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DIAMOND AND RELATED MATERIALS

Influence of the addition of CF_4 on the deposition of a-C:H layers using the expanding thermal plasma technique

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Abstract

Applying an expanding cascaded arc thermal plasma beam deposition technique, amorphous fluorohydrogenated carbon (a-C:H,F) layers were deposited from acetylene (C_2H_2) and tetrafluoromethane (CF_4). Deposition of the layers was monitored in situ by HeNe ellipsometry and the layers were analyzed ex situ by Fourier transform IR spectroscopy. It is found that the growth rate of the layers is independent of the addition of the CF_4 precursor. However, the structure of the layers is influenced by the addition of CF_4. It is found that the extinction coefficient decreases with increasing CF_4 flow. The composition of the layers is changed with respect to the bonding types in the layers. The addition of CF_4 leads to incorporation of F in the layers and also to the appearance of sp^2 CH bonds, which implies modification of the layers by CF_4.

Keywords: Amorphous hydrogenated carbon; Infrared transmission; In-situ characterization; Plasma jet

1. Introduction

In recent decades interest in the research of diamond-like carbon films of amorphous hydrogenated carbon (a-C:H) has grown because of their unique properties such as hardness, chemical inertness, electrical insulation, tunable optical constants and transparency [1–3]. This makes these films suitable for a wide range of applications, such as antireflection coatings and protective coatings. In recent years increasing interest has been shown in a-C:H films, deposited with a fluor-containing precursor. The properties of the resulting a-C:H,F films are changed with respect to for example the hydrophobicity and imperviousness [4]. These layers are of interest with respect to tribological applications [5].

In this paper the influence of the addition of CF_4 on the deposition of a-C:H layers onto silicon is described. We wish to determine the influence of an etching precursor (CF_4) during the deposition process. The layers are deposited with an expanding cascaded arc thermal plasma beam set-up. The deposition parameter varied is the CF_4 flow. All other process parameters are kept fixed. The topics discussed in this paper are the influence of the CF_4 flow on the IR absorption peaks in the wavenumber interval 2900–3000 cm^{-1}, and its effect on the thickness, refractive index and extinction coefficient of the layers deposited.

2. Experimental

Deposition of the layers is performed using an expanding cascaded arc thermal plasma beam technique. Fig. 1 shows a schematic overview of the set-up; the cascaded arc is positioned on the left. Through this arc in the plasma channel, argon (Ar) gas flows as carrier gas from the left to the right. At the beginning of the channel three cathodes are positioned which are biased. The exit of the arc (called the nozzle) is grounded. Other details can be found elsewhere [6,7]. The Ar gas in the arc is ionized, giving a plasma at a pressure of 0.5 bar. The Ar gas flow is 50 standard cm^3 s^{-1}, the arc current is 24 A and the electrical power is 1.5 kW.

When the plasma arrives at the exit of the arc, it expands into the expansion vessel. As this vessel is at a low pressure of 0.14 mbar, the expansion is supersonic [8]. At the exit the precursor gases necessary for deposition are added to the plasma. Both a constant flow of 3 standard cm^3 s^{-1} C_2H_2 and a variable flow of CF_4, in the range 0–2.9 standard cm^3 s^{-1} are added to the expanding plasma. After a shock, the plasma mixture, which consists of the gases mentioned and the radicals and ions produced, is transported subsonically [9] towards the substrate holder positioned on the right side in the vessel. Typical of this type of plasma is a low ion energy (about 1 eV) and a high ion flux.

