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Effect of substrate conditions on the plasma beam deposition of amorphous hydrogenated carbon

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A study on the effect of substrate conditions was performed for the plasma beam deposition of amorphous hydrogenated carbon (*a*-C:H) from an expanding thermal argon/acetylene plasma on glass and crystalline silicon. A new substrate holder was designed, which allows the control of the substrate temperature independent of the plasma settings with an accuracy of 2 K. This is obtained via a combination of a good control of the holder's yoke temperature and the injection of helium gas between thermally ill connected parts of the substrate holder system. It is demonstrated that the substrate temperature influences both the *a*-C:H material quality and the deposition rate. The deposition rate and substrate temperature are presented as the two parameters which determine the material quality. *In situ* studies prove that the deposition process is constant in time and that thermally activated etching processes are unlikely to contribute significantly during deposition. Preliminary experiments with an additional substrate bias reveal that an energetic ion bombardment of the growing film surface does not influence the deposition process. A tentative deposition model is proposed based on the creation and destruction of active sites, which depend on the particle fluxes towards the substrate and the substrate temperature. This model allows the qualitative explanation of the observed deposition results. © *1997 American Institute of Physics.*
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I. INTRODUCTION

Amorphous hydrogenated carbon (*a*-C:H) is generally recognized as a material with adjustable favorable properties. Potentially, *a*-C:H is a very hard (over more than 20 GPa) chemically inert, electrically insulating, wear resistant, and infrared transparent material with low friction behavior.[1–3] However, the exact material properties are strongly determined by the deposition conditions and may vary from soft-polymerlike to hard-diamondlike. Therefore, the final properties can be adjusted to the application foreseen. For example, hard wear resistant *a*-C:H is used as a protecting film on optical elements and as a wear resistant, low friction coating for mechanical systems.

In recent years various plasma deposition techniques have been developed for the deposition of *a*-C:H.[4] A general feature of most of these techniques is that biasing of the substrate is assumed to be indispensable to obtain diamondlike properties, i.e., a bias of the order of a hundred volt per deposited carbon particle is applied.[1,5–10] The energetic ions bombarding the film surface can fulfil various tasks: they can penetrate in the film causing subsurface reconstruction of the growing film resulting in diamondlike material, they can create dangling bonds at the surface, which act as growth sites and they can stitch physisorbed hydrocarbon radicals into the film.[11–13] The deposition rate typically is in the range of 0.1–1 nm/s. For a fruitful commercial use this is too low; a considerably higher deposition rate over large areas (>100 cm^2) would be desirable.

Recently, it has been shown that it is indeed possible to deposit *a*-C:H at a rate which is two orders of magnitude higher than conventional methods allow.[14,15] Using an expanding thermal plasma deposition rates up to 75 nm/s have been obtained without loss of material quality. The material properties even improve at increasing growth rate[14,16] and the films exhibit diamondlike quality.[15] Variation of the plasma settings and the subsequent change in material properties is obtained by varying the ionization degree of the expanding plasma and the admixed acetylene precursor flow. During the depositions no external substrate bias has been applied. The plasma self-bias is only several volts which is due to the low electron temperature. Therefore, the generally considered crucial energetic ion bombardment of the surface is absent. Furthermore, the best material quality is obtained when the residual ion density in front of the growing film is minimal.[14,17]

Next to the effect of a substrate bias, another substrate property is considered to be important during the deposition of *a*-C:H: the substrate temperature. In previous deposition experiments the substrate holder was water-cooled without applying an active temperature control.[15,16] It was observed that the temperature of the substrate holder only changed a few kelvin during one deposition. However, the thermal contact between the substrate and the substrate holder was poor, as the substrates were only clamped on the holder. From infrared interferometric experiments, it has been determined that the substrate temperature increases much more than is observed from a temperature measurement of the substrate holder. An increase of 5–10 K/s is much more realistic than the observed increment of the holder of several kelvin per minute.

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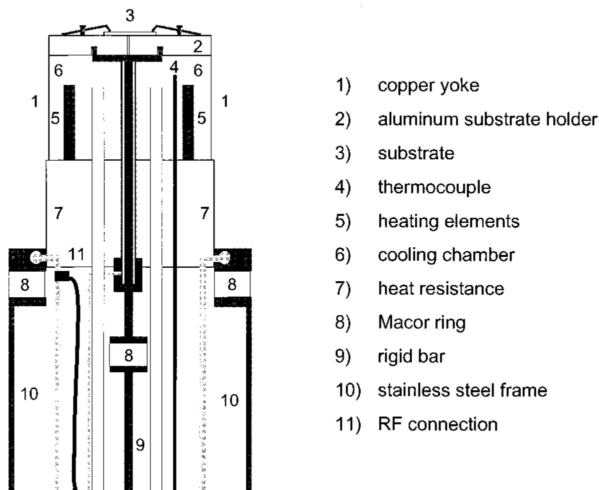

FIG. 1. A schematic drawing of the substrate holder.

To study the effect of the substrate conditions on the quality of plasma beam deposited a-C:H a new substrate holder has been designed. The main features of this holder are its temperature control in the range from 200 to 600 K and the radio frequency (rf) biasing up to -200 V. In this article, this substrate holder will be described in particular with respect to the thermal contact between substrate and substrate holder. The effect of the substrate temperature on our plasma beam deposited a-C:H will be discussed, and the results of an *in situ* study on the deposition and etching of a-C:H films will be presented. The results of preliminary deposition experiments with the application of a rf substrate bias will be given, too. Finally, a first attempt will be made to explain the temperature dependent properties in relation to the plasma chemistry and the surface reactions.

II. EXPERIMENT

A. Deposition setup

In a cascaded arc plasma source a subatmospheric thermal argon plasma is created. At the arc exit the plasma expands into an expansion vessel which is at a typical pressure of 25 Pa. In the expansion zone acetylene is admixed which is dissociated by interaction with argon ions.[14] The formed plasma mixture is transported towards a substrate holder where deposition takes place. An extensive description of the deposition setup has been presented elsewhere,[16] except for the substrate holder which is described in Sec. II B.

B. Substrate holder

The objective of the new substrate holder is both to control the substrate temperature and to apply a rf bias. In Figure 1 a schematic drawing is shown. The holder consists of the following parts: from top to bottom a copper yoke, a stainless steel heat resistor, an electrically insulating Macor ring, and a stainless steel frame which is connected to the expansion vessel.

