Deposition of amorphous carbon layers from C₂H₂ and CF₄ with an expanding thermal arc plasma beam set-up

Citation for published version (APA):

Gielen, J. W. A. M., Sanden, van de, M. C. M., & Schram, D. C. (1995). Deposition of amorphous carbon layers from C₂H₂ and CF₄ with an expanding thermal arc plasma beam set-up. *Thin Solid Films*, 271(1-2), 56-63. <https://doi.org/10.1016/0040-6090%2895%2906902-X>, [https://doi.org/10.1016/0040-6090\(95\)06902-X](https://doi.org/10.1016/0040-6090(95)06902-X)

DOI:

[10.1016/0040-6090%2895%2906902-X](https://doi.org/10.1016/0040-6090%2895%2906902-X)
[10.1016/0040-6090\(95\)06902-X](https://doi.org/10.1016/0040-6090(95)06902-X)

Document status and date:

Published: 01/01/1995

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Deposition of amorphous carbon layers from C_2H_2 and CF_4 with an expanding thermal arc plasma beam set-up

J.W.A.M. Gielen, M.C.M. van de Sanden, D.C. Schram

Eindhoven University of Technology, Department of Physics, PO Box 513, 5600 MB Eindhoven, The Netherlands

Received 13 January 1995; accepted 7 July 1995

Abstract

Amorphous fluorohydrogenated carbon layers are deposited on silicon and glass substrates using an expanding thermal arc plasma, burning on argon with a fixed flow ($3 \text{ standard cm}^3 \text{ s}^{-1}$) of acetylene and a varying flow ($0\text{--}2.9 \text{ standard cm}^3 \text{ s}^{-1}$) of tetrafluoromethane. The layers deposited are analyzed in situ by means of ellipsometry and ex situ by means of Fourier transform infrared spectroscopy, transmission of visible light, scanning electron microscopy and atomic force microscopy.

It is found that the growth rate of the layers is independent of the CF_4 flow added to the plasma. No dramatic variation in the refractive index, extinction coefficient and optical bandgap is observed with changing CF_4 flow. The molecular bonding structure is influenced by the addition of CF_4 , suggesting that the layers are modified by the addition of CF_4 .

Keywords: Amorphous materials; Carbon; Fluorine; Plasma processing and deposition

1. Introduction

Over the last two decades much research work has been carried out on diamond-like carbon (DLC) films of amorphous hydrogenated carbon (a-C:H), because of their unique properties [1]. They are in general hard, extremely chemical inert, electrically insulating, transparent and their optical constants, like the refractive index, are tuneable [2,3]. Possible applications are protective anti-reflection coatings and protective coatings for reduction of wear and corrosion, but also investigation on the use in microelectronics and nanolithography has been performed [2,3].

In the last decade, increasing interest has been shown in the effect of adding a fluorine-containing precursor to the deposition process of a-C:H films, which changes the properties of the DLC films. Fluorination of a-C:H layers decreases the surface energy, giving a lower contact angle of water on the surface and a decrement of the friction. Also the microwear is reduced. All this improves the tribological properties of the layers. Furthermore an increase in corrosion resistance of layers deposited on metals, has been observed [4]. Possible applications of fluorinated carbon films may be found in the field of file memories, large scale integration manufacturing, communication satellites and micromachines [5].

In this paper the deposition of fluorine-containing layers is described, applying an expanding thermal plasma, containing

argon as carrier gas and acetylene (C_2H_2) and tetrafluoromethane (CF_4) as precursors. Our main objective is to obtain more insight into the effect of a precursor which contains both an etching particle (F) and a depositing particle (C) on films deposited. This both with respect to bulk parameters, like the refractive index, and to the microstructure of the film. Is there any fluorine incorporated in the film or is there a modification of the film by fluorine? The plasma parameter varied in the experiments is the CF_4 precursor gas flow. The layers are analyzed with various techniques like ellipsometry and infrared spectroscopy.

