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Hard graphitelike hydrogenated amorphous carbon grown at high rates by a remote plasma

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Hydrogenated amorphous carbon (a-C:H) deposited from an Ar-C₂H₂ expanding thermal plasma chemical vapor deposition (ETP-CVD) is reported. The downstream plasma region of an ETP is characterized by a low electron temperature (~ 0.3 eV), which leads to an ion driven chemistry and negligible physical effects, such as ion bombardment (ion energy < 2 eV) on the depositing surface. The material properties in ETP-CVD can be controlled by varying the plasma chemistry. In this article we investigate the change in a-C:H material properties by varying the Ar/C₂H₂ gas flow ratio over a wide range (1.33–150), with emphasis on low gas flow ratios (1.33–5). By changing the Ar/C₂H₂ gas flow ratio, the gas residence time in the ETP expansion can be tuned, which in turn defines the chemistry of the ETP-CVD. Soft polymerlike a-C:H to moderately hard a-C:H films have been deposited by lowering the Ar/C₂H₂ gas flow ratio. Recently, under very low Ar/C₂H₂ gas flow ratios, a hard graphitelike a-C:H material has been deposited. The striking feature of this material is the infrared absorption spectrum in the C—H_x stretching region (2800–3100 cm⁻¹), which is a distinct narrow bimodal spectrum evolving from a broad spectrum for the moderately hard a-C:H. This transition was attributed to the absence of end groups (*sp*² CH₂ and *sp*³ CH₃), which favors an enhanced cross-linking in the film in a similar effect to elevated ion bombardment or annealing. Moreover, the hard graphitelike film has an increased refractive index (*n*) as high as 2.5 at 633 nm with a corresponding mass density of ~ 2.0 g/cm³. © 2010 American Institute of Physics. [doi:10.1063/1.3273412]

I. INTRODUCTION

Hydrogenated amorphous carbon (a-C:H) films combine a number of outstanding properties such as high chemical resistance, biocompatibility, mechanical hardness, and transparency in the infrared (IR). Due to their excellent tribological properties, a-C:H films are widely used as protective coatings for hard disks and magnetic media, machine parts, optical windows and fibers, etc.¹ In the past few years, a-C:H coatings have been implemented on biomedical and biosensor products.^{2,3}

The properties of a-C:H films can be adjusted over a wide range by tuning the *sp*³, *sp*², and *sp*¹ hybridized carbon and hydrogen content ([H]) in the film, by changing the processing conditions.^{1,4,5} The mechanical properties, such as hardness and elasticity, are related to *sp*³ C—C bonded sites, while the optical and electronic material responses, such as transparency and conductivity, depend on *sp*² C=C sites. The hydrogen content determines the stress and cross-linking within the a-C:H matrix. Therefore, a-C:H materials are often presented via a “ternary phase diagram” of

*sp*³-*sp*²-[H]. Moreover, the direct measurement of *sp*³-*sp*²-[H] content is experimentally demanding and in this respect the optical parameters, such as IR refractive index (*n*_{IR}) and optical bandgap, which are linked with a-C:H material quality, can be used instead. A high refractive index film is accompanied by a decrease in the hydrogen content, an increase in mass density, and an increase in *sp*³/*sp*² ratio. On the other hand, a low optical bandgap is related to increased *sp*² hybridized π -bonding. The *sp*² hybridization due to π -bonding enhances the intralayer interactions, whereas *sp*³ C—C σ -bonds account for strong interlayer networking. Generally a high refractive index and a low optical bandgap strongly correlate with enhanced mechanical and tribological properties such as nanohardness (*H*_a).

