DEPOSITION OF HARD AMORPHOUS CARBON THIN FILMS:
EFFECTS OF NOBLE GAS DILUTION

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Abstract
In this work we present an investigation on amorphous carbon films deposited in 13.56 MHz radiofrequency (rf) CH₄/Ar and CH₄/He plasmas: the processes variables were the methane dilution and the bias voltage, fixed at –100V and –400V. The effect of noble gas dilution on the structure and optical properties of a-C:H films was investigated by Raman spectroscopy, infrared (IR) absorption, UV-VIS transmittance and ellipsometry measurements. With respect to the bias effect, the experimental results indicate that the addition of argon and helium to the methane plasma allows an increase of the refractive index only at lower bias voltage. The structural changes induced by the noble gas dilution are generally more pronounced in Ar rich atmosphere, even if similar optical modifications are observed for films grown from CH₄/Ar and CH₄/He plasmas.

I. Introduction
Hydrogenated amorphous carbon (a-C:H) films have been of great interest since their advent, owing to their wide range of useful properties, such as high mechanical hardness, chemical inertness, and optical transparency [1]. It is known that a-C:H films have an extremely complex structure due to the different types of hybridization of carbon atoms: tetrahedral sp³, trigonal sp². The amount and bonding of hydrogen incorporated in these films plays a crucial role in stabilizing the tetrahedral sp³ bonds and thereby tailoring the film properties. Among the various methods used to prepare a-C:H films, the most common is the deposition from rf glow discharge of hydrocarbons, usually a CH₄ plasma. By manipulating the deposition parameters, a-C:H films can be produced with a broad range of properties ranging from polymer-like (hydrogen rich, low sp³ fraction, high optical gap) to diamond-like (high sp³ fraction, low hydrogen, low optical gap) films [2]. Unfortunately, in spite of the large effort made to optimize their structure and optical properties under a wide range of deposition parameters, a systematic study of the effects of precursor dilution by noble gases on the film microstructure and on optical properties is still lacking, even if a few results concerning the structural and compositional modifications induced in a-C:H films by Ar and He dilution have been published [3-6].
In the present work, we have studied a-C:H films from the viewpoint of bonding characteristics and optical properties. As a function of deposition parameters, the modification of both the chemical bond states and the vibrational properties upon methane dilution by Ar
and He noble gases were studied using infrared (IR) and Raman spectroscopy for a better understanding of the role of hydrogen content and the formation of various sp’ and sp’ carbon bonds in the films. The ellipsometric and UV-VIS transmittance measurements have then been exploited to probe the macroscopic optical behavior of the films, studying the evolution of the refractive index and film transparency as a function of methane fraction.

II. Experimental Details

Hydrogenated amorphous carbon (a-C:H) films were deposited on silicon substrates in an rf glow discharge system using two different mixtures of CH₄/Ar and CH₄/He. Substrates were kept on a water cooled powered cathode. The process controlled variable was the CH₄ dilution by noble gases varying the Ar and He fraction from 0% to 90%. The total gas flow was fixed at 28 sccm so that the same pumping speed and pressure (9Pa) could be used in all deposition processes. Two series of samples were grown keeping the rf bias voltage constant at -100V and at -400V, respectively. The deposition rate was calculated by a Tencor surface profile system, measuring the height of a step produced on a partially coated sample. The thickness of the deposited films varied from 30 nm to 300 nm, depending on deposition conditions. Infrared (IR) spectra were recorded using a Jasco 615 Fourier transform IR spectrometer. Raman spectroscopy measurements were carried out at room temperature in a nearly back scattering configuration with an angle of 90° with samples held in air. Unpolarized Raman spectra were obtained exciting the film with 100 mW of the 488.5 nm Ar⁺ laser line, analyzed with a Jobin-Yvon (Ramanor model HG2-S) double monochromator, equipped with holographic gratings (2000 lines/mm), and detected by a standard photon counting system. The refractive index was measured at a fixed angle of 70°, by a Philips SD 200x ellipsometer, operating at three different wavelengths: two in the infrared, 1530 and 1300 nm, and one in the visible at 632.8 nm. Finally, an UV-VIS Perkin Elmer 2000 spectrometer was used to evaluate the transparency of DLC coatings deposited on glass substrates. The related optical gaps were calculated basing on transmittance and thickness data [7].