2. Experimental

The deposition of the layers is performed applying an expanding thermal arc plasma. A schematic drawing of the set-up which consists of a cascaded arc plasma source, an expansion vessel and a water-cooled substrate holder is shown in Fig. 1. From the plasma source (argon carrier gas flow, $50 \text{ standard cm}^3 \text{ s}^{-1}$; arc current, 24 A; arc power, 1.5 kW; arc pressure, 0.5 bar) a thermal plasma beam expands into the vessel (pressure, 0.14 mbar), to which a constant acetylene flow ($3 \text{ standard cm}^3 \text{ s}^{-1}$) and a variable tetrafluoromethane flow ($0\text{--}2.9 \text{ standard cm}^3 \text{ s}^{-1}$) is admixed. This plasma mixture of Ar, C_2H_2 and CF_4 is transported with a subsonic velocity, of about 1000 m s^{-1} , towards the water-

Fig. 1. A schematic drawing of the deposition set-up.

cooled substrate holder [6,7]. There deposition takes place on 2.5×2.5 cm² substrates of silicon [100], from Wacker-Chemitronic GMBH in Germany, and glass, which are Menzel-Gläser microscope slides. The silicon is cleaned by wiping and rinsing with acetone, distilled water and ethanol. The cleaning of the glass slides is the same except that the acetone treatment is performed in an ultrasonic bath. More details on the deposition set-up can be found elsewhere [8–10].

The layers have been grown in two separate deposition sessions. In the first session the deposition time is 60 s, giving thin layers (< 1 μm) and in the second session the deposition time is 300 s, resulting in thick layers (> 1 μm). In each session the CF₄ precursor flow takes the values 0, 0.3, 0.6, 0.9, 1.4, 2.0 and 2.9 standard cm³ s⁻¹. During deposition the substrate temperature increases: for the thin layers about 9 K, for the thick layers approximately 22 K. After each deposition session the expansion vessel is cleaned during 15 min by burning an argon/oxygen plasma which removes the carbon and other particles from the vessel walls, ensuring equal wall conditioning for all layers deposited. The arc conditions during cleaning are: argon flow, 100 standard cm³ s⁻¹; arc current, 45 A; electrical power, 4 kW; and arc pressure, 0.5 bar. The oxygen is injected at a flow rate of 6 standard cm³ s⁻¹.

Both in-situ and ex-situ diagnostics have been applied on the deposited layers. In-situ He–Ne ellipsometry provides information on the growth rate and refractive index. Various ex-situ diagnostics have been performed. Fourier transform infrared (FTIR) spectroscopy reveals the bonding types in the layers and transmission of visible light experiments on the layers on glass give the optical bandgap. Scanning electron microscopy (SEM), performed on perpendicular cleaves of the layers on silicon, provides information on the homogeneity and thickness and atomic force microscopy (AFM) on the surface of the layers reveals the structure of the top surface.

Finally a separate experiment has been performed to study etching of the layers with an oxygen plasma. On a silicon

sample thin layers are deposited, which are subsequently etched, using the cleaning conditions mentioned earlier. The process is monitored in-situ with He–Ne ellipsometry. This experiment is done both for the 0 standard cm³ s⁻¹ CF₄ case and the 2.9 standard cm³ s⁻¹ CF₄ case.

3. Results

In this section the results of the analysis of the amorphous hydrogenated carbon films are presented with respect to their various diagnostics.

3.1. Ellipsometry

During the deposition process of the thick a-C:H, F films, the growth on the silicon substrate is monitored using in situ a rotating analyzer He–Ne ellipsometer, with which the change of polarisation of incident laser light, reflecting from the growing layer, is determined. From this the ellipsometric angles Ψ and Δ are obtained as a function of time, which are related to the reflection properties of the layers [11].

Simulation of the Ψ – Δ curves reveals the refractive index and the thickness of the layers [12]. For this a model for the growing layer is assumed which consists of a silicon substrate, with a complex refractive index of $3.88 - 0.018i$, a growing bulk layer and a top layer [13–15]. From the simulation six parameters are obtained: the refractive index, extinction coefficient and thickness of the top layer, the refractive index and extinction coefficient of the bulk layer and the total thickness of the bulk layer.