The temperature of the yoke is regulated by a combination of cooling and heating. Cooling is performed by liquid nitrogen which flows through the copper yoke; the cooling power is 700 W. The heating occurs via eight heating elements (Watlow EG40A5) of 250 W each, which are positioned circularly symmetric just below the top of the yoke. With a Chromel–Alumel thermocouple (Thermocoax®, Type K, SKI20/100/D) the temperature of the yoke is measured. Both the heating power as well as the liquid nitrogen flow are fixed in magnitude and are either fully on or off. Temperature control of the yoke is obtained via a control unit (West 5010 Industrial Controller), which determines the desired heating and cooling time periods from the actual yoke temperature. The yoke temperature is in the range from 200 to 600 K and is regulated within 1 K around the setpoint temperature. Characteristic heating and cooling times of the yoke are 170 s to increase the temperature by 100 K and 500 s to decrease the temperature by 100 K. This difference is due to the available cooling and heating power.

The substrates on which a film is to be deposited are not directly mounted on the copper yoke, but they are clamped on an aluminium substrate holder which is pulled against the copper yoke. This pulling occurs via a rigid bar (cf. Figure 1) which is forced downward with compressed air. The construction with the additional aluminium holder is necessary in view of a future load-lock system, by means of which in one time the substrate holder and the substrate can be mounted on the yoke without breaking vacuum.

For this construction with several solids clamped on each other the bad thermal contact between the various materials remains a problem. Without a good thermal contact the temperature difference between the substrate and the yoke can be very large, i.e., exceeding 100 K, when the plasma is switched on. This results in a nonreproducible and noncontrollable temperature variation of the substrate. Several techniques have been studied to improve the thermal contact.[18] One good way to improve the thermal contact is to glue the various parts on each other with a conductive paste. However, to remove the paste from the substrate after the deposition is very difficult. This implies that there are always some residual material left on rear side of the substrate. In view of *ex situ* analyses this is undesired as, e.g., the paste influences the transmitted infrared light through the substrate during infrared spectroscopy. For the connection of the holder to the yoke this method is also unsuitable as the holder and the yoke shall not be connected permanently. Another method is to put a flexible conductive material between the various solids. The best candidate for this is indium, which is very soft and has a high thermal conductivity ($\approx$82 W m^{-1} K^{-1}).[19]A disadvantage of using indium is that it melts around 430 K which is in the desired temperature range. Furthermore, it is rather expensive. A third opportunity is to inject a gas with a high thermal conductivity between the several solids. Various gases are suitable but the best candidates are hydrogen and helium. The thermal conductivity[19] of hydrogen is about 0.18 W m^{-1} K^{-1} and for helium it is in the range of 0.10–0.24 W m^{-1} K^{-1}, which is high compared to other gases. This is mainly due to their low masses, small neutral collision cross-sections, and high molar heat capacities. Hydrogen is a good and cheap candidate, but the interaction of hydrogen with an argon plasma has

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major undesired effects on the plasma composition as it decreases the ionization degree.[20,21] In contrast, helium is inert to an argon plasma as the ionization potential of helium is about 24.5 eV. The recombination energy of an argon ion is far less: 15.8 eV and in the expanding argon plasma no hot electrons are present.[22] Therefore, helium is used as an inter-solid thermal conductor.

The helium is injected along the rigid rod which has a small leak into the vessel at the vacuum transport rings. The gas arrives underneath the aluminium substrate holder and flows through the small leaks between the yoke and the holder towards the vessel, by which it provides the desired thermal contact. To obtain a helium flow between the substrate and the substrate holder a small bore is made in the holder below the substrate. To obtain a good thermal contact, only small helium flows are necessary, less than 5 scc/s (standard $cm^3\ s^{-1}$).

On the upper part of the substrate holder (yoke and stainless steel heat resistance) a rf bias can be applied with a rf unit (RF Power Products RF-5S). This unit consists of a power supply and a matching network to obtain a maximal power transfer to the load, i.e., the aluminium substrate holder. The maximal power that can be applied is 300 W. Measuring of the rf voltage on the substrate is performed with a high-voltage probe (Fluke PM9100).

III. DIAGNOSTICS

A. Infrared interferometry

Infrared interferometry is a technique which uses the interference features of infrared light reflected from a material in which multiple reflections have occurred.[23] In this article two applications of infrared interferometry will be used. One application is the determination of the temperature of a double polished silicon substrate. The other is the *in situ* study of the etching and deposition process of thin *a*-C:H films on a single side polished silicon substrate. In both cases the total reflected intensity is measured as a function of time. At an angle of about 70° normal to the substrate monochromatic infrared light of a Melles Griot HeNe laser ($\lambda_0 = 1.523\ \mu m$) is incident on the substrate. The total reflected light intensity from the substrate is measured with a photodiode.

For the determination of the substrate temperature the method proposed by Donnelly *et al.*[24] has been followed. A double polished silicon substrate has been heated or cooled and as a function of time the reflected infrared intensity has been measured. The multiple reflection features depend on the refractive index and thickness of the silicon. Especially, the refractive index value changes in the third decimal with small temperature variations, which influences the reflected infrared intensity significantly. From the measured reflected infrared intensity the temperature of the silicon has been determined as a function of time. To account for the nonlinearity in the temperature dependence of the refractive index over the applied temperature interval (200–600 K), a calibration has been performed.

To study the deposition and etching process with interferometry, an *a*-C:H film has been deposited on or etched from a single side polished silicon substrate. The interference features now arrive from multiple reflections in the *a*-C:H material. The substrate temperature has been kept constant and the measured reflected infrared intensity, therefore, is dependent on the film thickness only. This allows the determination of the film thickness as a function of time.

B. *Ex situ* film characterization

The deposited *a*-C:H films on glass and crystalline silicon have been analyzed *ex situ* with infrared spectroscopy. With a Biorad FTS-15/80 Fourier transform infrared spectrometer, the transmission of incident infrared light has been measured in the wavenumber interval from 400 to 5000 cm^{-1}. In the measured transmission spectra, multiple reflection features are clearly observed which are fully determined by the infrared refractive index and thickness of the material. Via a fitting procedure both properties have been determined from the measured spectra. A detailed description of the infrared spectroscopy measurements and the subsequent analysis via fitting has been presented elsewhere.[15] From the determined thickness the growth rate of the films has been obtained.

IV. SUBSTRATE TEMPERATURE

The effect on the substrate temperature when switching on an argon plasma (arc current: 48 A; argon flow: 100 scc/s; vessel pressure: 25 Pa) has been studied with interferometry. As an example the effect on the substrate temperature is shown in Figure 2(a) for a yoke temperature of 323 K. When the plasma is switched on the infrared reflected intensity changes indicating a temperature increase due to plasma heating. In Figure 2(b) this intensity variation has been translated into a temperature change. It is observed that the temperature increases by about 10 K. The time in which the temperature is within $1/e \times 10$ K is less than 10 s. The aluminium holder obtains nearly the same temperature as the substrate ($\Delta T < 2$ K). On the other hand, the yoke temperature does not change when the plasma is ignited. The temperature gradient between the substrate and the yoke represents the heat transport from the substrate to the yoke which originates from the plasma. It is found that the temperature increase for the given plasma condition is rather independent of the chosen yoke temperature, which itself is independent of the applied plasma. The substrate temperature increases by about 10 ± 2 K. When the arc current is varied the observed temperature increment changes a little but this is well within the given error margin.

