Influence of the H/C ratio in precursor gases on a-C:H films deposited by means of an expanding thermal plasma

INFLUENCE OF THE H/C RATIO IN PRECURSOR GASES ON a-C:H FILMS DEPOSITED BY MEANS OF AN EXPANDING THERMAL PLASMA

K.G.Y. Letourneur, S.C.M. Aerts, M.C.M. van de Sanden and D.C. Schram
Eindhoven University of Technology, Department of Applied Physics,
P.O. Box 513 - 5600 MB Eindhoven, The Netherlands.
Tel: (+31) 40 2 47 42 23 - E.mail: karine@etpserver.phys.tue.nl - Fax: (+31) 40 2 45 64 42

ABSTRACT

Amorphous hydrogenated carbon films (a-C:H) were deposited by means of an expanding thermal plasma with addition of different precursor gases such as C_2H_2, CH_4, C_2H_4 and C_2H_6 with and without H_2 addition. Infrared absorption spectroscopy and in situ ellipsometry have been used to provide information on the refractive index, the growth rate and the structure of the layers. It appears that the lower the H/C ratio in the plasma, the better are the films in terms of refractive index and growth rate. A slight improvement of the refractive index is observed with an increase of the substrate temperature from 0°C to 290°C whereas the growth rate decreases .

INTRODUCTION

One of the advantages of a-C:H films is the ability to tune their properties. Depending on the deposition conditions, soft polymer-like to hard diamond-like films can be obtained [1].
Among various techniques that can be used for deposition of carbon containing layers, the use of an expanding thermal plasma created by a cascaded arc is advantageous because of the high growth rates [1] and the spatial separation between plasma production, transport and deposition. Recently, efforts have been made to understand the mechanisms governing the formation of carbon layers. Hydrogen appears to have an important role in the surface processes [2]. Former investigations have shown that the hydrogen content of the deposited films is related to the film properties such as refractive index and hardness [3,4]. Hydrogen atoms can come either from hydrogen injection or from hydrocarbon dissociation. Previous studies carried out on an expanding thermal plasma with acetylene injection showed that layers of high quality could be obtained at high growth rates [1]. By doing experiments with other gases, such as CH_4, C_2H_4 and C_2H_6 with and without H_2 addition, the influence of the hydrogen content of the gas phase as well as of the hybridization state of the precursors on the hydrogen content of the layers has been investigated. The refractive index, being a measure for the hydrogen content of the film, has been investigated by means of infrared absorption spectroscopy and ellipsometry. To gain additional insight in the occurring processes, the influence the substrate temperature was also investigated.

EXPERIMENTAL

The deposition set-up

A remote argon plasma (flow = 100 scc/s) is generated in a DC thermal arc (cascaded arc) operated at high pressure (0.5 bar) [1]. For the used current (48 A), the ionization rate of the argon is approximately 10 % [4], resulting in an electronic density of 10^{22} m^{-3} and an electronic temperature of 1 eV in the plasma channel [6,7]. The plasma then expands in a low pressure vessel where the electron temperature drops down to 0.2-0.3 eV [5]. At 5 centimeters below the arc, 10 scc/s of precursor gases were symmetrically injected into the argon plasma.

The plasma is transported at a speed of 500 to 1000 m/s towards the water-cooled substrate holder, at 65 centimeters below the arc. The substrate temperature is accurately controlled within 5 K in the range 0°C - 295°C [8]. Depositions were performed on c-Si substrates (1 in × 1 in) during 1 to 15 minutes.

Diagnostics

Ex-situ characterization of the deposited films is performed with a Bruker Vector 22 Fourier Transform Infrared Spectrometer in the range of 370 to 7499 cm^{-1} at a resolution of 4 cm^{-1}. From the infrared absorption spectrum, the refractive index, the thickness and the predominant bonding configuration of the film (typically around 3000 cm^{-1} for $C\text{-}H_x$ bonding) can be obtained [9]. Provided that each oscillator strength is known, the bond densities could be estimated. Monitoring of the film growth is performed by means of an in-situ Rotating Compensator Ellipsometer [10,11]. From the temporal evolution of the $\Delta(\psi)$ plot, both the refractive index and the film thickness can be simulated. This was used to check the evolution of the growth rate.

RESULTS AND DISCUSSION

For each precursor gas, a set of films was deposited at varying temperatures. A second set was deposited at 250°C with addition of hydrogen to the hydrocarbons. Depositions with acetylene as precursor showed the higher refractive indexes and growth rates.

