HARD AMORPHOUS HYDROGENATED CARBON FILMS DEPOSITED WITH AN EXPANDING THERMAL PLASMA.

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Abstract

With a recently constructed deposition set-up, based on the expanding thermal plasma technique, amorphous hydrogenated carbon films have been deposited on glass and silicon substrates. The plasma is generated in argon to which acetylene is added in the jet region as a precursor gas. The plasma parameters varied are the flow of acetylene and the electrical current through the plasma. The films have been analysed ex-situ. Fourier Transform Infrared Spectroscopy reveals the bonding types, the thickness and refractive index of the films and from Nano-indentation experiments the hardness of the films is obtained. It is found that with decreasing arc current and increasing acetylene flow, the hardness, refractive index and growth rate of the films increase. It is shown that with increasing growth rate the quality (i.e. hardness, refractive index) of the grown layer increases

Introduction

Since several decades there has been a large interest in the production and properties of amorphous hydrogenated carbon films on various substrates. This interest stems from the specific properties of the films, as they can be very hard and transparent for visible and IR light. This makes them suitable for a wide range of applications like protective layers on glass plates and optical elements [1,2].

Recently, a deposition set-up has been constructed based on the expanding thermal plasma technique [3,4]. With this technique it is possible to deposit carbon films from an expanding argon plasma with a large growth rate (typ. 10-100 nm/s), to which precursor gases like methane and acetylene are added. In this contribution the first results are given of carbon films deposited with the newly designed set-up.

Experimental

The carbon layers are deposited using an expanding thermal arc plasma. In Figure 1 a schematic drawing is given of the deposition set-up, which consists of a cascaded arc plasma source, an expansion vessel and a substrate holder. Through the plasma source there is a constant flow of argon (100 scc/s) at a pressure of 0.4 bar, which is ionised to a degree varying from 5 to 15 % with increasing arc current. The plasma expands into the vessel (0.25 mbar), where in the nozzle acetylene is added. The formed plasma mixture flows towards a water-cooled substrate holder where deposition takes place on silicon and glass samples (about 6 cm^2). During the deposition runs two plasma parameters are varied: the arc current is varied from 25 to 65 A at a constant acetylene flow (1 scc/s) and the acetylene flow is increased from 1 to 5 scc/s at a constant arc current (45 A). A more extensive description of the set-up is given in [5]. The hardness of the deposited films is determined at the VITO institute in Mol (Belgium) with a Nano-indenter [6] and the structure of the films is obtained with Fourier Transform Infrared Spectroscopy.

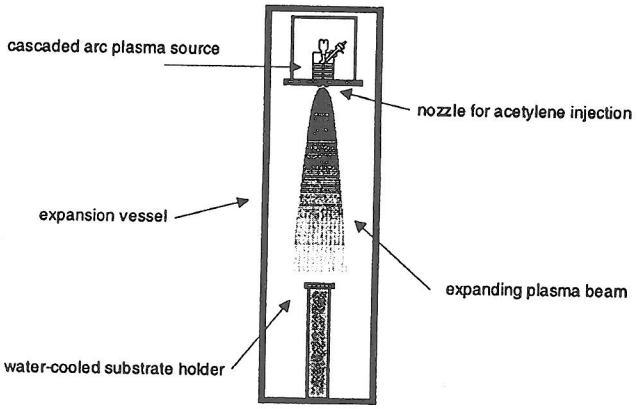

Figure 1 : Schematic drawing of the deposition set-up.

An essential difference between the expanding thermal plasma deposition and conventional deposition techniques using e.g. RF capacitively coupled discharges is the fact in which the monomers are dissociated. As the electron temperature is low [7] the monomers can not be dissociated by means of electron impact. Instead they are dissociated by a chain of charge exchange with the Ar^+ ion produced in the arc,

$$Ar^+ + C_2H_2 \rightarrow Ar + C_2H_2^+ \qquad (1)$$

followed by dissociative recombination of the formed molecular ion,

$$C_2H_2^+ + e \rightarrow CH + CH \qquad (2a)$$

$$\rightarrow \quad C_2H + H \qquad (2b)$$

$$\rightarrow \quad C_2 + H_2 \qquad (2c)$$

each with different rates. The formed molecules can be rovibrationally excited and, depending on the amount of ions left, undergo another sequence of charge exchange and dissociative recombination. The first step is the time limiting step with rates on the order of 10^{-15} - 10^{-17} m^3s^{-1}. This manner of dissociation of the injected monomer is very efficient and the material freedom is large: all molecules having an ionization potential which is lower than that of argon can be dissociated by reactions analoguous to Eqs. (1)-(2). Furthermore, by changing the monomer flow and the arc power or flow the dominant radical can be tuned. Note that the sequence of reaction Eq. (1)-(2) leads to a decrease of the ionization degree of the plasma. Therefore for the conditions mentioned the ion density close to the substrate will be on the order of the 10^{17}-10^{18} m^{-3} at electron temperatures in the range of 2000-3000 K.

