

Deposition of CN_x thin films by plasma-activated chemical vapour deposition using various precursors as carbon source

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CN_x -thin films have been deposited by plasma-activated chemical vapour deposition with capacitively or inductively coupled r.f. plasma. Acetylene, methane, carbon monoxide and tetracyanoethylene have been used as carbon precursor. A strong dependence of the layer properties on the precursor was found. In some films the nitrogen to carbon ratio was close to that of C_3N_4 . The highest nitrogen content was observed in films made from carbon monoxide as precursor in an inductively coupled argon/nitrogen plasma. The nitrogen was mainly incorporated with covalent nitrogen-carbon single bonds. X-ray diffraction measurements showed no reflections indicating crystallinity. In small grains (length $\sim 10 \mu\text{m}$) found on the layer surface the stoichiometry corresponded nearly to that of C_3N_4 , the oxygen content is very low. Further characterizations by TEM are intended.

1. Introduction

Many publications have reported the deposition of CN_x layers in trying to realize $\beta\text{-}C_3N_4$, a material that should have interesting properties such as high hardness, stability and good thermal conductivity [1]. The process used for deposition is mostly a physical vapour deposition (PVD) process. Usually high energetic nitrogen is produced by an ion source and carbon is taken from a target. Some examples are reactive carbon sputtering [2, 3], ion-beam-assisted deposition (IBAD) [4, 5] or laser ablation [6–8]. The deposited layers are amorphous, sometimes containing small crystalline grains and the highest overall nitrogen contents are about 50 at %. The great disadvantages of the PVD processes are well known: high or ultra-high vacuum is necessary which entails high costs, the growth rates are small and it is difficult to deposit on to non-planar formed substrates.

There have also been some attempts using chemical vapour deposition (CVD) techniques: thermal CVD producing soft films [9] and electron cyclotron resonance (ECR)-plasma CVD using methane (CH_4), producing smooth layers with a nitrogen content up to 48 at % [10, 11].

This work studied capacitively and inductively coupled r.f. plasma CVD of CN_x layers using different precursors. Nitrogen and nitrogen/argon mixtures have been activated in a non-thermal low-pressure plasma. As precursors, acetylene (C_2H_2), methane (CH_4), carbon monoxide (CO) and tetracyanoethylene-steam ($\text{C}_2(\text{CN})_4$) have been used. Si (100) wafer pieces served as substrates.

The aim of the investigation was to find a precursor and experimental conditions which lead to the deposition of crystalline stoichiometric C_3N_4 .

2. Experimental procedure

The deposition process was performed in two different 60 mm inner diameter quartz wall reactors with vertical gas flow. For the capacitively coupled plasma discharge, a reactor with water-cooled copper electrodes and an r.f. generator producing 1 kW maximum output power at 13.56 MHz connected via an automatic matchbox, were used. The inductively coupled plasma discharge took place in an electrode-less set-up with a coil with an inductivity of $1.3 \mu\text{H}$, powered by a frequency free-running generator in the 4.5 MHz range, also with 1 kW maximum power output.

The substrate holder was made from stainless steel with 40 mm diameter. A resistance heater was additional, mountable in the inner space of the substrate holder. An additional d.c. bias was realized in some experiments. Therefore, a d.c. power supply with 600 V maximum tension was connected to the substrate holder and a further electrode in the upper part of the reactor.

A two-stage vane pump was applied; the reactor pressure was controlled by an automatically acting motor butterfly valve. For the gas supply, high-purity gas was used. An overview of the experimental apparatus is shown in Fig. 1.

The achievable pressure range is 30–500 Pa; most experiments were carried out at 150 Pa as working pressure. Argon was added to nitrogen varying from 0–90 vol %. Within the adjustment of the precursor flow, a N/C ratio from 8–60 in the gas phase was achieved. In the capacitively coupled plasma, the power densities ranged from $0.5\text{--}2.5 \text{ W cm}^{-3}$, and in the inductively coupled plasma from $2.5\text{--}10 \text{ W cm}^{-3}$. In both cases it is possible to activate the precursor