III. Results
Figure 1 shows the film growth rate and conversion efficiency (growth rate divided by carbon containing precursor gas flow) for increasing Ar and He fraction in the plasma atmosphere. The measured growth rate decreases with the noble gas dilution. However, since the absolute carbon density depends on the fraction of CH\textsubscript{4}, the deposition rate normalized on the actual amount of carbon increases with the Ar and He partial pressure. This effect is mainly evident for the depositions carried out with Ar dilution.

The structural investigation was carried out by Raman spectroscopy recording the spectra of the films (Fig. 2) between 1000 and 2000 cm\textsuperscript{-1}, which exhibit the features commonly observed for amorphous carbon materials \[8\]. consisting in the D (disorder) and G (graphitic) Raman bands. The main G-band peak is positioned at about 1530-1550 cm\textsuperscript{-1}, while the D-band appears in form of a shoulder of the main G-band, located at about 1370 cm\textsuperscript{-1}. In order to take information on the evolution of the sp\textsuperscript{2} carbon bonding of the films as a function of noble gas fraction, each spectrum was least square fitted by two Gaussian curves superimposed to a background signal. In this way, we obtained the integrated intensity ratio \(I_D/I_G\) between the D and G bands, the peak position, \(\omega_G\), and the bandwidth, \(\Gamma_G\), of the G band, which are listed in table I.

**Figure 2:** Raman spectra of a-C:H films deposited from pure methane plasma and 10% CH\textsubscript{4} fraction with a rf bias voltage of a) –100V and b) –400V.

<table>
<thead>
<tr>
<th>CH\textsubscript{4} [sccm]</th>
<th>Ar [sccm]</th>
<th>He [sccm]</th>
<th>Bias Voltage –100V</th>
<th>Bias Voltage –400V</th>
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<tr>
<td></td>
<td>(\omega_G) [cm\textsuperscript{-1}]</td>
<td>(\Gamma_G) [cm\textsuperscript{-1}]</td>
<td>(I_D/I_G)</td>
<td>(\omega_G) [cm\textsuperscript{-1}]</td>
</tr>
<tr>
<td>28</td>
<td>1532</td>
<td>157</td>
<td>0.33</td>
<td>1532</td>
</tr>
<tr>
<td>4</td>
<td>1538</td>
<td>147</td>
<td>0.49</td>
<td>1546</td>
</tr>
<tr>
<td>4</td>
<td>1538</td>
<td>158</td>
<td>0.42</td>
<td>1544</td>
</tr>
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As shown in Table I the amorphous carbon film obtained by methane dilution exhibits a relatively narrow G band and a definite increase in the D band intensity. This effect is mainly pronounced for the samples grown in Ar rich atmosphere. Concerning the bias voltage effect.
it is evident that for a fixed plasma composition at -100V the G band position tends to decrease to lower energy and its width to widening, while a reduction of the $I_D/I_G$ ratio is observed.

![Graph](image)

**Figure 3:** Refractive index of a-C:H films deposited in both CH$_4$/Ar and CH$_4$/He plasmas as a function of CH$_4$ fraction.

As for optical properties figure 3 shows that at low bias voltage the refractive index of the film slightly increases with increasing noble gas dilution. On the contrary, at -400V, the values of the refractive index decreased abruptly for noble gas dilution higher than 50%. No relevant differences were observed depending on noble gas dilution used. Table II lists the optical gaps $E_{04}$ (the energy value at which the absorption coefficient assumes a value of 10$^4$ cm$^{-1}$): the main effect on optical gap is represented by the deposition bias voltage, while only small variations are reported for samples deposited with the highest methane dilution. The intensity of the recorded IR spectra normalized on the film thickness shown in Figure 4 indicates qualitatively a decrease in the bonded hydrogen content in the coating when the bias is raised and the increase of intensity and a variation of the main absorbing region to higher wavenumbers for Ar and He dilution at bias of -400V. It is worth noting that these C-H absorption bands are related only to carbon atoms bonded to one or more hydrogen atoms and do not reveal anything about the unbounded hydrogen in a-C:H network.

