# Localized carbon concentration gradients affecting nanocrystalline growth in Si-C-N films

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## INTRODUCTION

Gas turbines, the marine and oil sectors, and gas turbine wear, abrasion, and corrosion resistance are applications for multicomponent hard coatings. They are also utilized in rocket nozzle inserts, hypersonic vehicle nose caps, turbo-jet engines, and edges. We have previously used magnetron sputtering to deposit Si-C-N and Ti-B-Si-C coatings on silicon surfaces. These coatings demonstrated high hardness as well as fracture toughness, which were found using nanoindentation. **[1-5]**. The constituent phase of silicon oxycarbide (SiOC) along with TiC serve as a high temperature composite **[3].** The TiCN/SiBCN nanocomposite has also reported to possess a nano porous structure, which has high temperature ceramic aerogel having high surface area and low conductivity **[4].** The hard phases like SiC, $Si_3N_4$, TiN, cBN, CNx, $TiB_2$, and TiC, formed in the coatings are the reason for showing these properties which have been characterized subject to indentations in different modes **[6-10],** Coatings of these hard phases are also used in the microelectronic industry for MEMS components **[11, 12]** A real time analysis of these coatings considering porosity, which is parameter depicting material compactness is beneficial for coatings for high temperature applications **[13].** The porosity or void formation however is related to the atomic migrations that occur on a surface forming crystallites and the process of coalescence that follows it**.** An attempt has been made in this communication to study the porosity in the hard coatings and the deposition parameters affecting it

## MATERIALS & METHODS

Using a sintered SiC and Ti-B-Si-C target which act as the cathode in the evacuated ($10^{-6}$ Torr) RF magnetron sputtering chamber (Hindhivac, Bangalore), the Si-C-N and Ti-B-Si-C coatings were deposited on silicon substrates by using Argon as the ionizing gas. Nitrogen was introduced in specified $Ar/N_2$ ratios for the reactive sputtering to take place. The microscopic images were obtained using TEM (FEI, Technai. Netherlands). The films were subjected to nanoindentation experiments using the Nanoindenter XP (MTS/Agilent USA).

## RESULTS & DISCUSSIONS

A TEM image of Si-C-N film growth process has been shown in **Fig 1(a)[14]**. The atomic clustering due to localized carbon concentration gradients can be seen to take a linear pattern on otherwise an amorphous background. The process of atomic clustering with an increase in carbon percentage in Si-C-N films has recently been reported **[15]**.

The surface profile of the TEM image of Si-C-N coatings at three different regions are given in **Fig 1(b)**. The profiles A and B represent the regions far and near to the linearly clustered regions. The profile C on the other hand includes the clustered region and manifests the phenomenon by means of a wide inverted band which was deconvoluted into Gaussian peaks depicting the clustering process (**Fig 2**).

The differential intensity profiles showing the high and low (porous) concentration regions of the nucleation is given in **Fig 1(c).** A difference in the frequency and intensity of the peaks between profile A and B can be seen, indicating the atomic migration a bit more intense as one gets closer to the clustering region (**Fig 1d**). The profile C which represents the clustered region was found to be further subdivided in terms of the peaks formed which arises due to the process of coalescence of the crystallites. The variation of fitting parameters viz the FWHM and intensity (area) indicated the atomic migration to be persistent inside the clustering causing coalescence and crystal growth. However, their directions change forming more than one preferred site as the energy needs to be balanced. A difference in Raman spectra arising due to similar phenomena has been reported previously **[16, 17]**.