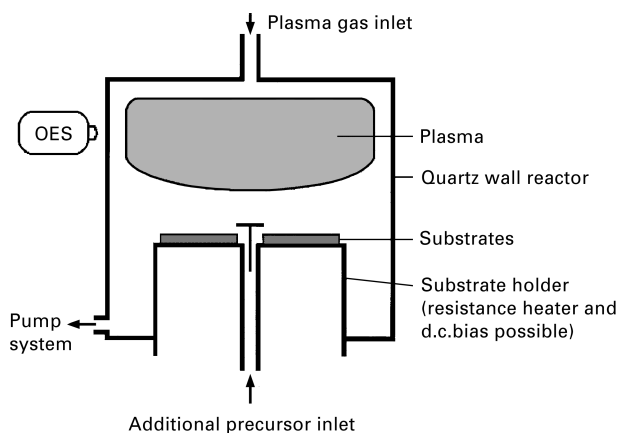


Figure 1 Overview of the experimental apparatus.

together with the nitrogen in the plasma, or to use it without activation through an additional outlet in the bottom of the substrate holder. Typically Si (100) from a commercially available 4 in. (~ 10.2 cm) wafer was used as substrate material, but also Si (111) or metallic substrates were possible. Normally the substrate was only heated by the plasma, so the temperature was between room temperature and 100°C . In some experiments, an external resistance heater was applied that enabled substrate temperatures up to 500°C . Layers with a thickness of $2\text{--}5\ \mu\text{m}$ were achieved, varying the deposition times from 30 min to 2 h, depending on the different deposition rates.

The layers have been investigated by electron probe microanalysis (EPMA with EDX, WDX) for the elemental composition, infrared absorption spectroscopy for the detection of cyano and amine contents, X-ray photoelectron spectroscopy (XPS) for the chemical bond analysis, glow discharge optical emission spectroscopy (GDOES) for the examination of depth profiles, X-ray diffraction (XRD) and transmission electron microscopy (TEM) for crystallinity.

In some preliminary examinations, the best plasma conditions with respect to high nitrogen excitation were sought by the evaluation of optical emission spectra from discharges without carbon precursor gas. A high argon content was found to be good for a high nitrogen excitation. Also the excitation increases with lower pressures in the reactor. A qualitative analysis of excited N_2 states and N_2^+ states showed that in the inductively coupled plasma, the ionization rates are much higher than in the capacitively coupled plasmas.

3. Results

The morphology of the deposited layers was examined first by SEM. The nitrogen and carbon composition and the contents of other elements (oxygen, chlorine, sputtered metals) were determined by EPMA.

The realized nitrogen contents exceed 50 at%. The highest nitrogen contents depending on the various precursors used are shown in Fig. 2. Normally the layers had a homogeneous surface as detected by SEM. Using carbon monoxide as precursor, small grains (size $\sim 10\ \mu\text{m}$) have been observed in some cases (Fig. 3).

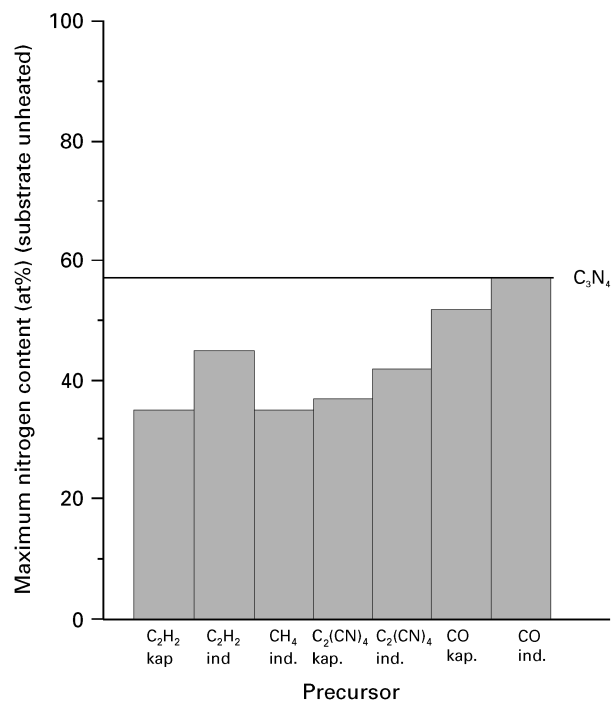


Figure 2 Comparison of the maximum nitrogen contents with an unheated substrate measured by EPMA. Kap: capacity coupled plasma; ind: inductively coupled plasma.



Figure 3 Micrograph of a CN_x layer surface containing small grains.

