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Plasma beam deposited amorphous hydrogenated carbon: Improved film quality at higher growth rate

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High quality diamondlike a-C:H has been deposited, at low ion bombardment energies, from an expanding thermal argon/acetylene plasma at high growth rate. It is observed that quality improvement, in terms of hardness, is equivalent to maximization of the refractive index. The highest refractive indices are obtained when the admixed acetylene flow and the argon ion flux emanating from the plasma source are comparable in magnitude, which suggests critical loading. This also indicates that the acetylene has to be dissociated only once. Combination with the observed quality behavior at higher deposition rates suggests that there is one preferred hydrocarbon radical for deposition, probably C_2H. © *1996 American Institute of Physics.*
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For several decades it has been known that amorphous hydrogenated carbon (a-C:H) has important adjustable properties like high hardness, chemical inertness, and infrared transparency.[1,2] Possible applications are found as protective antireflection coatings in, e.g., bar-code laser scanner devices, and in flat panel displays. Films of a-C:H are commonly produced via plasma deposition techniques at growth rates between 0.1 and 1 nm/s.[3] For practical technological applications, production costs must be minimized. This implies that the growth rate should be increased, while maintaining good film quality. This quality depends of course, on the application which is foreseen. For example, for wear resistant coatings a hardness above 10 GPa would be desirable. It will be shown that deposition of a-C:H films with an expanding thermal plasma[4] can fulfill this condition. In the past, this technique has been applied successfully for the deposition of diamond, graphite, amorphous hydrogenated silicon, and amorphous (fluoro)hydrogenated carbon.[5,6]

The deposition setup consists of a dc plasma arc, a vacuum chamber, and a substrate holder. The arc[4] generates a subatmospheric thermal plasma in argon (argon flow: 100 scc/s, electron density: $\approx 10^{22}$ m^{-3}, electron temperature: ≈ 1 eV), which expands into the vacuum chamber (pressure: 0.25 mbar) where acetylene is admixed, at about 5 cm from the arc exit. As the electron temperature in the chamber is low (≈ 0.2 eV) there are no electron induced processes.[7] The acetylene is only ionized via charge exchange

$$Ar^+ + C_2H_2 \rightarrow Ar + C_2H_2^+, \tag{1}$$

with a rate of $\sim 10^{-16}$ m^3 s^{-1}.[8] The formed acetylene ion rapidly recombines dissociatively with an electron

$$C_2H_2^+ + e^- \rightarrow C_2H + H$$
$$\rightarrow CH + CH$$
$$\rightarrow C_2 + H_2, \tag{2}$$
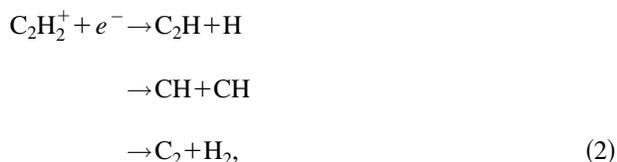
with a rate of about 3×10^{-13} m^3 s^{-1}.[9] As will be argued later, the $C_2H + H$ channel will probably be predominant. The active plasma mixture is then transported at a velocity of about 1000 m/s towards the water-cooled, grounded, nonbiased, substrate holder, which is positioned at 65 cm from the arc exit. No active temperature control is carried out, but from infrared interferometry, using a double polished silicon substrate, it is determined that the substrate temperature is always less than 100 °C.[10]

The films are grown on glass and crystalline silicon substrates (2.5×2.5 cm^2). The plasma parameters varied during deposition are the electrical current through the arc (20–88 A), which determines the ionization degree of the argon gas, and the admixed acetylene flow (2–20 scc/s), which is a measure for the hydrocarbon particle flux.

