Fast deposition of amorphous carbon films by an expanding cascaded arc plasma jet

Citation for published version (APA):

DOI:
10.1063/1.360637

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.
Fast deposition of amorphous carbon films by an expanding cascaded arc plasma jet

A. J. M. Buurona) and M. C. M. van de Sandenb)
Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

W. J. van Ooij
Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0012

H. M. A. Driessens and D. C. Schram
Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 29 April 1994; accepted for publication 13 March 1995)

Using an expanding cascaded arc plasma jet, amorphous hydrogenated and fluorohydrogenated carbon films were deposited on silicon, glass, and steel substrates at high rates of tens of nanometers per second and on large areas of up to 100 cm². The present work was aimed at depositing amorphous carbon films suited for optical and protective applications. Films deposited with the common argon/methane or argon/acetylene mixture tend to delaminate from the substrate when the film is thicker than about 1 μm. For this reason, also trials using other compounds like C₆H₆ (toluene), CF₄, and H₂, and mixtures of these, were carried out. Using toluene, several-μm-thick films with good adhesion to the substrate were deposited. With spectroscopic ellipsometry and infrared absorption spectroscopy optical parameters were obtained. Appropriate numerical models were developed for analyzing the data, taking into account interference fringes in the spectra due to multiple reflections in the thin film. The hydrogen and oxygen content in the films were determined with nuclear recoil techniques. Films deposited with the use of methane and acetylene are diamondlike with mainly sp³ bonding types, and a hydrogen content ranging from 36 to 26 at. % (with a low oxygen contamination of 1–2 at. %). Films deposited with the use of toluene are more polymerlike, with also sp² and sp³ bonding types. These films have a high hydrogen content (35 at. %), and can be partially oxidized (up to 13 at. %). In general, going from the polymerlike to the more diamondlike films, the refractive index increases from 1.3 to 2.2, and the band gap decreases from about 2 to 1 eV. By the admixture of hydrogen in the deposition plasma diamondlike films were produced with a larger band gap of 2.2 eV. The corrosion performance of the films was studied by storing them in a humidity cabinet. The corrosion resistance of films deposited with hydrocarbon/argon plasma mixtures appears to be limited. Thick films with a good corrosion resistance were produced by admixing a fluorine containing gas in the plasma. Analysis of the infrared absorption spectra showed that these films consist of amorphous fluorohydrogenated carbon. The presence of fluorine radicals in the plasma may lead to a chemically enhanced surface mobility, leading to a less porous film structure, and resulting in lower internal stresses. The growth rates and the corrosion performances of the films appear to be different for substrates of different types of steel. This may be attributed to different initial growth mechanisms, as a consequence of the difference in electrical and thermal conductivity of the two substrate types used here. © 1995 American Institute of Physics.

I. INTRODUCTION

Plasma polymerization is a relatively new technique for surface modification and for deposition of amorphous hydrogenated carbon films (a-C:H films).¹⁻³ Compared to conventional gas-phase deposition methods, the plasma deposited films are known to be highly cross linked. In general the films are insoluble and pinhole free, and adhere well to most substrates. The a-C:H films have an extensive field of potential applications, because of their unique combination of specific properties such as hardness, low friction coefficients, chemical inertness, biocompatibility, and optical transparency in a wide wavelength range.⁴ Some practical applications of a-C:H films are: overcoats on thin-film media for magnetic recording,⁵ protective and antireflection coatings for optical devices working in the infrared,⁶ insulating layers in electronic devices,⁷ and coatings for biomedical purposes.⁸

The deposition rate with conventional plasma reactors like rf, microwave, or dc glow discharge reactors however are low (at maximum a few nanometers per second)⁹,¹⁰ and hamper large-scale industrial applications of a-C:H films. In the last decade, at the Eindhoven University of Technology a method has been developed, using an expanding cascaded...
arc plasma jet, with which all types of carbon coatings are produced at deposition rates which are orders of magnitude higher than with the conventional methods. For a-C:H films the growth rates of up to 200 nm s⁻¹ were achieved on areas of 100 cm². Conventional gases like methane and acetylene were admixed in the argon carrier gas. The aim of this sequence was to find parameter settings with which thick films (3−4 µm) could be deposited, with a good adhesion to the substrate, and with optimum combinations of film properties aimed at optical applications. The optical parameters were determined using spectroscopic ellipsometry and infrared absorption spectroscopy. From the results of the latter, information on the predominant bonding types in the film was derived. Finally, the hydrogen and oxygen contents in the film were determined by nuclear scattering and recoil techniques.

In a second study the corrosion behavior of cold-rolled steel (CRS) and electrogalvanized steel (EGS), coated with a film of amorphous carbon was investigated. Research on the feasibility of depositing films with these qualities on steel for anticorrosion protection has increased rapidly in recent years. Recently, films deposited with trimethylsilane were reported to have a good corrosion performance. These films were deposited in a parallel plate reactor, or in a de bell type reactor. The deposition rates obtained (about 1 µm h⁻¹) were rather low. In the present study, the corrosion performance of carbon coatings deposited with the cascaded arc method are investigated with respect to substrate type and pretreatment and, type and flow rate of the admixed compound. Compounds admixed in the argon carrier gas were CH₃, C₂H₆, C₃H₈, and CF₄, and mixtures of these. In order to map the requirements on elemental composition and structure to this specific aim, the films were also studied using glow discharge optical spectroscopy (GDOS) and electron impedance spectroscopy (EIS). In some cases, also scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (TOF-SIMS) were carried out. In this article we first address specific numerical models for analyzing the results of the optical diagnostics. In these models multiple reflection in a thin film is taken into account, and the effect of interference fringes is eliminated from the final results. Subsequently the deposition reactor, conditions, and the specifications of the various diagnostics are addressed. The results on the optical and protective properties of the films are discussed consecutively, both in relation to their elemental and structural composition.