The homogeneity of the depth profiles of the layers was proved by r.f. glow discharge optical emission spectroscopy (GDOES). These measurements (Fig. 4) indicate a good homogeneity of the layers. The determination of the element composition was not possible because no standards are available for the r.f. GDOES.

Further characterizations are given below for each precursor in detail.

3.1. Acetylene as precursor

The highest nitrogen content achieved was about 35 at%, but the infrared absorption spectroscopy (Fig. 5) showed that much of the nitrogen was incorporated as cyanide. The carbon is typically sp^2 hybridized and also CH- and NH- absorption peaks appeared in the infrared (IR) spectra. Dynamic hardness measurements resulted in values up to $100\ \text{H}_{\text{V}0.5}$ due to soft polymer material.

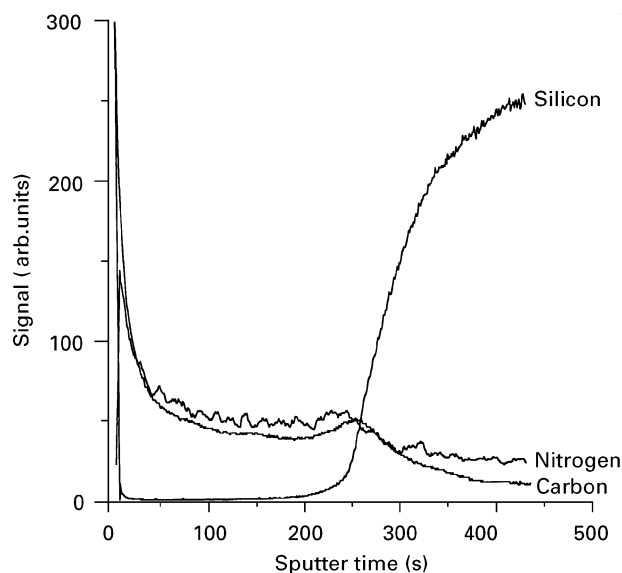


Figure 4 R.f. GDOES (LECO GDS 750) depth profile of a CN_x layer.

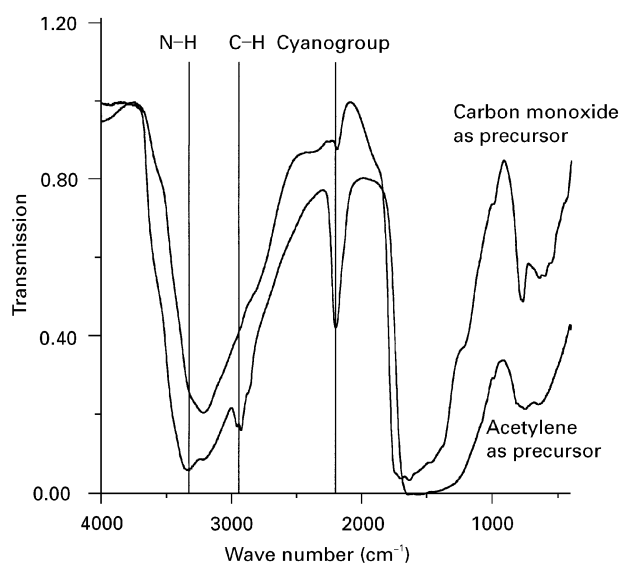


Figure 5 IR transmission spectroscopy measurements of two CN_x layers deposited from different precursors. The resolution was limited by the thermal line width.

To deposit layers at substrate temperatures of 600 K, the positive ions have to be accelerated by a negative substrate bias. The layers obtained were harder (600 $H_{V0.5}$) but the deposition rate decreased and the nitrogen content became lower than 20 at %. In the infrared spectra, fewer CN triple bond absorption peaks appeared, mostly C–C and C–N single- and double-bond absorption peaks being observed.

3.2. Methane as precursor

In the methane molecule, the carbon is sp^3 hybridized, but the H/C atomic ratio is four times higher than in acetylene. The conditions of the deposition of CN_x layers were much more sensitive to the reactor pressure, substrate position and substrate temperature.

The films, deposited at 40 Pa in an 80% Ar and 20% N_2 plasma with 300 W inductively coupled plasma power at room temperature, contained only

35 at % nitrogen and much hydrogen. In the films, the carbon is typically sp^2 bonded, strong CH– and NH–, absorption peaks appeared in the infrared absorption spectra.