The distance from the nozzle to the substrate holder is about 80 cm. On this substrate holder deposition takes

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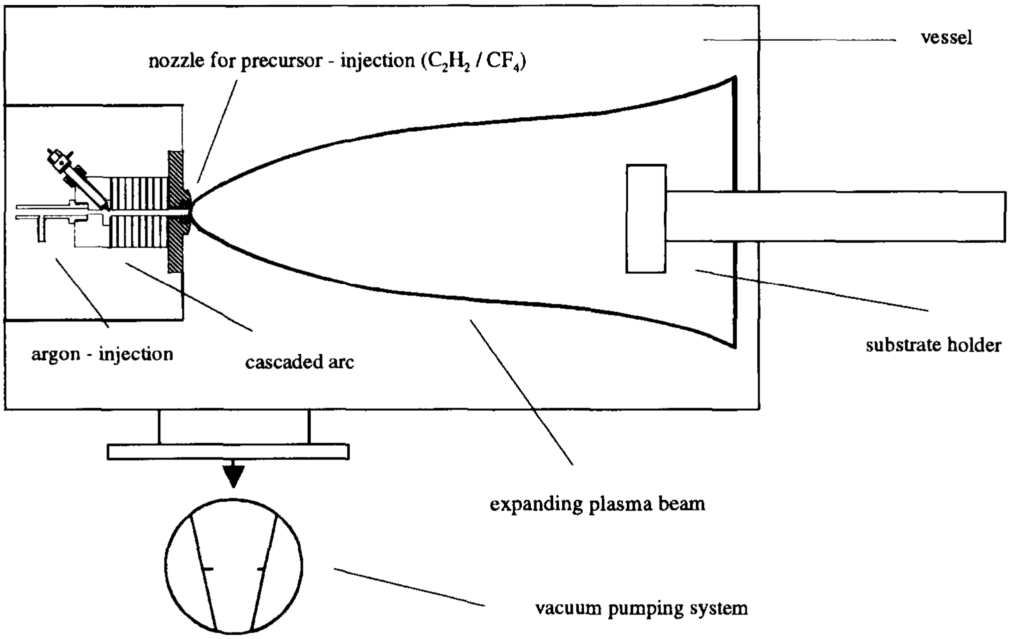

Fig. 1. Schematic drawing of the expanding cascaded arc thermal plasma beam deposition set-up.

place onto 2.5 × 2.5 cm^2 pieces of [100] oriented silicon from Wacker Chemitronic, which are cleaned with acetone, ethanol and distilled water.

The layers are deposited in a deposition time of 300 s. The variable CF_4 flow takes the values 0, 0.3, 0.6, 0.9, 1.4, 2.0 and 2.9 standard cm^3 s^{-1}. The other parameters are constant for all depositions. The temperature of the substrate increases from 13 to 35 °C during the deposition process. After each deposition the expansion vessel is cleaned by burning an Ar–oxygen plasma for 15 min. The Ar flow is then 100 standard cm^3 s^{-1}, the oxygen flow is 6 standard cm^3 s^{-1}, the arc current is 45 A and the electrical power is 4 kW. This increases the reproducibility significantly.

The deposition of the layers is monitored in situ with HeNe ellipsometry and ex situ by Fourier transform IR (FTIR) spectroscopy.

3. Results and discussion

3.1. In situ HeNe ellipsometry

The growth of the layer is monitored by HeNe ellipsometry. This technique reveals the change in polarization of incident laser light, when it reflects at the growing layer surface. The quantities determined are the ellipsometric angles Ψ and Δ as a function of deposition time [10]. The properties of the growing layer are obtained from studying Ψ–Δ curves. This is done by simulating the curves [11]. For these simulations a model is assumed for the layer which is deposited. This model consists of a silicon substrate, with a complex refractive index of 3.88 − 0.018i, a growing bulk layer and a top layer, on top of each other.

To obtain good agreement between simulation and measurement, the optical parameters of the bulk and top layer are varied. In Fig. 2 a typical example is shown of measured and simulated Ψ–Δ curves. From this picture it is evident that the simulation is in better agreement with measurement when the curve approaches the convergence point, which means that the layer becomes thicker. This is explained by the fact that the model used for simulation assumes a constant top layer, from the start of the deposition, and the effect of this decreases with increasing thickness of the bulk layer.