II. ANALYSIS OF THE OPTICAL PROPERTIES OF THE FILMS

A. Spectroscopic ellipsometry

With ex situ spectroscopic ellipsometry the optical parameters of the deposited films, such as refractive index, absorption coefficient, and band gap were determined. The theory of this method has been described extensively. Briefly, the method determines the change in polarization of linearly polarized light upon reflection on the system film substrate. This polarization change is expressed in the complex reflection ratio ρ:

\[ ρ = R_p / R_s, \]  

where \( R_p \) and \( R_s \) are the complex reflection coefficients for the light components polarized parallel and perpendicular to the plane of incidence, respectively (For a semi-infinite medium they are directly equal to the Fresnel reflection coefficients). So ρ is a complex quantity and is generally expressed in the ellipsometric angles Ψ and Δ:

\[ ρ = \tan(Ψ) \exp(jΔ). \]  

In measurement setups either a rotating analyzer or a rotating polarizer system is used. In both methods a periodic signal on the detection device arises. By Fourier analysis of this signal the ellipsometric Fourier coefficients \( a \) and \( b \) are determined. If the polarizer angle is set at 45°, these coefficients are related to the ellipsometric angles Ψ and Δ by the following relationships:

\[ a = -\cos(2Ψ), \]  
\[ b = \sin(2Ψ) \cos(Δ). \]

The parameters refractive index \( n \) and the extinction coefficient \( k \), enter the formulas through the Fresnel reflection coefficients. The band gap can be determined using the Tauc relation:

\[ \sqrt{αE} = G(E - E_g) \]  

with α the absorption coefficient (in cm⁻¹), \( α = 4πk/λ \), λ is the wavelength in vacuum of the incident light (in cm⁻¹), \( E \) is the photon energy (in eV), \( E_g \) is the band gap (in eV), \( G \) is a density-of-states coefficient (in cm⁻¹/² eV⁻¹/²). Because of the limited thickness of the deposited layers, interference oscillations appeared in the signals as a function of wavelength, due to multiple reflections within the film. The method in which substrate and film are considered mathematically by one semi-infinite bulk medium is no longer adequate. The system substrate layer has to be described by a multilayer system. This prohibits a straightforward determination of \( n, k, \) and \( E_g \) using the equations above. The problem can be solved by reversing the solution method. This means that a fit procedure to the measured data can be applied, starting from a given set of thicknesses and optical parameters. From these values the expected values of the coefficients \( a \) and \( b \) can be calculated and by an iterative least-squares algorithm an optimum fit to the measured data can be obtained. Mathematically the multilayer system can be described most conveniently in terms of complex optical impedance factors for each layer. In the past, computer programs have been written to analyze the data of He-Ne in situ ellipsometry. Recently, the program has been adapted for calculations over a large wavelength range. A variable number of parameters can be included in the model: Often the system substrate layer is extended with a top layer, with different optical parameters. The theory of Bruggeman sup-

J. Appl. Phys., Vol. 78, No. 1, 1 July 1995

Buron et al.
plies a means for characterizing these surface parameters. The top layer is then described by a void fraction of 50% and a limited thickness (of some nanometers). However, it appeared that for the present amorphous carbon films, the implication of this top layer did not improve the fit quality significantly, so we omitted it in the fits. The following parameters were then included in the fit procedure.

1. The thickness of the film \( d \).
2. The refractive index \( n \), in first approximation taken constant over the wavelength range.
3. The density-of-states factor \( G \).
4. The optical gap \( E_g \).

Initial values for \( n, G, \) and \( E_g \) can be estimated from the amplitude of the fringes, and from the level and the slope of the \( a \) and \( b \) coefficients. The interference oscillations permit an initial film thickness estimate using

\[
d = \frac{\lambda_i \lambda_{i+1}}{\lambda_i - \lambda_{i+1}} \frac{1}{2n^2}.
\]

(6)

with \( \lambda_i \) and \( \lambda_{i+1} \) the wavelength of two successive interference maxima. As a measure for the quality of the fit the least-squares error function

\[
\chi^2 = \frac{1}{N} \sum_{i=1}^{N} \left[ (a_i^{\text{calc}} - a_i^{\text{exp}})^2 + (b_i^{\text{calc}} - b_i^{\text{exp}})^2 \right]
\]

(7)

was adopted, with \( a \) and \( b \) the Fourier coefficients, \( N \) the number of data points, and the superscripts \( \text{exp} \) and \( \text{calc} \) denoting experimental and calculated \( a \) and \( b \) values, respectively. Weighing was not applied, because the absolute instrument noise (equal over the entire frequency interval) was predominant over the effect of the relative inaccuracies in \( a \) and \( b \).

### B. Infrared absorption spectroscopy

Infrared (IR) absorption spectroscopy supplies a means to determine the abundance of bonding types in a coating.\(^{23,24}\) The transmitted intensity \( I_T \) through a layer of thickness \( d \) is described by the well-known exponential relationship

\[
I_T = I_0 \exp(-\alpha d),
\]

(8)

with \( I_0 \) the intensity of the incident beam. The absorption coefficient \( \alpha \) is related to the extinction coefficient \( k \) by \( \alpha = k \frac{4\pi n}{\lambda} \).

As in the case of the ellipsometric spectra, the measured IR absorption spectra are disturbed by interference oscillations, caused by multiple reflection in the layer. Assume that the incident light passes through a layer system air-substrate-coating-air subsequently. The various reflection and transmission coefficients on the interfaces have to be taken into account. To this end, the components of the system are denoted by the indices \( a, s, \) and \( c \) (and again \( a \), respectively). The transmittance \( I_T/I_0 \) of the system under investigation, assuming perpendicular incidence of the light, is then given by (cf. Ref. 18):

\[
\frac{I_T}{I_0} = \exp(-\alpha d_a) \|t_{as}\|^2 \|t_{sc}\|^2 \|t_{ca}\|^2 \frac{1 - 2 \Re[r_{ca}r_{cs} \exp(-j\phi)] \exp(-\alpha d) + \|r_{ca}\|^2 \|r_{cs}\|^2 \exp(-2\alpha d)}{1 - 2 \Re[r_{ca}r_{cs} \exp(-j\phi)] \exp(-\alpha d) + \|r_{ca}\|^2 \|r_{cs}\|^2 \exp(-2\alpha d)},
\]

(9)

with \( r_{xy} \) and \( t_{xy} \) the (complex) reflection and transmission coefficients when the light encounters the interface from medium \( x \) to medium \( y \), which are all related to \( n \) and \( k \) by the Fresnel relations: \( \phi = 4\pi nd/\lambda \) is the real part of the phase change on passing two times through the coating.