Good quality a-C:H films in terms of nanohardness are deposited by enhancing the *sp*³ C—C bonding and decreasing the hydrogen content.¹ Conventionally, C—C σ -bonds in a-C:H are generated by bombarding the surface using energetic ions during deposition. The subimplantation model, proposed by Lifshitz *et al.*,⁶ assumes subsurface implantation of energetic species by means of three energy-loss mechanisms to the surface: atomic displacements, phonon excitations, and electron excitations. This essentially generates an increase in mass density due to an increase in *sp*³ C—C bonds. In addition, Robertson¹ explained that an optimum energy of around 100 eV per depositing carbon atom is required for producing a high density coating with enhanced

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sp^3 C—C bonds, leading to excellent mechanical and tribological properties. An alternative thermal spike model, proposed by Hofsäss *et al.*,⁷ assumes that all excess energies generated by ion impact are converted to thermal energy, which then diffuses outwards, favoring sp^3 bonding during atomic rearrangements. According to this model, the required energy for sp^3 bond formation falls in the range 50–2000 eV. McKenzie *et al.*⁸ suggested a model where the compressive stress generated during film growth is the cause of the high sp^3 bond content in the films. Here the optimum energy for sp^3 bond formation lies in the interval 15–70 eV. In another model, proposed by Koponen *et al.*,⁹ the formation of diamondlike bonding is attributed to transient high pressure created by the energetic ion impact. Relaxation to the energetically favored graphitic state is assumed to proceed through a succession of metastable states. Even the more recent molecular simulations by Marks¹⁰ show that a threshold energy of around 6 eV is required for the formation of sp^3 bonding in a-C:H films. The simulations are based on a model of surface insertion in which energetic burial leads to the simultaneous processes of sp^3 promotion, densification, stress generation, and surface growth. All the above models are based on deposition methods (e.g., filtered cathodic arc vacuum, capacitively coupled radiofrequency source, electron cyclotron wave resonance source, etc.) where the growth mechanism is controlled by physical processes, such as high energy ion bombardment. Moreover, even under high energy ion bombardment, the choice of precursor is critical. A comparative study shows C_2H_2 as a better candidate over CH_4 and C_6H_6 , which reveals that chemistry plays an important role during deposition even under such conditions.¹¹ For industrial applications, these ion or physical based deposition techniques have the downside of slow growth rates, typically up to a few nm/s.¹

Depositing a-C:H films at high growth rates without compromising the material quality has been a scientific and technological challenge, where the expanding thermal plasma chemical vapor deposition (ETP-CVD) has emerged as a promising technique.¹² In the ETP-CVD moderately hard films have been achieved at high growth rates above 10 nm/s entirely by tuning the plasma chemistry.⁴ These growth rates have been achieved for various materials, e.g., a-C:H, a-Si:H, SiO_x :C:H, etc.^{13,14}

A low electron temperature is the main difference between ETP-CVD and other remote plasmas with almost an order higher electron temperature.¹⁵ The low electron temperature also accounts for no energetic ion bombardment (ion energy < 2 eV) during ETP-CVD operation.¹⁶ In the recent years, ETP-CVD in Ar- C_2H_2 mixtures has shown the ability to grow good quality a-C:H films.^{4,17–20} Studies dedicated to reaction mechanism involved in such plasmas have been taken up by our group at several occasions.^{4,17–27} Ionization of acetylene molecules via electron impact is not possible due to the low electron temperature. Since the C—H bond strength in acetylene is 5.7 eV, thermal dissociation of acetylene is also ruled out, because heating of acetylene molecule occurs via electrons in which only about 0.3 eV is transferred. De Graaf *et al.*¹⁹ showed that physical processes such as ionization and excitation in ETP-CVD in Ar- C_2H_2