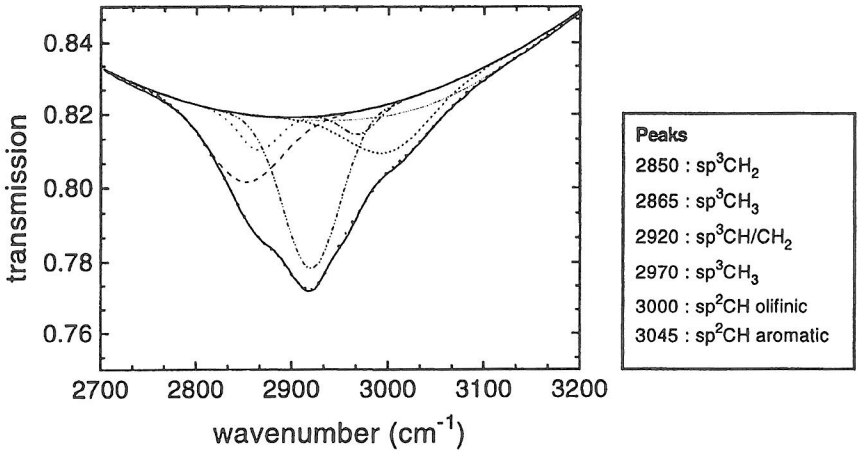

Figure 2 A typical example of a fitted infrared spectrum

Results

From infrared transmission in the wavenumber interval from 2800 to 3400 cm^{-1} the C-H bonds in the amorphous carbon layers are obtained. By a fitting process, based on a model including multiple reflection and in which the absorption peaks are described by Gaussian line shapes [8,9], the measured spectra are analysed. In fig. 2 a typical example of a spectrum both measured and fitted is shown.

From the multiple reflection behaviour the thickness and the refractive index of the layers deposited are obtained. In fig. 3 the growth rate, determined using the

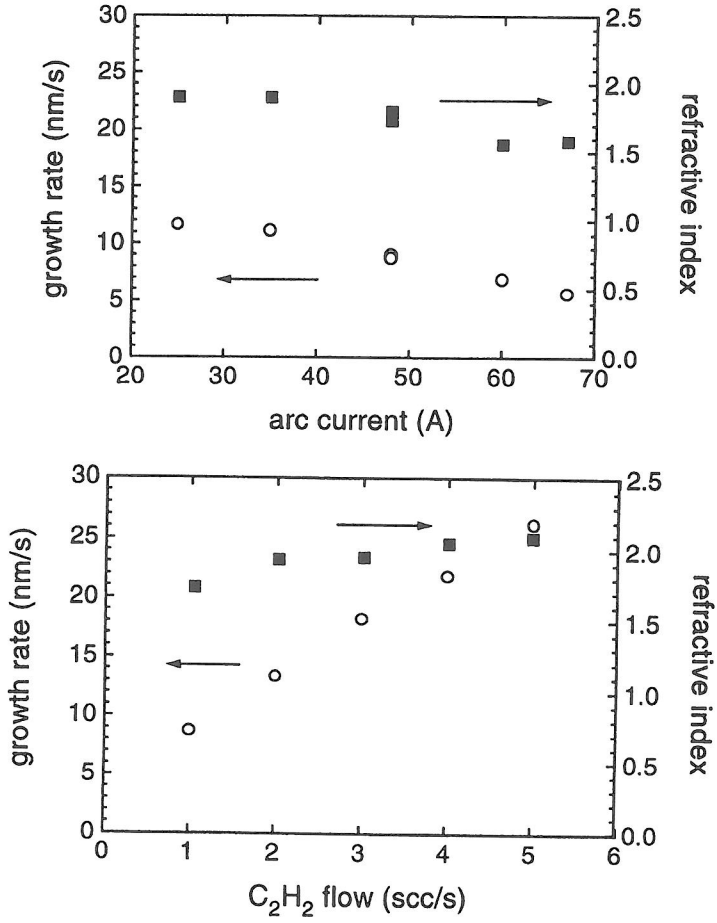

Figure 3 The growth rate and refractive index vs. the arc current and the acetylene flow. Other settings see text.

thickness, and the refractive index are found to increase with decreasing arc current and increasing acetylene injection. The thickness as determined from the IR measurements was checked using a Talystep equipment and good agreement was found.