The ratio \( I_T/I_0 \) can be corrected for the attenuation of the beam through the substrate. This was done by measuring the transmission through an uncoated piece and a coated piece of silicon out of the same wafer. Using the ratio of the reference intensity \( I_{U_0} \), transmitted through the uncoated substrate, and the incident intensity \( I_0 \),

\[
\frac{I_U}{I_0} = \exp(-\alpha d_u) \|t_{as}\|^2 \|t_{sa}\|^2,
\]

(10)

in which \( d_u \) and \( d_s \) are the substrate thicknesses in the uncoated and coated substrate section, respectively (\( d_u \approx d_s \) in general), the coating transmittance \( I_T/I_U \) can directly be deduced from Eq. (9). The applicability of an \( a \)-C:H layer as an optical coating is obvious. If the refractive index of the coating has a suitable value, intermediate of that of the substrate and that of air, the transmittance of the system substrate coating will be higher than the transmittance of the bare substrate. All of the parameters (except the thicknesses) are a function of frequency (wave number), so \( \alpha = \alpha_\nu \), etc. Using Eqs. (9) and (10) the coating transmittance \( I_T/I_U \) can now be converted into the absorption coefficient \( \alpha_\nu \). Two approaches are possible: When the thickness \( d \) and refractive index \( n \) of the coating (and substrate) are known, \( \alpha_\nu \) can be solved point by point by a simple computer iteration of Eq. (9). For a C:H materials, the profile of \( \alpha_\nu \) in an absorption band can be fitted approximately by a Gaussian function.\(^{25}\) When the thicknesses are not exactly known, the spectrum can be fitted starting from a suitable set of initial values for the thicknesses, refractive indices, and Gaussian absorption profiles in the vibrational bands. An estimate for the film thickness can be found using Eq. (6). A starting value for the refractive index can be estimated on basis of the amplitude of the interference fringes. The overall level mismatch caused by the difference \( d_s - d_u \) and, possibly by some residual overall absorption in the IR, can be adjusted by a flat or a linear background, giving one or two extra fitting parameters. Substituting the initial parameter estimates in Eqs. (9) and (10), the transmittance can be simulated over an entire wavelength range, and by a subsequent least-squares fit,
optimum values of the profiles of the absorption coefficient are obtained. In this way the Gaussian absorption bands are convoluted towards the measured transmittance.

III. EXPERIMENT

A. The expanding cascaded arc set-up for deposition

In Fig. 1 an outline of the cascaded arc deposition reactor is shown. The main features of the expanding cascaded arc technique for deposition are the separation of the three phases production, transport, and deposition of active species. The argon carrier gas enters the cathode space of the cascaded arc at a pressure of about 0.5 bar. A plasma is generated in the channel of a cascaded arc and expands through the anode annule into a vacuum chamber (pressure of the order of 100 Pa). The monomer is injected in the anode and ionized and dissociated by the plasma. In the expanding plasma jet excited and ionized atomic and molecular radicals are transported towards the substrate, where deposition occurs at high rates. To maintain a low deposition temperature (necessary for a-C:H deposition), the substrate is water cooled. The reactor settings for a-C:H deposition are given in Table I. All flow rates are given in standard cm$^3$s$^{-1}$, that is the flow rates are normalized on a pressure of 1 bar at room temperature and are denoted by means of {} braces.

As a specific parameter for characterizing the deposition with the expanding cascaded arc plasma jet, while varying a large number of parameters, often the inverse power-flow factor $Q$ is used. It is similar to the inverse of the $W/FM$ ratio, which is the common parameter in the case of stationary rf and dc deposition methods: $W$ is the power, $F$ is the monomer flow rate, and $M$ is the molecular weight of the monomer. The factor $Q$ is defined as $F/AV$ with $F$, the net carbon flow rate, $A$ the argon flow rate, and $W$ the power of the arc. In contrast to, e.g., Ref. 17, we cannot simply state that a high $Q$ factor leads to a precursor-similar structure in the film. In our case the monomer dissociation degree is much higher, and various mechanisms contribute to the observed relationships between reactor settings and carbon film properties. As in our case the power and the argon flow were kept constant, we can present our results as a function of the hydrocarbon flow rate. The net carbon flow rate in a flow of 0.151 ml min$^{-1}$C$_2$H$_4$ is equal to the net carbon flow rate in a flow of 2 cm$^3$s$^{-1}$C$_2$H$_2$. A flow rate of 1 cm$^3$s$^{-1}$C$_2$H$_2$ is equivalent to a $Q$ factor of $\sim 5 \times 10^{-6}$ W$^{-1}$. More details on the deposition reactor, the reactor settings, and the relations with the deposited materials are given elsewhere. $^{14,15}$

In the present project, two sequences of deposition experiments were carried out. The first sequence was aimed at optimizing the properties of the films suited for optical applications, the second at depositing films on steel substrates providing a good anticorrosion protection. A major demand for the films in both sequences was that they have a good adhesion to the substrate.

In the first sequence acetylene (C$_2$H$_2$) and toluene (C$_7$H$_8$) were used as admixtures. With acetylene a series of thin (~500 nm) films was deposited, in order to update the results found in the past. $^{14,15}$ In a second series, thick films (>1 $\mu$m) with a good adhesion to the substrate were deposited with the use of toluene. The most promising trials of both series were repeated with admixture of hydrogen as an extra feed gas in order to try and deposit more diamondlike films with enhanced $sp^3$ bonding. Each trial batch consisted of one B-doped (100)-silicon substrate (2.5×2.5 cm$^2$ and one glass substrate (Menzel-Gläser microscopy glasses; 3×1 in.). The diagnostics were all carried out on the coatings on the silicon samples; the glass samples were mainly meant for a qualitative judgment of the adhesion and the transparency of the coating. The range of the applied reactor settings is given in Table I, with the notice that in this sequence the chamber pressure was always 100 Pa.

In the second main sequence, the corrosion-performance study, films were deposited using various hydrocarbon flow rates, and with CF$_4$ as an extra admixture. In each batch, substrates of two types of steel, each with dimensions 5×5 cm$^2$ were placed: The steel types used were cold-rolled, low carbon steel (CRS) of automotive grade and electrogalvanized steel (EGS), both manufactured by Armco Research and Technology (Middletown, OH). To facilitate various film diagnostics, also a substrate of silicon was added. In this second sequence the chamber pressure was reduced to 22 Pa, in order to enlarge the deposition area.

B. Adhesion improvement by pretreatment

Adhesion of a-C:H films to the substrate is a major issue in the study of the applicability of these films for protective purposes. A distinction can be made between the polymer-like, hydrogen-rich films, which are deposited in low $Q$-factor trials, and the diamondlike, hydrogen-lean films at the high-$Q$ side of the reactor parameter range. $^{12,15}$ In gen-
er polymerlike films are soft and adhere reasonably well to the substrate. Using gaseous precursors like CH₄ and C₂H₂, with our method this is valid for thicknesses of up to about 1 μm. Particularly the diamondlike films contain internal stresses, and have a tendency to delaminate at thicknesses of only a few hundreds of nanometers.