From the results above, it is concluded that the helium flow between the various solids results in a good thermal contact as the substrate temperature is only slightly changed by an incident argon plasma and this change is known and reproducible. The temperature of the substrate can be well controlled. The effect on the substrate temperature of admixing a deposition precursor cannot be measured via interferometry, as deposition of *a*-C:H also implies multiple reflections in this material which influence the reflected light

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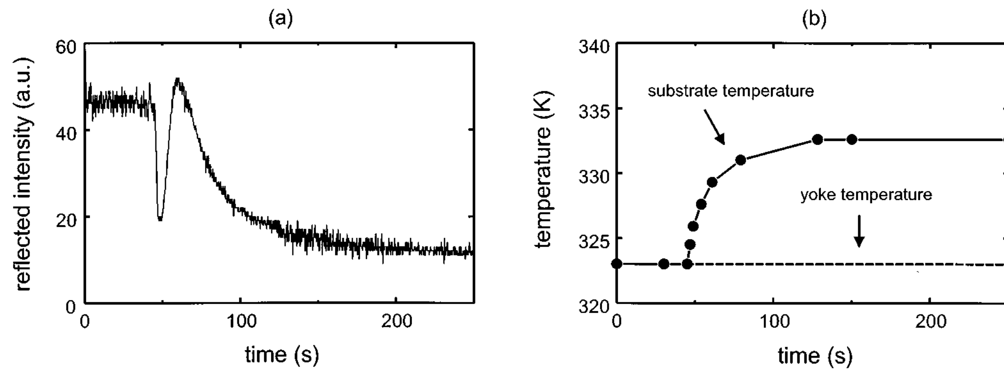

FIG. 2. The time-dependent effect of starting an argon plasma on the measured reflected infrared intensity (a) and the substrate temperature (b).

intensity next to the temperature variation. However, the temperature of the aluminium holder is well coupled to the substrate temperature, and does not change by more than 2 K on the time scale of the deposition which is of the order of 1 min. This shows that the substrate temperature is constant within the error margin during deposition, and the actual substrate temperature is easily determined from the yoke temperature via the relation

$$T_{\text{substrate}} = T_{\text{yoke}} + \Delta \quad (1)$$

with $T_{\text{substrate}}$ the substrate temperature and T_{yoke} the yoke temperature. Δ is a constant and gives the difference between the yoke and substrate temperature which is approximately 10 K.

V. RESULTS

A. Deposition of *a*-C:H and the influence of substrate temperature and growth rate

With the thermostration method described in the previous section, the influence of the substrate temperature on the film deposition process has been studied. The films have been deposited on glass substrates of 2.5×2.5 cm^2 which have been cleaned via the procedure described in Ref. 15. In this reference also the deposition procedure has been described in detail. During the deposition experiments two plasma parameters have been varied: the arc current and the admixed acetylene flow. Both parameters have been chosen such that either critical loading or underloading conditions are present.[14,16] An overview of these parameter settings is given in Table I. In Table I critical loading refers to the parameter setting where the ion flow emanating from the arc approximately equals the injected acetylene flow. Underloading refers to settings for which the acetylene flow is smaller than the ion flow. It is demonstrated in Refs. 14 and 16 that in case of critical loading the best films in terms of hardness and refractive index are produced. The deposited films have a typical thickness of about 1.5 μm and in general adhere well to the substrate. For each plasma setting condition the substrate temperature has been varied from 223 to 573 K. Via *ex situ* infrared spectroscopy the infrared refractive index and thickness of the films have been obtained.

TABLE I. The applied arc current and admixed acetylene flow during the deposition of *a*-C:H.

Arc current (A)	Acetylene flow (scc/s)	Critical loading/ underloading
22	4.7	Critical loading
48	4.7	Underloading
48	10.0	Critical loading
66	15.0	Critical loading
87	20.0	Underloading

In Figure 3(a) the infrared refractive index is presented as a function of the substrate temperature for the various plasma settings. The critically loaded films at 48 A arc current have a higher refractive index than the underloaded films at 48 A for all temperatures, which confirms earlier observations[14] and demonstrates that this is a temperature independent fact. For the lowest arc current, i.e., 22 A, the refractive index is found to be independent of the substrate temperature. For the other deposition conditions the refractive index exhibits more or less an increasing trend with an increasing substrate temperature. In the underloaded 48 A case the refractive index saturates from about 360 K. The critically loaded 48 A case seems to have a maximum at about 500 K. The trend in the critically loaded 66 A case is not quite clear. Finally, the underloaded 87 A case exhibits a weak maximum between 400 and 500 K. The general trend in the refractive index seems increasing with temperature increase with a slight indication for a maximum value around 500 K. An extensive comparison with literature data is difficult as there is not much data available on the substrate temperature dependence of the refractive index. Von Keudell *et al.*[25] found a refractive index which is rather constant for several temperature regimes. At certain temperatures a change occurs; a higher refractive index is observed at higher temperatures. This observation is not in agreement with our findings.

In Figure 3(b) the growth rate of the deposited films is presented as a function of the substrate temperature. For all plasma settings a clear decrease in the deposition rate is observed with increasing substrate temperature. This decrease can be up to 50% over a temperature range of 350 K. The decrease of growth rate is accompanied by an increasing refractive index [Figure 3(a)] and, thus, increasing material

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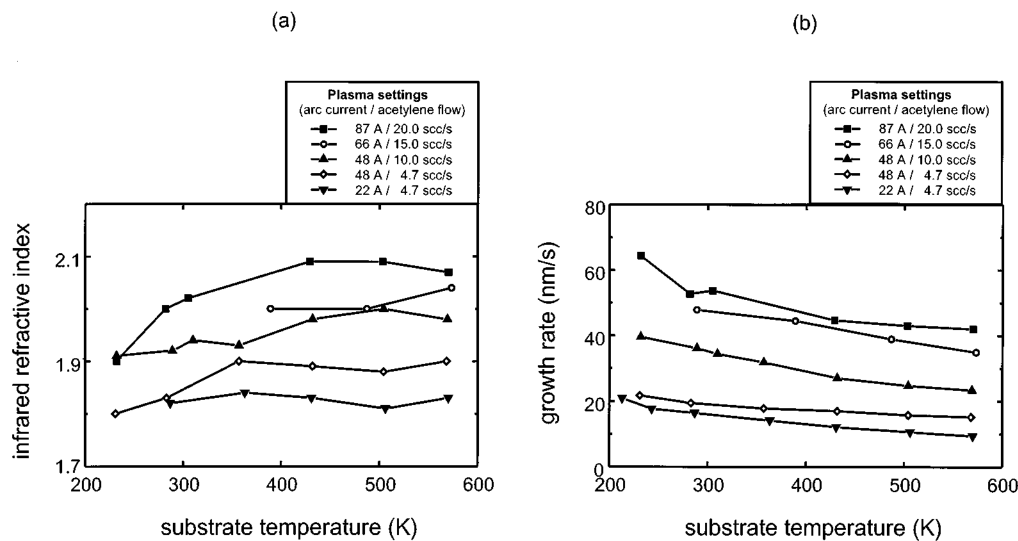