Characterization of the film properties is performed via various *ex situ* diagnostics.[11] It is found that all properties show clear relations with the refractive index, independent of which plasma parameter (arc current or acetylene flow) is varied. The refractive index is obtained from infrared absorption spectroscopy and is known to be an indicator for film quality.[12] The microhardness, determined via nanoindentation,[13] is found to increase with increasing refractive index from about 4 to 13 GPa (see Fig. 1), which implies a shift from soft polymerlike material to hard diamondlike. All
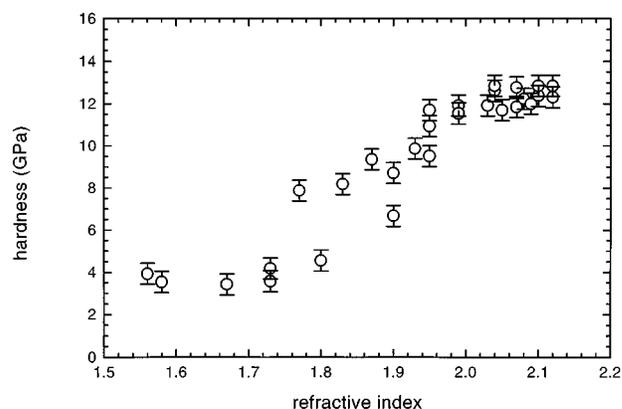

FIG. 1. The microhardness of the films vs the infrared refractive index.

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TABLE I. Properties of plasma beam deposited diamondlike a-C:H films and other PECVD techniques (Refs. 17–19).

Film property	Plasma beam deposition	PECVD
Hardness	13 GPa	10–20 GPa
Optical band gap	1.0–1.3 eV	1.1 eV
Mass density	1.7 g/cm^3	1.4–1.9 g/cm^3
sp^3:sp^2:sp^1	75:22:3	68:30:2
CH:CH$_2$:CH$_3$	54:44:2	60:40:0
Hydrogen content	23-34 at. %	27 at. %
Refractive index (visible)	2.05	2.0
Refractive index (infrared)	1.95–2.09	1.67–2.69

FIG. 3. The infrared refractive index vs the growth rate. Both the arc current (20–88 A) and the admixed acetylene flow (2–20 scc/s) are varied.

films are found to adhere well to the substrate. The hydrogen density (bonded and nonbonded) and the optical band gap decrease at increasing refractive index. The latter is in agreement with the observed increment in the sp^2/sp^3 ratio, which indicates an enhanced cluster formation.[14,15] From infrared absorption spectroscopy indeed an increment in aromatic sp^2CH bonds is found. Furthermore, it is observed that the widths of the deconvoluted infrared C–H absorption peaks increase with increasing refractive index, which also indicates harder material.[16]

In Table I, the determined properties for diamondlike a-C:H films (high refractive index), using the different film diagnostics, are summarized. Also, the typical diamondlike properties of films deposited with other PECVD techniques are given.[17–19] It is obvious that plasma beam deposited diamondlike a-C:H is of similar quality. However, note that no external substrate bias is applied during deposition. In general a bias of $\sim$100 V per deposited C atom is needed to obtain diamondlike properties.[20–24]

The highest a-C:H hardness is observed at the highest refractive index. Thus, improving film quality is equivalent to maximizing the refractive index. In Fig. 2 the latter property is given as a function of the admixed acetylene gas flow at various arc currents. For each applied arc current a similar trend with increasing acetylene flow is found: the refractive index first increases until a maximum is reached, then it decreases.

