Quality improvement of plasma-beam-deposited amorphous hydrogenated carbon with higher growth rate

Citation for published version (APA):

Gielen, J. W. A. M., Sanden, van de, M. C. M., Kleuskens, P. R. M., & Schram, D. C. (1996). Quality improvement of plasma-beam-deposited amorphous hydrogenated carbon with higher growth rate. *Plasma Sources Science and Technology*, 5(3), 492-498. <https://doi.org/10.1088/0963-0252/5/3/016>

DOI:

[10.1088/0963-0252/5/3/016](https://doi.org/10.1088/0963-0252/5/3/016)

Document status and date:

Published: 01/01/1996

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.

Quality improvement of plasma-beam-deposited amorphous hydrogenated carbon with higher growth rate

J W A M Gielen, M C M van de Sanden, P R M Kleuskens and D C Schram

Eindhoven University of Technology, Department of Physics, PO Box 513, 5600 MB Eindhoven, The Netherlands

Received 10 October 1995, in final form 26 February 1996

Abstract. An improved plasma beam deposition set-up, based on an expanding thermal plasma, is presented. Amorphous hydrogenated carbon films have been deposited on glass and crystalline silicon, under variation of the arc current and admixed acetylene flow. The films have been analysed *ex situ* with infrared absorption spectroscopy, broadband visible light transmission and nano-indentation measurements. These techniques reveal the growth rate, refractive index, bonded C–H density, optical bandgap and hardness. The growth rate and refractive index are found to increase with decreasing arc current and increasing acetylene flow admixture. The quality of the films in terms of refractive index and hardness increases with increasing growth rate and inverse energy coefficient, whereas the bonded hydrogen concentration and optical bandgap then decrease. From comparison of the growth rate dependency with the inverse energy coefficient dependency, we conclude that the growth rate is the preferred parameter in terms of which to describe the film properties because it is directly related to the plasma composition.

1. Introduction

The introduction of diamond-like hydrocarbon films by Aisenberg [1] rapidly increased the interest in the deposition and analysis of these films [2]. The reason for this is that amorphous hydrogenated carbon films (a-C:H) have favourable properties. The films are very hard, chemically inert, electrically insulating, transparent to infrared light and their optical properties such as the refractive index can be tuned [3]. Furthermore, they can be deposited at low substrate temperatures ($\leq 300^\circ\text{C}$), in contrast to diamond films. Possible applications of the films are found in the field of protective and anti-reflection coatings on glass plates, of, for example, bar-code laser scanner devices, and on other materials, but also in the field of file memory [4] and flat panel displays. In most cases a-C:H films are grown using plasma deposition processes [5]. The obtained growth rate is in general in the range $0.1\text{--}1\text{ nm s}^{-1}$. However, for commercial applications, higher growth rates will be very important.

At the Eindhoven University of Technology, a deposition technique has been developed which is based on an expanding thermal plasma [6]. With this technique carbon films have been deposited, varying from amorphous

hydrogenated films [7] to graphite [8], diamond [9] and fluorohydrogenated films [10, 11].

When reviewing the results of the last ten years obtained with our expanding thermal plasma beam deposition technique, efforts have been made to interpret the properties of the deposited a-C:H films with respect to plasma parameters. This led to the introduction of the so-called inverse energy coefficient Q [9], which is defined by

$$Q = \frac{F(\text{C}_x\text{H}_y)}{PF(\text{Ar})}. \quad (1)$$

In this equation $F(\text{C}_x\text{H}_y)$ is the admixed hydrocarbon flow, $F(\text{Ar})$ is the applied argon gas carrier flow and P is the arc power. This coefficient, which only depends on the arc parameters and the admixed hydrocarbon gas flow, is an inverse measure for the amount of energy available per deposition event. Both the refractive index and the hardness of the films were found to increase and the optical bandgap to decrease with increasing Q ; the films become harder, more dense and less transparent. This dependence on Q suggests a thermal picture, namely that the film quality is determined by the energy per deposition event, irrespective of the specific chemical composition of the plasma. The aim of the current study is to find a correlation between

Figure 1. A schematic drawing of the deposition set-up.

film properties and plasma parameters, such as radical and ion fluxes or the growth rate, instead of plasma input parameters. In this paper a new improved deposition set-up will be described and the deposition of hard amorphous hydrogenated carbon films on glass and crystalline silicon, using this new set-up, will be presented.

2. The deposition set-up

The deposition of a-C:H is performed with an expanding thermal plasma. A sub-atmospheric-pressure argon plasma is created in a cascaded arc source and expands into a chamber at low pressure, where a hydrocarbon monomer is added. The formed mixture of reactive particles flows at subsonic velocities towards a substrate.