When using hydrogen-containing precursors, it seems difficult to suppress hydrogen incorporation without detriment to the layer properties.

3.3. Carbon monoxide as precursor

To avoid the hydrogen incorporation, carbon monoxide (CO) was tested as precursor. An interesting feature of the CO molecule is the nature of the chemical bond: a σ -bond and two π -bonds. The CO molecule is isoelectronic to the nitrogen molecule; the carbon is negatively charged and the oxygen positively charged. This bond character allows a gas phase reaction of a CO molecule with a positive nitrogen ion (atom N^+ or molecule N_2^+). The electrical charge leads to an attractive electrostatic interaction, and this reaction is automatically a three-particle impact, so the momentum and energy conservation can be fulfilled.

The layers deposited with CO as carbon precursor were nitrogen rich; some of the layers had a composition close to that of stoichiometric C_3N_4 . The oxygen content measured by EPMA did not exceed 8 at %. In some small grains shown in the scanning electron micrograph (Fig. 3), the oxygen incorporations measured by the EDX system (Fig. 6) were negligible.

The content of cyanide in the layers detected by IR absorption spectroscopy was small (Fig. 5). No N–H or C–H peaks appear. The analysis of the carbon and nitrogen single and double bonds from the IR spectra was not possible.

In order to obtain more information about the chemical bonds, some layers were also characterized by XPS. The results are shown in Fig. 7a and b. The C 1s core level is in the energy range from 285–290 eV. A fit of four carbon bonds was applied by Marton *et al.* [12] to obtain good agreement between

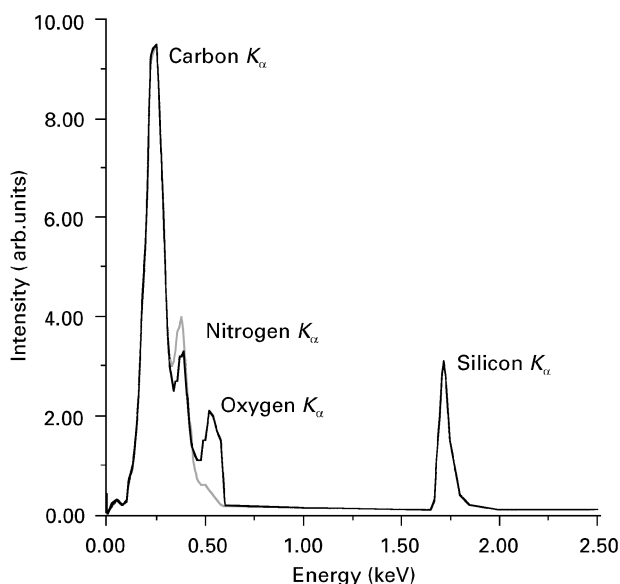


Figure 6 Comparison of the EDX spectra of (—) layer and (---) grains. (EDX spectrometer on Philips XL 30).

