Process control of CVD deposition of Nanocrystalline diamond films by optical emission spectroscopy

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Abstract: In this work NCD films were deposited in a MW-CVD plasma chamber from an Ar/H₂/CH₄ plasma and the signals of the C₂ dimer in the plasma were analyzed with optical emission spectroscopy (OES) during deposition. By controlling the process parameters the intensity of the C₂ emission line was systematically varied and a correlation of plasma parameters with film properties was found in an empirical way for the given reactor and the chosen conditions.

Keywords: Nanocrystalline diamond films, Optical Emission Spectroscopy

1. Introduction

Diamond grown by chemical vapor deposition (CVD) and other techniques is due to its excellent combination of properties a candidate for a number of applications.

One major problem with the conventional (microcrystalline) diamond films in many applications is their high surface roughness. Also the homogeneous deposition of diamond films on substrates with high aspect ratio is difficult with films consisting of relatively large grains.

By depositing diamond films from Argon rich plasmas it was possible to produce nanocrystalline diamond (NCD) films with grain sizes between approximately 5-100 nm [1] or even below named ultra-nanocrystalline diamond (UNCD). The fact that diamond films could be deposited from plasmas where only small amounts of hydrogen were added and the fact that the strongest visible emission line in the optical spectrum in the NCD growth conditions is the C₂ line lead to a new deposition model with the C₂ dimer as main growth and nucleation species [2, 3]. Although recent paper disagree, doubting that the C₂ molecule is in any way participating in the growth of NCD referring to it as an spectator molecule [4, 5, 6], the role of the dimer is still discussed.

To re-evaluate the role of the C₂ dimer for the given reactor an the chosen growth conditions a correlation was tried to be found between the C₂ emission lines measured by optical emission spectroscopy and the growth rate of the nanocrystalline films. Though the simplicity of OES makes it a popular method for plasma diagnostic, usually the emission intensities alone provide only limited insight into the plasma parameters. The reason for that is that the emission intensity depends strongly on both exitation and nonradiative deexcitation rates as well as radiative decay rates and therefore does not give direct information on ground state species concentrations. But Goyette et al. were able to find a linear correlation between the emission intensities of the C₂ dimer at 515 nm from the microwave plasma with the absolute C₂ concentration in Ar/H₂/CH₄ plasma [7]. These absolute C₂ concentrations were obtained by white-light absorption spectroscopy. The results confirm the reliability of the (0,0) Swan band for relative determination of C₂ density with high sensitivity under conditions used for plasma-enhanced chemical vapour deposition of diamond used for NCD.

The influence of the deposition parameters pressure and gas flow of the process gas was investigated on the C₂ emission line in the plasma. It must be pointed out that the reaction and diffusion rates of H and C₂ are very different, so ratios of emission intensities taken at the plasma centre are not necessarily representing the true concentrations reaching the diamond surface.

In fact, Zhou et al. [8] performed mass spectrometer measurements that showed that most of C₂ were eliminated at the edge of the plasma ball through chemical reaction due to frequent collisions in the high-pressure plasma environment although the C₂ emission dominated the OES spectra.

Nevertheless a correlation of the measured emission lines and process parameters was found.

Residual stress is a critical parameter in thin film deposition and especially important for technical applications of nanocrystalline diamond films like tribological coatings, SAW devices or MEMS. High residual stress can lead to cracking or even to delamination of the film from the substrate.

Residual stress in diamond films results from two effects – a thermal part and an intrinsic part. The thermal part is due to the high deposition temperature of diamond and the different thermal expansion coefficients of diamond and the substrate. The thermal stress is usually compressive for diamond films because typical substrates have higher values of the thermal expansion coefficient. The intrinsic stress is tensile and its origin can be described by the grain boundary relaxation model [9]. A more detailed analysis of the residual stress in NCD films can be found in [10].

Experimental setup

2. Deposition Process

Nanocrystalline diamond films were deposited with a 2.45 GHz IPLAS CYRANNUS® I-6" plasma source. The functional principle of this microwave plasma source is based on a resonator with annular slot antennas [11]. This special setup allows the use of plasma from low pressure (10⁻² mbar) to atmospheric pressure (1 bar) and above.

