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FIELD EMISSION STUDIES OF NITROGEN-DOPED DIAMOND-LIKE CARBON FILMS DEPOSITED USING $CH_4/N_2/Ne$ AND $CH_4/NH_3/Ne$ RF PLASMAS

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Hydrogenated diamond-like Carbon (DLC) films have been deposited on Si substrates using CH_4-based radio-frequency plasmas. The films have been doped with nitrogen by addition of either N_2 or NH_3 into the source gas mixture, producing films with up to 16% and 25% N content, respectively. The effect of additions of Ne to these gas mixtures has been investigated as a possible method to increase the growth rate and the N-content of the films. We find that addition of Ne increases the film growth rate until the Ne flow rate equals that of the CH_4, giving maximum growth rate increases of 70% and 200% for NH_3 and N_2 containing gas mixtures, respectively. At the same time the field emission threshold voltage decreases by a factor of ~ 0.5 and 2, respectively. With further increases in Ne flow rate, the film growth rates decrease in both cases, whilst the threshold voltage increases. Micro-combustion measurements show that the N content within the films is proportional to the percentage of the N-containing precursor in the gas phase, but is independent of Ne concentration.

1 Introduction

Diamond-like carbon (DLC) has been suggested as a possible cathode material for use in field emission displays (FEDs) and devices because of its low surface work function, low temperature deposition, and compatibility with existing micro-electronic processing technology [1]. However, in order to obtain optimum electron current at minimum applied electric field, without surface damage [2], it is necessary to dope the DLC film using suitable p- or n-type dopants [3]. Incorporation of nitrogen into some DLC films has been reported to greatly enhance both its conductivity and its electronic performance [4,5]. As a result, there have been a number of recent reports [6-8] describing attempts to N-dope DLC by additions of nitrogen-containing gases (such as N_2, NH_3 and CH_3NH_2) into the process gas mixture. Films produced in this manner can have up to 40% nitrogen content, whilst others have been reported to have field emission threshold onsets as low as 4 V μm^{-1}. Ideally, on cost and safety grounds, one would like to use N_2 as the nitrogen dopant source. However, the stability of the N_2 bond means that it proves difficult to dissociate by low power plasma methods and the nitrogen often incorporates into the DLC film in an electronically inactive form, probably as N_2 species, rather than as N atoms. However, a recent paper [9] has shown that the addition of Ne to nitrogen ECR plasmas enhances the production rate of atomic nitrogen. The authors of this paper suggested that, due to a coincidental resonance between an energy level in Ne and one in N_2, Penning ionisation of the Ne aided the decomposition of N_2 into N atoms resulting in a 4-fold increase in N^+ in the plasma. In the present paper, we aim to see if this effect can be utilised to increase the N-doping level of DLC films produced from N-containing gas mixtures upon adding Ne. To do so, we investigate the effect upon the observed growth rate, N content and field emission characteristics of films grown both with N_2/CH_4 and NH_3/CH_4 source gas mixtures with varying amounts of Ne added to the feedstock.

2 Experimental

The DLC films were deposited using a 13.56 MHz capacitively-coupled radio frequency (RF) parallel plate plasma reactor. Gases (CH$_4$, Ne and N$_2$ or NH$_3$) were metered into the chamber using mass flow controllers at a process pressure of 60 mTorr. The flow of CH$_4$ remained constant at either 5 or 10 sccm, whilst that for Ne and the N-containing gases were varied between 0-65 sccm. An applied RF power of 40~100 W produced a DC self-bias on the powered electrode of –50 V (CH$_4$/N$_2$ or NH$_3$) or –150 V(CH$_4$/Ne/N$_2$ or NH$_3$), which was kept constant during the period of the deposition. The substrate was mirror-polished 1 cm^2 single crystal Si (100), cleaned prior to deposition using isopropanol. Depending upon the exact conditions, a deposition time of 90 mins resulted in DLC films between 100 nm and 2 μm thick, as determined by cross-sectional scanning electron microscopy (SEM).

