Dendritic growth in Si-(CN) thin films

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Abstract

A rare dendritic growth in sputter deposited SiCN and CVD deposited CN were observed. The rapid rate of nucleation and growth process led to instabilities in the growth pattern and the surface energy release rate was more through convection than diffusion It opens up new field of fractal study in the case of CN and SiCN based materials and thin films.

Keywords: Cu thin films, sputtering, copper oxide, dendritic growth

Previous publications have shown formation of nanocrystalites on amorphous matrix in Si-CN nanocomposites deposited by magnetron sputtering. A sputter model for atomic layer deposition has also recently developed. In this communication we have taken a closer look into the growth mechanisms of the sputter deposited films. SiCN thin film deposition has been explained in details earlier [1-7].

A rare dendritic growth has been observed in some areas in SiCN and CN films deposited by RF magnetron sputtering and plasma enhanced CVD respectively on Si (100) substrates (Fig1). Dendritic growth usually occurs in metals due to interfacial interaction between the molten state and the solid state. The films were deposited in a high vacuum (HV) chamber with initial base pressure of 10^{-6} mbar. The sputtering was done in Argon and Nitrogen atmosphere with a sintered SiC target [2-6].

Fractal growth in carbon based organic thin films is quite uncommon and not well understood. Carbon nitride and Silicon carbon nitride based materials and films have shown novel multifunctional properties and have been prepared by various techniques. However no reports showing dendrite growth in SiCN or CN films are present till date to the best of our knowledge. A SiCN thin film, although not truly an organic film, has got resemblance in properties to hydrocarbons thin films as a small fraction of hydrogen is present in the top surface layer due to trapped residual water molecules. These hydrogen atoms can react with carbon present in the film. The presence of Nitrogen below 20 at % in the case of CNx films on the other hand, makes it equivalent to a nitrogen free carbon film. The formation of a CH compound is therefore quite possible at the surface of the SiCN film. Recent reports have shown fractal growth of hydrocarbon pentacene ($C_{14}H_{22}$) on Si (100) substrates which finds application in the growth organic optoelectronic thin film devices[8].

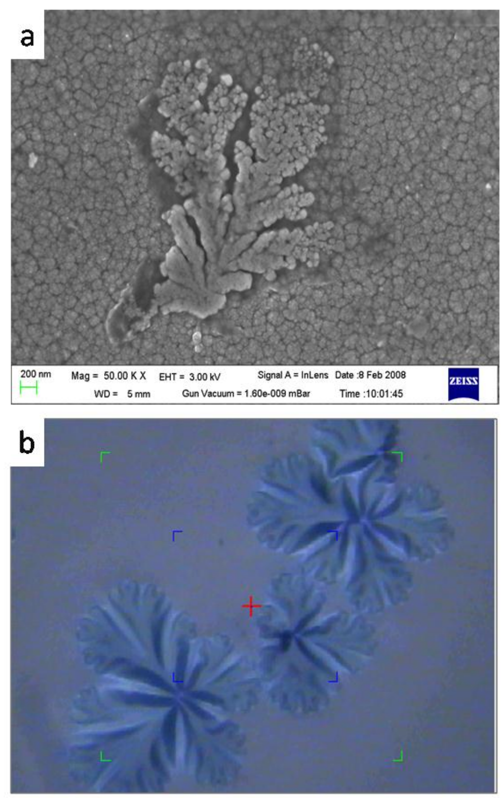

Fig 5: Dendritic growth observed in (a) PVD grown SiCN films and (b) CVD grown CN films

The dendritic growth in SiCN films might have greater impact in this context being a optoelectronic material itself with a tunable band gap. It opens up new field of fractal study in the case of CN and SiCN based materials and thin films.

Dendritic growths were observed in SiCN films grown by magnetron sputtering at high substrate temperature of 400°C. The micrographs were captures by FESEM (Zeiss, Germany).The rapid rate of nucleation and growth process led to instabilities in the growth pattern and the surface energy release rate was more through convection than diffusion. The nature of dendritic growth was however different for CVD growth CNx films. The dendrites were much larger in size and were associated with film delamination form the substrate most probably due to high amount of stress being generated in the film. On close observation of the dendritic SiCN structure one can see that there are two different regimes. The first one starts from the bottom to the middle where the nanograins are not distinctly visible. In the other regime the grains are prominent which starts in the middle and extends upto the branched structure. The reason behind having two different nature of structure can be attributed to the diffusion the adatoms undergo during film growth. Dendritic growth usually takes place during solidification of a supercooled liquid. Supercooling is a process of lowering the temperature of a liquid below its melting point without solidification. As the liquid solidifies the dendrite grows in structure. So somehow a large temperature gradient might have risen during the thin film growth which has melted a part of the film. The melted part in the process of solidification again could have given the dendritic structure. The parameter which defines nondimensional super cooling is called the Stefan number S_t[9]. There are reports of dendritic growth in thin films where temperature and film thickness have been found to contribute significantly[10]

References

1. AS Bhattacharyya, S Kumar, S Jana, PY Kommu, K Gaurav, S Prabha, VS.Kujur, P.Bharadwaj, Sputter based Epitaxial Growth and Modeling of Cu/Si Thin Films, *Int. J. Thin. Fil. Sci. Tec* 4 (3), 2015,173-177
2. A. S Bhattacharyya, S.K.Mishra, S. Mukherjee Journal of Vacuum Science and Technology A, 28 (2010) 505-509.
3. Bhattacharyya, A.S Mishra, S.K Das, G.C Mukherjee, S. Hot Properties. European Coatings Journal, 2009, 3,108-114.
4. Bhattacharya, A.S. Das, G.C. Mukherjee, S. Mishra, S.K. Effect of radio frequency and direct current modes of deposition on protective metallurgical hard silicon carbon nitride coatings by magnetron sputtering, Vacuum 2009 83 1464-1469.
5. Bhattacharyya, A.S. and Mishra, S.K. Raman studies on nanocomposite silicon carbonitride thin film deposited by RF magnetron sputtering at different substrate temperatures. Journal of Raman Spectroscopy 41 (2010) 1234–1239.
6. Bhattacharyya, A.S. Mishra, S.K. Mukherjee, S. Das, G.C. A comparative study of Si–C–N films on different substrates grown by RF magnetron sputtering Journal of Alloys and Compounds 2009, 478, 474–478.
7. A.S.Bhattacharyya, K. Gaurav, P. Kommu, Compound TiO_x film growth dynamics in Sputtering , 2015, DOI: 10.13140/RG.2.1.5077.8082
8. Frank- J, Meyer zu Heringdorf, M. C. Reuter & R. M. Tromp, *Nature*, 2001, 412, 517-520
9. Nabeel Al-Rawahi, Gretar Tryggvason, Numerical Simulation of Dendritic Solidification with Convection: Two-Dimensional Geometry, Journal of Computational Physics 180, 471–496 (2002) doi:10.1006/jcph.2002.7092
10. Qi-jing Lin, Weixuan Jing, Shu-ming Yang, Zhuang-de Jiang, Chen-ying Wang Agglomeration and Dendritic Growth of Cu/Ti/Si Thin Film Volume, Journal of Nanomaterials2014, Article ID 518520, 8 pages http://dx.doi.org/10.1155/2014/518520