Mirror polished Si(100) with a thickness of 425 µm was used as substrate. To enhance the nucleation of diamond the substrates were ultrasonically scratched for 30 min with a scratching solution consisting of diamond powder (~ 20 nm grain size), Ti powder (~ 5 nm particle size) and methanol in a weight percent ratio of 1:1:100 (wt%). Af-
terwards the substrates were ultrasonically cleaned for 15 min in Acetone. During deposition the substrates were kept on a molybdenum substrate holder. Prior to the deposition the substrates were etched in a H₂/Ar plasma for 30 min. After this cleaning step the process parameters were switched to the deposition parameters.

The nanocrystalline films shown here were deposited from an Ar/H₂/CH₄ plasma with fixed concentration. To investigate the influence of the process parameters on the possible precursor C₂ the pressure and the gasflow were varied as shown in table 1.

The MW-power was kept constant at 1.5 kW and the films were deposited for 5 h.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>175 mbar – 225 mbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasflow</td>
<td>250 sccm – 1750 sccm</td>
</tr>
<tr>
<td>H₂ fraction</td>
<td>2.5 %</td>
</tr>
<tr>
<td>CH₄ fraction</td>
<td>0.8 %</td>
</tr>
<tr>
<td>Ar fraction</td>
<td>96.7 %</td>
</tr>
<tr>
<td>MW power</td>
<td>1.5 kW</td>
</tr>
<tr>
<td>Deposition time</td>
<td>5 h</td>
</tr>
<tr>
<td>Substrate</td>
<td>15 min scratched silicon(100)</td>
</tr>
</tbody>
</table>

Table 1 Process parameters

The spectrometer was coupled to the process chamber via a glass fibre and the whole system was calibrated as usual with a tungsten strip lamp.

3. Film analysis

All deposited films were investigated by SEM to get information about the morphology and to determine the film thickness by making cross views of the films.

To affirm the nanocrystalline structure of the deposited films all films were characterized by a Jobin Yvon LabRam two wavelength scanning micro Raman spectroscopy. The Raman spectra were obtained in the range of 900-1800 cm⁻¹ with a step size of 1 cm⁻¹. Two laser wavelengths were used with an Ar Laser (λ=514.5 nm) and a HeNe Laser (λ=632.8 nm). The spectra measured are not shown in this publication.

The properties of the matrix of the nanocrystalline films are mainly determined by the sp³/sp² ratio of bonded carbon and the total content of incorporated hydrogen in the film. In comparison to the Raman Spectroscopy which is probing only the C-C bonds in the matrix the IR-Spectroscopy is sensitive for the C-H bonds. The C-H stretching modes around 2800 cm⁻¹ to 3300 cm⁻¹ were investigated to characterize the matrix of the deposited films. The measurements shown in this work were performed with a Bruker FTIR spectrometer EQUINOX® IFS55 that allows to measure spectra between 370 cm⁻¹ and 7500 cm⁻¹.

Stress measurements were performed with a SSID ("Surface Stress Induced Optical Deflection") setup [12]. By measuring the deflecting angle of a laser on a substrate the curvature of a substrate can be measured. With respect to Stony’s equation [Equation 1] one can calculate the residual stress in the film with respect to substrate properties (Elastic modulus E_{sub}, Poisson ratio ν, substrate thickness t_{sub} and to the film thickness t_{film}) [13].

\[
σ = \frac{E_{sub} t_{film}^2}{1 - ν} \left( \frac{t_{sub}}{t_{film}} \right) \left( \frac{1}{R_{post}} - \frac{1}{R_{pre}} \right) \]  

[Equation 1]

For thick films the film bending moment and resultant flexure stress are no longer negligible and the film/substrate structure must be treated as a composite beam as Windischmann and coworkers worked out for diamond films [14].

Because the film thickness investigated in this work is larger than 20 μm for most of the films the Brenner-Stoneroff equation must be used to avoid substantial errors in the calculated stress.

\[
S = S_0 \left( 1 + 4R \frac{t_{film}}{t_{sub}} - \frac{t_{film}}{t_{sub}} \right) \]  

[Equation 2]

where R is the ratio of the film and substrate biaxial moduli (6.08 for polycrystalline diamond on (100) silicon) and S₀ is the stress derived from the Stoney equation.

The residual stress consists of two components: the thermal stress due to the different thermal expansion coefficients of the substrate and the film, and the intrinsic stress. By calculating the thermal stress, one can determine the intrinsic stress by subtracting the calculated thermal stress from the measured residual stress [8] [12] [15].