In Fig. 2 the refractive index and extinction coefficient of the bulk layer obtained from the simulations are shown at the He–Ne wavelength of 632.8 nm as a function of the CF₄ precursor flow. The refractive index is found to be roughly constant when increasing the CF₄ flow. Its value of 2.1 in the case of 0 standard cm³ s⁻¹ CF₄ addition is in agreement with

Fig. 2. The bulk refractive index and extinction coefficient from ellipsometry vs. CF_4 flow.

earlier results [8,9,16–18]. The extinction coefficient decreases with increasing CF_4 flow. Further on this is found to be in agreement with an increasing optical bandgap. The thickness of the bulk layer is presented in Fig. 3 and proves to be independent of the CF_4 flow. With respect to the top layer properties (not shown), it is found that the refractive index remains constant at 1.4 ± 0.1 , while the extinction coefficient increases with CF_4 addition, from -0.02 to -0.07 . The thickness, finally, slightly increases with increasing CF_4 flow, from 30 to 40 nm. The top layer is considered to be the part of the growing layer which is still under construction. Its structure is not yet in its final form and gives rise to less dense material, as is obvious from the optical properties which have lower values than the bulk material. The increment of the top layer thickness with increasing CF_4 addition, may indicate a more open structure of the film grown, which results in a larger penetration depth of the modifying particles and this makes the top layer larger.

From the simulations it is concluded that the addition of CF_4 has no large influence on the optical properties of the layers deposited. Also the thickness is independent of the CF_4 addition, implying that the addition of a primarily etching precursor CF_4 does not influence the growth rate. These results indicate that CF_4 modifies the growth of the layers rather than etches them, which will also be shown from other techniques applied. A reason for the CF_4 not to etch may be that there is no ion bombardment [19] on the surface as the only bias on the substrate is the self-bias of the plasma, which is only several volts.

In the simulation process all parameters are varied independently. However, using the effective medium theory [20], we can assume a formal relation between the properties of the top and bulk layer. The top layer then is constructed partly from bulk material and partly from voids, resulting in less dense material. The relation between the optical properties of the top and bulk layer is given by the effective medium approximation (EMA) of Bruggeman. From this theory a volume fraction f is determined, which reveals the fraction of bulk material and voids in the top layer [21]. This volume fraction, calculated from the simulation results, is plotted in Fig. 3 as a function of the CF_4 flow. It is found that f

Fig. 3. The bulk thickness and the void fraction from ellipsometry vs. CF_4 flow.

is reasonably constant at 0.55 when varying the CF_4 flow, indicating that the top layer is quite open and porous, confirming the relative large top layer thicknesses.

When analysing Ψ and Δ individually as a function of time it is found that during the deposition process the growth rate is constant. Combining this result with the independence of the total thickness of the films with varying CF_4 precursor admixture, a uniform growth rate is observed. This results in a growth rate of about 5 nm s^{-1} for the deposition of amorphous fluorohydrogenated carbon layers.

3.2. Fourier transform infrared spectroscopy

Applying FTIR spectroscopy, using a Bruker IFS 66 interferometer [22,23], the transmission of infrared light ($500\text{--}4000 \text{ cm}^{-1}$) has been measured for the layers deposited on silicon with respect to plane silicon, at a resolution of 4 cm^{-1} . The transmission varies between 0.8 and 1.4, having a sinusoidal form caused by multiple reflection and showing anti-reflection behaviour.

From the multiple reflection of the light in the layers deposited, the thickness and refractive index of the layers are obtained. This is done by fitting the transmission spectrum measured in those regions with no molecular bonds. Using elementary optics, the transmission is described by

transmission

$$= \frac{|t_1|^2 |t_2|^2}{|t_R|^2} \frac{\exp[2\text{Im}(\phi)]}{1 - 2\text{Re}[r_1 r_2 \exp(-2i\phi)] + |r_1|^2 |r_2|^2 \exp[4\text{Im}(\phi)]} \quad (1)$$

The quantities t_1 , t_2 and t_R are the transmission coefficients for the boundaries between silicon and the layer, layer and air, and silicon and air respectively; the quantities r_1 and r_2 are the reflection coefficients from the layer to silicon and the layer to air. They are all given by the Fresnel equations [24]. The quantity ϕ is defined by $2\pi n d / \lambda$, with n the complex index of refraction of the layer, d the thickness of the layer and λ the wavelength of the incident infrared light. The fitting is performed by means of a commercial software package running on a PC 486.

The description above assumes that the system to be fitted consists of a perfect flat layer on a perfect flat silicon surface. However fitting the spectra is then impossible. This is caused by two reasons: one there exists a top layer on top of the bulk layer, and two between the silicon substrate and the layer there is an undefined interface layer. To overcome this problem, a correction factor is inserted in the fitting equation, being a second-order polynome, adapting the reflection coefficients. This finally results in a fitting equation with four variables. One fact is very important during fitting. The solution of Eq. (1) depends sensitively on nd rather than on n and d , separately, which is confirmed when redoing the fitting, using the thicknesses calculated from the ellipsometry and keeping them constant in the fitting process. From these calculations the error in n and d is determined. In Fig. 4 the results of n and d for the thick layers are presented as a function of the CF_4 flow. It is obvious that both the thickness and refractive index again are not significantly changed by adding CF_4 , which confirms the behaviour found from ellipsometry.