Figure 2 suggests the following mechanism for the deposition of plasma beam deposited a-C:H. At a fixed arc current, a constant flux of argon ions emanates from the plasma source. From Langmuir probe measurements[25] this flux is
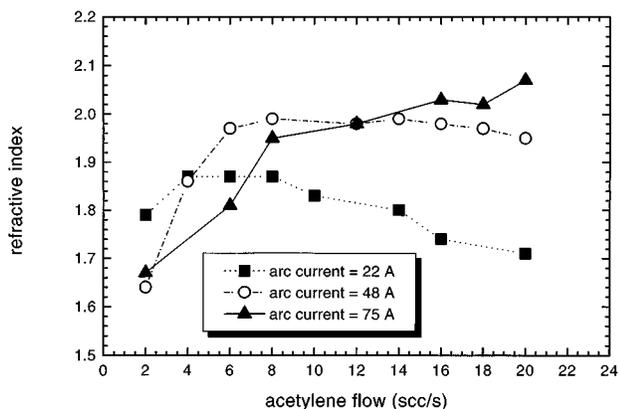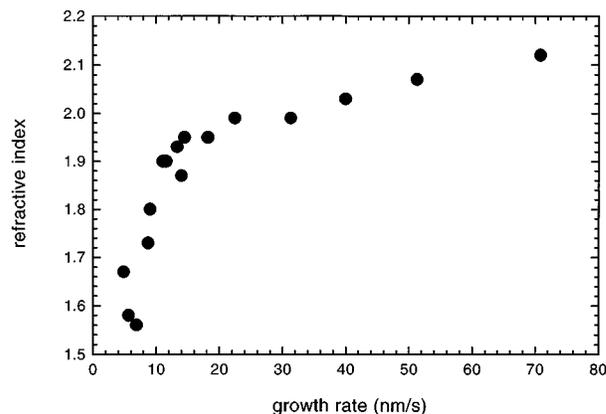
found to vary from 5% to 25% of the argon neutral flux at increasing arc current (22–75 A). Ionization of the acetylene molecules occurs via reaction (1), directly followed by the dissociative recombination via (2). The maximum refractive index is observed at an admixed acetylene flow which is comparable to the argon ion flux emanating from the source. This suggests a critical loading of acetylene with respect to the argon ion flux in the plasma. This also indicates that the acetylene has to be dissociated only once and that the radicals thus formed are responsible for a good film quality. Both underloading and overloading of the plasma with acetylene, in comparison with the argon ion flux, is proven to be unfavorable for film quality. Underloading results in an enhanced ionization and dissociation of the formed hydrocarbon radicals and overloading probably results in clustering or direct deposition of acetylene.[26] The mean free path for acetylene to react with an argon ion is about 20 cm. Probe measurements at 25 cm from the acetylene injection point show that in the case of critical loading more than 90% of the argon ion density is lost,[25] excluding further ionization and dissociation of the formed radicals. This shows that the deposition process is dominated by radicals.

The one step ionization and dissociative recombination of acetylene [Eqs. (1) and (2)] can result, as already mentioned, in various reaction products. The exact branching ratio of each product reaction path is presently unknown. However, based on energetic, statistical phase space and stereometric arguments,[27] there are strong indications that C$_2$H is the most important radical.

The existence of one preferred deposition radical might also be concluded from the refractive index behavior with respect to growth rate variation. The latter is a measure for the hydrocarbon particle flux towards the growing film surface which contributes to growth. The refractive index is found to increase with increasing growth rate (see Fig. 3). At higher rates the quality still improves but less dramatic. This could indicate that the plasma composition is well established, with respect to one certain growing particle, e.g., C$_2$H (ethinyl). The growth rate increment then is a result of an enhanced particle flux towards the substrate, which influences the film quality only marginally. The result in Fig. 3 is very important, as presently, better a-C:H films are deposited

FIG. 2. The infrared refractive index vs the admixed acetylene flow, for three arc current settings.

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at higher deposition rates (currently the maximum hardness is 13 GPa at a rate of 75 nm/s).

In conclusion, the use of an expanding thermal plasma, without substrate bias and thus low ion bombardment energies, allows the deposition of diamondlike a-C:H with similar properties as other PECVD techniques, but at a deposition rate which is at least two orders of magnitude higher. It is observed that quality improvement is equivalent with maximizing the refractive index. At a specific source setting, this maximum is reached when the admixed acetylene flow and the argon ion flux from the plasma source are comparable (critical loading). This indicates a one step dissociation mechanism of acetylene. Combination with the observed quality improvement behavior at higher growth rates, suggests that there might be one dominant hydrocarbon radical (probably C_2H) which is responsible for good diamondlike a-C:H.

[1] J. C. Angus and Y. Wang, in *Diamond and Diamond-like Films and Coatings,* NATO ASI Series B, Vol. **266**, edited by R. E. Clausing, L. L. Horton, J. C. Angus, and P. Koidl (Plenum, New York, 1991), p. 173.