mixture are induced by argon ions created in a cascaded arc source. The argon ion-induced chemistry is triggered via charge exchange reactions between argon ions and acetylene molecules where the total ionization energy of the argon ion (15.76 eV) is transferred to the formed acetylene ion. The acetylene ion subsequently recombines dissociatively with the electrons producing C, CH, C_2 , and C_2H radicals. The radical species were experimentally measured using threshold ionization mass spectroscopy and cavity ring down spectroscopy.^{23–28} A similar primary reaction mechanism is also supported by the theoretical calculations.²⁹ The further chemistry is dependent on the argon ion to acetylene loading (Ar^+/C_2H_2 or Ar/C_2H_2 gas flow ratio at constant arc current), which has also been proved to be a key issue in achieving high deposition rates and an enhanced material quality. At low acetylene flows, where argon ions are abundant, the further reaction between Ar^+ and the primary products dominates.^{4,23–29} Moreover, the end products do not further react in the plasma phase, similarly to the primary products. Under these conditions the deposited films are reported to be soft polymerlike. In contrast, under a high acetylene loading, the reactions between the primary products and the undissociated acetylene take place, generating secondary products such as C_3 , C_3H , and, to a lesser extent, also C_5 and C_5H radicals in the plasma expansion. Since these radicals are also resonantly stabilized they are relatively nonreactive to acetylene in the gas phase; therefore they are abundantly present at a substrate level. The radicals containing three carbon atoms are proposed to contribute significantly to the growth of hard (characteristically high refractive index) a-C:H films. Moreover, Benedikt *et al.*²⁸ established that the C_3H_x ($x=0,1$) radicals have among them the highest density, and these radicals have been directly related to the enhanced refractive index (at 633 nm).

The established reaction channels indicate a considerable amount of atomic hydrogen as a by-product during the ETP-CVD operation in Ar- C_2H_2 .^{23–28} However, the role of hydrogen on material quality is still not fully understood. In the case of carbon nanotubes, for example, it is known that atomic hydrogen can be absorbed on the nanotube walls and it promotes the transformation of C=C sp^2 bonded sites into sp^3 hydrogenated sites.^{30–32} In this regard, the mechanism of hydrogen removal from the expanding plasma and from the films is one of the key issues. Under the conditions where C_3H_x ($x=0,1$) radicals strongly contribute to film deposition, the relatively low hydrogen content measured in the films also needs further understanding. To study the simultaneous role of three carbon-containing radicals and hydrogen on material quality, the C_2H_2 gas residence time in the ETP is critical. A closer evaluation of results on material properties reveals a trend of saturation for critical parameters such as optical bandgap, n_{IR} , [H], and hardness H_a , with decreasing Ar/ C_2H_2 gas flow ratio.^{4,18,25} In contrast, the deposition rate keeps on increasing with C_2H_2 dosing, because of the constant increase in the flux of C_3H_x depositing radicals. Since hydrogen concentration in the film saturates and C_3H_x constantly increases with C_2H_2 dosing, the H/ C_3H_x ($x=0,1$) decreases at a substrate level with increasing C_2H_2 loading. This suggests that the gas residence time

in the plasma expansion and hydrogen removal from the downstream plasma are the keys for achieving the right chemistry. In this respect, the influence of (externally) introduced hydrogen in the expanding plasma has been studied for the plasma and film chemistry using molecular dynamics simulations by Neyts *et al.*³³ It can be concluded that the specific plasma chemistry of an ETP-CVD in Ar-C₂H₂ mixture is dominated by the hydrocarbon radicals, and therefore, to achieve different compositions of sp^3 - sp^2 -[H], the chemistry of the plasma has to be tuned accordingly.

