

Preparation of CNSi_x using a RF hollow cathode

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Abstract

During the last few years a large number of methods have been attempted to produce C_3N_4 films. Many of these have involved the use of ion bombardment, silicon substrates and, through the use of CH_x precursors, significant concentrations of atomic hydrogen. Under these conditions it is well known that silicon can be etched from the substrate, enter the gas phase and be incorporated in the growing film, indeed such effects have been reported by a variety of groups. There is at least one report of the formation of CNSi crystals with silicon concentrations up to $\sim 10\%$, with the indication that the presence of silicon may help to stabilise the beta structure.

In this work we report the preparation of deposits of CNSi_x using RF chemical vapour deposition (CVD) in a graphite hollow cathode. The concentration of silicon incorporated in the deposit was controlled, primarily, by varying the amount of silicon exposed to the plasma inside the hollow cathode. The experimental conditions used are similar to those used previously to prepare C_3N_4 deposits. However, in this case substrates other than silicon were used to avoid additional inclusion of this element from the substrate. The films were analysed using energy dispersion spectroscopy (EDS), X-ray diffraction, scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. The variation of the film properties as a function of the experimental parameters, such as plasma power, substrate temperature, exposed area of the silicon source material and methane concentration in the gas mixture, is described. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

During the last decade carbon nitride films have been an active area of research due to the theoretical predictions of the extreme properties of crystalline C_3N_4 [1]. Although there are several reports [2–4] of samples prepared with a composition equal or close to a C/N ratio of 0.75, there have been very few convincing reports of the formation of a crystalline deposit with C_3N_4 composition. A number of the articles reporting crystal formation have involved the use of silicon substrates under conditions where it might be expected that the silicon would be sputtered or eroded and re-incorporated in the deposit [5]. In fact, at least one study reported that a crystalline deposit could be formed on silicon, or other neighbouring non-silicon substrates,

if silicon was present, but not without the silicon [6]. Similarly, it has been reported that the CN deposit formed on silicon can contain between 5 and 10% silicon, with this element substituting carbon in the formed compound, resulting in $(\text{C}_x\text{Si}_{1-x})_3\text{N}_4$.

Along the same lines recently there has been interest in SiCN materials because they display some new characteristics distinct from crystallised mixtures of Si_3N_4 –SiC [7–9]. Most of this work has involved high silicon contents, but several papers concerning the microstructure of ultrafine particles, or deposits, suggest that the characteristics of the materials are related to the more complicated Si, C and N atomic chemical arrangements found, in contrast to the case of mixtures of pure Si_3N_4 –SiC phases [9–12].

In this work we have attempted to study the formation of carbon nitride deposits with silicon elemental concentrations in the range 0 to 25%, under conditions which had been found to produce crystalline C_3N_4 within a carbon-rich amorphous matrix.

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2. Experiment

The hollow cathode apparatus has been described in detail elsewhere [2], but consists of a water-cooled copper block containing the graphite hollow cathode, internal diameter 0.8 cm and length 5 cm, connected to a 1 kW RF power supply. This block is mounted on a water-cooled flange so that the generated plasma flows directly onto the substrates mounted on the heater, 2.0 cm below the open end of the cathode. A graphite end block with a 0.3 cm aperture was mounted in the flange. Optical emission spectroscopy (OES) measurements showed that this block appears to act as an electron mirror, generating a higher density plasma within the cathode; the nitrogen emission peak intensities are significantly increased with the end block. The experimental conditions used in this study were similar to those found earlier to produce the highest average nitrogen content CN deposits: 400–600 W RF power, 30 sccm N_2 (99.999% purity), 0.3–1.2 sccm CH_4 (99.999% purity), pressure 5 Torr (our earlier work was performed at 0.5 Torr but improvements in the cathode permitted higher pressures) and substrate temperatures from 600 to 1100°C. The substrate temperature was determined by calibrating the substrate holder thermocouple, and the heater current values, using a thermocouple placed on top of a molybdenum substrate under the experimental conditions but without plasma. Similar temperature measurements were also made immediately after switching off the plasma, and indicated that plasma heating raised the substrate temperature by approximately 150°C. Molybdenum rather than silicon substrates, 1 cm × 1 cm × 0.03 cm, were used throughout, so that the silicon content of the deposits could be determined. Samples were prepared without silicon, with a 0.3 cm wide by 0.8 cm long piece of silicon wafer inserted in the hole in the end block, and with an additional 0.8 cm wide by 2.0 cm long piece of silicon placed within the hollow cathode. For each case deposits were prepared as a function of the RF power, substrate temperature and methane content in the gas mixture.

