobashi, M. S. Goorsky, and S. Kodambaka. Kinetics of Zr-Al intermetallic compound formation during ultra-high vacuum magnetron sputter-deposition of Zr/Al2O3(0001) thin films. ***Acta Materialia* 152**, 34-40 (2018).

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Publications (submitted/in preparation):

1. H. Zaid *et al.*, Growth of elastically-stiff, nanostructured, high-entropy alloy nitride, (VNbTaMoW)N/Al2O3(0001) thin film, **submitted (2021).**
2. M. Chen, J. Wheeler, D. Sangiovanni, J.-M. Yang, S. Kodambaka, and G. Po, *Orientation-Dependent Highly anisotropic thermomechanical behavior of TaC*, **in preparation**.
3. K. Tanaka *et al*., *van der Waals layer promoted hetero and homoepitaxy*, **in preparation**.

INVITED SEMINARS/PRESENTATIONS:

1. "*In situ* High-Temperature Scanning Tunneling Microscopy Studies of two-dimensional hexagonal boron nitride (hBN) growth kinetics and surface dynamics on Pd(111)," NANOTR-15, 15th Nanosci. and Nanotechnol. Conf., Antalya, Turkey, Nov. 03-06, 2019.
2. "*In situ* microscopy as a materials characterization tool: fundamental understanding of 2D layer growth kinetics and nanomechanics of ceramics," Oklahoma State Univ., Tulsa, OK, Sept. 4, 2019.
3. "*In situ* microscopy: a powerful approach for understanding materials phenomena," Texas A&M, College Station, TX, March 4, 2019.
4. "*In situ* scanning tunneling microscopy studies of growth and characterization of two-dimensional hexagonal boron nitride layers," ICN+T2018, Brno, Czech, July 23-27, 2018.
5. "Ultra-high vacuum dc magnetron sputter-deposition and microstructural characterization of Zr and ZrCx thin films," THERMEC'2018, Paris, France, July 8-13, 2018.
6. "*In situ* microscopy: an old approach to develop new insights into the growth of 2D layered materials and the mechanical behavior of refractory carbides," UC Davis, Davis, CA, May 29, 2018.
7. "*In situ* Scanning Tunneling Microscopy Studies of hBN Layer Growth Kinetics and the Influence of Substrate on Electronic Structure of the Layers," 233rd ECS meeting, Seattle, WA, May 13-17, 2018.