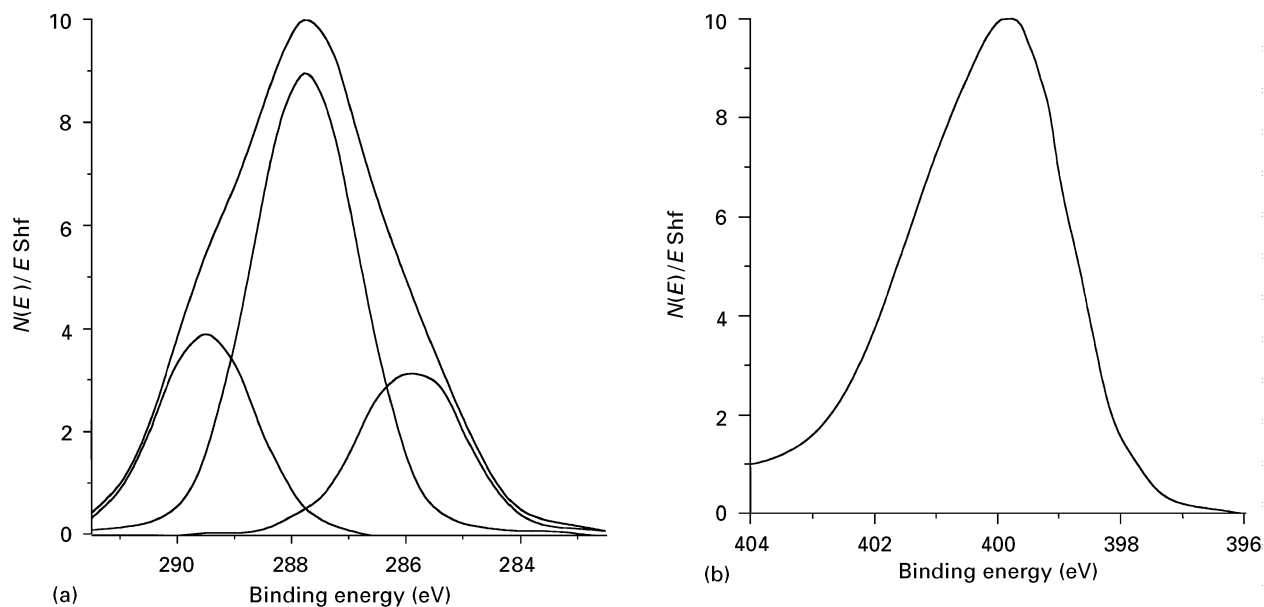


Figure 7 XPS measurements made by a PHI 5600 CI instrument with Mg K_{α} radiation, 12 eV pass energy and an effective energy resolution of 0.8 eV (FWHM); (a) carbon 1s core level and line fit of three gaussian peaks to the measured curve, (b) nitrogen 1s core level. The binding energy values were shifted (shf) to the correct values.

measured and fitted curves. In the layers deposited with CO as carbon source, the peak at 284.6 eV due to C–C bonds was almost undetectable; only two different types of CN single bonds and some CO bonds were found. Most of the CN single bonds appeared at 287.7 eV, which is the C sp^3 type as necessary, for example, for β - C_3N_4 [12, 13], but the C sp^2 type at 285.9 eV was also represented.

The N 1s core level is between 398 eV and 403 eV. For the layers examined, no fit was necessary because only the nitrogen sp^3 level appeared at 400.0 eV, which is not the right nitrogen type for the predicted β - C_3N_4 [12]. A C_3N_4 compound of sp^3 hybridized carbon and nitrogen was also predicted [13]; the calculated material properties are comparable to that of the predicted β - C_3N_4 .

The layers deposited from CO were visually transparent; no delamination was observed. Hardness measurements were not successful because the layers were brittle and crack even at low indenter loads. Neither the XRD nor the TEM revealed crystalline parts in the layers; preparation of one of the small grains for TEM examination has not yet been possible.

3.4. Tetracyanoethylene as precursor

Within the search for a precursor consisting only of nitrogen and carbon, tetracyanoethylene ($C_2(CN)_4$) was tested. Under normal conditions $C_2(CN)_4$ is a solid powder, that sublimates at 272 °C. Under reduced pressure the sublimation temperature is lowered. For the use of tetracyanoethylene, a precursor crucible was mounted into the substrate holder to evaporate the solid precursor. In the pressure range used for the presented experiments, the evaporation temperature was about 100 °C, which was the typical substrate holder temperature, so no external heating was necessary.

The deposited layers were cracked and completely delaminated after only a few hours, so the characterization was quite difficult. The highest nitrogen content was 45 at %, but the IR absorption measurement showed large amounts of cyanide. Supposedly, the cyanogroups from the precursor were not dissociated before the deposition and were therefore incorporated into the layers. The hardness of the layers was not higher than 100 $H_{V0.5}$.

4. Conclusion

As an important result of the plasma-activated CVD investigations it can be concluded that the deposition process, composition and properties of the CN_x layers are considerably influenced by the choice of the precursor, much more than by changes in the plasma conditions. Using favourable precursors (e.g. carbon monoxide) and suitable plasma conditions, it is possible to deposit amorphous CN_x layers with a N/C ratio close to that of C_3N_4 , with only small amounts of other elements. An important fact is the absence of C–C bonds in these layers; this is necessary for the realization of each of the predicted carbon nitrides.

Higher substrate temperatures lead to a strong decrease of the deposition rate, so it is necessary to change the deposition conditions or to use further techniques to obtain suitable growth rates.

Finally, it is interesting to test other possible precursors and to deposit CN_x layers at temperatures at or above 800 K to suppress incorporation of undesired elements and to produce crystalline material. The higher temperature leads to a strong decrease of the deposition rates; the use of further techniques with selected deposition parameters seem to be necessary to obtain suitable growth rates.

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