FABRICATION AND CHARACTERIZATION OF POLYMERIC AND NANOSTRUCTURED CARBON NITRIDE THIN FILMS: A SIMPLE DIFFERENCE IN ELECTRODE DISTANCE

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ABSTRACT

This work gives an insight on the fabrication and characterization of two distinctly different hydrogenated carbon nitride CN_x:H structured films showing either polymeric, p-CN_x:H or nanostructured, ns-CN_x:H film growth. These structures were obtained using radio frequency (rf) plasma enhanced chemical vapour deposition employing a parallel-plate electrode configuration, under the same deposition parameters except for the change in the electrode distance. It was this simple change in the distance which induced the structural transformation from p-CN_x:H films obtained at distance of six to three cm, to the ns-CN_x:H films produced at two to one cm. Each type of film showed its own unique characteristics. For the p-CN_x:H films deposited at an electrode distance of 5 cm, their PL spectra showed two main peaks assumed to be attributed to the presence of sp^2 clusters and nitrogen bonding in the films. Further studies showed that the optimized rf power and nitrogen-to-methane N_2:CH_4 gas-flow-rate ratio to obtain p-CN_x:H films with the highest PL intensities were 80 W and 0.70, respectively. There appeared to be no direct correlation between the PL properties and optical energy gap. However, the PL characteristics were dependent on the N content in the films. From extensive bonding studies carried out on these films, it was found that N is incorporated most significantly through nitrile, isonitrile and sp^2-C=N bonding configurations. Also, these films were thermally stable when annealed in nitrogen up to temperatures of 500 °C, though the PL intensities start to decline even from 200 °C. The recombination centers which produced these high PL intensities were attributed to the CH_n, C=N and the isolated and/or fused aromatic rings bonded to nitrile (−C≡N) which may contribute significantly as recombination centers.

While the studies of p-CN_x:H films were focused on their PL characteristics, a more fundamental approach was taken in the study of ns-CN_x:H. These novel ns-CN_x:H films were obtained at low deposition temperatures without the use of metal-catalyst or template, and could be grown directly on the bare silicon and quartz substrates. The focus of the study of these ns-CN_x:H films was on the formation of vertically aligned CN_x:H nanorods and their growth mechanism. The optimized parameters for the formation these nanorods were determined to be at P_{rf} of 80 W and N_2:CH_4 ratio of 0.70. This coincided with the maximum N content and preferential bonding of isonitrile bonded to fused or isolated aromatic rings in the films. These nanorods were made up of C nanographitic sp^2 clusters embedded in a carbon-nitrogen amorphous matrix which surrounded, encapsulated and held them together. The growth mechanism of these vertically aligned nanorods was proposed.

In the optimization studies of both materials, one fascinating conclusion was uncovered. The optimized deposition parameters for both exceptional characteristics of these structured films were the same. It is the simply the difference in electrode distance at these optimal P_{rf} and N_2:CH_4 ratio, which induces the formation of these two significantly different structured films.

ABSTRAK

Kerja penyelidikan ini memberi pemahaman yang mendalam terhadap fabrikasi dan pencirian dua jenis karbon nitrida berhidrogen (CN_x:H) yang jelas berbeza dari segi struktur filemnya samaada filem polimerik (p-CN_x:H) atau berstruktur nano (ns-CN_x:H). Struktur-struktur ini telah diperolehi dengan menggunakan kaedah pemendapan frekuensi radio wap kimia secara peningkatan plasma dengan konfigurasi kepingan elektrod selari, dimana parameter pemendapan yang digunakan adalah sama kecuali beza jarak diantara elektrod. Perubahan jarak ini dengan mudahnya mendorong transfomasi struktur filem dari p-CN_x:H yang diperolehi pada jarak enam hingga tiga cm kepada filem ns-CN_x:H yang dihasilkan pada jarak dua hingga satu cm. Kedua-dua jenis filem menunjukkan ciri-ciri unik yang tersendiri. Bagi filem p-CN_x:H yang dimendapkan pada jarak elektrod lima cm, spectra PL menunjukkan dua puncak utama yang dipercayai berkait rapat dengan kehadiran kelompok-kelompok sp^2 dan ikatan nitrogen dalam filem-filem tersebut. Kajian lanjut menunjukkan kuasa rf (K_{rf}) dan kadar nisbah campuran aliran gas nitrogen terhadap gas metana (N_2:CH_4) yang optima bagi menghasilkan filem p-CN_x:H dengan PL yang berkeamatan paling tinggi masing-masing adalah 80W dan 0.70. Didapati tiada hubungan terus diantara sifat PL dan jurang tenaga optikal. Walaubagaimanapun, sifat PL bergantung kepada kandungan N dalam filem-filem tersebut. Melalui kajian ikatan kimia yang terperinci, didapati penggabungan N yang sangat penting berlaku melalui konfigurasi ikatan nitrile, isonitrile dan sp^2-C=N. Didapati juga, filem-filem ini stabil sehingga suhu 500 ºC walaupun keamatan PLnya menurun seawal suhu 200 ºC. Pusat penggabungan semula yang menghasilkan keamatan PL yang tinggi dikaitkan dengan kehadiran CH_n, C=N dan nitrile (-C≡N) yang terikat kepada lingkaran aromatik yang terpencil dan/atau terpadu yang mungkin merupakan penyumbang terpenting sebagai pusat-pusat penggabungan semula.