FIG. 3. The infrared refractive index (a) and the growth rate (b) of the a-C:H films as a function of the substrate temperature. The deposition settings are given in Table. I.

density. However, the effect of this density variation on the growth rate is 4% at maximum, and cannot explain the observed growth rate variation of 50% with substrate temperature variation. Temperature dependent a-C:H deposition experiments with an expanding thermal plasma seeded with methane by Kersten *et al.*, several years ago also revealed a decrease in deposition rate with substrate temperature increment.[26] However, compared to the present results the decrease was much stronger, i.e., the deposition rate decreased by more than 15 nm/s when the temperature rose less than 30 K. The present depositions from an argon/acetylene plasma reveal a similar decrease but for temperature increments exceeding 200 K. An explanation for this difference is currently not available, but it could be due to different deposition mechanisms involved when using methane or an improper substrate temperature measurement by Kersten *et al.*[27]

Comparison of the temperature dependence on the growth rate with literature data concerning other plasma deposition techniques confirms our observations, that a substrate temperature increase results in a lower deposition rate. However, in general the absolute decrease is much lower in our case. Planck *et al.*[28] attribute this negative temperature dependence to the chemical erosion of the films by atomic hydrogen and carbon self-sputtering. The latter cannot be an explanation in our case as no substrate bias has been applied which implies no energetic ion bombardment and, thus, no sputtering. Möller and Von Keudell[11,25,29] proposed a model for the deposition of a-C:H which explains that growth occurs from an adsorbed layer by ion stitching of radicals into the growing film. The adsorbed density of the various radicals in this adsorbed layer is temperature dependent, and at elevated substrate temperatures enhanced desorption leads to depletion of the adsorbed layer and, thus, to lower deposition rates. Mantzaris *et al.*[30] have modeled the growth rate also via an adsorbed layer model. They show that the deposition rate decreases drastically with increasing substrate temperature which again is due to a strong increase in desorption of neutral particles from the adsorbed layer. Recently, von Keudell *et al.*[31] have done temperature dependent a-C:H deposition studies in which the growth has been monitored *in situ* with HeNe ellipsometry. Again, they find a decreasing growth rate at elevated substrate temperatures. They explain this decrease via a temperature dependent hydrogen induced erosion process in combination with a temperature independent deposition process. Opposite to earlier models[11,25,29] they conclude that an adsorbed layer does not necessarily exist. On the effect of thermally activated etching with hydrogen we will comment below. So far, the observed decrease in deposition rate with increasing substrate temperature is only in qualitative agreement with the available literature data but in absolute sense not; we observe a smaller temperature dependence. Further on a possible tentative mechanism for our deposition process will be discussed.

In previous experiments[14] it has been observed that a clear correlation exists between the refractive index of the deposited a-C:H material and the deposition rate: the refractive index increases at higher deposition rate. These films have been deposited with poor substrate temperature control. For the current deposition experiments at various substrate temperatures, the refractive index is presented as a function of growth rate in Figure 4(a). For each individual substrate temperature the refractive index of the material increases with increasing growth rate. The results presented in Ref. 14 also have been plotted in Figure 4(a). The refractive index for the films deposited with good substrate temperature control exhibits a similar trend, as found for the films without a good substrate temperature control. A perfect match of the latter results to one specific substrate temperature curve is not found, but it seems reasonable to conclude that the film depositions of Ref. 14 have been performed at substrate temperatures well above 450 K. This is much higher than the earlier assumed temperatures below 375 K. This assumption was based on the presence of sp^1CH bonds in the films;

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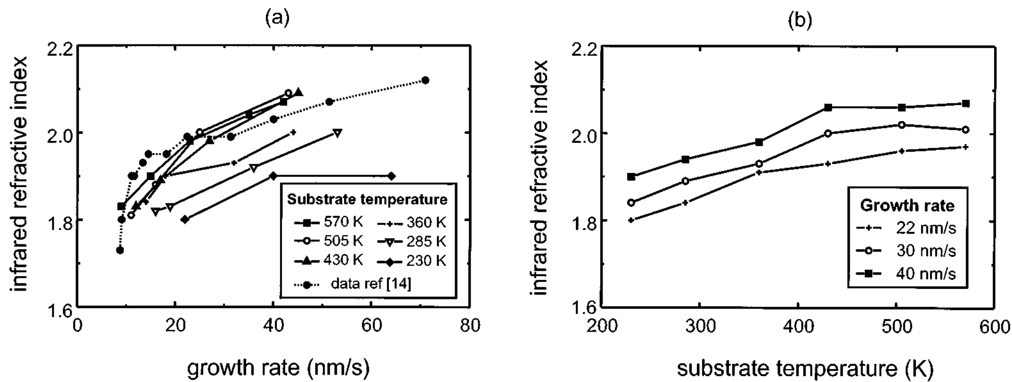

FIG. 4. The refractive index vs the growth rate at constant substrate temperature (a) and vs the substrate temperature at constant growth rate (b). The deposition settings are given in Table I.

Dischler concluded that the presence of these bonds implies a substrate temperature during deposition below 375 K.[32]

The trends in Figure 4(a) clearly show that the refractive index of the deposited *a*-C:H increases with increasing substrate temperature and with increasing deposition rate. The latter seems in contradiction with the results from Figure 3, which exhibit that at elevated substrate temperatures the deposition rates decrease while the refractive index increases. However, these trends are observed for individual deposition settings, i.e., arc current and acetylene flow settings, while the trends in Figure 4(a) are not related to individual deposition settings, anymore. From the refractive index as a function of growth rate curves in Figure 4(a); the refractive index at constant growth rate is determined as a function of the substrate temperature by means of interpolation. This has been done for three deposition rates: 22, 30, and 40 nm/s. The result is shown in Figure 4(b). As expected from Figure 4(a), the refractive index increases with the substrate temperature with a saturation behavior at elevated temperatures. But from Figure 4(a) it is also obvious that a higher growth rate leads to a higher refractive index.

To conclude: the quality of *a*-C:H in terms of refractive index is dependent on both the applied substrate temperature during deposition and the obtained deposition rate. Increment of each individual parameter leads to better films.