Gielen *et al.*⁴ showed that the a-C:H material quality in terms of IR refractive index and hardness improves with increasing growth rate, which is directly related to acetylene loading. In his study Ar/C₂H₂ gas flow ratio in the range 130–6 (mainly by keeping Ar gas flow in the arc fixed at 100 sccs) has been covered, corresponding to very soft polymerlike to moderately hard films, in a respective flow trend.^{4,17,18,20} The optical bandgap showed an inverse behavior with respect to the refractive index, which agrees with the compositional change from polymeric sp^3 CH-like film toward a network containing a considerable fraction of sp^2 bonds.⁴ The improvement in the material quality was attributed to transformed polymeric sp^3 CH to graphitic sp^2 bonds. These results on film compositions were obtained from the measured IR absorption in the C—H_x stretching region (2700–3200 cm⁻¹). It was also established that the hydrogen content decreases with an increasing IR refractive index, but the C—H_x stretching region broadens for the harder films.¹⁸ The soft polymerlike films are characterized by the presence of about 45 at. % of hydrogen, whereas the moderately hard films contain about 30 at. %. A range of materials from soft polymerlike to moderately hard a-C:H could be deposited utilizing the ETP technique. Precisely, hardness in the range 4–13 GPa, Young's modulus in the range 60–120 GPa, IR refractive index in the range 1.55–2.1, optical bandgap (E_{04}) in the range 1.4–2.2 eV, hydrogen content in the range 45–30 at. %, and mass density in the range 1.1–1.7 g/cm³ have already been achieved. In high pressure conditions even an ultrahigh deposition rate of 70 nm/s has been demonstrated.¹⁷

Recently, we have reported a hard well cross-linked graphitelike a-C:H material, which has a nanohardness of about 16 GPa, and has a unique IR absorption spectrum.³⁴ This IR spectrum shows two separated peaks corresponding predominantly to sp^3 CH and sp^2 CH stretching modes and is characterized by the absence of end groups (sp^2 CH₂ and sp^3 CH₃). Refractive index as high as ~ 2.35 at 3 μ m was measured indicating a high mass density (measured ~ 2.0 g/cm³) and a low hydrogen incorporation (measured 22 at. %). These results were obtained by tailoring the ETP-CVD chemistry in Ar-C₂H₂ mixture to conditions favorable for C₃H_x ($x=0,1$) radical production. Distinct from previous works, very low Ar/C₂H₂ gas flow ratios have been used (in the range 1.33–30, mainly by lowering the Ar flow in the arc). This further increases the C₂H₂ gas residence time in the expansion aiming to achieve increased C₃H_x ($x=0,1$) radical density at the substrate level and thus enhanced refractive index and hardness.

In this paper we extend our understanding on this re-

cently reported unique form of hard graphitelike a-C:H material deposited under reduced gas flow ratio. We report on a peculiar dispersion relation in the vacuum ultraviolet-visible and IR spectra, obtained under low gas flow ratios, i.e., results that are typically reported only for the depositions under high ion bombardment or elevated annealing temperature. Moreover, the evolution of the C—H_x stretching region is presented with the purpose of illustrating the effect of the gas flow ratio on the film composition from polymerlike to moderately hard layers and finally to the hard graphitelike material. Other material properties, such as the nanohardness, optical bandgap, and mass density, are also presented as a function of the refractive index.

In Sec. II, the experimental setup and the techniques used for film characterization are presented. This is followed by results in Sec. III, which are then discussed and conclusions are drawn in Sec. IV.

II. EXPERIMENTAL

The ETP-CVD technique belongs to the class of remote plasmas, where thermal plasma is generated in a cascaded arc (typical arc current $I_{arc}=50$ –90 A and voltages in the range 40–60 V) at subatmospheric pressure in argon with typical values for electron temperature $T_e \approx 1$ eV and electron density $n_e \approx 10^{22}$ m⁻³. The argon gas, with a degree of ionization of typically 10%, flows through a 4 mm diameter and 24 mm long arc channel and expands into a low pressure (remote) chamber with typical pressure of tens of Pa, $T_e \approx 0.3$ eV and $n_e \sim 10^{17}$ – 10^{19} m⁻³.^{15,21,22} Due to the large pressure difference, the argon plasma expands supersonically at the source exit and after a stationary shock the expansion continues subsonically in the reaction vessel, where acetylene is introduced downstream by means of an injection ring (Fig. 1). The experimental setup is described in detail elsewhere.^{12,18} Due to low electron temperature the substrate self-bias is low, meaning low energy ion bombardment at the substrate level, as demonstrated by the measured ion energy distribution (IED) in Fig. 2. The IED is measured by means of a retarding field energy analyzer (RFEA), which clearly shows abundant low energy ions distributed around 2 eV. The used RFEA is described by Gahan *et al.*³⁵