Now two different ways have been used to obtain the absorption by the molecular bonds in the deposited films. The first method is a qualitative description of the total spectrum measured, by calculating the difference between the multiple reflection spectrum obtained by fitting and the measured transmission. This results in spectra with absorption peaks only. In Fig. 5 these spectra are given for an increasing CF_4

Fig. 4. The refractive index and thickness from IR spectroscopy vs. CF_4 flow.

Fig. 5. Relative absorption for varying CF_4 flow.

flow. Table 1 shows the characterisation of the peaks and their wavenumbers, which is based on Refs. [3,27].

Analysing Fig. 5 and Table 1 reveals several facts. First, with increasing CF_4 flow, the absorption in the interval from 1000 to 1400 cm^{-1} increases, indicating increasingly more fluorine in the layer, being $-\text{CF}$, $-\text{CF}_2$ and $-\text{CF}_3$ bonded. Second, there is a strong peak at 2927 cm^{-1} indicating sp^3 - CH_2 bonds. This peak is rather symmetric in shape, when no CF_4 is added. However, when the CF_4 flow is increased, the shape of the peak becomes more anti-symmetric, its intensity decreases and the curve broadens. Simultaneously, a peak at 1600 cm^{-1} , indicating sp^2 - $\text{C}=\text{C}$ bonding, appears and increases in intensity. This is the reason for the anti-symmetrizing of the 2927 cm^{-1} peak as around 3000 cm^{-1} an sp^2 - CH bonding appears. The peak at 3300 cm^{-1} shows the presence of an sp^1 - $\text{C}\equiv\text{C}$ bonding in the layer.

To determine the amount of C-H bonds in its various forms, a quantitative method to determine the absorption by molecular bonds is applied. The measured transmission spectra are fitted in the wavenumber interval from 2500 to 3500 cm^{-1} . Each molecular bond is represented by an extinction coefficient of Gaussian shape. In the wavenumber interval concerned three bonds were assumed. This procedure results in good fits compared to the measured spectra. From the extinction coefficient the absorption coefficient is determined [24]. In Fig. 6 a typical example of the fitting result is pre-

Table 1
Peak positions and characterisation

Peak number	Wavenumber (cm^{-1})	Characterisation
1	3660	$-\text{O}-\text{H}$
2	3300	$\equiv\text{C}-\text{H}$ (sp^1)
3	2927	$-\text{CH}_2$ (sp^3)
4	2350	$\text{C}-\text{O}_2$
5	1700	$\text{C}=\text{O}$
6	1600	$\text{C}=\text{C}$ (sp^2)
7	1450	$-\text{CH}_2$ or $-\text{CH}_3$ (sp^3)
8	1200–1400	$-\text{CF}_3$ (sp^3)
9	1100–1200	$-\text{CF}_2$ (sp^3)
10	1000–1100	$-\text{CF}$ (sp^3)
11	900	$\text{C}-\text{C}$ (sp^3)

Fig. 6. An example of a fit result. Upper part, measurement and fit; lower part, deconvoluted peaks and summed absorption.

sented. The upper curves show the measured and fitted spectrum. The lower part gives the deconvoluted absorption peaks and the sum of these absorption peaks.

The most remarkable result of the fitting procedure is the fact that the position of the peak, fitted in the interval from 2 900 to 3 000 cm^{-1} , is varying. It is found that its position increases, almost linear, in wavenumber from 2 926 to 2 977 cm^{-1} , when the CF_4 flow increases from 0 to 2.9 standard $\text{cm}^3 \text{s}^{-1}$, as is shown in Fig. 7. Considering the peak at 2926 cm^{-1} , which corresponds to an $\text{sp}^3\text{-CH}_2$ bond [3,25], two explanations are possible to describe this effect, when CF_4 is added.