An improved set-up has recently been constructed. In contrast to its predecessor, its main orientation is vertical, with the arc at the top and the substrate holder at the bottom. This facilitates the implementation of a load-lock system, because the samples can now simply be laid down. A state-of-the-art control system, allows reliable performance of reproducible deposition experiments. Magnet field coils have been placed around the expansion vessel for plasma confinement by an axial magnetic field.

A schematic drawing of the improved deposition set-up is shown in figure 1. The main parts are the cascaded arc plasma source, which is placed in a moveable source holder, the expansion chamber, the gas injection system, the substrate holder, the pumping system, the system control unit and the magnet field coils.

The cascaded arc plasma source, first introduced by Mäcker [12], used at the Eindhoven University of Technology [6] consists of a stack of eight water-cooled circular copper plates, insulated from each other by boron nitride rings, with a bore in the centre 4 mm in diameter. The plasma channel is approximately 5 cm long. Argon

carrier gas, up to 200 standard cm^3 per seconds (scc s^{-1}), flows from the three cathodes towards the earthed anode and is ionized by use of an electrical current. The plasma is thermal at a temperature of about 1 eV and at a high pressure (typically 0.5 bar). The degree of ionization depends on the arc power and argon flow and varies from 5 to approximately 25%.

The expansion chamber, within which the pressure may vary in the range 1–100 Pa, consists of three separate segments, made of stainless steel. From top to bottom they are 42, 22 and 54 cm long, respectively, with an inner diameter of 32 cm. In all segments openings are made for various applications, for example for optical emission spectroscopy, *in situ* ellipsometry and probe measurements.

For the injection of gaseous precursors, a gas-handling system has been built, which allows the addition of up to five different precursors to the plasma: hydrogen, methane, acetylene, tetrafluoromethane and oxygen. The gas flows may be up to 20 scc s^{-1} and the injection position in the chamber is variable. One position allows the injection through the nozzle, causing the gas to be admixed before the supersonic expansion. The second position is at 5–10 cm from the nozzle, via an injection ring (see figure 1). This causes the gas to be admixed in the subsonic relaxation zone of the plasma.

After the stationary shock, the formed plasma mixture is transported at subsonic velocities (500–1000 m s^{-1}) towards the substrate holder [6]. This holder is earthed and consists of a water-cooled copper plate 10 cm in diameter upon which an aluminium substrate holder is mounted. Crystalline silicon, glass or metal substrates can be clamped onto the holder.

The pressure in the expansion chamber is controlled via a vacuum pumping unit, which consists of two main pumping lines. One line is formed by two mechanical booster pumps (Edwards EH2600, 2600 $\text{m}^3 \text{h}^{-1}$; Edwards EH500A, 500 $\text{m}^3 \text{h}^{-1}$) and one rotary piston pump (Edwards, 240 $\text{m}^3 \text{h}^{-1}$) and is used to control the pressure during deposition within the range 1–100 Pa, via a moveable valve. The other line consists of a turbomolecular pump (Leybold Turbovac 1500, 90 $\text{m}^3 \text{h}^{-1}$) and a rotary pump (Edwards, 40 $\text{m}^3 \text{h}^{-1}$) and is used to maintain a base pressure of 10^{-6} mbar.

The experiment is controlled via a system which consists of a programmable logical control (PLC) unit, which is operated via a personal computer. In the PLC unit all actions of the system (vacuum unit, gas handling, cascaded arc, magnetic field, vessel and substrate conditions and in the future also the load-lock operation) are controlled and the conditions of the system are monitored permanently. The interaction of the user with the set-up is performed via a personal computer on which the commercial software package Intouch[®] is running to perform actions and to obtain data from the system.

At four positions magnet field coils have been positioned around the expansion chamber. There are four coils in top of the vessel, two coils at 40 cm and two at 60 cm from the top and finally two coils at the bottom of the vessel. The electrical current through each coil may be up to 400 A. The maximum magnetic field on the axis of the vessel then is about 300 Gauss.

The described set-up has been compared with its predecessor and other equivalent set-ups via Langmuir probe measurements [13] in a pure argon plasma. Good agreement is found with the results in [14].

3. Deposition of a-C:H

Amorphous hydrogenated carbon films have been deposited on glass and on crystalline silicon substrates. The general plasma settings were as follows: argon carrier flow 100 scc s⁻¹, arc pressure 0.5 bar, chamber pressure 0.25 mbar and distance from nozzle to substrate 65 cm. The substrate holder is water-cooled. During deposition the temperature of this holder increases owing to heating by the plasma. Deposition is started at 25 °C and the temperature increment, which is mainly dependent on the deposition time, is less than 40 °C.