Plasma Chemistry

Due to the low electron temperature in the expansion zone, the hydrocarbon dissociation does not occur by electron impact but by charge transfer between an argon ion and a C_xH_y molecule. In this reaction, a molecular ion is formed which recombines dissociatively with an electron, resulting predominantly in C_2H radicals in the case of an acetylene plasma [1]. Concerning the other precursor gases, the following assumptions are made for the active radicals during deposition [12]: CH_3 in the case of CH_4, C_2H_5 in the case of C_2H_6 and C_2H_3 in the case of C_2H_4. If we assumed that radicals are responsible for deposition, the radicals with the highest H/C ratio will also lead to the highest H/C ratio in the films. So for instance, films deposited with methane are expected to have a higher hydrogen content (and thus a lower refractive index) than films deposited with C_2H_6 and C_2H_4. However, for a right picture, the hybridization state of the different radicals has also to be taken into account. A radical with an unsaturated C=C or C≡C bond arriving at the substrate can stick to the surface. This could be followed by a breaking up of the unsaturated bond thus creating two dangling bonds at the surface (cf fig. 1). Hydrogen atoms can easily react on those dangling bonds. In this way of thinking, depositions with C_2H_2 would give films predominantly containing sp^2 hydrogenated bonds, whereas with CH_4, C_2H_4 and C_2H_6, the films would contain sp^3 hydrogenated bonds. Since the refractive index is related to the hydrogen content and to the carbon density of the film, we can thus expect that depositions from acetylene would have a higher quality than with ethene, ethane or methane, which happens to be in agreement with the experiments.

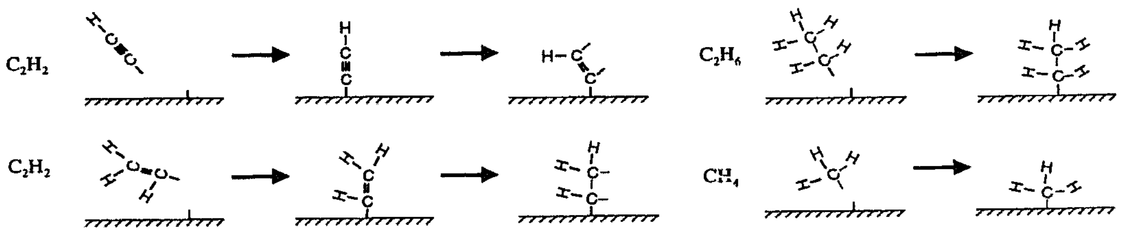

figure 1: *Proposed mecanisms for the different radicals arriving at the surface*

Refractive index, growth rate versus temperature

In our case, for all the used precursor gases, an increase in the substrate temperature leads to an increase in refractive index, a decrease of growth rate and a change in the structure of the films, as evidenced by a decrease in the intensity ratio of the 2900 cm^{-1} peaks (C-H bonding) over the 1600 cm^{-1} peaks (C=C bonding). An explanation for the temperature dependence of the refractive index could be that the desorption of hydrogen from the surface is higher at higher temperature (because of thermal activation) thus inducing a higher refractive index. The saturation of the refractive index at higher temperatures as found in former experiments with acetylene [8] could not be confirmed within the used temperature range. The decrease of the growth rate with the temperature was also observed in an ECR reactor [13] and was attributed to the temperature enhanced hydrogen etching.

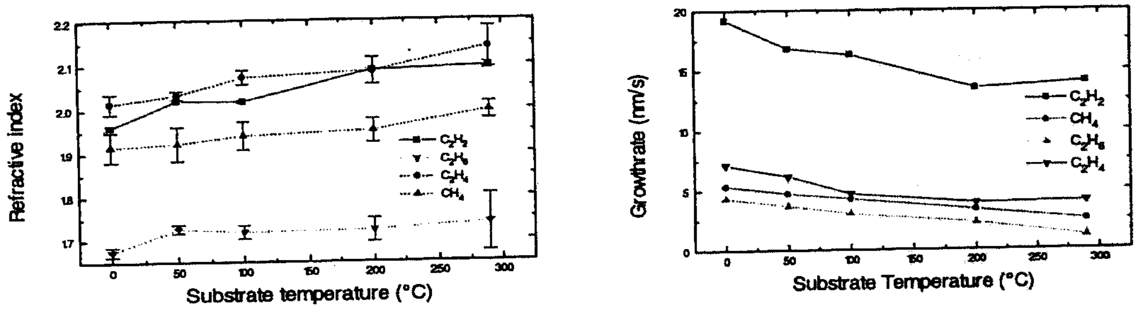

figure 2: *Influence of temperature on the refractive index and the growth rate for all used gases*

Refractive index, growth rate versus H/C ratio

From figure 3, we tentatively conclude that, in our case, the lower is the hydrogen to carbon ratio, the higher is the growth rate and the refractive index. A decrease of the H/C ratio of a factor 4 leads to an increase in the growth rate of 25%. The hybridization state of the precursor gas is influencial: methane is obviously reacting in a different way than the other precursors. This might be attributed to an overloading of the plasma with hydrocarbons. The carbon supply in the case of methane is twice as low as for other gases and could thus lead to more dissociation of the hydrocarbons resulting in better refractive index and growth rate.