It is well-known that a thorough cleaning of the substrate before depositing an a-C:H layer is essential for the adhesion of the film. For the glass and silicon substrates 5 min ultrasonic cleaning in an organic solvent (trichloroethylene) was carried out. For the CRS and EGS substrates this treatment must consist of a few stages. In order to remove stamping oil, the substrates were first cleaned ultrasonically in trichloroethylene (purity >99.5%) for 5 min. As a second stage, the substrates were cleaned in a 100/5 Ar/H₂ plasma for 5 min, with a substrate temperature rising to ~300 °C. In a third pretreatment stage, in which it was attempted to create an intermediate steel-carbon layer. The bias potential was limited to ~200 V in order not to damage the growing layer. On the other hand, it is not sure whether this bias value was high enough to really implant the ions. After switching off the bias the actual deposition was carried out during some tens of seconds.

C. Film diagnostics

For determining the optical parameters of the film, ellipsometry measurements were carried out by the group Surface Physics of the Department of Physics of the Eindhoven University of Technology. The setup used was practically identical to the one previously described. A rotating polarizer system (static analyzer at 45° orientation) with a stagnant cascade arc as a high-intensity light source was used. The angle of incidence was 68.3°, and wavelength dependent signal detection occurred by means of a photodiode array. The ellipsometric Fourier coefficients a and b were determined over the wavelength range from 300 to 1100 nm (from 4.5 to 1 eV).

For determining the bonding types in the film, IR spectra were recorded with a Bruker IFS 66 Fourier transform interferometer, with a resolution of 4 cm⁻¹, using again a stagnant cascade arc as a light source.

In order to determine the hydrogen content and possible oxygen incorporation in the films (both bonded and not bonded), nuclear recoil techniques were carried out using a beam of high energy α particles, produced by the AVF cyclotron of the Department of Physics of the Eindhoven University of Technology. In each measurement two techniques were used simultaneously, nuclear backscattering for calibration purposes and (noncoincident) elastic recoil detection (ERDA) for the actual concentration determination. Two different experimental configurations, beam energies and detection methods were used, for the detection of the heavy elements oxygen and carbon, and the light element hydrogen, respectively. More information on these techniques can be found in the literature.

The diagnostics for testing the corrosion resistance of the films were all carried out by Armco Research and Technology and related laboratories.

---

TABLE II. Survey of the trials for the optical applications; [CH₄], [C₂H₂], [C₃H₆], and [H₂], flow rates; d and Rd, film thickness and growth rate on silicon as obtained from the ellipsometric fits; t₆, duration of deposition; T, deposition temperature; p, chamber pressure, p = 100 Pa. All other reactor settings are given in Table I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[C₁H₂] (cm³s⁻¹)</th>
<th>[C₂H₂] (mlmin⁻¹)</th>
<th>[C₃H₆] (cm³s⁻¹)</th>
<th>[H₂] (cm³s⁻¹)</th>
<th>d (nm)</th>
<th>Rd (nm s⁻¹)</th>
<th>t₆ (s)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E8</td>
<td>...</td>
<td>0.068</td>
<td>...</td>
<td>...</td>
<td>180</td>
<td>190</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E9</td>
<td>...</td>
<td>0.151</td>
<td>...</td>
<td>...</td>
<td>120</td>
<td>180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E10</td>
<td>...</td>
<td>0.227</td>
<td>...</td>
<td>1660</td>
<td>5.5</td>
<td>300</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>E11</td>
<td>...</td>
<td>0.302</td>
<td>...</td>
<td>1730</td>
<td>9.6</td>
<td>180</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td>E12</td>
<td>...</td>
<td>0.378</td>
<td>...</td>
<td>2300</td>
<td>15</td>
<td>150</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>0.36</td>
<td>...</td>
<td>370</td>
<td>2.9</td>
<td>125</td>
<td>160</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td>0.90</td>
<td>...</td>
<td>370</td>
<td>6.2</td>
<td>59</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>1.90</td>
<td>...</td>
<td>395</td>
<td>14</td>
<td>29</td>
<td>110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F4</td>
<td>3.6</td>
<td>...</td>
<td>265</td>
<td>19</td>
<td>14</td>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F5</td>
<td>6.6</td>
<td>...</td>
<td>310</td>
<td>44</td>
<td>7.3</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F6</td>
<td>10.9</td>
<td>...</td>
<td>245</td>
<td>61</td>
<td>4.0</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>10.9</td>
<td>...</td>
<td>500</td>
<td>15</td>
<td>32.5</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G2</td>
<td>6.6</td>
<td>...</td>
<td>50</td>
<td>2.0</td>
<td>26</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G3</td>
<td>3.6</td>
<td>...</td>
<td>49</td>
<td>1.0</td>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>...</td>
<td>0.151</td>
<td>3</td>
<td>2380</td>
<td>9.6</td>
<td>240</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>H3</td>
<td>...</td>
<td>0.151</td>
<td>3</td>
<td>8120</td>
<td>9.0</td>
<td>900</td>
<td>...</td>
<td></td>
</tr>
</tbody>
</table>
Glow discharge optical spectroscopy (GDOS) was used for depth profiling of the films. In the GDOS diagnostic (cf., e.g., Ref. 33) the film is sputtered by a beam of high energy argon ions. Typical operating parameters are a voltage of 700 V and a current of 30 mA. The device used is a LECO GDS-1000 glow discharge spectrometer. A qualitative picture of the sputtered elements is obtained by observing the optical emission of the glow discharge. In this way a depth profile of the elements in the film is obtained as a function of time. It should be noted that the GDOS technique has a widely varying sensitivity for the different elements and can only be used for a qualitative analysis. For instance, it appears to be very insensitive to hydrogen. On the other hand it is known that small amounts of nitrogen in a plasma can lead to strong optical emission bands.

The corrosion performance of the films was tested qualitatively by storing them in a humidity cabinet (85% relative humidity, 60 °C) for 96 h.

EIS yields information on the barrier properties of the films. This is a relatively novel method. The most important parameter is the pore resistance $R_p$. This quantity is equal to the modulus of the impedance of the system in the limit of zero frequency. This parameter is a direct measure for the porosity of the layer and consequently for the corrosion performance.

Preliminary TOFSIMS measurements were carried out on one sample in order to investigate the possible merits of this technique for the analysis of amorphous carbon films. The measurements were performed on a Kratos PRISM instrument.