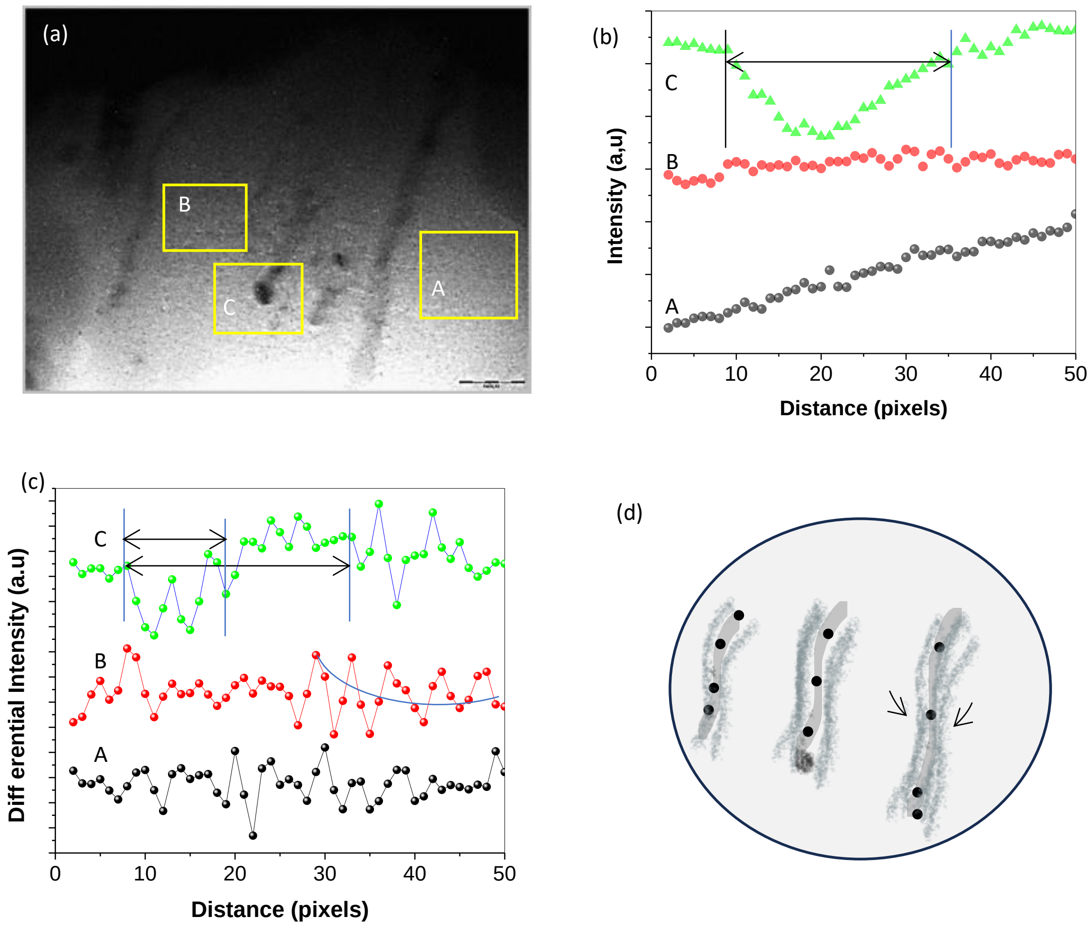
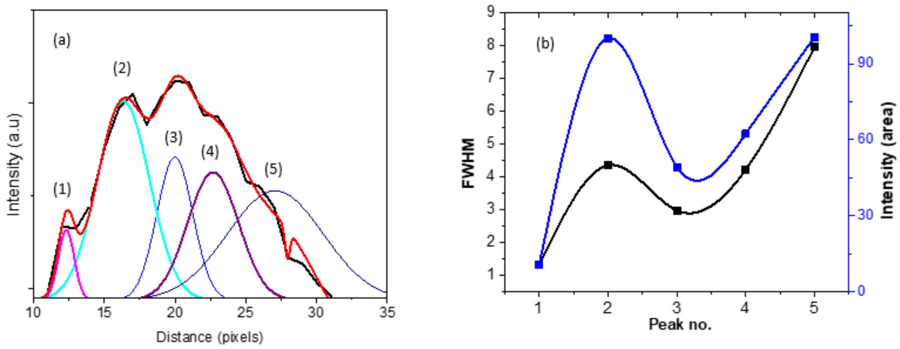



**Fig 1**(a) TEM image of Si-C-N **[14]** (b) surface profiles of marked regions (A, B and, C) (c) differential surface profiles depicting porosity (d) schematic of growth process on an amorphous Si-C-N




| Peak | FWHM | Intensity (area) |
|---|---|---|
| 1 | 1.33 | 10.78 |
| 2 | 4.36 | 100 |
| 3 | 2.98 | 49.26 |
| 4 | 4.23 | 62.39 |
| 5 | 7.98 | 100.6 |

**Fig 2**. (a) Gaussian plot fits of the intensity profile representing carbon clustering along with (b) the variation of fitting parameters

## CONCLUSIONS

The atomic migration giving rise to crystallite formation having its own mechanics based upon thermodynamic aspects can causes formation of voids or pores. It changes its course of action inside an atomic cluster for energetic reasons giving rise to formation of nanocrystallites.

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## DECLARATIONS

### Compliance with Ethical Standards

The manuscript has not been submitted in parallel either in full or partially to any other journal.

### Conflict of interest

There is no conflict of interest among the authors

### Research Data Policy and Data Availability Statements

Data shall be provided on request

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## REFERENCE

1. D. V. Kanyanta, “Hard, superhard and ultrahard materials: An overview,” in *Microstructure-Property Correlations for Hard, Superhard and Ultrahard Materials*, Springer, 2016, pp. 1-23.