The samples were analysed using a Nicolet 510P Fourier transform infrared (FTIR) spectrophotometer using a diffuse reflectometry accessory, a Siemens D500 X-ray powder diffractometer using Cu $K\alpha$ radiation and a Leica-Cambridge Stereoscan 440 scanning electron microscope equipped with an energy dispersive X-ray analyser for the elemental composition measurements. The energy dispersion spectroscopy (EDS) analysis was calibrated using NaCN and melamine ($C_3N_6H_6$).

The optical plasma studies were performed using a Hamamatsu R955 photomultiplier tube mounted on a 0.5 m Acton Research SpectraPro-500, equipped with a 1200 grooves/mm grating blazed at 500 nm, plus the associated computer interface, software and mercury calibration light source. A 3 m long by 0.2 cm silica

fibre bundle and quartz lens system was used to collect the light from the plasma, with observation being through a quartz window on the reaction chamber.

3. Results

Various peaks between 350 nm and 420 nm from the second positive series of neutral molecular nitrogen could be clearly seen in the optical emission spectrum taken with silicon in the hollow cathode, and fairly strong peaks at 707 and 715 nm from atomic nitrogen [13,14]. The 388.3 and 421.6 nm bands of the CN violet system were also clearly observed, the former being much more developed. The two strongest atomic hydrogen peaks at 656 and 486 nm were discernible as small peaks, and various peaks associated with molecular hydrogen could be seen in the spectra. Small peaks were observed at 470, 518, 562 and 644 nm, which may be from the C_2 molecule. Similarly, we could tentatively identify peaks due to Si at 730 and 743 nm as well as the formation of SiH_2 at 554 and 580 nm [13]. All the peak intensities increased almost linearly with the plasma power. Fig. 1 shows the variation of the normalised intensities of the N_2 , N, CN, H_2 , H, C_2 , SiH_2 and Si peaks as a function of the percentage of methane in the gas mixture. The atomic nitrogen, SiH_2 and Si signals all decrease in a similar manner with increasing CH_4 %, but the CN, H_2 and C_2 signals increase to a maximum at 4% CH_4 and decrease for high concentrations. The atomic hydrogen signal rapidly increases to a saturation level at a CH_4 concentration of 1% and the SiC and N_2 signals show a mutually inverse relation with the methane content. Although this latter observation implies that there is a common process between these three components of the plasma, further studies are required to clarify the details.

The IR reflection spectra of samples with different

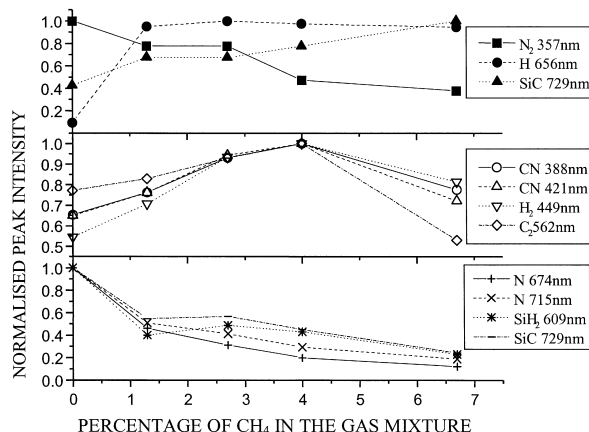


Fig. 1. The variation of the normalised intensities of the emission from N_2 , N, CN, H_2 , H, C_2 , SiH_2 and Si as a function of the methane gas percentage, using 400 W and 5 Torr.