Film composition was determined by microcombustion, giving the percentage N, C and H in the film to an accuracy of ~1 wt%. Field emission testing was performed in a high vacuum chamber (working pressure 10^{-7} Torr) comprising a moveable grounded substrate holder situated beneath a copper anode. The sample was attached to the holder using conducting paint (front contact), and positioned a few tens of μm beneath the anode using a micrometer *z*-drive feedthrough. The anode voltage was ramped from 0-2.5 kV using a computer, and the emission current from the surface of the film was collected and measured using a picoammeter. Care was taken to ensure that the voltage and current density did not exceed a value which might cause damage to the film surface [2]. The films often required a number of voltage ramps to 'condition' or 'activate' [10] the film surface, after which subsequent current/voltage (*I-V*) curves became stable and reproducible. Over 20 *I-V* curves were taken from the same emission site, at different positions on the same sample, and at substrate-anode separations of 20, 40 and 60 μm. The data were then averaged to obtain a value for the threshold voltage for each film, defined as the minimum voltage required to produce an emission current of 10 nA (equivalent to ~5 μA cm^{-2}). Because the various plasma parameters are all interconnected, varying one parameter (say Ne content) can affect many other features of the deposition process. The most important of these is the growth rate, since field emission properties are known to depend upon film thickness. Previous work in our laboratory showed that for front-contacted DLC films there is a linear relationship between the film thickness and the field emission threshold values. Therefore, a simple method to correct for the effects of variations in film thickness is to normalise the threshold voltage values by dividing by the measured film thickness.

3 Results

The N-doped films deposited at high DC bias values were uniform in thickness, smooth on a nm scale, and often exhibited a variety of colours depending upon their thickness. They were hard (could not be scratched with steel tweezers), but were softer in comparison to undoped films previously grown with pure CH$_4$. Some of them, particularly those deposited at high DC bias values sometimes cracked or delaminated due to internal stresses. In general, we found that N$_2$-derived films were harder than NH$_3$-derived films.

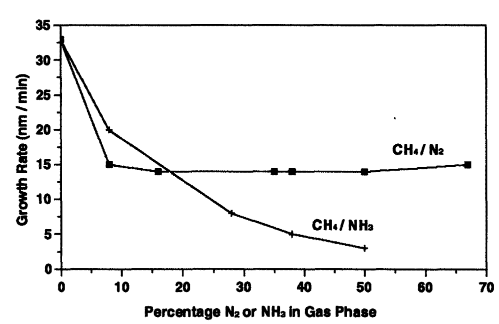


Figure 1. Growth rate of DLC films as a function of the percentage of nitrogen dopant source in the gas mixture of N_2 and NH_3 added to a constant 5 sccm of CH_4. Conditions were: DC Bias = -50 V, RF power = 70-100 W, growth time = 30 mins, pressure = 60 mTorr.

We shall first present data for CH_4/N_2 and CH_4/NH_3 gas mixtures in the absence of Ne. Figure 1 shows the growth rates of various DLC films as a function of different N_2 or NH_3 proportions in the gas mixture, with the methane flow being held constant. For both gases there is an initial decrease in growth rate as NH_3 or N_2 is added. For NH_3 additions, the decrease continues smoothly, but for N_2 additions the growth rate flattens out after a value of ~10% and further N_2 additions make no difference to the growth rate.

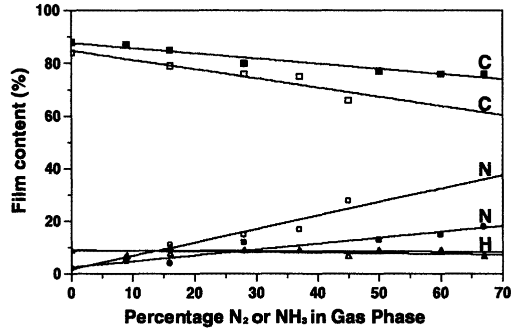
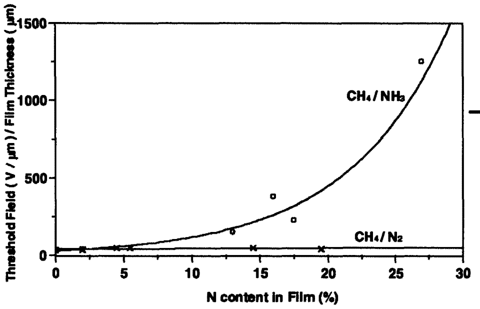


Figure 2. Composition of DLC films deposited using different amounts of N_2 and NH_3 added to a constant 5 sccm of CH_4. Conditions are as given in Fig.1. CH_4/N_2 (filled symbols): □=C, □=N, □=H; CH_4/NH_3 (open symbols): □=C, O =N, Δ=H.