To deposit hydrocarbon films, acetylene is admixed into the expanding argon plasma. Interaction of this precursor in the expansion zone with argon ions results in the ionization and subsequent dissociation of acetylene. A mixture of hydrocarbon ions and radicals is created in this way.

Ionization of acetylene molecules via interaction with electrons is not possible, because these electrons only have energies of approximately 0.2 eV [14]. The ionization occurs in a charge exchange reaction with argon ions via

at a rate $k_{ion} \approx 10^{-16} \text{ m}^3 \text{ s}^{-1}$, which is the only exothermic ionization reaction possible [15,16]. The total recombination energy of the argon ion (15.76 eV) is assumed to be transferred to the formed acetylene ion. Dissociation of acetylene by intermolecular reactions is not probable, because the rate is less than $10^{-17} \text{ m}^3 \text{ s}^{-1}$ and the argon ion density is larger than the acetylene density [17,18]. Thermal dissociation of acetylene is also considered to be of minor importance, because heating of the acetylene molecule occurs via electron collisions, in which only 0.2 eV is transferred; the C–H bond energy in acetylene is 5.7 eV.

The formed acetylene ion recombines dissociatively with an electron with the following possible reaction results:

at a rate of $3 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$ [19]. All formed radicals and ion complexes can be electronically and/or rovibrationally excited. No clear evidence exists on the branching ratio of the various reaction paths. However, the order presented in equation (3) is expected to be most probable, on the basis of energetic, statistical phase space and stereometric arguments [20]. Depending on the argon ion and acetylene fluxes, the formed radicals in equation (3) can be ionized and dissociated further.

Two different plasma parameters have been varied during a-C:H deposition. First, the electrical current through the arc, which is a measure of the degree of plasma

ionization, was varied from 25 to 67 A. This implies that the power coupled into the arc varied from 1 to 5 kW and that the dissociative capacity increased, because the argon ion density increased. The acetylene flow was kept constant at 2 scc s⁻¹. Second, the admixed acetylene flow was varied from 2 to 10 scc s⁻¹. The arc current was kept constant at 48 A, which implies an arc power of approximately 3 kW. All deposited films had a thickness of about 2 μm.

The films were analysed *ex situ* in three different ways. The refractive index, thickness and bonded hydrogen content were obtained from infrared absorption spectroscopy and the optical bandgap determined via visible light transmission measurements. Furthermore, the hardness of the films, corrected for elastic recoil, was obtained with a nano-indenter. The first two techniques were applied to the films deposited on glass, the last one to the films on crystalline silicon.

Analysis of the infrared transmission spectra was performed via fitting. A mathematical description of the transmission was applied, which was based on multiple reflection in the deposited film [10]. The refractive index and thickness were determined from those parts of the spectra in which no absorption by molecular bonds occurs. Absorption by bonds from possible *ex situ* oxidation was also excluded from the fitting. The bonded hydrogen content follows from a fit in the molecular bonding area.

In figure 2 the growth rate and refractive index are shown as functions of the arc current and the admixed acetylene flow. Both quantities are found to decrease with increasing arc current. When the acetylene flow admixed into the plasma is increased, the refractive index and growth rate increase. An increasing growth rate with increasing acetylene admixture is caused by the increment of hydrocarbon particles available in the plasma. The observed decrease in the growth rate with arc current increment shows that there being more argon ions does not suffice to ensure faster growth. The ratio of argon ions and acetylene molecules also proves to be important. A possible explanation is that there being too many argon ions with respect to the acetylene density results in further dissociation of the formed radicals in (3), which is not beneficial for the growth rate, because, for example, more atomic hydrogen is formed, which etches the growing film. However, a full explanation of the growth rate behaviour with arc current increment cannot yet be given.

The refractive index is a measure of the volume density N of oscillators in the film, which is given by [21]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{Nq_e^2}{3e_0m_e} \sum_j \left(\frac{f_j}{\omega_{0j}^2 - \omega^2} \right). \quad (4)$$

In this equation q_e and m_e are the electron charge and mass, ω and ω_{0j} are the incident light frequency and resonant frequency of the oscillators respectively and f_j is the oscillator strength. From this relation it follows that

$$N \propto \frac{n^2 - 1}{n^2 + 2}. \quad (5)$$

In figure 3(a) the oscillatory density, both from the films deposited with arc current variation and from those