4. Plasma characterization

Goyette et al. compared the optical emission intensity of the d'III → a'II (0,0) vibrational band of the C₂ system with the absolute C₂ concentration in Ar/H₂/CH₄ plasma used in NCD deposition and found that it correlates linearly for variations of several plasma parameters [7]. A detailed investigation of the plasma processes during nanocrystalline diamond deposition from Ar/H₂/CH₄ can be found in [8]. By investigating the plasma with quadrupole mass spectroscopy and optical emission spectroscopy Zhou et al. were able to find an explanation for CH₄ decomposition in hydrogen-poor plasmas, in these plasmas electron impact seems to be mainly responsible for the CH₄ dissociation other than hydrogen abstraction with atomic hydrogen.

In this work the influence of the process parameters (pressure and gasflow) on the carbon dimer d'III → a'II Swan band emission at 516 nm was systematically investigated. From that a correlation of the C₂ emission line intensity with deposition rate and the mechanical stress in the films was found by this method.

Results and discussion

Deposition parameters and plasma parameters

Despite the fact that Goyette et al. were able to show the use of OES for relative determination of the C₂ density in the special case of nanocrystalline diamond CVD deposition it is in general not valid to ratio the emission intensities of species from a plasma as a function of process conditions and to draw quantitative conclusions from this. Actinometry - where the emission intensities of each species are scaled by the intensity of emission from a suitable inert gas – is a possible solution. In this work the Argon line at 751.4 nm was used to scale the measured C₂ emission line. Unfortunately the intensity of the Argon line at
751.4 nm is weak for all spectra taken in this work and the measured values are prone to statistical error. It would be preferable to use the intensities of the C\textsubscript{2} (516 nm) line and the H\textalpha{} (656.3 nm) line because them being strong in the spectra.

Therefore it was measured, if the C\textsubscript{2}/Ar intensity and the C\textsubscript{2}/H\textalpha{} ratio show the same trend for the spectra taken.

Fig. 1 shows the influence of the pressure on the measured C\textsubscript{2}/Ar and the C\textsubscript{2}/H\textalpha{} intensities. All OES measurements were done with a MW-Power of 1.5 kW and the measured intensities were normalized to the maximum.

It is observed that increasing the pressure results in a stronger C\textsubscript{2} emission intensity for the C\textsubscript{2}/Ar ratio as well as the C\textsubscript{2}/H\textalpha{} ratio. The emission intensity increases by nearly an order of magnitude when changing the pressure by 50 mbar from 175 mbar to 225 mbar. Because both ratios show the same trend for the parameter field used for the depositions shown in this work the C\textsubscript{2}/H\textalpha{} is used to correlate plasma properties with the film properties due to its higher applicability by the stronger intensities.

Fig. 1 Normalized to maximum C\textsubscript{2}/Ar and C\textsubscript{2}/H\textalpha{} intensity measured by OES

Fig. 2 shows the C\textsubscript{2}/H\textalpha{} ratio as measured by OES. One can see that the gasflow as well as the pressure have an influence on the ratio. The intensity is increasing by a factor of 2 with gasflow being increased from 300 to 1500sccm. Pressure has a similar influence on the intensity and a maximum of intensity is found at 200 mbar.

Fig. 2 Influence of the process parameters pressure and gasflow on the intensity ratio of the C\textsubscript{2} (516.5 nm) line and the H\textalpha{} (656.3 nm) line taken from the Optical Emission spectroscopy

Plasma parameters and properties of NCD films

After characterizing the plasma by measurement of the C\textsubscript{2} line intensity by Optical Emission Spectroscopy the influence of the plasma parameters on the film properties was investigated. First the growth rate for NCD films was correlated to the C\textsubscript{2}/H\textalpha{} during deposition as shown in Fig. 3. At first the growth rate is increasing with the amount of dimers. A maximum of 3.5 µm/h for the growth rate was found around a C\textsubscript{2}/H\textalpha{} value of 54. At higher C\textsubscript{2} densities the growth rate of NCD diamond is decreasing again.

Large amounts of graphitic carbon were deposited in the deposition chamber at high C\textsubscript{2}/H\textalpha{} values which suggests that the deposition of graphitic carbon is favourable in these growth conditions.

Based on these results it appears that the growth rate can be adjusted and maximized directly by controlling the amount of carbon dimers in the plasma.

Fig. 3 Growth rate dependents from the C\textsubscript{2}/H\textalpha{} taken from the Optical Emission Spectroscopy

Another film property investigated in correlation to the carbon dimer density in the plasma is the intrinsic stress in the NCD films.