In Figure 2 is shown the compositions of various DLC films grown with different N_2 or NH_3 proportions in the gas mixture. As the amount of N_2 increases from 0-70%, the amount of N incorporated into the film increases slowly and linearly, from 0-18% (±1%), with corresponding decreases in H and C. NH_3 additions follow a similar trend, except that the N incorporation is roughly double that seen for N_2, giving a maximum value of 27% for 45% NH_3 in the gas phase (the highest value we used). It is clear that NH_3 is more effective than N_2 as a source of N incorporation in films.



CH$_4$/NH$_3$		CH$_4$/N$_2$	
N content (%)	thickness (nm)	N content (%)	thickness (nm)
1.6	980	1.6	980
12.4	588	5.2	460
14.6	255	4.2	420
16.1	193	9.6	719
25.5	82	13.5	410
		14.9	603
		19.7	490

Figure 3. Average electron emission threshold voltages (for 10 nA current) for DLC films as a function of N content, produced using N$_2$ or NH$_3$ additions. Conditions are as in Fig.1. The threshold fields have been normalised by dividing the field by the film thickness, and the film thicknesses are shown in the table on the right.

Figure 3 shows the average field emission threshold voltages (scaled for film thickness) with varying N content in the DLC films. It is seen that addition of N$_2$ into the gas mixture has very little effect upon the threshold field over the range measured, with it remaining constant at ~40 V µm^{-1}, whereas addition of NH$_3$ increases the threshold field considerably. This suggests that when using N$_2$ the nitrogen is incorporated into the film in an inactive form, such as N$_2$ units, which do not alter the electronic properties significantly. However, NH$_3$ does appear to allow N to be incorporated in an electronically active form, but unfortunately it worsens the field emission properties rather than enhances them. This is in contrast to previous reports which showed that nitrogenated DLC films have improved emission characteristics [6]. This discrepancy may be due to variations in film properties (thickness, compositions, ratio of sp^2/sp^3 carbon, *etc*) derived from very different deposition methods. Our study also suggests that the field emission properties cannot be accounted for by the N contribution alone, and highlights the need for thickness normalisation to ensure that the true effects of doping are being observed.

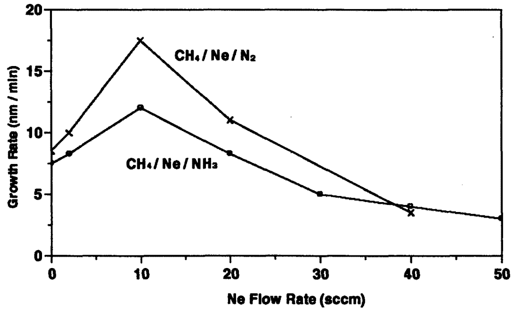


Figure 4. Growth rate of DLC films as a function of Ne addition to CH$_4$/N$_2$ and CH$_4$/NH$_3$ plasmas. DC bias = -150 V, RF power = 40-100 W, time = 90 mins, pressure = 60 mTorr, gas flow rates: CH$_4$ = 10 sccm, N$_2$ = 5 sccm, NH$_3$ = 1 sccm.

Figure 4 shows that for both N$_2$ and NH$_3$ containing process gas mixtures, the growth rate increases with Ne addition until the flow of Ne equals that of CH$_4$. In the case of CH$_4$/N$_2$ plasmas this enhancement in growth rate is almost a factor of two. One explanation could be that the electropositive Ne is supplying extra electrons to the plasma, thus stabilising the discharge allowing greater ionisation and fragmentation of species. Alternatively, it could be a result of increased Ne$^+$ ion bombardment onto the film surface. At higher Ne flows, the growth rate decreases again, presumably due to progressive dilution of the C/N species within the plasma that are required for deposition, or that the rate of sputtering by Ne^+ ions begins to exceed that of deposition.