Combining the growth rate and refractive index (n) a measure for the number of oscillators in the layer is found: $(n^2-1)/n^2+2)$. This quantity is given in in fig. 4. It is found that the number of oscillators increases when the growth rate increases, but seems to saturate for higher growth rates. This is quite surprising as there seems to be a relation between two layer parameters, while in the deposition process two plasma settings (arc current and acetylene flow) are varied independently.

From fitting the infrared spectra the intensity for each C-H bond is obtained. Integrating these intensities an indication for the total amount of hydrogen bonded to carbon particles is obtained. This total infrared absorption intensity is plotted in fig. 5,

showing that at higher growth rate the hydrogen incorporation decreases. This could be an explanation for the increment of the refractive index found as less C-H bonds make the material more dense. And again the total hydrogen incorporation seems to scale growth rate. The last results are obtained from hardness measurements. In fig. 6 the obtained hardness is given as a function of the growth rate of the layers. The hardness is found to increase with increasing growth rate.

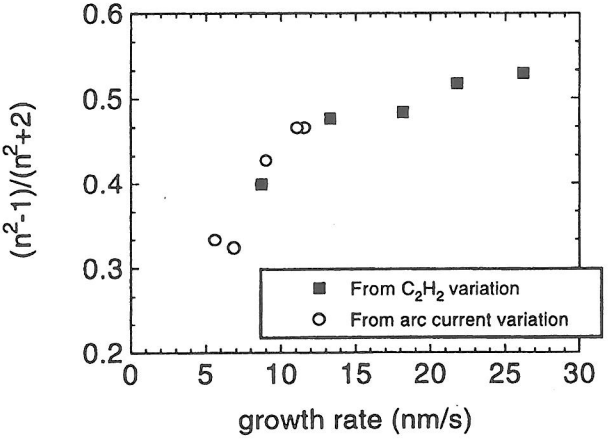

Fig. 4 The number of oscillators $(n^2-1)/(n^2+2)$ vs. the growth rate

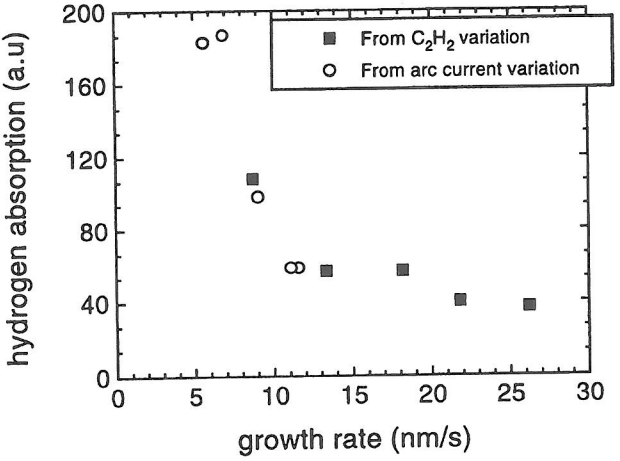

Fig. 5 Bonded hydrogen as a function of growth rate

Conclusions

Amorphous hydrogenated carbon films have been deposited on silicon and glass applying an expanding thermal plasma. The growth rate and refractive index decrease with increasing arc current and decreasing acetylene flow. The number of oscillators in

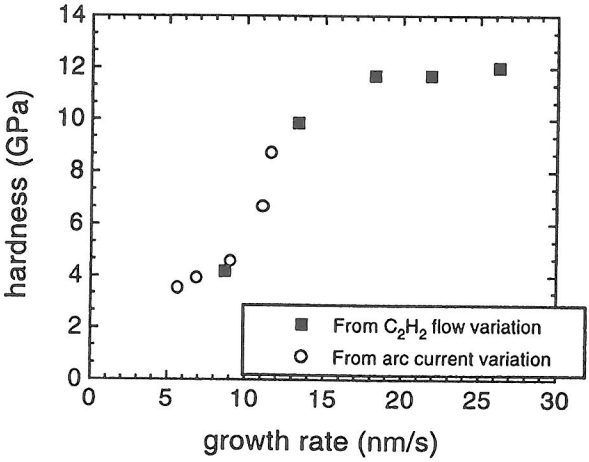

Fig. 6 The hardness as a function of the growth rate

the layers is found to increase with the growth rate. Also the hardness then is found to increase. However the amount of hydrogen bound to carbon is found to decrease with the growth rate. Combining all results it seems that harder layers are obtained when the growth rate increases and the hydrogen amount decreases.

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