SEM was applied for studying the morphology.

IV. RESULTS

A. The properties of a-C:H films aimed at optical applications

1. Results of the spectroscopic ellipsometry and the infrared absorption spectroscopy

In Table II a survey of the coatings studied for their suitability for optical purposes is given. In Fig. 2 an example of a representative fit to the measured $a$ and $b$ coefficients is shown. It can be observed that the fit is satisfactory and that the model is adequate for the present purpose. The fit can probably be improved by using the program options of a frequency dependence of the refractive index, and of the top layer. The drawback is that the number of fit parameters increases. Another disturbing factor may be the fact that the spectroscopic data are very sensitive to a slight error in the angle of incidence. Moreover, the validity of the Tauc relation is limited. This hinders the selection of the appropriate wavelength range, since this depends again on the (unknown) band gap. So future refinements on the application of this method are desirable. Nevertheless, the accuracy of the fit was sufficient to obtain approximate results on the thicknesses, band gaps, and refractive indices of the films.

In Fig. 3 the deposition rate as function of the flow rates is shown, as obtained from the best-fit thickness of the ellipsometric data. It can be observed that the deposition rate increases almost linearly with the hydrocarbon flow rate up to large values. The area of deposition was $\sim 100 \text{ cm}^2$. In Fig. 4 the refractive index and the band gap are shown as a function of the flow rates of acetylene and toluene. The values of $G$ were in the order of $150-300 \text{ cm}^{-1/2} eV^{-1/2}$. The value of $280 \text{ cm}^{-1/2} eV^{-1/2}$, commonly reported for amorphous carbon films, was not always appropriate. For acetylene the same tendencies for the refractive index and the band gap as found in the past were obtained. For toluene, the refractive index is hardly dependent on the flow rate. The band gaps actually found are somewhat higher and may be more realistic, because most of the films are transparent for
and the most prominent absorption bands of an a-C:H film (trial Ell).

FIG. 5. Example of a wide wave-number-range fit of interference fringes
cal spectrum of an a-C:H film is shown over a wide wave

TABLE III. Peak assignment for the infrared C-H absorption bands ob-
served in our a-C:H layers. The first block gives the stretching vibrations,
the small second block gives the observed bending vibrations (from Ref. 35).

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>3300</td>
<td>sp¹CH</td>
</tr>
<tr>
<td>H5</td>
<td>2970</td>
<td>sp²CH₂</td>
</tr>
<tr>
<td>H7</td>
<td>2920</td>
<td>sp¹CH₃</td>
</tr>
<tr>
<td>H8</td>
<td>2875</td>
<td>sp²CH₃</td>
</tr>
<tr>
<td>H9</td>
<td>2850</td>
<td>sp³CH</td>
</tr>
<tr>
<td>H10</td>
<td>1620</td>
<td>sp²C=C olefinic</td>
</tr>
<tr>
<td>C2</td>
<td>1580</td>
<td>sp²C—C aromatic</td>
</tr>
<tr>
<td>B1</td>
<td>1370</td>
<td>sp³CH</td>
</tr>
<tr>
<td>B2</td>
<td>1450</td>
<td>sp³CH₂</td>
</tr>
</tbody>
</table>

red and orange light. The band gap decreases with an increasing hydrocarbon flow rate. For toluene the same tendency can be noted.

For optical purposes the ratio of the diamondlike sp³ bonding and the polymeric and graphitic sp¹ and sp² bonding types is of utmost importance. Particularly, the presence of delocalized π electrons in aromatic rings (e.g., in graphite) will reduce the band gap drastically. With infrared absorption spectroscopy the prevalent bonding types in the film can be determined. Extensive studies of the assignment of the IR absorption bands observed in a C:H layers were carried out by Dirschler et al. 10,24,35 Table III gives a selection, summarizing the C—C and C—H bonding types observed in our a-C:H layers.

Using the method described in Sec. II B, the IR absorption bands were determined absolutely by convolving them towards the measured IR absorption spectra. In Fig. 5 a typical spectrum of an a-C:H film is shown over a wide wave number. The power of the fit method in eliminating the interference fringes is also demonstrated. The results of the fits of the various trials can be summarized using band integrated intensities (or ratios) and band widths as relevant parameters.

It appeared that for all films deposited with acetylene (sequence F, Table II), only the sp³ bands around 2900, 1450, and 1370 cm⁻¹ are present. This confirms the finding 12 that films deposited with our technique, using acetylene, are predominantly diamondlike. In this case the ratio of the band integrated absorption coefficient of the 2920 cm⁻¹ sp³CH₁₂ and of the 2970 cm⁻¹ sp³CH₃ band should give an indication for the degree of cross linking (more C—C bondings). In Fig. 6(a) these band integrated absorption coefficient ratios are given as a function of the acetylene flow rate (solid symbols). No clear dependence of this ratio on flow rate can be observed. This may be due to the thickness differences of the films and the relative influence of a top layer and a substrate-film sublayer of different composition. In Fig. 6(b) the band widths are given as a function of the acetylene flow rate. The widths of the bands increase with increasing flow rate, indicating a harder (more diamondlike) film. 35 The top values of the band widths all decrease, for example the maximum of the 2920 cm⁻¹ sp³CH₁₂ band decreases from about 1000 to about 300 cm⁻¹.

Preliminary trials (sequence G) were carried out in order to try and improve the optical properties of the deposited films, by admixing various amounts of hydrogen in the plasma, following the experiences from crystalline diamond deposition trials. 15 In Fig. 6 the results for three values of the acetylene flow rate, upon addition of 14 cm³ s⁻¹ H₂ are shown (open symbols). It can be observed that the ratio of the integrated intensities of the sp³CH₁₂ and sp³CH₃ bands increases, that is the films become more diamondlike with an increasing H/C ratio in the plasma. Only for one film (G2) also the ellipsometric spectrum was recorded. The refractive index appeared to be low (1.5) but the band gap was enlarged from 1.2 to 1.6 eV (with G = 280 cm⁻¹ eV⁻¹/2). The growth rate was reduced to about 2 nm s⁻¹, so the hydrogen flow rate may have to be optimized. This result looks promising and future trials with this mixture are recommended.