B. Deposition and etching of *a*-C:H studied *in situ* with interferometry

An *in situ* study of the deposition of *a*-C:H films would reveal only the time dependence of the deposition process. On single side polished silicon *a*-C:H films have been grown and the deposition process has been monitored *in situ* with infrared interferometry. The substrate temperature is kept constant at 523 K and the refractive index (n) is assumed to be independent of the film thickness. This implies that the reflected infrared intensity during deposition is a direct measure of the film thickness if the refractive index is known. The thickness (d) is obtained from the fringe number m as a function of time and is given by

$$d=\frac{\lambda_0}{2\sqrt{n^2-\sin^2\theta}}m \tag{2}$$

with θ the angle of incidence of the laser beam normal to the film surface: $m=l+0.5$ for minima and $m=l$ for maxima in the reflected intensity with l an integer starting at 0. For three

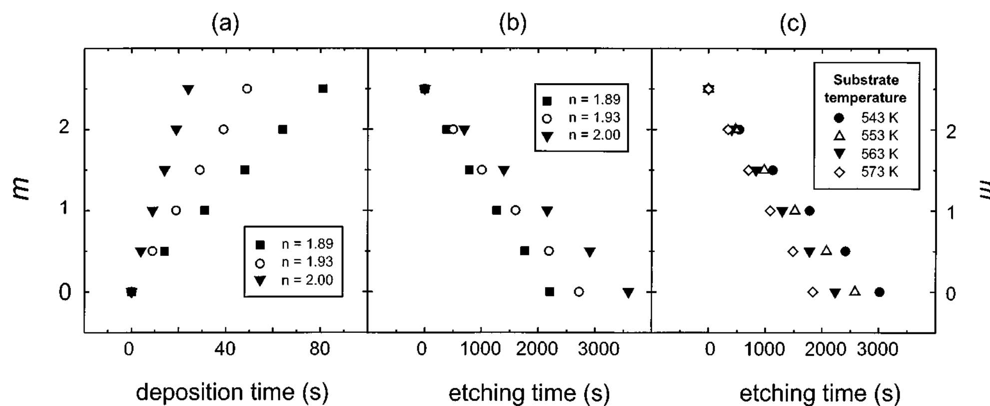

FIG. 5. The extreme values in the reflected infrared intensity as a function of time during (a) the deposition of *a*-C:H on silicon at constant substrate temperature; (b) the etching of *a*-C:H on silicon at constant substrate temperature; and (c) the etching of *a*-C:H on silicon at various substrate temperatures.

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plasma conditions an a-C:H film has been deposited. In Figure 5(a) the fringe number is given as a function of time. A linear fit to the data points reveals that they are equidistant. This implies that the film growth is homogeneous in time. From infrared absorption spectroscopy, the refractive indices of the deposited films are known [cf. Figure 3(a)]. The applied infrared light in interferometry (1.523 μm is equal to 6566 cm^{-1}) is not in the interval used in the spectroscopy experiments. Nevertheless, the error made by the use of the refractive indices from Figure 3(a) will be negligible as the infrared refractive index of a-C:H depends only weakly on the wavenumber. The growth rate of each film is determined from the slope in Figure 5(a) applying Eq. (2). A steeper slope implies a higher deposition rate. For the respective refractive indices of 1.89, 1.93, and 2.00 the calculated growth rate is 15, 23, and 43 nm/s. These results are in good agreement with the rates obtained from infrared absorption spectroscopy.

Subsequent to each deposition, the films have been etched with an argon/hydrogen plasma (argon flow: 100 scc/s; arc current: 48 A; hydrogen flow: 10 scc/s) at a constant substrate temperature of 523 K. The process is also monitored with infrared interferometry. In Figure 5(b) the extreme values in the reflected infrared intensity are presented as a function of time. The negative slope indicates a decreasing film thickness; a steeper slope implies faster etching. A linear fit to the measured extrema reveals that, just as the deposition of a-C:H, the hydrogen induced etching occurs at constant rates. The etch rate is found to decrease with increasing refractive index of the deposited a-C:H. For a refractive index of 1.89, 1.93, and 2.00 the respective etch rates are 0.58, 0.42, and 0.30 nm/s.

The hydrogen induced erosion of carbon is suggested to occur via the formation of CH_3 (methyl) groups which desorb from the surface.[31,33] The decrease in etch rate for material with higher refractive indices, thus harder material, can be explained in our case by an increase in the number of sp^2C=C bonds and a lowering of the hydrogen content in the material [cf. (Ref. 15)]. On one hand sp^2C=C bonds must be transformed into sp^3C–C bonds which are hydrogenated and finally desorb. On the other hand more hydrogen means that more hydrogenated sp^3 groups are already present and, thus facilitate the etching of these groups by additional atomic hydrogen. During the etching process of a hard film one part of the hydrogen flux is used to transfer the sp^2C=C into sp^3C–C bonds, and the other part is used for hydrogenation of the latter bonds into methyl groups which desorb.[31,33] Hard-diamondlike a-C:H, therefore, is etched more slowly than soft-polymerlike a-C:H under equal etching conditions; the former contains more sp^2C=C bonds and less hydrogen.

From Figure 3(b) it has been demonstrated that the growth rate decreases at increasing substrate temperature. Several authors have been cited and they all suggest that this is due to a thermally activated desorption or erosion process. Von Keudell *et al.*[31] even show that in their case the decrease in deposition rate is totally due to an increasing etch rate by atomic hydrogen, while the deposition rate does not change with substrate temperature. Their deposition rates are

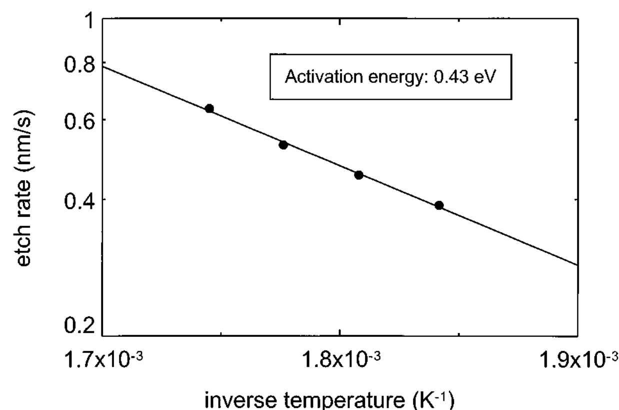
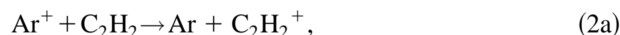


FIG. 6. The etch rate as a function of the substrate temperature presented in an Arrhenius plot.

quite low, less than 1 nm/s. To check whether in our case etching by atomic hydrogen is responsible for the decrease in deposition rate hydrogen induced etching experiments have been performed at various substrate temperatures. The etching process is monitored with infrared interferometry. For substrate temperatures of 543, 553, 563, and 573 K an a-C:H film has been deposited at an arc current of 48 A and an acetylene flow of 4.7 scc/s. Under these conditions the refractive index is known to be constant at 1.89 [cf. Figure 3(a)]. The deposited film thickness is approximately 1.2 μm. After each deposition the film has been etched at its respective substrate temperature with an argon/hydrogen plasma (argon flow: 100 scc/s; arc current: 48 A; hydrogen flow: 10 scc/s). The fringe number versus etching time is given in Figure 5(c). The etch rates are found to increase with increasing substrate temperature from about 0.2 to 0.6 nm/s in the temperature range from 543 to 573 K. In Figure 6 the etch rate is given as a function of the inverse substrate temperature in an Arrhenius plot. From this plot the activation energy of the hydrogen induced etching process is determined to be about 0.43 eV. This is in agreement with the activation energy for atomic hydrogen etching obtained by von Keudell *et al.*[31] The absolute etch rates are higher as observed by von Keudell *et al.*,[31] but this is due to a higher atomic hydrogen flux towards the substrate in our case.