From the simulations the bulk parameters are determined. In Fig. 3 the refractive index n and the extinction coefficient k of the bulk layer are given at $\lambda = 632.8$ nm, with varying CF_4 flow. The refractive index is fairly constant or slightly decreasing and the extinction coefficient decreases with increasing CF_4 flow. The value of refractive index of about 2 is rather high, as the layer is grown with low ion energy. Normally, a minimum bias of 100 eV is necessary to obtain these indices [12]. Tentatively, one could conclude from this that the high ion energy does not determine the value of n and that the high ion flux may play a role (in combination with low ion energy) [13].

3.2. Fourier transform IR spectroscopy

After deposition, the layers are analyzed ex situ by FTIR spectroscopy. The transmission of the IR light is determined, which is defined as the ratio of transmission through the silicon substrate plus sample to transmission

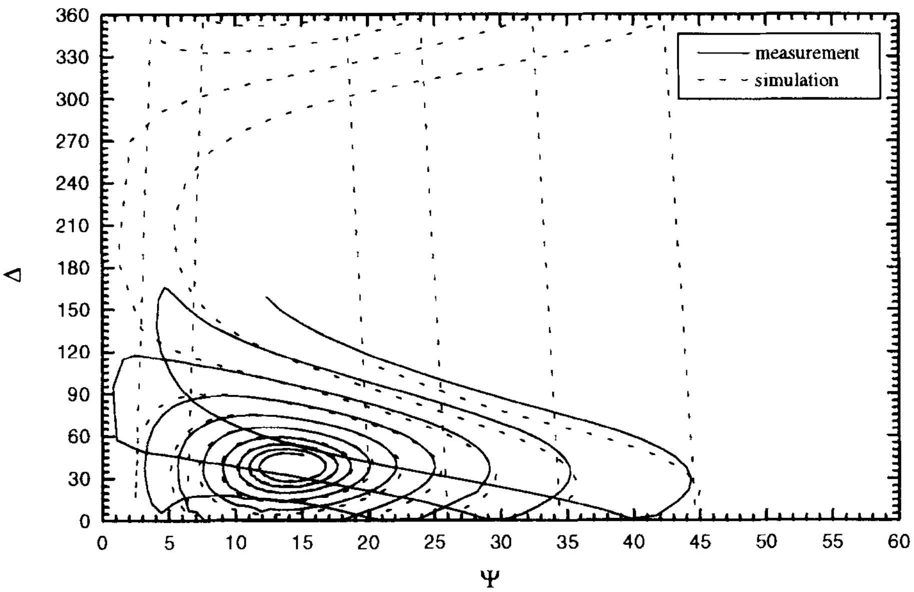

Fig. 2. A typical example of a Ψ-Δ curve both measured and simulated.

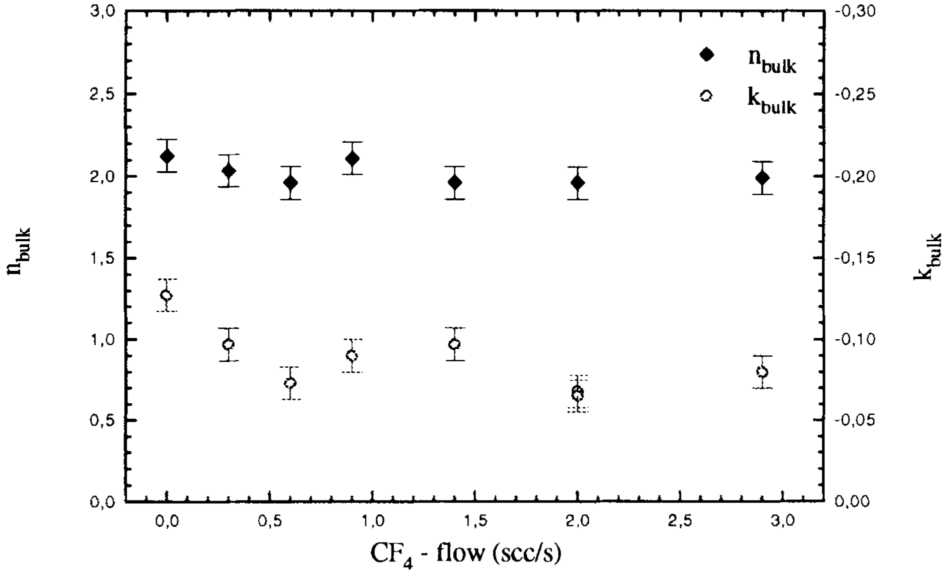

Fig. 3. The refractive index (left axis) and the extinction coefficient (right axis) of the bulk layer vs. CF_4 flow.

through a plane silicon substrate. It is found that the transmission for certain wavenumbers is higher than unity, which is caused by the antireflection behavior of the layer deposited.