Analyzing the IR spectra of the films deposited with toluene as an admixture (sequence F, Table II), it appeared that these films all have a polymeric character. Besides various sp³CH₃ bands also the aromatic and olefinic sp²C=C bands at 1580–1620 cm⁻¹ and the sp¹CH band at about 3300 cm⁻¹ can be observed (cf. Fig. 5). Besides the absorption coefficient ratio of the 2920 sp³CH₁₂ cm⁻¹ band and the 2970 cm⁻¹ sp³CH₃ band, in this case also the ratios with the sp³CH₁₂ band at 3300 and the sp²C=C bands around 1600 cm⁻¹ give an indication for the degree of cross linking. In Fig. 7(a) these ratios are given as a function of toluene flow rate. It is clear that the films become more diamondlike.
with higher flow rates. In this case, the widths of the bands [Fig. 7(b)] do not show a clear dependence on the flow rate. Simultaneously the absolute values of all the absorption coefficients appeared to decrease with increasing flow rate. For example, the maximum absorption coefficient of the 2920 \( sp^3 CH\equiv CH \) band decreases from about 600 to about 300 \( cm^{-1} \) with higher flow rates. In this case, the widths of the bands 2875, 2920, and 2970 \( cm^{-1} \) band, respectively.

A substantial improvement was again obtained by admixture hydrogen (using a small amount, taking into account the lower deposition rate for toluene). Two trials (H2 and H3) were carried out with an admixture of 3 cm\(^3\) s\(^{-1}\) Hz and 0.151 ml min\(^{-1}\) C\(_6\)H\(_6\) into the plasma. After the test H2, trial H3 was carried out aimed at depositing a thick (and protective) film, with good optical properties and a good adhesion. A deposition period of 15 min resulted in a thick \((8.1 \mu m)\) film with a good adhesion to glass and silicon substrates.

From the elipsometry data a refractive index of 1.55 and an optical band gap of 2.2 eV (with \( G=600 cm^{-1/2} eV^{-1/2} \)) were determined. Originally the films are yellow transparent, confirming this value for the optical gap. Similar results have been reported in Ref. 36.

In principle the exact number density of bondings \( C_H \) (and also \( C_c \)) per cm\(^3\) can be calculated from the band integrated absorption coefficient, and in this way a density estimation should be possible. To this end following formula (e.g., Ref. 37) can be used

\[
C_H = A, \int \frac{\alpha_v}{\nu} d\nu,
\]

with \( A \), the inverse absorption cross section and \( \nu \) the frequency (or, equivalently, the wave number) of the incident light. For the stretching modes of the three CH, \((x=1,2,3)\) bonding states, an average value of \( A_x=10^{21} cm^{-2} \) can be adopted. For our coatings, \( C_H \) number densities of the order of \( 5\times10^{22} cm^{-3} \) are then obtained. In Ref. 10 densities for a-C:H layers of typically 1.5-1.8 \( g cm^{-3} \) are reported, with comparable values for the band integrated C-H absorption coefficients. The C-C vibrations are lying in the range 700-1500 \( cm^{-1} \), and in the actual measurements we could not resolve these, probably due to the low infrared absorption cross section for this type of bonding.

2. The atomic C/H and C/O ratios as determined by the nuclear recoil techniques

In Fig. 8 some typical carbon/oxygen-ERDA spectra are shown. The high intensity peak at about 5.4 MeV is caused by elastically recoiled C atoms which pass through the thin foil detector and only reflect a relative impression of the layer thickness. Profiling is obtained by the spectra of the inelastically recoiled carbon atoms (with emission of gamma radiation). These exhibit an intensity distribution independent of the recoil energy, showing that the bulk of the film is homogeneous over the thickness. The slowly decreasing low-energy edge of especially the carbon signals may be due to layer thickness or density variations in the substrate-film interface (except the gradual decrease observed for the reference oxide, which is due to the variation of the cross section with energy). From the ERDA measurements the total numbers of carbon, oxygen, and hydrogen atoms per cm\(^2\) and their ratios were obtained. Measurements were carried out only for a selected number of the deposition trials. It should be noted that for the actual specific measurement technique special thin films of about 50 nm were required. In Table IV the results are summarized. So the trials in column I of Table IV are reproductions of those in Table II, with a very short deposition time (a few seconds). The ERDA measurements for carbon and oxygen were carried out one day after the deposition of the films. Also the hydrogen content of samples E9, H2, and F1 was measured on the same day.
The hydrogen content of the other samples were measured three months later. As a check the H/C ratio of sample F1 was determined in both measurement series. The H/C ratios were 0.56 and 0.57, respectively, showing the good reproducibility of the results of this technique and indicating that the hydrogen content in the films does not change substantially with time. It can be observed that with increasing acetylene flow (F1 through F6) the hydrogen contents in the films decrease, indicating an increasing diamondlike character, in agreement with the IR results and Refs. 12 and 15. The absolute values of the H/C ratio are much lower than in Ref. 12, where a different measurement technique was applied. The actual values around 0.5 are more realistic and of the same order as the ones reported in other literature.10 In general the oxygen content in the films is small. The high oxygen content (13 at. %) for sample E9, deposited using toluene may be due to the relatively large amount of double and triple carbon bonds in the deposited film. By exposure to air these may be oxidized. Another possibility is that the oxygen was already dissolved in the (liquid) toluene.

In Ref. 23 it is reported that it is possible to relate the C-H number densities as obtained by the IR transmission measurements using Eq. (11) and the H/C ratio as determined by the ERDA measurements quantitatively to each other. The following relationship is given:

\[
\int \frac{a \nu}{d} \nu \approx \int \frac{6H}{c} \text{ERDA}.
\]

For our films this relationship appears to be only roughly valid. This may be due to the fact that with ERDA also the unbonded hydrogen is detected.

### B. The parameters of a-C:H,F coatings for anticorrosion protection

#### 1. Introduction

Trials aimed at producing a good anticorrosive film were carried out, using both hydrocarbons and fluorocarbons as admixtures. Films produced with the latter admixture are known to exhibit a moisture-repulsive behavior which might imply also a good corrosion performance. In Table V a survey of the most important trials is given. The films of trials D5 through D12 were deposited on large steel substrates (5×5 cm²) and these were analyzed by several techniques. Only for D7 a stable thermocouple temperature measurement was obtained, but the other temperatures can be estimated to be of the same order (depending on deposition time).