Fig. 4 Influence of the C\textsubscript{2}/H\textalpha{} taken from the Optical Emission Spectroscopy on the intrinsic stress in the film.

It was found that the tensile stress can be adjusted directly by controlling the carbon dimer density in the plasma (Fig. 4). All deposited films have tensile intrinsic stress. For low ratios of C\textsubscript{2} to H\textalpha{} (around 42) the tensile stress is rather low at 250MPa. With increasing C\textsubscript{2}/H\textalpha{} the intrinsic stress is also increasing up to a maximum around a C\textsubscript{2}/H\textalpha{} value of 52. The maximum of tensile stress in our films was measured with 550 MPa. As mentioned before the deposited films appear to be more graphitic for high dimer concentrations. This has also an effect on the in-
trinsic stress in the film. Above a $C_2/H_α$ value of 52 the general trend shows that the intrinsic stress is decreasing again back to a value of 250MPa.

The intrinsic stress in polycrystalline films is usually dominated by two contributions that can be described by the two models: The Ion Peening model that describes the bombardment of high energetic particles leading to over-dense films and thus to compressive stress in the films and the grain boundary mismatch model [16] predicting a direct connection between the grain size and the tensile stress – the smaller the grains the higher the tensile stress. Because of the low mean free path at the given pressure of 200 mbar, strong thermalization of the particles must be assumed and thus ion peening can be neglected as in the case of microcrystalline diamond [17].

It was investigated if a connection between the grain boundary density and the intrinsic stress can be found. FTIR spectra were analyzed to find out how the matrix changes with the deposition parameters. All deposited films show a strong absorption band between 2750 and 3100 cm$^{-1}$ indicating various C-H stretching modes. The spectra were deconvoluted using 9 Gaussian peaks with frequencies and assignments given by Ristein et al. [18] and the peaks added up to a total integrated absorption. Considering that the matrix structure is not changing and only the ratio of matrix and diamond crystals is influenced by the deposition parameters, the measurements are giving direct information about the proportion of matrix and diamond grains in the film.

Fig. 5 Integrated Total Absorption as taken from FTIR in correlation to intrinsic stress

Fig. 5 shows that the tensile stress in the films is directly connected to the integrated total absorption coming from the FTIR measurements. This measurement is in consistency to the predictions of the grain boundary mismatch model where smaller diamond crystals lead to a higher grain boundary density – and therefore higher tensile stress.

To investigate if the diamond grains behave as predicted by the grain boundary mismatch model the size of the crystals were measured by XRD measurements. The spectra used in this work are obtained by a Phillips Diffractometer PW 1710 using Co K$α$ radiation. The FWHM of the $<220>$ peak was taken to calculate the grain size. Fig. 6 show that the grain size of all deposited films is between 16nm and 26nm. Comparative measurements were done with a SEM to proof the diamond grain size to be correct.

![Fig. 6 Influence of the grain size on the intrinsic stress](image)

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![Fig. 7 SEM picture of NCD film surface](image)

Fig. 7 shows a film with diamond grains clearly of a size around 20nm.

The measurements shown in Fig. 6 are contra-intuitive and contradict with the predictions of the grain boundary mismatch model. It is shown that films with bigger crystals have higher tensile stress.

Taking the results from Fig. 5 and Fig. 6 it is clearly shown that the grain boundaries mismatch model by Hoffmann needs to be modified for this special field of nanostructured material. It was measured that the predicted results for grains surrounded by a thin grain boundary are no longer true for a 3-dimensional matrix with embedded diamond. In this case the inner structure and geometry needs to be taken into account and the model needs to be adapted.

**Conclusion**

The measurements made in this work show how the OES spectra of the deposition plasma are influenced by the process parameters.

It was also shown that the film properties of the deposited NCD films such as growth rate and residual stress can be controlled by plasma parameters determined by OES,
especially the C/H₀ value.

Furthermore the results clearly prove that predictions derived from the grain boundary mismatch model are not able to explain the experimental results. This model, developed by Hofmann for fine-grained films, predicts greater tensile stress in films with smaller grains and a higher grain boundary density. The results found here suggest that the model needs to be adapted to nanomaterials consisting of a 3-dimensional matrix structure with embedded diamond – this allows a new degree of freedom: variation of the volume of the matrix between the diamond grains and the inner structure of the matrix.

References