Figure 2. The growth rate and refractive index versus (a) the arc current (25–67 A, acetylene flow 2 scc s⁻¹) and (b) acetylene flow (2–10 scc s⁻¹, arc current 48 A) determined from infrared spectroscopy. The plasma settings were argon flow 100 scc s⁻¹, arc pressure 0.5 bar, vessel pressure 0.25 mbar, distance from nozzle to substrate 65 cm and substrate temperature 25–65 °C.

with acetylene flow variation, is given as a function of the inverse energy coefficient Q . The result is comparable to earlier observations [9], whichever parameter is varied. However, the maximum Q is more than a factor of two greater. As already mentioned, the inverse energy coefficient is an arc-related parameter, which gives no direct information about the plasma composition or growing film. Therefore, we will now discuss the behaviour of the film properties as a function the growth rate, which is a measure of the hydrocarbon flux towards the substrate.

In figure 4(a) the oscillatory density, both for the films deposited with arc current variation and for those with acetylene variation, is presented as a function of the growth rate. Figure 4 clearly shows that the oscillatory density increases with increasing growth rate, implying that the film grows more compact when the flux of particles, which contribute to growth, arriving at the substrate surface

increases. This effect is independent of the variation both of the arc current and of the admixed acetylene flow. At 8 nm s⁻¹ growth rate the two measured data points refer to different films, deposited at equal plasma settings (arc current 48 A, acetylene flow 2 scc s⁻¹), which shows reproducibility.

The increment in refractive index is caused either by an increase in the sp²/sp³ ratio or by a decrease in the hydrogen content of the film [22, 23]. The bonded hydrogen density is obtained from fitting the infrared spectra in the molecular bonding regions [24], by combining the results for all individual C–H bonds (sp¹, sp² and sp³). It is shown in figure 4(b) as a function of the growth rate. It is evident that the hydrogen concentration decreases with increasing growth rate. Again, a film property has been found to be related to the growth rate. In figure 3(b) the hydrogen density is given as a function of Q .

Figure 3. The oscillator density (a), hydrogen content (b), optical bandgap (c) and hardness (d) versus the inverse energy coefficient Q . The plasma settings were arc current 25–67 A, acetylene flow 2–10 scc s⁻¹, argon flow 100 scc s⁻¹, arc pressure 0.5 bar, vessel pressure 0.25 mbar, distance from nozzle to substrate 65 cm and substrate temperature 25–65 °C.

Broadband visible light transmission is used to determine the optical bandgap, according to Tauc's method [25], for films on glass. In figure 4(c) the bandgap is presented as a function of the growth rate. It is found that the bandgap decreases with increasing growth rate. This suggests that the sp^2/sp^3 ratio increases [22] and is in agreement with an increasing refractive index. So, the optical bandgap depends also on the growth rate variation. When the bandgap is given as a function of Q (figure 3(c)), again good agreement with earlier results is observed [9].

Finally, the hardness of the films was measured with a nano-indenter, taking into account the elastic recoil [26]. In figure 4(d) the hardness is given as a function of the growth rate. It can be seen that the hardness increases with increasing growth rate, which proves again the relation that

exists between the film properties and the growth rate. At higher growth rate, saturation of the hardness is observed. In figure 3(d) the hardness is plotted as a function of the inverse energy coefficient and the observed behaviour is again in agreement with earlier observations [6].

In figure 4 a comparable behaviour of the film properties is observed, as a function of the growth rate: at lower rates a large gradient is found, which decreases at higher rates and finally even results in property saturation. An explanation could be that, at small rates (namely with high arc current and low acetylene flow) the plasma contains a rich composition of hydrocarbons, which influences the properties a lot. At higher rates (namely with lower arc current and higher acetylene flow), the plasma composition becomes more defined, containing a dominant

Figure 4. The oscillatory density (a), hydrogen content (b), optical bandgap (c) and hardness (d) versus the growth rate. The plasma settings were arc current 25–67 A, acetylene flow 2–10 scc s⁻¹, argon flow 100 scc s⁻¹, arc pressure 0.5 bar, vessel pressure 0.25 mbar, distance from nozzle to substrate 65 cm and substrate temperature 25–65 °C.

fraction of a certain precursor for growth. An increasing growth rate, then, is the result of an enhanced particle flux, which no longer affects the film quality. The latter could explain the observed saturation in the hardness and suggest that, for high a-C:H quality, a certain particle is needed for growth (such as C₂H, see equation (3)). However, the exact reason is not known.

It has been shown that it is possible to describe the a-C:H film properties with respect both to the inverse energy coefficient Q , which is a plasma input parameter, and to the growth rate, a growth parameter. However, the growth rate is much more closely related to processes in the plasma, because it is a measure of the flux of the hydrocarbon particles which contribute to deposition. Therefore the growth rate is the preferred parameter for the

description of film properties. Furthermore, it is observed that better films are made at higher rates.