#### 2. Results of the GDOS

In Fig. 9 a typical GDOS spectrum for a film deposited on a CRS substrate is shown (trial D7). From correlating the GDOS sputter time with the thickness of the layer as estimated by a SEM photograph, it could be deduced that about 1 μm of an amorphous carbon film is sputtered in about 35 s. Using the fact that the sputter rate is approximately constant for films of the same type, estimates for the growth rate of all of the films were deduced. In Fig. 10 (cf. Table V) the obtained growth rates on the CRS substrates are given as a function of the hydrocarbon flow rate. The GDOS spectrum reveals some specific features. The peak in the first seconds is an artifact during stabilization of the ion beam. Correlations of oxygen, nitrogen, and iron can be observed. The

<table>
<thead>
<tr>
<th>Sample</th>
<th>[C₂H₅] (cm³ s⁻¹)</th>
<th>[C₂H₆] (ml min⁻¹)</th>
<th>[CF₄] (cm³ s⁻¹)</th>
<th>d (CRS, EGS) (nm)</th>
<th>Rₙ (CRS, EGS) (nm s⁻¹)</th>
<th>tₑ (s)</th>
<th>Vₑ (V)</th>
<th>Tₑ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D5</td>
<td>3.0</td>
<td>...</td>
<td>...</td>
<td>610, 450</td>
<td>12, 9</td>
<td>50</td>
<td>-70</td>
<td>70</td>
</tr>
<tr>
<td>D6</td>
<td>6.0</td>
<td>...</td>
<td>...</td>
<td>910, 850</td>
<td>20, 28</td>
<td>10</td>
<td>-110</td>
<td>...</td>
</tr>
<tr>
<td>D7</td>
<td>3.0</td>
<td>...</td>
<td>0.6</td>
<td>1060, 830</td>
<td>21, 17</td>
<td>10</td>
<td>-50</td>
<td>110</td>
</tr>
<tr>
<td>D8</td>
<td>6.0</td>
<td>...</td>
<td>0.6</td>
<td>1000, 830</td>
<td>22, 19</td>
<td>10</td>
<td>-50</td>
<td></td>
</tr>
<tr>
<td>D9</td>
<td>1.5</td>
<td>...</td>
<td>0.6</td>
<td>480, 270</td>
<td>8, 4</td>
<td>10</td>
<td>-100</td>
<td></td>
</tr>
<tr>
<td>D10</td>
<td>...</td>
<td>1.0</td>
<td>...</td>
<td>540, 450</td>
<td>9, 7</td>
<td>10</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>D11</td>
<td>...</td>
<td>0.4</td>
<td>...</td>
<td>1440, 2090</td>
<td>36, 32</td>
<td>10</td>
<td>-800</td>
<td></td>
</tr>
<tr>
<td>D12</td>
<td>...</td>
<td>0.4</td>
<td>0.6</td>
<td>60, 120</td>
<td>0.5, ...</td>
<td>10</td>
<td>-10</td>
<td></td>
</tr>
</tbody>
</table>

---

TABLE IV. Results of the ERDA measurements; flow rates C₂H₆ in ml min⁻¹, other (gas) admixtures in cm³ s⁻¹.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Feed gas C number + flow rate (10¹⁰ cm⁻³)</th>
<th>O number (10¹⁰ cm⁻³)</th>
<th>H number (10¹⁰ cm⁻³)</th>
<th>α/H/C</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>0.9 C₂H₆</td>
<td>300</td>
<td>4.5</td>
<td>168</td>
<td>0.015</td>
</tr>
<tr>
<td>F4</td>
<td>3.6 C₂H₆</td>
<td>830</td>
<td>25</td>
<td>374</td>
<td>0.040</td>
</tr>
<tr>
<td>F6</td>
<td>10.8 C₂H₆</td>
<td>2400</td>
<td>36</td>
<td>860</td>
<td>0.015</td>
</tr>
<tr>
<td>G1</td>
<td>10.8 C₂H₆+14 H₂</td>
<td>1600</td>
<td>43</td>
<td>400</td>
<td>0.027</td>
</tr>
<tr>
<td>E9</td>
<td>0.151 C₂H₆</td>
<td>290</td>
<td>64</td>
<td>156</td>
<td>0.22</td>
</tr>
<tr>
<td>H2</td>
<td>0.151 C₂H₆+3 H₂</td>
<td>480</td>
<td>37</td>
<td>210</td>
<td>0.076</td>
</tr>
</tbody>
</table>
former are probably due to residual gases in the deposition chamber. The latter is an indication of a porous film. Physical sputtering of iron during the deposition of the film is very unlikely, in view of the low bias potential and hence ion energy. Further, it can be observed that the substrate film interface appears diffuse. This may be a consequence of the third pretreatment, the bombarding of the substrate with carbon ions, but possibly it is an artifact of the method (rapid simultaneous sputtering of film and substrate). All the films deposited on CRS substrates showed a spectrum similar to the one of Fig. 9, with slight variations in contaminations signals. In films deposited at a higher chamber pressure, these signals were relatively lower (as expected).

In Fig. 11 the spectrum of the film grown simultaneously on the EGS substrate is shown. Besides the contaminations already mentioned, a very interesting feature can be observed in the substrate-film region. The carbon signal shows a pronounced rise. This may be an artifact due to the conductivity of the substrate, but more likely it is an indication for the presence of a substrate-material dependent interfacial layer. This hypothesis is supported by the fact that the film deposited on EGS was always thinner than the one deposited on CRS (in the same trial). As the absolute value of this difference is approximately constant, it points to some kind of incubation time before the growth starts on zinc. These two phenomena indicate that the initial growth may be different on CRS and EGS substrates, as a consequence of the difference in electrical and thermal conductivity of the substrate. Subsequently, the initial growth mechanism may have influence on the growth mode of the bulk of the film.

3. Results of the corrosion performance studies

In Fig. 12 the qualitative results of the corrosion tests are shown. Bare CRS substrates show severe corrosion in this test [Fig. 12(d)]. The corrosion performance of films deposited with an argon/hydrocarbon plasma (e.g., D11) is moderate, particularly of the thicker films. Most probably not the thickness but the adhesion is a very important factor, in addition to the film composition. Samples D7 and D9 showed a good corrosion resistance. These were films produced with acetylene, with additional admixture of CF4. Preliminary XPS measurements indicate a content of 10 at. % F, 3% N, 12% O, and 75% C for sample D7. In Fig. 13 the IR transmission spectrum of a typical a-C:H:F film (trial D9; on the silicon reference sample) is given. It appears that besides low-amplitude C—H bands also the C—F band at 1200 cm⁻¹ is present.
cm\(^{-1}\) (Ref. 38) is prominently present. In the IR spectrum of trial D7, typically hardly any absorption at all could be distinguished. Concerning the good corrosion performance of the fluorinated amorphous carbon films several explanations are possible.