First, increasing the CF_4 flow increases the number of F particles in the plasma, which are able to replace an H atom in the sp^3 bond. As F is a more electronegative particle than H, the C–H bonding distance will decrease [26], which results in a higher bonding energy, leading to an increasing peak wavenumber. This explanation describes a shift of the bonding energy. Some proof for this mechanism is found in Fig. 5, where the appearance and increasing intensity of CF_x bonds between 1 000 and 1 400 cm^{-1} is seen when CF_4 is added. This effect is also found when looking at gaseous molecules. In CH_4 the primary C–H stretching vibration is at a lower wavenumber than the same vibration in CH_3F [27].

The second explanation of Fig. 7 is that the F particles change the structure of the carbon to carbon bond. As not all C_2H_2 molecules are decomposed by the plasma, which is explained later, there appear sp^1 bonds in the layer. When F appears in the vicinity of such an sp^1 bond, it could break this bond, resulting in an $\text{sp}^2\text{-CH}$ bond, which is situated around 3 000 cm^{-1} . So next to the sp^3 peak, which is already available, an sp^2 peak appears. With the fitting routines applied it was impossible to make any distinction between these two peaks and so the peak fitted is a convolution of both. Increasing the CF_4 flow results in more sp^2 bondings formed, leading to an increasing wavenumber. For this explanation proof is also found in Fig. 5. The appearance of the absorption peak at 1 600 cm^{-1} indicates an $\text{sp}^2\text{-C}=\text{C}$ bond. The peaks found in the interval from 2 900 to 3 000 cm^{-1} show an increasing anti-symmetry, also indicating the increment of sp^2 bonds.

So the addition of CF_4 results in two modifications of the growth of the films. Fluorine is incorporated in the layer via

the exchange of a hydrogen atom by a fluorine atom. The sp^1 bonds in the layers are transformed into sp^2 bonds. The other two peaks from the fits are found around 3 300 and 3 520 cm^{-1} . The first one is assigned to an $\text{sp}^1\text{-C}\equiv\text{C}$ bond, due to not fully dissociated C_2H_2 . Its intensity decreases with increasing CF_4 addition as a result of the transformation to sp^2 bonds, also confirming the second explanation. The second peak is not identified up to now, but is most likely due to some pollution of the vessel by nitrogen or other gasses.

3.3. Transmission of visible light

The transmission of visible light through the thick a-C:H layers deposited on glass is studied, which reveals two other important optical parameters: the optical bandgap and the Urbach edge. A cascaded arc is used as a broad-band light source [28]. The transmitted light is detected via a prism monochromator and a photo-diode array, in the wavelength range 400–800 nm.

The optical bandgap (E_g) is determined using the Tauc method [29]. In Fig. 8 the calculated values are presented with varying CF_4 flow. The optical bandgap is slightly increasing when more CF_4 is added, which is in agreement with the decreasing extinction coefficient determined from the in-situ ellipsometry experiments and the incorporation of fluorine, which leads to electronic states with higher energy.

The Urbach edge is a measure for the degree of amorphousness of the layer deposited: a larger Urbach edge indicates a more amorphous layer. In Fig. 8 the results are given, and they are found to be constant at approximately 0.31 eV. Again it is demonstrated that the addition of CF_4 does not influence the optical properties in a dramatic way.

Comparing the results for the optical bandgap with literature, good agreement is found. Seth and Babu [2] found a slightly increasing bandgap up to 60% CF_4 addition in their experiments, being around 1.43 eV. Looking at the ratio of etching and depositing particles in the plasma, the behaviour of the optical bandgap with flow increment is in agreement with the plasma used in our experiments. The absolute value for the bandgap is slightly higher. Sah et al. [30] found a bandgap of about 1.25 eV, being rather constant up to 50%

Fig. 7. Change of the fitted peak position vs. CF_4 flow.

Fig. 8. Optical bandgap and Urbach edge vs. CF_4 flow.

Fig. 9. Thickness of the layers via transmission of visible light vs. CF₄ flow.

fluorine atoms. This is comparable with our experimental conditions again confirming the results found.

The thickness of the layers is also obtained from these experiments. In Fig. 9 the thickness is drawn as function of the CF₄ flow. Again, the thickness is found to be constant, when varying the CF₄ flow, confirming earlier results, but now on glass samples. The average thickness is 1.48 ± 0.14 μm. The average thickness of the layers on silicon is found to be 1.54 ± 0.15 μm, as will be shown later. So the layers have the same thickness on both silicon and glass samples and this means that the growth rate is independent of the substrate type used.

