

DOPING AND ANNEALING AMORPHOUS CARBON FILMS FOR ELECTRONIC APPLICATIONS

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INTRODUCTION

Amorphous carbon (a-C) or diamond-like carbon (DLC) thin films may contain differing ratios of tetrahedral sp^3 , trigonal sp^2 , and linear sp^1 hybridized bonds [1]. This is in contrast to other Group IV amorphous materials, such as silicon and germanium, which can only hybridize tetrahedrally. Consequently, the electronic and mechanical properties of the films can be tuned; in a sense drawing from the often contrasting but appealing properties of diamond and graphite. Much of the work to date has focused on developing, improving and understanding a host of deposition techniques [2], but the results to date have not been encouraging from the point-of-view of creating a high quality electronic device material.

This is primarily caused by the high density of defect states in the band-gap; a somewhat surprising outcome given that the three possible bonding configurations should help reduce co-ordination defects or dangling bonds in the structure, and improve the semiconducting properties of the material.

One approach to reduce these defects is to produce hydrogenated variants (a-C:H) in which the dangling bonds are terminated by hydrogen [3]. However, compared to the success this technique has had with a-Si [4], intra-gap defects have still remained at unacceptably high levels in carbon-based films.

If high quality, low defect a-C films can be produced, there is an opportunity for electronic doping of the material and creating useful working devices [5]. Interestingly, indications are that nitrogen doping of a-C and a-C:H (giving a-C:H:N) has been relatively successful, and that the incorporation of nitrogen further reduces the number of defects and produces a material close to that sought.

Hence, work has begun to look at improving the quality of deposited a-C:H:N films and further enhancing their electronic properties by post-annealing for short times at moderate temperatures.

EXPERIMENTAL

A series of a-C:H:N films with different nitrogen contents have been produced by magnetically confined radio-frequency plasma enhanced chemical vapour deposition (rf-PECVD), and characterised by a variety of different techniques [5]. As with most samples produced by investigators using PECVD, a water-cooled substrate table was used to ensure the temperature at the surface of the films did not exceed $\sim 50^\circ\text{C}$.

Films grown on quartz substrates were then post-annealed under nitrogen ambients using 4- and 8-lamp rapid thermal annealers for relatively short durations. The temperatures chosen were moderate to minimise graphitisation of the carbon film as well as adsorption of H; but, so that localised re-arrangement of the metastable structure may be promoted. The chosen annealing stages for the preliminary study are outlined below in Table 1.

sample set 1:

Stage	Temperature	Time
1	as-deposited	-
2	100°C	300 s
3	250°C	300 s
4	400°C	300 s

Table 1 - details of the annealing stages for various a-C:H:N samples.

At each stage the films were analysed by optical absorption spectroscopy to determine their optical band-gap. The variation in the optical band-gap with annealing temperature, and that obtained by other investigators have also been compared.

RESULTS AND DISCUSSION

The optical absorption for an a-C:H film and an a-C:H:N film after each of the numbered annealing stages in Table 1 is shown in Figure 1. Of particular interest is the fact that both films showed a slight but definite

increase in the optical band-gap after the first anneal (compare the energy of each plot at 10000 cm^{-1} , for example, which gives the E_{04} optical band-gap). This effect appeared to occur regardless of the presence of nitrogen in the films and work continues to investigate if the nitrogen concentration plays a more significant rôle in the microstructure of a-C.

The optical absorption of a series of films of different nitrogen concentration after annealing stages 3 (part a) and 4 (part b) is shown in Figure 2. In the former, the nitrogen-free film (1) retained a higher E_{04} value than those containing nitrogen (the three lines labelled '2' were with 4, 7, and 14 at. % N). This indicates that the nitrogen containing films were initially more sensitive to annealing. Figure 2b shows a further closure of the optical band-gap after annealing at 400°C . The films 1-4 contained 0, 4, 7, and 14 at. % N respectively.