The typically observed etch rates for our films, thus are on the order of 1 nm/s at the highest substrate temperature of about 573 K at an admixed hydrogen flow of 10 scc/s. At lower temperatures the etch rates strongly decrease. From considerations of energy and phase space, it is inferred that the dissociation of C_2H_2 by means of argon ions and electrons mainly creates C_2H radicals and H atoms[17,34,35] [note that electrons have only a temperature of approximately 0.2 eV (Ref. 22) and therefore, are incapable of dissociation of C_2H_2]:



$$Ar^+ + C_2H_2 \rightarrow Ar + {C_2H_2}^+, \quad (2a)$$

$$ {C_2H_2}^+ + e \rightarrow C_2H + H. \quad (2b)$$

At the surface these hydrogen atoms may etch while the C_2H radicals infer deposition. If we describe the deposition process according to Von Keudell *et al.*,[31] the decrease in

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deposition rate is totally due to an increase in hydrogen induced etching. This implies that an Arrhenius plot of the deposition rates of Figure 3(b) has to reveal the activation energy for hydrogen erosion. The average calculated activation energy is about 16 meV. This is more than 25 times less than the 0.43 eV obtained from the experiments. Therefore, it is concluded that only thermally induced hydrogen etching cannot explain the observed decrease in deposition rate with temperature increment. There seems to be a weak temperature dependent process which results in the observed decrease in deposition rate. This subject will be discussed below.

C. Influence of an energetic ion bombardment on *a*-C:H film deposition

To study whether an energetic ion bombardment influences the deposition process of *a*-C:H material by means of an expanding thermal argon plasma, a preliminary experiment has been performed with the application of an additional rf bias on the substrate during deposition. For two deposition conditions (the underloaded and critically loaded 48 A arc current cases) *a*-C:H material has been deposited on crystalline silicon (argon flow: 100 scc/s; vessel pressure: 25 Pa). The applied rf power has been varied from 0 to 100 W. This results in a negative bias in front of the substrate up to 120 V. The deposited films have been analyzed *ex situ* with infrared spectroscopy. In both the critically loaded and the underloaded deposition cases no dramatic change has been observed in the deposited *a*-C:H material under variation of the applied rf bias; the refractive index is constant within the error margins. It should be noted here, that at the typical ion density of 10^{17}–10^{18} m^{-3} and electron temperature of approximately 0.2 eV, the Child–Langmuir sheath thickness close to the substrate is much smaller (0.02 cm) than the mean free path for ions (2 cm) at a pressure of 0.25 mbar and a gas temperature of 0.2 eV.

For the critically loaded case this is not surprising. In Ref. 17 it has been demonstrated that the ion density halfway the expansion in this case has decreased until 10% of the initial density which is equivalent to about 2×10^{18} m^{-3}. When the plasma arrives at the substrate the density will have decreased even more. With a thermal velocity of the argon ions of about 1400 m/s [the ion temperature is about 0.3 eV (Ref. 22)], an upper limit of the argon ion flux towards the substrate is calculated to be 3×10^{21} m^{-2} s^{-1}. The density of C_2H radicals is calculated on the basis of a minimal dissociation degree of 70% which is about 5×10^{19} m^{-3}.[34] With a thermal velocity of about 1700 m/s the flux of C_2H radicals towards the substrate is about 9×10^{22} m^{-2} s^{-1}. The flux of radicals contributing to growth towards the growing film is at least by more than an order of magnitude higher than the ion flux. This could explain why an additional rf bias only has marginal influence on the particle fluxes towards the substrate and, thus on the deposition process.

In the underloaded case one might expect a larger influence of an ion bombardment as the ion flux ($\approx1\times10^{22}$ m^{-2} s^{-1}) towards the substrate is comparable in magnitude to the C_2H flux ($\approx3\times10^{22}$ m^{-2} s^{-1}). However, the ion flux mainly consists of argon ions.[17,34] The penetration depth of these ions into the material is rather small due to their high atomic mass.[36] This implies that subsurface reorganization reactions cannot occur. The ion bombardment only affects the surface conditions which obviously seems not to result in major property changes. This could suggest that an adsorbed layer is not present.

From these first experiments, it has to be concluded that an additional rf substrate bias during plasma beam deposition of *a*-C:H material does not influence the film properties opposite to findings with other deposition techniques. But as only two deposition conditions have been studied, it is necessary to perform an extensive study into the effect of an additional rf bias in the near future. For the moment the influence of an energetic ion bombardment is considered as unimportant for the deposition of diamondlike *a*-C:H by means of an expanding thermal plasma.

VI. TENTATIVE MODEL FOR THE DEPOSITION OF *a*-C:H

Until recently our deposition results were explained in terms of the amount of input energy which is available per deposited carbon particle. This leads to the introduction of the inverse energy coefficient.[16] It was found that the *a*-C:H material quality improves (higher hardness and refractive index, lower optical band gap, and hydrogen content) when the amount of input energy per deposited carbon particle decreases.[37,38] A disadvantage of connecting the material properties and the deposition process to the inverse energy coefficient is that this description does not account for the plasma chemistry, the substrate conditions, and the plasma-surface reactions. Only a relation between the arc plasma input parameters and the final film parameters is given. In Ref. 16 it has been demonstrated that the dependence on the inverse energy coefficient can be translated into a dependence on the deposition rate, which is a deposition property rather than a plasma input parameter; it accounts for the flux of growing particles towards the growing film. From Figure 4 it has been shown that not only the growth rate determines the deposited material properties but also the substrate temperature. These observations imply that the inverse energy coefficient on itself is not sufficient to describe the deposition process, as the substrate conditions are of importance to the film properties independent of the plasma composition. The description of the deposition process on the basis of plasma input parameters only, thus is not allowed. Below our first speculative ideas are presented on the deposition process by means of an expanding thermal argon plasma fed with acetylene taking into account both the plasma composition, in terms of the deposition rate, and the substrate conditions, in terms of the substrate temperature. A tentative deposition model is proposed which is based on six plasma-surface reactions which are considered to be dominant.