4. Conclusions

An improved deposition set-up for amorphous hydrogenated carbon, based on an expanding thermal plasma, has been presented. Amorphous hydrogenated carbon films have been deposited on crystalline silicon and glass. The plasma input parameters varied are the arc current and the admixed acetylene flow. An increment in arc current decreases both the growth rate and the refractive index of the films; and increasing acetylene flow increases the growth rate and refractive index.

The refractive index and hardness of the films are found to increase at an increasing growth rate and inverse energy coefficient; the hydrogen concentration and the optical bandgap then are found to decrease. So, both parameters describe the film properties. However, the inverse energy coefficient is only a plasma input parameter whereas the growth rate is directly related to the plasma composition and is therefore to be preferred. Furthermore, it is found that better films are deposited at higher deposition rates.

Acknowledgments

The authors would like to thank E H A Dekempeneer and J Meneve from the VITO institute in Mol (Belgium) for performing the hardness measurements. Also, the skilful technical assistance of M J F van de Sande, A B M Hüskén and H M M de Jong is greatly acknowledged. The Foundation of Fundamental Research on Matter (FOM) and the Royal Netherlands Academy for Arts and Sciences (KNAW) are acknowledged for their financial support.

References

- [1] Aisenberg S and Chabot R 1971 *J. Appl. Phys.* **42** 2953
- [2] Angus J C and Wang Y 1991 *Diamond and Diamond-like Film and Coatings* ed R E Clausing *et al* (New York: Plenum) p 173
- [3] Angus J C, Koidl P and Domitz S 1986 *Plasma Deposited Thin Films* ed J Mort and F Jansen (Boca Raton, FL: CRC) p 89
- [4] Miyake S and Kaneko R 1993 *Thin Solid Films* **212** 256
- [5] Catherine Y 1991 *Diamond and Diamond-like Film and Coatings* ed R E Clausing *et al* (New York: Plenum) p 193
- [6] Kroesen G M W, Timmermans C J and Schram D C 1988 *Pure Appl. Chem.* **60** 795
- [7] Buuron A J M, Beulens J J, Meeusen G J, van de Sanden M C M and Schram D C 1994 *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **54** 115
- [8] Buuron A J M, Beulens J J, Groot P, Bakker J and Schram D C 1992 *Thin Solid Films* **212** 282
- [9] Beulens J J, Buuron A J M and Schram D C 1991 *Surf. Coating Technol.* **47** 401
- [10] Gielen J W A M, van de Sanden M C M and Schram D C 1995 *Thin Solid Films* **271** 56
- [11] Buuron A J M, van de Sanden M C M, van Ooij W J, Driessens R M A and Schram D C 1995 *J. Appl. Phys.* **78** 528
- [12] Mäcker H 1956 *Z. Naturf. a* **11** 457
- [13] Hershkowitz N 1989 *Plasma Diagnostics* vol 1 ed O Auciello and D L Flamm (Boston: Academic)
- [14] van de Sanden M C M, de Regt J M and Schram D C 1993 *Phys. Rev. E* **47** 2792
- [15] Rosenstock H M, Draxl K, Steiner B W and Herron J T 1977 *J. Phys. Chem. Ref. Data* **6** 93
- [16] Maier W B 1965 *J. Chem. Phys.* **42** 1790
- [17] Miller S A 1965 *Acetylene, Its Properties, Manufacture and Uses* (London: Ernest Benn)
- [18] Tachibana K, Nishida M, Harima H and Urano Y 1984 *J. Phys. D: Appl. Phys.* **17** 1727
- [19] Mul P M and McGowan J W 1980 *Astr. Phys. J.* **237** 749
- [20] Herbst E 1978 *Astrophys. J.* **222** 508
- [21] Hecht E 1987 *Optics* (Amsterdam: Addison-Wesley)
- [22] Robertson J and O'Reilly E P 1987 *Phys. Rev. B* **35** 2946
- [23] Fourches N and Turban G 1994 *Thin Solid Films* **240** 28
- [24] Gielen J W A M, Kleuskens P R M, van de Sanden M C M, van IJendoorn L J, Schram D C, Dekempeneer E H A and Meneve J 1996 to be published
- [25] Tauc J 1972 *Optical Properties of Solids* ed F Abelès (Amsterdam: North-Holland)
- [26] Loubet J L, Georges J M and Meile G 1986 *Microindentation Techniques in Materials Science and Engineering* ed P J Blau and B R Lawn (Philadelphia, PA: ASTM)