3.4. Microscope studies

Visual information of the films is obtained via scanning electron microscopy (SEM) and atomic force microscopy (AFM), applying a Nanoscope AFM. Perpendicular cleaves, of both thin and thick layers deposited on silicon, are analyzed via SEM. From scans along the surface, it is found that the layers are uniform in thickness, revealing that a homogeneous deposition process on the scale studied takes place. In Fig. 10 the thickness of both the thin and thick layers as a function of the CF₄ flow is given. The thickness is independent of the CF₄ flow, confirming earlier results, again indicating that CF₄ not influences the growth rate, but just modifies its structure. For the thick layers an averaged growth rate of 5.1 ± 0.5 nm s⁻¹ is found and for the thin layers 6.2 ± 0.9 nm s⁻¹. These

Fig. 10. The thickness of the layers from SEM vs. CF₄ flow.

two values are in agreement, indicating that the growth rate for both thin and thick layers is the same.

The surface of some thin layers and thick layers is studied via AFM. The surface structure is found to be a randomly ordered arrangement of round spots. No columnar growth is observed. Increasing the CF₄ flow decreases the mean height difference which means a smoother surface. This view is also confirmed by looking at the depth distribution, which indicates a lower maximum depth at larger CF₄ flow. The mean roughness is a few nanometres and, with increasing CF₄ flow, this decreases slightly, again indicating a smoother surface. Just looking at the surface scan reveals that the spot size decreases in diameter when increasing the CF₄ flow. It should be noted that the roughness found is much smaller compared with the thickness of the top layer calculated from the simulation of the ellipsometry results. When analysing the data concerning the thin layers, similar results are obtained. Increasing the CF₄ flow gives a smoother surface, decreasing the height differences and the mean roughness.

3.5. Etching with oxygen

A separate experiment, to obtain more information on the bonding structure, is performed in which layers are etched after deposition. The etch rate is known to be dependent on both the number of hydrogen bonds and the sp²/sp³ ratio [31]. Thin layers have been deposited during 60 s and then the plasma conditions have been changed to etching conditions; the mentioned cleaning settings. The etching process is monitored with in-situ He–Ne ellipsometry. From this experiment it is found, that the etch rate is independent for various CF₄ additions and is 1.47 ± 0.03 nm s⁻¹.

4. Discussion

The thickness of the thick layers has been determined with four independent techniques, revealing that the growth rate is independent of the substrate, silicon or glass, used. In Fig. 11 all the thicknesses calculated are presented in one graph. This shows not only that the growth rate does not

Fig. 11. The thickness of the thick layers, from SEM, in-situ He–Ne ellipsometry, IR spectroscopy and visible light transmission vs. CF₄ flow.

change with increasing CF_4 flow, but that four independent diagnostics produce the same results. When averaging this means that the average growth rate for the layers is $5.1 \pm 0.5 \text{ nm s}^{-1}$.

The constant deposition rate is confirmed in the literature. Seth and Babu [2] find a nearly constant deposition rate for $\text{CF}_4/\text{C}_4\text{H}_6$ mixture ratios up to a ratio of etching particles to depositing particles of 24:11. Sah et al. [30] find an only slightly increasing deposition rate for an etching to depositing ratio of 1:1. The maximum ratio in our depositions is 5:4 which is between the ratios mentioned above. So the addition of F particles does not influence the number of particles deposited, it only modifies the structure.

Insight into the appearance of several absorption peaks found with infrared spectroscopy can be obtained as follows. This analysis is only meant to be a first modelling of the growth process and is not complete. The plasma in the arc is produced by the ionisation of argon via:

The quantity ΔE gives the endothermic (positive signed) energy for the ionisation reaction. From the arc then a mixture of Ar, Ar^+ and e^- expands into the vessel. In the nozzle C_2H_2 and CF_4 are added and undergo a charge exchange reaction with Ar^+ . The possible exothermic reactions [32] are:

The formed C_2H_2^+ reacts by recombining dissociatively with an electron via:

And the CF_3^+ ions react via:

The formed molecular radicals are electronically and vibrationally excited and have sticking probabilities close to 1.