Previously, the following facts have been demonstrated:[14–16,34] First, diamondlike *a*-C:H can be deposited from an expanding argon/acetylene plasma which is dominated by radicals. Second, during the deposition process no significant contribution of temperature induced hydrogen etching is present; and third, preliminary deposition experi-

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ments with an additional substrate bias have revealed that an additional ion bombardment of the growing film surface does not influence the final film properties. Most models for the plasma deposition of *a*-C:H material, which have been presented in literature infer the presence of an energetic ion bombardment of the growing film surface to obtain diamond-like *a*-C:H. These models, therefore, cannot be used to describe the deposition process from an expanding plasma.

Recently, Von Keudell[36] has proposed an alternative mechanism for the deposition of *a*-C:H. To his opinion not only the energetic ion bombardment of the film surface is important but also the creation and preservation of so-called ''active sites:'' the dangling bonds at the film surface where a radical can chemisorb. The ion bombardment has two effects during deposition: it displaces hydrogen atoms from the film surface creating the necessary active sites and it induces subsurface reorganization to a certain depth. The latter processes are not possible without an energetic ion bombardment. On the other hand, the creation of active sites at the surface can also occur without an ion bombardment. Von Keudell *et al.*[31] proposed that in their electron cyclotron resonance (ECR) deposition process with acetylene as deposition monomer the dominant deposition radical is C_2H. If this radical chemisorbs on a dangling bond, the triple carbon-to-carbon bond may reduce into a double bond resulting in new dangling bonds. In this process the deposition of a C_2H radical does not decrease the active site density and the film growth can continue. This process of chemisorption of C_2H radicals occurs without the necessity of an energetic ion bombardment. The approach of describing the growth in terms of active sites on the growing film surface will be used in the proposed model, which is described below.

In Refs. 34 and 35 it has been demonstrated that the interaction of argon ions and electrons with acetylene in the expansion zone of an expanding thermal argon plasma, mainly results in the formation of ethynyl (C_2H) radicals and hydrogen atoms. It should be stressed here that we speculate on the dominant presence of C_2H and H as the main products produced by dissociating C_2H_2 by means of argon ions and electrons [Eqs. (2)], and that these two particles are the only particles which interact at the growing film surface. For simplicity, the contribution of other particles in the deposition process is, therefore, neglected in the following tentative deposition model.

The model for the description of the deposition of *a*-C:H from an expanding thermal plasma has to account for the following observations, which link the material properties in terms of the infrared refractive index, hydrogen content, sp^2/sp^3 ratio, the deposition rate, the substrate temperature and plasma input parameters:

(1) The deposition rate decreases with increasing substrate temperature for constant plasma settings [Figure 3(b)].
(2) The infrared refractive index increases with increasing deposition rate for a constant substrate temperature [Figure 4(a)].
(3) The infrared refractive index increases with increasing substrate temperature for a constant deposition rate [Figure 4(b)].

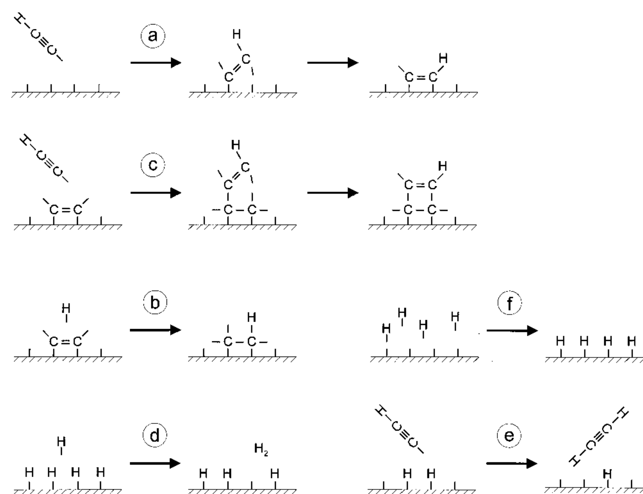

FIG. 7. Overview of the plasma-surface reactions.

(4) The hydrogen content of the material decreases with increasing growth rate at a constant substrate temperature.[16]
(5) The ratio of sp^2 bonded carbon sites and sp^3 bonded carbon sites increases with increasing deposition rate for a constant substrate temperature.[14,15]

As stated, the only particles which are assumed to participate in the deposition process are the C_2H radical and the H atom. It is assumed that only interactions on impact occur; this implies so-called ''direct incorporation.'' In Figure 7(a) schematic overview is given of the six plasma-surface reactions which are used for the modelling. Three surface quantities are considered: the fraction of active sites (dangling bonds) ϑ_{DB}, the fraction of sp^2 sites ϑ_{sp^2}, and the fraction of hydrogenated sites ϑ_{H}. The total potential density of surface sites ν_0 can be estimated from the film density and is for *a*-C:H material about 4×10^{19} m^{-2}. The change of the various surface quantities as a function of time in general can be given by

$$\nu_0 \frac{d\vartheta}{dt} = \Gamma P \vartheta, \tag{3}$$

in which ϑ is the fraction of the regarding surface quantity, Γ the incoming flux of the concerning plasma species, and P its interaction probability. In the next paragraphs the various surface reactions will be discussed.

First, there is the incorporation of C_2H radicals into the film [Figure 7(a)]. When a C_2H radical from an incident C_2H radical flux (Γ_{C_2H}) meets an active site it can chemisorb. This process has a bonding probability P_{C_2H}. The creation of the new C–C bond on the surface is an exothermic process in which about 4 eV is released. The energy is used to break the triple bond into a double bond. This process needs less than 3 eV. At the same time, one of the formed dangling bonds reconstructs with the surface, either by bonding to a neighboring dangling bond or by replacing a hydrogen atom. The net result of the C_2H incorporation in the film

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is the loss of one active site and the production of one sp^2 bond. This process is one of the growth steps as no etching of carbon atoms occurs.

Second, a sp^2 site can be transformed into a sp^3 site (so-called hydrogenation) by the interaction with an H atom [Figure 7(b)] or a C_2H radical [Figure 7(c)]. In case of hydrogen the incoming H atom breaks the double bond into two dangling bonds and chemisorbs to one of them. The hydrogen fraction in the film then increases. This process depends on the available H particle flux (Γ_H) and the hydrogenation probability $P_{H,h}$. The net result is the creation of one dangling bond and one hydrogenated site and the loss of one sp^2 bond. In case of interaction with C_2H, the C_2H radical breaks the double bond into two single bonds and is bond to one of them. The triple bond of the ethynyl is broken, too, and one of the formed active sites is bond to the surface in a similar way as the direct incorporation of ethynyl. The net result is the creation of one dangling bond, the loss of one sp^2 bond and the insertion of one C_2H particle. This process is proportional to the incoming C_2H flux and the hydrogenation probability $P_{C_2H,h}$ and implies film growth as no etching occurs. Both hydrogenation by H and C_2H lead to the formation of sp^3CH_x bonds.