[2] J. C. Angus, P. Koidl, and S. Domitz, in *Plasma Deposited Thin Films,* edited by J. Mort and F. Jansen (CRC, Boca Raton, FL, 1986), p. 89.

[3] Y. Catherine, in *Diamond and Diamond-like Films and Coatings,* NATO ASI Series B, Vol. **266**, edited by R. E. Clausing, L. L. Horton, J. C. Angus, and P. Koidl (Plenum, New York, 1991), p. 193.

[4] J. W. A. M. Gielen, M. C. M. van de Sanden, P. R. M. Kleuskens, and

[D. C. Schram, Plasma Sources Sci. Technol. **5** (1996) (in press).

[5] J. J. Beulens, A. J. M. Buuron, M. J. de Graaf, G. J. Meeusen, M. C. M. van de Sanden, A. T. M. Wilbers, and D. C. Schram, High Temp. Chem. Proc. **1**, 105 (1992).

[6] J. W. A. M. Gielen, M. C. M. van de Sanden, and D. C. Schram, Thin Solid Films **271**, 56 (1995).

[7] M. C. M. van de Sanden, J. M. de Regt, and D. C. Schram, Plasma Sources Sci. Technol. **3**, 501 (1994).

[8] W. B. Maier, J. Chem. Phys. **42**, 1790 (1965).

[9] P. M. Mul and J. Wm. McGowan, Astrophys. **237**, 749 (1980).

[10] E. S. Aydil, J. A. Gregus, and R. A. Gottscho, Rev. Sci. Instrum. **64**, 3572 (1993).

[11] J. W. A. M. Gielen, M. C. M. van de Sanden, P. R. M. Kleuskens, L. J. van IJzendoorn, D. C. Schram, E. H. A. Dekempeneer, and J. Meneve (unpublished).

[12] K. Donnelly, D. P. Dowling, E. Davitt, T. P. O'Brien, and T. C. Kelly, Proc. Adv. Mater. Proc. Technol. 769 (1993).

[13] J. L. Loubet, J. M. Georges, and G. Meile, ASTM Spec. Techn. **889**, 72 (1986).

[14] J. Robertson and E. P. O'Reilly, Phys. Rev. B **35**, 2946 (1987).

[15] J. Robertson, Diam. Relat. Mater. **4**, 297 (1995).

[16] B. Dischler, E-MRS Meeting **17**, 189 (1987).

[17] P. Koidl, C. Wild, R. Locher, and R. E. Sah, in *Diamond and Diamond-like Films and Coatings,* NATO ASI Series B, Vol. **266**, edited by R. E. Clausing, L. L. Horton, J. C. Angus and P. Koidl (Plenum, New York, 1991), p. 243.

[18] J. Robertson, in *Diamond and Diamond-like Films and Coatings,* NATO ASI Series B, Vol. 266, edited by R. E. Clausing, L. L. Horton, J. C. Angus, and P. Koidl (Plenum, New York, 1991), p. 331.

[19] O. Stenzel, R. Petrich, and M. Vogel, Opt. Mater. **2**, 125 (1993).

[20] N. Fourches and G. Turban, Thin Solid Films **240**, 28 (1994).

[21] P. Reinke, W. Jacob, and W. Möller, J. Appl. Phys. **74**, 1354 (1993).

[22] A. von Keudell, W. Jacob, and W. Fukarek, Appl. Phys. Lett. **66**, 1322 (1995).

[23] S. Xu, M. Mundhausen, J. Ristein, B. Yan, and L. Ley, J. Non-Cryst. Solids **164-166**, 1127 (1993).

[24] L. Martinu, A. Raveh, A. Dominique, L. Bertrand, J. E. Klemberg-Sapieha, S. C. Gujrathi, and M. R. Wertheimer, Thin Solid Films **208**, 42 (1992).

[25] J. W. A. M. Gielen, M. C. M. van de Sanden, W. M. M. Kessels, and D. C. Schram, Mater. Res. Soc. Symp. Proc. (to be published).

[26] S. A. Miller, *Acetylene, it's Properties, Manufacture and Uses* (Ernest Benn, London, 1965).

[27] E. Herbst, Astrophys. J. **222**, 508 (1978).