The ionisation degree of the plasma is about 3% [33], which means that in the nozzle a flux of $3.6 \times 10^{19} \text{ ions s}^{-1}$ is available. The C_2H_2 gas flow added is 3 standard $\text{cm}^3 \text{ s}^{-1}$, which is equivalent to $7.2 \times 10^{19} \text{ s}^{-1}$. When only C_2H_2 is added and we assume that every argon ion charge exchanges, just 50% of the injected C_2H_2 is dissociated. So a reasonable number of inert C_2H_2 molecules is always available in the plasma, which could interact at the substrate surface resulting in $\text{sp}^1\text{-C}\equiv\text{C}$ bonds. Furthermore it is obvious that after the first ionisation and recombination step, triple-bonded carbon exists in the plasma, explaining the sp^1 bonds in the layers. Also single-bonded carbon is formed resulting in $\text{sp}^3\text{-CH}_x$ in the films. The addition of CF_4 to the plasma, gives rise to F,

CF , CF_2 particles, which are either incorporated in the films, producing the CF_x absorption, or which modify the structure of the films.

A last remark is made on the fact that the refractive index is around $n = 2$, also for the layers only from acetylene. This is rather high as no substrate bias is applied. In the literature it is found that normally a substrate bias of at least 100 eV is needed [34,35]. An explanation for this is not yet found, but one possible reason could be that only the ion energy flux is the determining parameter as was recently shown by Fourches and Turban [34].

5. Conclusions

Amorphous fluorohydrogenated carbon films have been deposited on silicon and glass substrates, using an expanding thermal plasma. The plasma is primarily burning on argon to which acetylene and tetrafluoromethane is added. The parameter varied in the deposition sessions is the CF_4 flow, from 0 to 2.9 standard $\text{cm}^3 \text{ s}^{-1}$, while the other parameters are kept constant. The deposition time is 60 s giving thin layers and 300 s giving thick layers.

It is found that the growth rate of the layers is independent of the CF_4 gas flow, between 5 and 6 nm s^{-1} for both thin and thick layers. The growth rate is also independent of the substrate type, silicon or glass, and the growth process is homogeneous. The refractive index of the layer is constant with increasing CF_4 flow. However the extinction coefficient decreases slightly, when more CF_4 is added. This is confirmed by a slight increment in the optical bandgap, which is about 1.2 eV.

The addition of CF_4 to the plasma influences the position of C–H bonds in the wavenumber interval from 2 900 to 3 000 cm^{-1} . The absorption peaks show a shift in their position to higher wavenumbers when more CF_4 is added to the plasma. This can be explained in two ways. One explanation is the replacement of an H by an F particle. The other one is the transformation of an sp^1 into an sp^2 bond. Proof for the first explanation is found in the appearance of CF_x peaks and for the second one in the appearance of sp^2 peaks and decreasing sp^1 peaks.

Comparison of all results suggests that the addition of CF_4 only influences the growth resulting in a modification of the growth process. From our experiments it is concluded that simultaneous etching during deposition is minimal.

Acknowledgements

The authors would like to thank Océ/Van der Grinten Nederland, for financial support. Also J. Verhoeven and coworkers at the FOM/AMOLF institute in Amsterdam are acknowledged for providing the atomic force microscopy facilities, Mrs. M. Blijlevens of the Chemical Department at the Eindhoven University of Technology for her aid with the

scanning electron microscopy and Hans de Boer for providing the equipment for the Fourier transform infrared spectroscopy. The Foundation for Fundamental Research on Matter (FOM) and the Royal Netherlands Academy for Arts and Sciences (KNAW) are acknowledged for their financial support. The skilful technical assistance of Ries van de Sande, Bertus Hüskens and Herman de Jong is greatly acknowledged and the students Alf Kockelkoorn and Remco Grimm are thanked for taking part in the analysis of the layers.