Third, there is the abstraction of hydrogen from the surface. This can either occur by H atoms [Figure 7(d)] or C_2H radicals [Figure 7(e)]. In both cases one dangling bond is created. The respective abstraction probabilities are given by $P_{H,a}$ and $P_{C_2H,a}$. The processes are proportional to the regarding incoming particle fluxes.

Fourth, hydrogen passivation occurs [Figure 7(f)]. This process results in the loss of one dangling bond. It is proportional to the passivation probability $P_{H,p}$ and the incoming hydrogen flux.

Each of the processes given above results in the gain or loss of dangling bonds, sp^2 sites and hydrogenated sites. For each of these sites a balance equation can be derived from the plasma-surface interactions for the regarding fraction. In a stationary situation which is the case during film growth the fraction of each site is constant. It can be demonstrated that only the incorporation of C_2H and the hydrogenation reactions lead to the incorporation of hydrogen in the film; the passivation and abstraction reactions are in balance, which implies that the net flux of incorporated hydrogen is equal to the net removal of hydrogen by these reactions.

The growth rate of the films is proportional to the flux of incoming C_2H radicals on one side, and the direct incorporation of C_2H radicals and the hydrogenation by C_2H radicals on the other side

$$R \propto \Gamma_{C_2H}(P_{C_2H}\vartheta_{DB} + P_{C_2H,h}\vartheta_{sp^2}). \tag{4}$$

Solving the balance equations and substitution of the obtained fraction of dangling bonds and sp^2 sites in this equation for the growth rate reveal

$$R \propto \Gamma_{C_2H} \frac{2P_{C_2H,h} + yP_{H,h}}{P_{C_2H,h} + yP_{H,h}} \frac{1}{\frac{1}{P_{C_2H}} + (P_{C_2H,h} + yP_{H,h}) + y\frac{P_{H,p}}{P_{C_2H}}(P_{C_2H,a} + yP_{H,a})}. \tag{5}$$

The quantity y represents the ratio of the incoming atomic hydrogen flux and C_2H flux.

With this expression observation one can be explained: the growth rate decreases with increasing substrate temperature at constant plasma settings. The latter condition implies that the quantity y does not vary. It is proposed that the sticking probability of the C_2H radical is the temperature dependent quantity in Eq. (5), i.e., P_{C_2H} decreases with increasing substrate temperature. All other quantities are assumed to be temperature independent. A decreasing sticking probability of C_2H radicals increases the denominator of Eq. (5), which implies a decrease of the deposition rate. With the assumptions on the temperature dependence of the various quantities above also the other four observations can be explained qualitatively.

When the substrate temperature is kept constant an increment of the deposition rate only can be achieved by decreasing y. This follows from the results in Refs. 14, 34, and 35: an increase of the deposition rate is equivalent to shifting the plasma settings from underloading to critical loading, which implies that the number of enhanced dissociation reactions decreases, and thus the relative presence of hydrogen to C_2H decreases; this decrease of y is also observed from preliminary reabsorption measurements of the hydrogen production under variation of the acetylene admixture. It can be demonstrated that a decrease of y leads to an increase of ϑ_{DB} and ϑ_{sp^2} and a decrease of ϑ_H. At a constant substrate temperature the following can be concluded for the material properties with increasing deposition rate: the sp^2 content, and thus sp^2/sp^3 ratio of the film increases (observation 5), the hydrogen content decreases (observation 4). Both the increase of sp^2/sp^3 ratio and the decrease of the hydrogen content result in a higher refractive index (observation 2). The variation of the properties under variation of the deposition rate at constant substrate temperature, thus are understood.

Regarding the substrate temperature dependence at constant deposition rate, from this model the following can be stated: an increasing substrate temperature results in a decreasing deposition rate. To keep the deposition rate constant the plasma composition has to be changed: y has to decrease. The effect of decreasing y is known: the refractive index increases which explains observation 3.

In the a-C:H material also a small amount of sp^1 bonds

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is present at lower temperatures which disappears at elevated temperatures. This suggests that a second temperature dependent process is present: the transformation of sp^1 into sp^2 bonds. This process also explains an increase in material quality at elevated temperatures: polymerlike sp^1 bonds are transformed into diamondlike sp^2 bonds. A third process that may depend on the substrate temperature is the cross-linking of the C_2H radical, when it bonds to an active site or hydrogenates a sp^2 bond [cf. Figure 7(a) and 7(c)]. At higher temperatures the cross-linking increases leading to better material.

It is concluded that the tentative model depicted above allows the qualitative description of the observed dependencies between the material quality, growth rate, and substrate temperature. The assumption that the sticking probability of the C_2H radical is the only temperature dependent property seems to be sufficient for the current description. It is not claimed that the presented collection of plasma-surface reactions with their proposed temperature dependencies is complete but for the moment they satisfy. A quantitative check of the proposed model has not yet been possible due to the lack of numerical data on the various reaction probabilities.

VII. CONCLUSIONS

The effect of substrate conditions on the plasma beam deposition of *a*-C:H has been studied. Therefore, a new substrate holder has been designed. Temperature control of the substrate is obtained via an active control of the yoke temperature in combination with the injection of a small helium gas flow between the solids of concern. The substrate temperature is known at an accuracy of 2 K independent of the plasma settings.

Amorphous hydrogenated carbon films have been deposited at various plasma settings under variation of the substrate temperature. It has been found that the substrate temperature influences the deposition process but less dramatic as is known from literature. For one plasma setting the *a*-C:H refractive index increases while the deposition rate decreases with substrate temperature. Further analysis reveals that the material properties in terms of the infrared refractive index depend on two deposition parameters: the growth rate and the substrate temperature. Increment of both parameters results in *a*-C:H with a higher refractive index, and thus better material.

An *in situ* study has revealed that the growth and etching processes with an expanding thermal plasma are homogeneous at constant plasma settings: during the deposition/etching of an *a*-C:H film the deposition/etching rate is constant in time. Furthermore, it has been found that hydrogen etching of the *a*-C:H cannot explain the observed decrease in deposition rate with increasing substrate temperature. The measured rate for hydrogen etching is less than 1 nm/s compared to a decrease in deposition rate up to 20 nm/s. Other thermally activated etching processes are also rather unlikely as the activation energy for this process only needs to be about 16 meV.

Preliminary experiments have been performed with the application of an additional substrate bias during the deposition process. Although, biases up to 120 V have been applied no influence on the deposited *a*-C:H material has been found.

A first tentative model has been presented for the plasma beam deposition of *a*-C:H without the need for an additional substrate bias. The basis for this model consists of the creation and destruction of active sites, i.e., dangling bonds. The species involved are the C_2H radical and the H atom. For the temperature dependence the sticking probability of C_2H is considered to be variable. The presented model allows the qualitative explanation of the observed deposition results under substrate temperature and deposition rate variation.

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