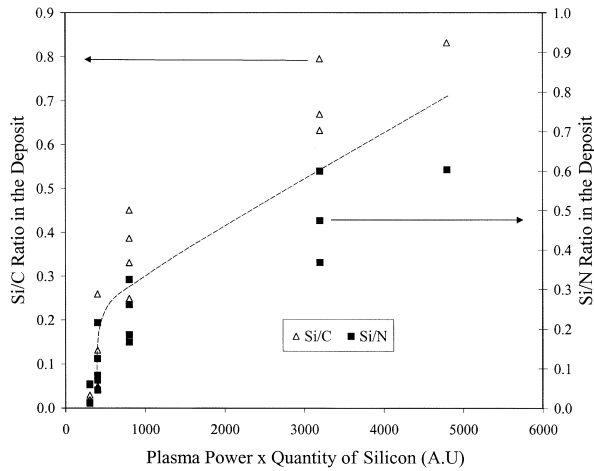


Fig. 2. The variation of the Si/C and Si/N ratios as a function of a combination of the plasma power and the area of silicon exposed to the plasma. The line is included as a guide to the eye.

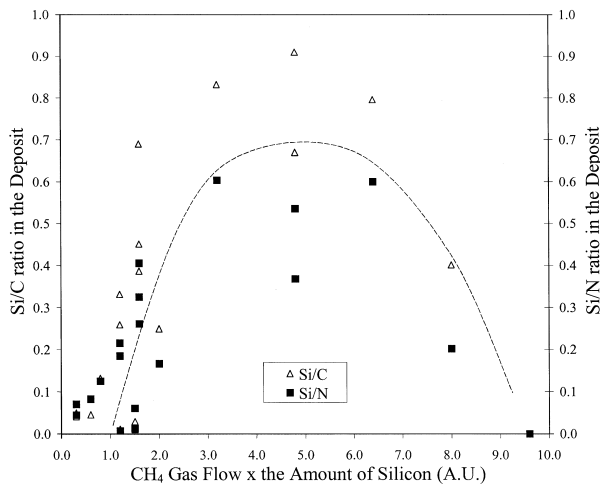


Fig. 3. The variation of the Si/C and Si/N ratios as a function of a combination of the methane flow and the area of silicon exposed to the plasma. The line is included as a guide to the eye.

compositions were similar, with major absorption peaks at around 700 cm^{-1} (graphite+N), 800 cm^{-1} (Si–N or $\text{C}\equiv\text{N}$), 1150 cm^{-1} (C–N), 1580 cm^{-1} (G peak of graphite or $\text{C}=\text{N}$) and 2200 cm^{-1} ($\text{C}\equiv\text{N}$), together with a broad band from 3000 to 3500 cm^{-1} (N–H and/or O–H). However, the samples with the highest silicon content showed more intense absorption in the region 800 – 1000 cm^{-1} and a small peak at $\sim 570\text{ cm}^{-1}$, both of which are indications of the formation of Si–N bonds.

Figs. 2–4 show the results of the compositional analysis, presented as the ratios of Si/C, Si/N and C/N, as a function of the product of the plasma power and the area of silicon, the product of the methane flow and the area of silicon used, and the measured silicon content of the deposit, respectively. The Si/C and Si/N ratios are small for both low methane gas flows and a combina-