1. The partial saturation of the carbon bondings by F atoms, instead of H atoms may have led to lower internal stresses, diminishing the delamination, which would lead to direct exposure of the CRS substrate to the environment.

2. The growth mechanism for films deposited with the use of CF\(_4\) may be different, due to the simultaneous etching by the fluorine radicals. This view is supported by the following SEM images. In Figs. 14(a) and 14(b) images of the coatings on the silicon reference samples of trials D11 and D7 are shown. It can be observed that for D11 a typical columnar growth mechanism has occurred, which starts from island growth and results in columnar grains with curved domes on top.\(^{40}\) Typical for this growth mode are the existence of voids and, corrosive species are not effectively blocked. The film deposited with CF\(_4\) [Fig. 14(b)] appears to be very smooth. It is likely that by the simultaneous etching by the fluorine radicals and subsequent reorganization of the nanostructures, the columnar growth mechanism can be avoided. An explanation is that the mobility on the growing surface can be enhanced by a chemical mechanism.\(^{41}\) The resulting film will be more uniform and dense, and provide a better anticorrosion protection.

3. The substrate is etched by the fluorine radicals, creating a very high density of defects, which act as gettering sites, resulting in a more uniform initial growth. In the subsequent film bulk morphology the growth of large-scale separate columns is avoided. A more gradual and regular structure may arise, without or, with less voids, minimizing the diffusion of ambient air. A similar effect can be noted in the case of diamond deposition. An enhanced nucleation density on the substrate results in the growth of smoother films. In Ref. 42 successful utilization of the high etching activity of fluorine on silicon for this purpose was reported.

The growth rate in trials with CF\(_4\) addition was of the same order as in the trials without CF\(_4\) addition (compare ▼ and ▲ in Fig. 10). This finding implies that, in order to obtain a high quality film, the growth rate does not necessarily have to be reduced.

4. Results of the EIS

As a preliminary study, for the first time carbon films (on the EGS samples) were subjected to EIS. In Fig. 15 the modulus of the impedance, ||Z||, is shown as a function of frequency, for various trials. The values for the best CRS films D7 and D9 however, are not very high. The highest value has been obtained for film D11. The corrosion performance of this film on CRS was low. These paradoxal results may be due to difficulties in the interpretation on the results of this novel method. Another explanation is that these results confirm the hypothesis that the growth mode on CRS is different from that on EGS. The specimen D11 was produced using toluene (meaning a relatively high Q factor), without admixture of fluorines. The only factor deviating from other trials using toluene, was the bias in the pretreatment stage. Accidently the bias was set at a high value of \(-800\)\(^{\text{V}}\). (Obviously, this improved not only the pore resistance but also the growth rate.)

5. Results of the TOF-SIMS

As a test measurement, the spectrum of a typical a-C:H film, deposited with a low hydrocarbon flow (low Q factor)
was recorded (reactor settings approximately those of sample \( \Gamma 2 \)). In the positive ion spectrum, the predominant radicals in this film appeared to be \( \text{C}_4\text{H}_3, \text{C}_2\text{H}_3 \) and with a lower intensity \( \text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_3\text{H}_2 \). The former two point to an abundance of carbon \( sp^2 \) bondings over the \( sp^3 \) bonding form, indicated by the latter three species. This finding is consistent with the results of the IR measurements, which showed that low \( Q \)-factor films are more polymerlike. Some aromatic compounds were found, too. In the negative ion spectrum of this film large contaminations of oxygen and nitrogen, and also chlorine and sulphur were found. As TOFSIMS is a surface sensitive technique (upper 3 Å), this points to reactions of the top layer with the ambient air. It is known that at the surface of plasma deposited films, highly reactive free radicals occur.

V. CONCLUSIONS

(1) Polymerlike and diamondlike \( a\)-\( \text{C}:\text{H} \) coatings can be deposited at high rates of tens of \( \text{nm s}^{-1} \) with the cascaded arc deposition technique using acetylene as a carrier gas. Using toluene results in the deposition of polymerlike films.

(2) In general the adhesion of the films deposited with toluene is very good, even for films with a thickness of several \( \mu \text{m} \). Using acetylene results in films with a moderate adhesion.

(3) The optical and protective properties of the films can be improved by admixing additional feed gases to the argon/hydrocarbon plasma. Addition of hydrogen leads to more diamondlike films with a larger optical band gap.

(4) To obtain a high corrosion resistance, the addition of a fluorine containing gas is beneficial. Three explanations are offered:

(i) The incorporation of fluorines leads to \( a\)-\( \text{C}:\text{H}, \text{F} \) films with much smaller internal stresses compared with those of \( a\)-\( \text{C}:\text{H} \) films, and avoiding delamination.

(ii) The deposition process consists of simultaneous etching and redeposition, leading to a chemically enhanced surface mobility and a different growth morphology, resulting in a less porous structure.

(iii) By etching of the substrate by the fluorine radicals the number of sites from which the growth starts, is increased, resulting in a more uniform growth.

(5) Different film types were obtained on the CRS and the EGS substrates. On the latter the initial growth appears to require an incubation period. This may be due to the difference in (both electrical and thermal) conductivity of the substrate.

(6) The initial growth of an amorphous carbon film may be an important factor in determining the subsequent film morphology. By controlling the growth in this stage, the film properties for the bulk of the film may be predefined.

(7) A thick film is not a prerequisite for a high corrosion resistance. On the contrary, these films tend to detach from the substrate, providing pathways for corrosive species. Thin films are adequate and with the high growth rates obtained with the cascaded arc method, economically feasible industrial production of these films is within reach.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the collaboration with Armco Research and Technology (Middletown, OH) and related laboratories, where all measurements of the corrosion study were carried out. Further they wish to thank all the persons of the Dept. of Physics, Eindhoven University of Technology who were involved in the other measurements, that is of the Surface Physics group, Professor H. H. Brongersma, Dr. C. Flipse and Dr. P. Musters, of the Nuclear Physics group, Professor M. J. A. de Voigt and Dr. L. v. Uitdenbogdor, and of the EPG Plasmaphysics group, Professor F. J. de Hoop and H. den Boer, and Dr. J. J. Beulens of Daresbury Laboratory (U.K.) for the XPS measurements. The skillful technical assistance of M. J. F. van de Sande is gratefully acknowledged.


FIG. 15. EIS spectra of \( \text{a}:\text{C}:\text{H}, \text{F} \) coatings on EGS substrates.

39 J. J. Beulens (private communication, Daresbury Laboratory, U.K., 1993).