2. S.K. Mishra, A.S. Bhattacharyya, P. Mahato, L.C. Pathak, Multicomponent TiSiBC superhard and tough composite coatings by magnetron sputtering, *Surface and Coatings Technology*, Volume 207, 2012, 19-23

3. Xiaoliang Sun, Gang Yang, Zhengkai Tian, Wenxia Zhu, Dong Su,In-situ formation of titanium carbide in carbon-rich silicon oxycarbide ceramic for enhanced thermal stability, *Journal of the European Ceramic Society*,42, 15, 2022, 6935-694. https://doi.org/10.1016/j.jeurceramsoc.2022.08.027.

4. Sun, Xiaoliang and Zhu, Wenxia and Wang, Huijie and Yan, Xiao and Su, Dong, In Situ Formation of the TiCN Phase in SiBCN Ceramic Aerogels Enabling Superior Thermal and Structural Stability up to 1800 °C, *ACS Applied Materials \& Interfaces*,15, 9,12221-12231, 2023 https://doi.org/10.1021/acsami.2c22601

5. Mishra, Suman K., A. S. Bhattacharyya, P. K. P. Rupa, and L. C. Pathak. "XPS studies on nanocomposite Si–C–N coatings deposited by magnetron sputtering." *Nanoscience and nanotechnology letters* 4, no. 3 (2012): 352-357.

6. R. Dash, K. Bhattacharyya, A.S. Bhattacharyya, Film failure at earlier and later stages of nanoindentation in static and sliding mode. *Eng Fail Anal* (2023) 150, 107353 https://doi.org/10.1016/j.engfailanal.2023.107353

7. Ritambhara Dash, A. S. Bhattacharyya Crack growth based on indentation along substrate and nanocrystallites in Titanium diboride thin films, *Fatigue & Fracture of Engineering Materials & Structures*. (2023) 46 (7) 2714-2719 https://doi.org/10.1111/ffe.13986

8. R. Dash, K. Bhattacharyya, A. S. Bhattacharyya. Fracture associated with static and sliding indentation of multicomponent hard coatings on silicon substrates, *Fatigue & Fracture of Engineering Materials & Structures* (2023) 46: 1641-1645. https://doi.org/10.1111/ffe.13960

9. A.S. Bhattacharyya. Sliding indentation: Failure modes with study of velocity and loading rate, Surface Topography: Metrology and Properties. 9 (2021) 035052 https://doi.org/10.1088/2051-672X/ac28aa

10. R. Dash, K. Bhattacharyya, A S. Bhattacharyya, Synergistic fractural features observed in Ti-B-Si-C hard coatings on enhancing the sharpness of nano indenters, Int J. Ref Met & Hard Mater, 116, 2023 106373

11. R. Dash, A. S. Bhattacharyya. Failure regions resembling geometrical shapes in sliding nanoindentation of Si-C-N thin films used for N/MEMS, *Tech Phy Lett*, 2022 10.21883/PJTF.2022.15.53122.19132

12. Abhay K. Rajak, Ritambhara Dash, Ashwini Kumari, A.S. Bhattacharyya, Sensitivity in nanomechanical pedestal MEMS cantilever, *Materials Today Communications*, Volume 38, 2024, 107891, https://doi.org/10.1016/j.mtcomm.2023.107891.

13. Licheng Shi, Yun Long, Yuzhang Wang, Xiaohu Chen, Qunfei Zhao,On-line detection of porosity change of high temperature blade coating for gas turbine, Infrared Physics & Technology, Volume 110, 2020, 103415, https://doi.org/10.1016/j.infrared.2020.103415.

14. A.S. Bhattacharyya, Kushal Bhattacharyya, Mixed-Mode Fracture behaviour of Si-C-N coatings, *Next Materials* 2023 https://doi.org/10.1016/j.nxmate.2023.100038

15. Dhruva Kumar, Soham Das, Bibhu P. Swain, Spandan Guha, Unveiling the multifaceted impact of C2H2 flow on SiCN CVD coatings: Mechanical mastery and beyond, Ceramics International, Volume 50, Issue 4, 2024, 6526-6542, https://doi.org/10.1016/j.ceramint.2023.11.399.

16. Dash R, Mohanta P, Bhattacharyya A. Analysis of Raman spectra with surface and nanocrystalline growth in carbon nitride thin films with nitrogen flow rate . ChemRxiv. Cambridge: Cambridge Open Engage; 2022; . https://doi.org/10.26434/chemrxiv-2022-7123z

17. Bhattacharyya, A.S. and Mishra, S.K. (2010), Raman studies on nanocomposite silicon carbonitride thin film deposited by r.f. magnetron sputtering at different substrate temperatures. J. Raman Spectrosc., 41: 1234-1239. https://doi.org/10.1002/jrs.2588