IV. Discussion

Concerning the noble gas dilution effect on growth rate and conversion efficiency, Ar ions may be present to bombard the surface of films and excite the adsorbed monomers, creating radicals which may react with incoming radicals in the plasma to form bonding on the films surface. This mechanism may enhance the conversion efficiency. If this mechanism is considered, due to a lower momentum transfer from impinging ions, a reduction in the film deposition rate is expected for He dilution. In both cases clearly a change in the branching ratio of the active species is occurring depending on the noble gas used [9]. The observed dependence of the optical constants of a-C:H film on noble gas dilution reflects to a large extent the microstructural changes of the films. It is known [10] that the main structural feature of amorphous carbon films is the presence of both $sp^3$ and $sp^2$ carbon. For films deposited without noble gas dilution, the material is highly $sp^3$ bonded with only low fraction of $sp^3$ bonded carbon dispersed into the $sp^3$ matrix. For these films, the small number of $sp^2$ sites limits the formation of graphitic clusters. Upon noble gas dilution the a-C:H $sp^3$ diamond-like matrix collapses and the $sp^2$ carbon domains increase. A higher mass of Ar with respect to He results in the progressive raise of the $I_D/I_G$ ratio, indicating the formation of graphitic domains and the increase in their size and number. This clearly stands for bias voltage of -400V, while at lower bias a similar even if less pronounced effect was observed.
This interpretation should also take into account the area of main absorbing IR region indicating that a change in the C-H bonding configuration occurs with methane dilution. The data obtained for the films grown at -400V suggest that the modification of the structure induced by the noble gas dilution leads to an increase of the film hydrogen content. Hence, first of all, a gradual decrease of the interconnectivity in the carbon network occurs simply increasing the methane dilution. As a consequence, at lower methane fraction, with the

![Figure 4: IR spectra of samples deposited: a) from pure methane plasma and 10% CH₄ fraction at -400V; b) from pure methane plasma at -100V and -400V.](image)

increase of the hydrogen content the films have a lower transparency and less dense structure. According to what found with Raman spectroscopy, the consequent formation of larger number of sp² sites enhances the growth of graphitic clusters so that the measured refractive index and optical gap remain low with respect the films grown in noble gas free atmosphere. At lower bias an opposite behavior of the refractive index as a function of noble gas dilution could be explained in terms of a formation of hydrogen rich polymer-like structure consisting of low sp² carbon fraction, with high band gap for films deposited from pure methane plasma [11].

**Table II:** Optical gap of a-C:H films grown from pure methane plasma and 10% CH₄ fraction in CH₄/Ar and CH₄/He plasmas with a rf bias voltage of -100V and -400V.

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<tbody>
<tr>
<td>28</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
<td>0.9</td>
</tr>
<tr>
<td>4</td>
<td>24</td>
<td>0</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>24</td>
<td>0</td>
<td>1.3</td>
<td>1.0</td>
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As can be seen from the figure 4 and table II, both the hydrogen content and the band gap decrease with increasing bias voltage. For an increase in the negative self-bias of the
substrates, the growing films are exposed to more ion bombardment, which removes the weakly bonded hydrogen. This loss in hydrogen causes a reduction in the band gap [12].

V. Conclusion

In summary, the effect of Ar and He addition on the optical and structural properties of methane plasma deposited hydrogenated amorphous carbon films has been investigated. The deposition rate of the coatings, normalized on the carbon precursor flow rate, indicated that a different plasma chemistry occurs for the Ar and He dilution of pure methane plasma. For a bias voltage of ~ 400V, the measured values of the refractive index decreased abruptly for noble gas dilution higher than 50%. On the contrary, at low bias voltage the value of the refractive index of the film shows a slight increase with respect to what measured for sample grown from pure methane. IR spectra show that noble gas dilution produces an increase of the hydrogen content with a consequent reduction of the film density. The combined ellipsometry and Raman results may be interpreted by an increase of the sp² graphitic domains as a function of noble gas dilution.

References


2000