For the wavenumber interval 2500–3500 cm^{-1}, the measured spectrum is fitted. The mathematical description is based on a model with multiple reflection. For the interval mentioned, three absorption peaks are assumed. The shape of these peaks is taken to be gaussian. From the fitting, the extinction coefficient is determined, which is transformed into an absorption coefficient. In Fig. 4 the results of the fitting procedure are shown for the case with no CF_4 added to the plasma. The peak found at 3300 cm^{-1} is assigned to an sp^1 C≡C bond, which appears as a result of the fact that not all the C_2H_2 is dissociated and also because C≡C is produced from plasma reactions. The peak around 3500 cm^{-1} is not yet assigned.

For the peak found in the interval 2900–3000 cm^{-1} some remarkable behavior is found. When the CF_4 flow is varied from 0 to 2.9 standard cm^3 s^{-1}, the position of the peak fitted shifts from 2926 cm^{-1} to 2977 cm^{-1}. This is shown in Fig. 5. This effect can be explained in several ways. When no CF_4 is added, the peak at 2926 refers to an sp^3 C–H_2 bond. When CF_4 is added several things might happen. First, increasing the CF_4 flow increases the number of F particles in the plasma, which may be able to bond to the sp^3 mentioned or substitute for an

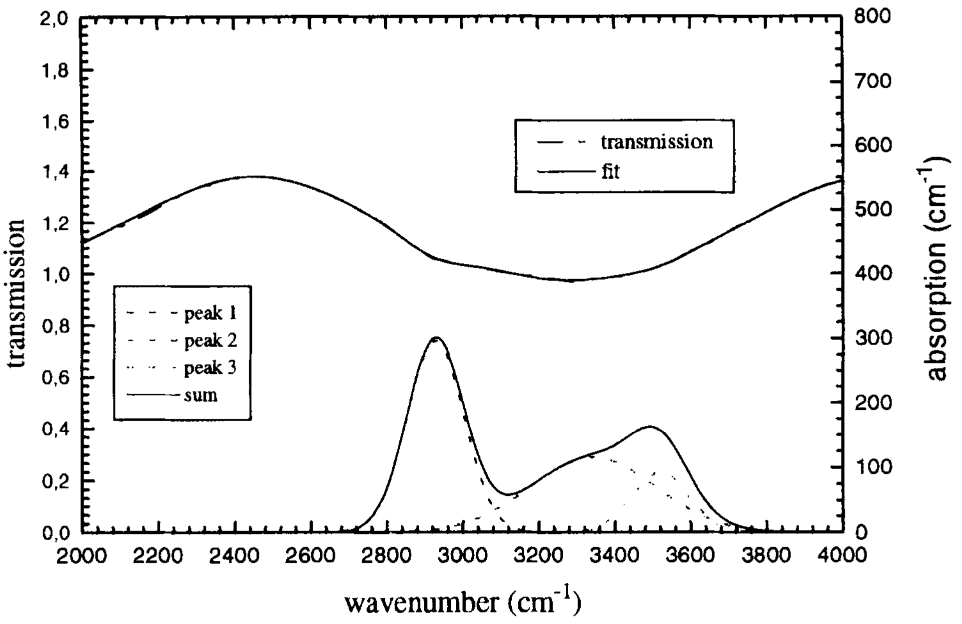

Fig. 4. Absorption peaks fitted in the wavenumber interval 2500–3500 cm^{-1}. The upper part gives the transmission both measured and fitted. The lower part gives the three deconvoluted peaks and their sum.