References

- [1] J. Mort and F. Jansen, *Plasma deposited thin films*, CRC Press, Boca Raton, FL, 1986.
- [2] J. Seth and S.V. Babu, *Thin Solid Films*, 230 (1993) 90.
- [3] B. Dischler, R.E. Sah and P. Koidl, in C.J. Timmermans (ed.), *Proc. of ISPC-11*, Eindhoven, 1985, p. 45.
- [4] A.J.M. Buuron, M.C.M. van de Sanden, W.J. van Ooij, R.M.A. Driessens and D.C. Schram, *J. Appl. Phys.*, in press.
- [5] S. Miyake and R. Kaneko, *Thin Solid Films*, 212 (1993) 256.
- [6] M.C.M. van de Sanden, J.M. de Regt and D.C. Schram, *Phys. Rev. E*, 47 (1993) 2792.
- [7] G.M.W. Kroesen, D.C. Schram, A.T.M. Wilbers and G.J. Meeusen, *Contrib. Plasma Phys.*, 31 (1991) 27.
- [8] G.M.W. Kroesen, D.C. Schram and M.J.F. van de Sande, *Plasma Chem. Plasma Proc.*, 10 (1990) 49.
- [9] J.J. Beulens, G.M.W. Kroesen, P.C.N. Crouzen, H. Vasmel, H.J.A. Schuurmans, C.B. Beijer and J. Werner, *J. Appl. Pol. Sci.*, 46 (1990) 527.
- [10] A.J.M. Buuron, J.J. Beulens, P. Groot, J. Bakker and D.C. Schram, *Thin solid Films*, 212 (1992) 282.
- [11] R.M.A. Azzam and N.M. Bashara, *Ellipsometry and polarized light*, North-Holland, Amsterdam, 1977.
- [12] G.M.W. Kroesen, G.S. Oehrlein, E. de Frésart and M. Haverlag, *J. Appl. Phys.*, 73 (1993) 8017.
- [13] G.J. Meeusen, *Thesis*, Eindhoven University of Technology, 1994.
- [14] A.M. Antoine, B. Drevillon and P. Cora I Cabarrocas, *J. Appl. Phys.*, 61 (1987) 2501.
- [15] E.D. Palik, *Handbook of Optical Constants and Solids*, Academic Press, London, 1991.
- [16] A.J.M. Buuron, G.J. Meeusen, J.J. Beulens, M.C.M. van de Sanden and D.C. Schram, *J. Nucl. Mater.*, 200 (1993) 430.
- [17] J.J. Beulens, A.J.M. Buuron and D.C. Schram, *Surf. Coat. Technol.*, 47 (1991) 401.
- [18] A.J.M. Buuron, J.J. Beulens, M.J.F. van de Sande, D.C. Schram and J.G. van der Laan, *Fusion Technol.*, 19 (1991) 2049.
- [19] M. Haverlag, D. Vender and G.S. Oehrlein, *Appl. Phys. Lett.*, 61 (24) (1992) 2875.
- [20] D.E. Aspnes, J.B. Beeten and F. Hottier, *Phys. Rev. B*, 20 (1979) 3292.
- [21] Harland G. Tompkins, *A User's Guide to Ellipsometry*, Academic Press, San Diego, CA, 1993.
- [22] J.T. Houghton and S.D. Smith, *Infrared Physics*, Oxford University Press, Oxford, 1966.
- [23] N.L. Alpert, W.E. Keiser and H.A. Szymanski, *IR Theory and Practice of Infrared Spectroscopy*, Plenum Press, New York, 1973.
- [24] Eugene Hecht, *Optics*, Adison Wesley, Amsterdam, 1987.
- [25] A.J.M. Buuron, *Thesis*, Eindhoven University of Technology, 1993.
- [26] G. Lucovsky, *Solid State Commun.*, 29 (1979) 571.
- [27] Gerhard Herzberg, *Molecular Spectra and Molecular Structure, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, London, 1945.
- [28] A.T.M. Wilbers, G.M.W. Kroesen, C.J. Timmermans and D.C. Schram, *Meas. Sci. Technol.*, 1 (1990) 1326.
- [29] J. Tauc, in F. Abelès (ed.), *Optical Properties of Solids*, North-Holland, Amsterdam, 1972.
- [30] R.E. Sah, B. Dischler, A. Bubenzer and P. Koidl, *Appl. Phys. Lett.*, 46 (1985) 739.
- [31] E.B.D. Bourdon, A. Raveh, S.C. Gujrathi and L. Martinu, *J. Vac. Sci. Technol. A*, 11 (1993) 2530.
- [32] H.M. Rosenstock, K. Draxl, B.W. Steiner and J.T. Herron, *Energetics of gaseous ions*, *J. Phys. Chem. Ref. Data*, 6 (1977).
- [33] J.J. Beulens, M.J. de Graaf and D.C. Schram, *Plasma. Sources Sci.*, 2 (1993) 180.
- [34] N. Fourches and G. Turban, *Thin Solid Films*, 240 (1994) 28.
- [35] P. Reinke, W. Jacob and W. Möller, *J. Appl. Phys.*, 74 (1993) 1354.