CONCLUSION

Short-term annealing at moderate temperatures has resulted in a small but significant increase in the measured optical band-gaps of the a-C:H:N films. This indicates that there is scope to improve the quality of a-C:X films with post-deposition treatments; to date investigators have more usually concentrated on the deposition parameters. Previous annealing experiments by others have usually comprised of more severe long-

term baking of samples resulting in the graphitisation of the films [6] and the closure of the optical band-gap. Work continues to explore these possibilities, and try to gain more insight into the behaviour with regards to film-composition. In-situ analytical heating experiments are planned to further broaden the understanding of the microstructural modifications of the thin films.

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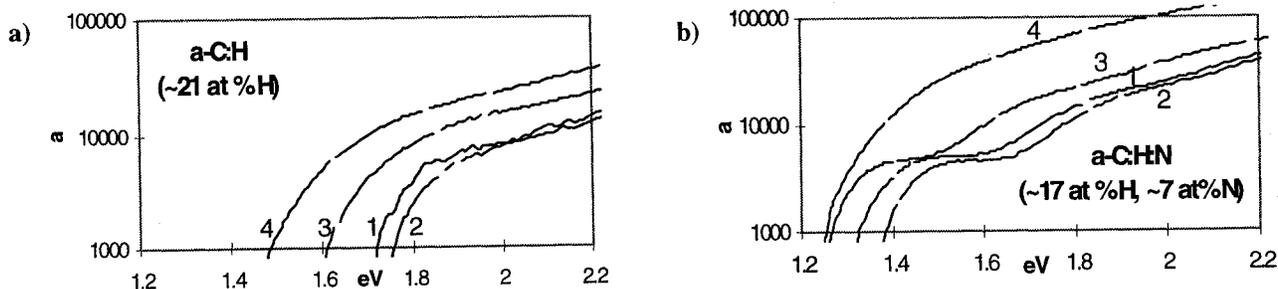


Figure 1 - a-C:H (a) and a-C:H:N (b) optical absorption spectra after the annealing stages (1-4) described in table 1.

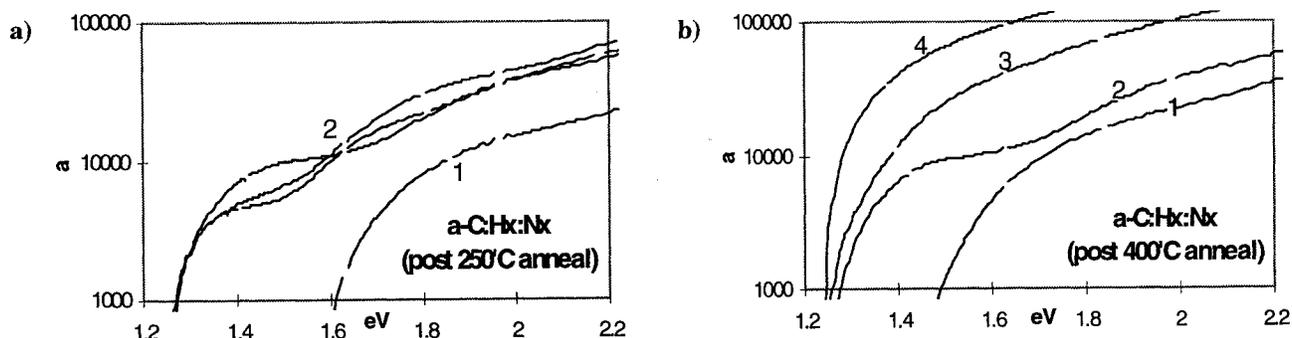


Figure 2 - a-C:H:N optical absorption spectra (a) after annealing stage 3 for a-C:H (line 1) and a-C:H:N (lines in group 2), and (b) after annealing stage 4 for a-C:H (line 1), and a-C:H:N with ~4 (line 2), ~7 (line 3) and ~14 (line 4) at % N.