Berbeza dengan kajian terhadap filem p-CN_x:H yang tertumpu kepada sifat-sifat PL, pendekatan yang lebih asas telah diambil dalam kajian terhadap ns-CN_x:H. Filem-filem ns-CN_x:H yang belum pernah dikaji ini telah di perolehi pada suhu pemendapan yang rendah tanpa menggunakan pemangkin logam atau templit dan boleh dimendap secara terus di atas substrak silikon dan kuarza yang terdedah. Kajian terhadap filem-filem ns-CN_x:H ini adalah tertumpu kepada pembentukan filem rod-nano CN_x:H yang tegak menjajar serta mekanisma pertumbuhannya. Parameter optima bagi menghasilkan rod-nano ini adalah K_{rf} bernilai 80 W dan nisbah N_2:CH_4 bernilai 0.70. Ini sejajar dengan kandungan maksima N dan kecenderungan ikatan isonitrile yang terikat kepada lingkaran aromatic yang terpencil dan/atau terpadu didalam filem tersebut. Rod nano ini terdiri daripada kelompok C sp^2 nano-grafitik yang terbenam didalam matrik amorfus karbon-nitrogen yang mengelilingi, mengkapsul dan mengikat kelompok-kelompok ini bersama. Mekanisma pertumbuhan rod-nano yang tegak menjajar ini dicadangkan.

Dalam kajian pengoptimaan kedua-dua bahan ini, satu kesimpulan yang menarik didedahkan. Parameter pemendapan optima bagi ciri-ciri unik kedua-dua struktur filem ini adalah sama. Perbezaan jarak antara elektrod pada nilai-nilai optimum P_{rf} dan nisbah N_2:CH_4 tersebut yang mendorong pemendapan filem yand jelas perbezaan strukturnya.

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LIST OF PUBLICATIONS

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Chapter 6: Section 6.4 and 6.5

1. **Catalyst-free formation of vertically-aligned carbon nanorods as induced by nitrogen incorporation**
   Carbon, Volume 49, Issue 6, Pages 1842-1848, May 2011
   Ritikos, R., Rahman, S.A., Gani, S.M.A., Muhamad, M.R., Yap, Y.K.
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Chapter 5: Section 5.4

2. **Effect of annealing on the optical and chemical bonding properties of hydrogenated amorphous carbon and hydrogenated amorphous carbon nitride thin films**
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Chapter 5: Section 5.3

3. **Influence of Nitrogen/Methane ratio on the properties of hydrogenated amorphous carbon nitride deposited by r.f. PECVD technique**
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Chapter 4

1 **Transformation of carbon nitride thin films into vertically-aligned nanorods**
   Ritikos, R., Rahman, S.A., Gani, S.M.A., Muhamad, M.R., Yap Y.K.,
   To be submitted to *Acta Materialia* for reviewing
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Chapter 6: Section 6.3

2 **Influence of Nitrogen Incorporation for the Catalyst-free Synthesis of Vertically-aligned Nitrogen Doped Carbon Nanostructures** (unedited title)
   Richard Ritikos, Yoke Khin Yap, Muhamad Rasat Muhamad, Siti Meriam Ab. Gani and Saadah Abdul Rahman
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On different gas (ethane and nitrogen) mixture as precursors

3 **Effects of N_2 flow-rate on the properties of CN_x thin films prepared by rf PECVD from ethane and nitrogen**
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Paper in writing

On aspects of applications

4 **Effects of thermal annealing on the properties of highly reflective nc-Si:H/a-CN_x:H multilayered films prepared by r. f. PECVD technique**
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