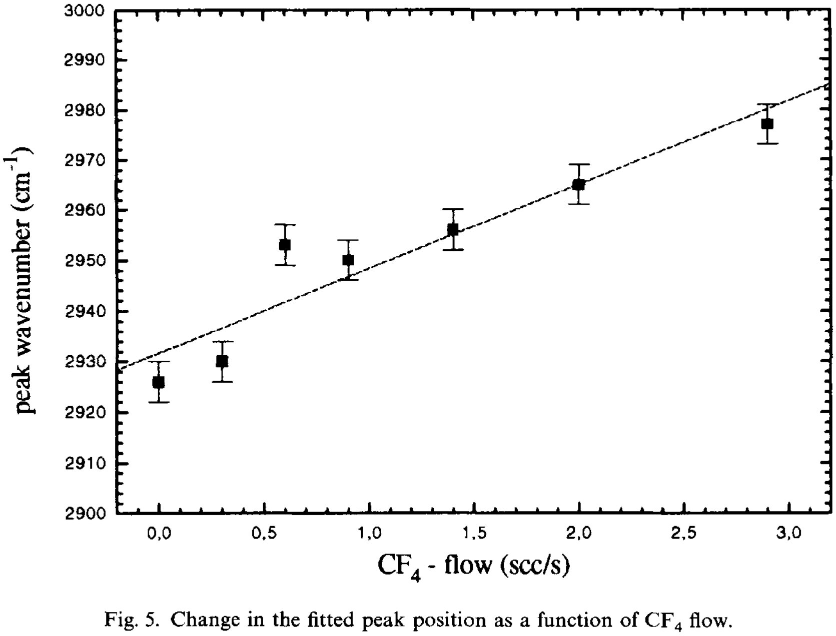

Fig. 5. Change in the fitted peak position as a function of CF_4 flow.

H atom. The positive charge of the F atom causes the C–H bonds to become stronger, which is translated in an increasing peak wavenumber, indicating a higher absorption energy. A second explanation could be that the appearance of F particles changes the structure of the sp^1 bond of the C_2H_2 molecules, resulting in an sp^2 CH bond, which is found around 3000 cm^{-1}. Increasing the CF_4 flow may result in more of the reactions leading to an increment of the peak wavenumber. For the first explanation some proof may be found in the appearance of $C–F_x$ bonds in the IR spectrum between 1000 and 1400 cm^{-1} when CF_4 is added. For the second explanation proof is also found in the IR spectrum, when looking at the origin of an absorption peak at 1600 cm^{-1} indicating a C=C bond. These explanations have assumed a real shift in the peak. It is also possible, and perhaps even more likely, that one peak is not shifting to another, but that next to one peak another peak is appearing, which is for an sp^2 or sp^3 bond. For this, proof is also found in the IR spectra, which show anti-symmetry of the peak mentioned, indicating the presence of more peaks.

One other result which follows from both the ellipsometry and IR spectroscopy is the fact that the growth rate of the layers is independent of the addition of CF_4. The growth rate is found to be about 5 nm s^{-1}. So the CF_4 precursor, which is basically an etching agent, does not influence the number of particles deposited. When looking at the results from the diagnostics with respect to the refractive index, extinction coefficient and shift of the absorption peaks, the growth itself is influenced. What is most probably the case is a modification of the deposition process by the CF_4 precursor and the particles produced from this in the plasma. For example, H atoms are substituted by F atoms, or bonding types are transformed from sp^1 to sp^2. These are likely to happen concurrently.

4. Conclusions

Amorphous fluorohydrogenated carbon layers were deposited from C_2H_2 and CF_4, using the expanding cascaded arc thermal plasma beam deposition technique. The parameter varied was the CF_4 flow. It was found that the addition of CF_4 does not influence the growth rate. The deposition process is likely to be influenced by the CF_4 in such a way that the layer deposited is modified in its structure as the bonding types obtained via IR spectroscopy change with varying CF_4 flow. The extinction coefficient decreases with increasing CF_4 flow, but the refractive index is hardly affected.

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