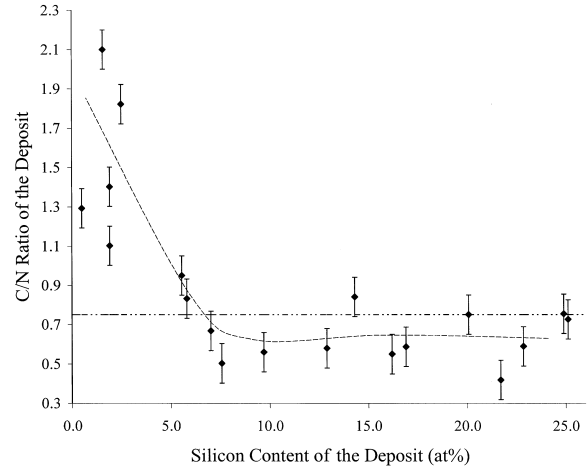


Fig. 4. The variation of the C/N ratio of the deposit with the measured silicon content. Lines are included as a guide to the eye and to indicate the value, 0.75, expected for C_3N_4 .

tion of high gas flow and large amounts of silicon in the cathode, with a clear maximum in the ratios for the middle range of the combination of gas flows and exposed silicon. The same ratios increase as the combination of plasma power and exposed silicon increases, with this increase being more rapid initially. The last figure probably represents the most important observation of this study in that it shows that the C/N ratio decreases for small increases in the silicon content of the deposit, and that for silicon concentration greater than 6% the C/N ratio is almost constant and approximately equal to 0.75; the value expected for C_3N_4 .

4. Discussion

Although the intensities of the OES peaks cannot be directly used to quantify the amount of a given species in the plasma, the relative intensities observed under similar experimental conditions do provide an indication of the variation of the abundance of the species. Therefore we can conclude that the efficiency of the sputtering processes, both physical and chemical, that produce the silicon, carbon, CN and nitrogen containing precursor species are directly proportional to the plasma power. However, since the deposition rate does not increase proportionally with the power but appears to saturate at 400 W, the process of growth of the deposit is strongly controlled by nucleation and the relative concentration of the precursors. The growth process can therefore be best described as chemical rather than physical vapour deposition. Although OES data was not taken as a function of the amount of silicon present in the cathode, it can be expected that the silicon signals and therefore the quantity of silicon species produced would increase. This idea, with the results of the variation of the OES signal with the plasma power, is

supported by the results shown in Fig. 2. As the power and the amount of silicon increase, so the concentration of silicon precursors increases and therefore the relative concentration of this element increases in the deposit. The initial increase in the relative silicon content of the deposit as a function of the product of the methane flow and amount of silicon, Fig. 3, can be readily understood as arising from an increase in the amount of silicon precursors in the gas flow. However, the observed maximum signifies that at high CH_4 flows the composition of the precursors changes to inhibit the incorporation of silicon in the deposit. From the OES results shown in Fig. 1 it can be seen that the emissions from the silicon and nitrogen species are fairly constant at the high CH_4 gas flows, but the C_2 and CN signals decrease significantly. This behaviour implies that the source of the carbon for the deposit is either C_2 or CN, and since the intensity of the C_2 OES signal is very small it is probable that the CN molecule is the main precursor.

The IR results indicate that the deposit mainly contains carbon bonded to nitrogen within an amorphous carbon matrix, but that at high silicon concentrations this element probably substitutes the carbon, rather than the nitrogen, in the CN compound.

The results given in Fig. 4 demonstrate that when the silicon content of the deposit is less than $\sim 5\%$ the formation of a carbon-rich deposit is favoured, but for higher Si concentrations the C/N ratio is close to that of C_3N_4 .

5. Conclusions

The presented results show that controllable low levels of additional elements can be introduced into carbon nitride compounds by the insertion of solid pieces of appropriate materials in either the end plug or the hollow cathode of the system. The gas phase precursors are generated by a combination of physical and chemical sputtering in the source. Nevertheless, it can be concluded that the deposit growth process is princi-

pally controlled by the chemical reactions that occur between the vapour precursors in the substrate gas interface. It is probable that the included silicon in the deposit substitutes the carbon atoms in the CN compound and is mainly bonded to the nitrogen. Similarly, the results indicate that the principal precursor for the formation of the carbon nitride deposit is the CN molecule. Finally, we have shown that the incorporation of small amounts of silicon in the carbon nitride deposit promotes the inclusion of nitrogen and leads to a C/N ratio similar to that expected for C_3N_4 .

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