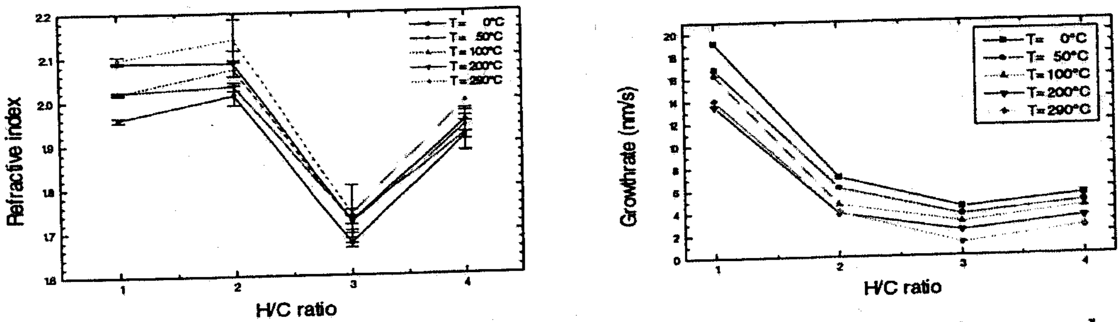

figure 2: *Influence of the H/C ratio on the refractive index and the growth rate*

H_2 addition

To investigate whether the H/C ratio or the hybridization state of the precursor gas is responsible for the quality of the layers, hydrogen was added to acetylene in order to have the same H/C ratio as in the used hydrocarbons. Addition of hydrogen to acetylene clearly results in a lower refractive index and a higher growth rate than obtained with precursor gases having the same H/C ratio (fig.3). From this, we conclude that the hybridization state of the precursors is indeed of importance for the deposition processes.

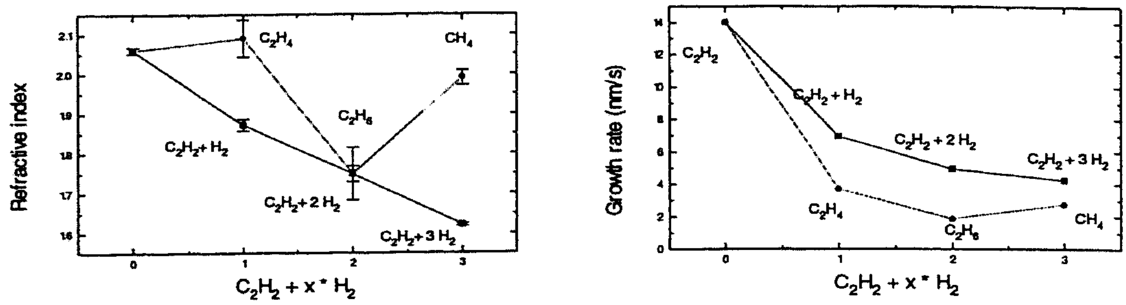

figure 3: *Effects of hydrogen addition on the refractive index and the growth rate*

The remaining challenge is to identify what are the main radicals formed in the plasma in the case of the different gases as well as their sticking probabilities. For the establishment of a complete description of the processes, suitable data on the predominant radicals, reaction cross sections and main surface reactions would be needed.

CONCLUSION

With the help of a cascaded arc, we produced carbon containing layers from different gases in order to study the influence of hybridization and of the H/C ratio in the precursors on the quality and growth rate of the films. A low H/C ratio in the plasma and a high temperature appear to be the best conditions to work at. It appears that the hybridization state of the precursor gas does matter and not only the H/C ratio.

ACKNOWLEDGMENTS

Financial support from the Foundation for Fundamental Research of Matter (FOM-Rolling Grant) is gratefully acknowledged.

REFERENCES

[1] J.W.A.M.Gielen, M.C.M. van de Sanden, DC Schram Appl Phys Lett 69,152 (1996)
[2] A.von Keudell, MSC 11, Proceedings, Nim-B
[3] R.C.Cheschire, W.G. Graham. T. Morrow, Appl Phys Lett. 66, 3152 (1995)
[4] E.Dekempeneer, R.Jacobs, J.Smeets, J.Meneve, L.Eerstels, Thin solid films 217 (56) (92)
[5] J.J.Beulens, D.Milojevic, D.C.Schram and P.M.Vallinga, Phys Fluids B,3(1991)
[6] M.C.M.van de Sanden, Thesis Eindhoven University of Technology (1991)
[7] G.M.W.Kroesen, C.J.Timmermans, D.C.Schram, Pure and Appl. Chem. 60, 795 (1988)
[8] J.W.A.M. Gielen, W.M.M.Kessels, M.C.M.van de Sanden and D.C.Schram,
[9] J.W.A.M. Gielen, P.R.M.Kleuskens, M.C.M.van de Sanden, L.J.van IJzendoorn, D.C.Schram, E.H.A. Dekempeneer and J.Meneve, J. of Appl. Physics, in press
[10] R.M.A.Azzam, N.M.Bashara, *Ellipsometry and Polarized light*, (1979)
[11] A.G.M.Kiers, *Bouw van een 'Rotating Compensator Ellipsometer'*, to be published
[12] T.Schwarz-Selinger, *Einfluss der Quellgase auf die plasmagestuetze deposition von Kohlenwasserstoffschichten*, Munchen (1996)
[13] A.von Keudell, W. Jacob, J.Appl.Phys. 79,1092 (1996)
[14] M.Mc Master, W.Hsu, M.Coltrin, D.Dandy, C.Fox, Diamond Rel. Mater. 4, 1000,(1995)