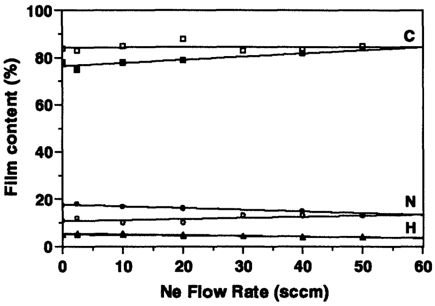
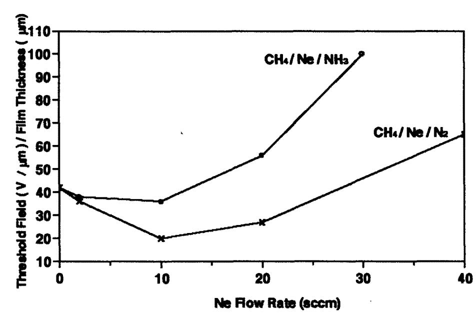


Figure 5. Film composition as a function of Ne addition for $CH_4/Ne/N_2$ and $CH_4/Ne/NH_3$ plasmas, conditions as in Fig.4. $CH_4/Ne/N_2$ (filled symbols): □=C, □=N, □=H; $CH_4/Ne/NH_3$ (open symbols): □=C, O =N, Δ=H.

Figure 5 shows how the composition of the films varies with Ne addition. It can be seen that in both cases the Ne has very little effect upon the N-content of the films. For all Ne flows, the composition remains roughly constant at ~84% carbon, ~5% hydrogen and ~11% nitrogen. This shows that for our system the Ne is not aiding nitrogen incorporation, and is therefore not helping in the dissociation of N_2 (or NH_3), in contrast to the findings of Fan and Newman [9]. This may be because we were using an RF plasma system rather than an ECR system. Perhaps in our lower power RF system, the resonance between an excited state of Ne and a state in N_2 works less efficiently. Also, our 3 gas mixture system ($CH_4/Ne/N_2$ or $CH_4/Ne/NH_3$) is considerably more complex than that used in Ref.[9], and this may be another factor that decreases the efficiency of the Ne-to-N_2 energy transfer.



$CH_4/NH_3/Ne$		$CH_4/N_2/Ne$	
Ne flow (sccm)	thickness (nm)	Ne flow (sccm)	thickness (nm)
2	784	0	794
10	1079	2	882
20	762	10	1590
30	444	20	948
		40	295

Figure 6. Average electron emission threshold fields (at 10 nA) versus Ne flow rate for $CH_4/Ne/N_2$ and $CH_4/Ne/NH_3$ plasmas, conditions as in Fig.4. The threshold fields have been normalised by dividing the field by the film thickness which are given in the table on the right.

Figure 6 shows how the average threshold fields vary with Ne addition for the two different gas mixtures. Here we see a similarity between the behaviour of these two systems, in that an initial decrease in threshold fields is observed as the flow rate of Ne increases, with a minimum occurring when the Ne flow rate equals that of CH_4. With further increases in Ne flow, however, the threshold voltages rapidly increase. Compared to the threshold field values for N_2-derived and NH_3-derived films (Fig.3), the films grown using Ne show lower voltage thresholds. It can also be seen from Fig.6 that the improvement in threshold voltage is greatest for the N_2-derived films, which is consistent with the observations of the enhanced growth rate in Fig.4. Since the C, N and H contents in the films from these two systems are similar, there must be other reasons to account for the variation in threshold voltage with Ne flow. One possible explanation could be structural modification of the DLC film by ion bombardment from energetic Ne^+ ions. This might be beneficial up to a certain flow rate but, thereafter, the increasing amount of sputtering that would hinder deposition may amorphise the film structure so worsening the electron transport properties.

4 Conclusions

For films deposited in our RF parallel plate reactor without Ne present, it appears that NH_3 is a more efficient precursor gas for incorporation of N into the DLC films than N_2. Also, with NH_3 the nitrogen becomes incorporated in an electronically active form, which actually worsens the field emission properties of the film. This is in contrast to N_2, which appears to incorporate nitrogen in an inactive form which does not affect the field emission properties. These observations are consistent with the idea that use of NH_3 incorporates nitrogen as atomic N or NH, whereas molecular N_2 is incorporated as N_2. For films deposited with Ne additions, we find that Ne increased the deposition rate by a factor of up to 2, and decreased the threshold voltage by a similar factor, so long as the flow of Ne did not exceed that of CH_4. However, Ne had very little effect upon the film composition, and did not significantly improve the nitrogen doping concentration. This suggests that the enhancement of N atom production rate observed for Ne additions in ECR plasmas offers only limited benefits in RF plasmas used for DLC growth. The effects of the addition of Ne upon growth rate and field emission probably reflect the stabilising effect of the Ne upon the discharge and increased ion bombardment of the film surface.

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