The plasma chemistry defining the film properties is mostly controlled within the ETP downstream plasma region. The gas residence time in the expanding plasma is controlled by varying the Ar/C₂H₂ gas flow ratio at a fixed arc current and chamber pressure. However, processes such as recirculation, recombination, and diffusion dominant in the background are also found to influence the film chemistry. Hence, the quality of the films will be presented with respect to Ar/C₂H₂ gas flow ratio. The Ar and C₂H₂ gas flow was varied in the ranges 20–100 and 0.7–15 sccs, respectively. All the depositions were performed on silicon substrates (orientation $\langle 100 \rangle$, with an ~ 2 nm native oxide on top) at constant substrate temperature of 250 °C. The reason for choosing the substrate temperature and reactor gas pressure will also be discussed later (cf. Sec. III).

Characterization of the film properties is performed via several *ex situ* diagnostics. The refractive index and extinc-

FIG. 1. (Color online) Schematic of an ETP-CVD reactor.

tion coefficient reported here are obtained from spectroscopic ellipsometry (SE).³⁶ The measurements were carried out using a rotating compensator SE (J. A. Woollam M-2000U), with photon energy in the spectral range 1.25–5 eV, at an angle of incidence of 75°. The ellipsometry spectra are interpreted in WVASE software (Woollam Co.) by regression analysis using a multilayer optical model that assumes an ambient/roughness/a-C:H film/native SiO₂/c-Si substrate structure. The effect of substrate temperature is taken into account while modeling the native oxide/c-Si structure. The surface roughness is modeled using the Bruggeman effective medium approximation. The a-C:H film optical constants are determined by Tauc–Lorentz (TL) model derived by Jellison and Modine,³⁷ which proposes an expression for the imaginary part ε_2 of the complex dielectric function given by

FIG. 2. (Color online) IED demonstrating low ion energy. These measurements are made at the substrate level for a pure argon discharge at a chamber pressure of 20 Pa.

TABLE I. Bonding types and their corresponding wavenumbers in the IR stretching region (partially taken from Ref. 40).

Bonding type	Stretching vibration wavenumber (cm ⁻¹)
sp^3 CH ₂ symmetric	2850–2855
sp^3 CH ₃ symmetric	2875
sp^3 CH	2900 ± 15
sp^3 CH ₂ asymmetric	2920
sp^2 CH ₂ olefinic, symmetric	2955–2960
sp^3 CH ₃ asymmetric	2970–2975
sp^2 CH olefinic	3000–3040
sp^2 CH ₂ olefinic asymmetric	3030–3085
sp^2 CH aromatic	3000–3100

$$\varepsilon_2 = \frac{AE_0C(E - E_g)^2}{(E^2 - E_0^2)^2 + C^2E^2E} \frac{1}{E} \quad (1)$$

if $E > E_g$ and $\varepsilon_2 = 0$ if $E < E_g$. In this expression, E_0 is the peak transition energy, C is the broadening term, and A is related to the transition probability of the TL oscillator. The real part ε_1 of the dielectric function is calculated by the Kramers–Kronig dispersion relation. It was shown that TL model parametrization provides the most reliable results for a-C:H films.³⁸ The SE measurements provide information about thickness (growth rate), refractive index, extinction coefficient, and roughness of the studied a-C:H films. From the extinction coefficient k the E_{04} optical bandgap can be determined, defined as the photon energy at which the absorption coefficient $\alpha (=4\pi k/\lambda)$ is equal to 10^4 cm⁻¹, where λ is the wavelength.

The IR absorption is measured using Fourier transformed infrared (FTIR) spectroscopy. A Bruker Tensor 27 provided the transmission spectra of the films in the range 370–7000 cm⁻¹, with a resolution of 4 cm⁻¹. The spectra normalized to the background show clear interference patterns, which are caused by multiple reflections in the film. Absorptions by C—H_x stretching vibration modes are clearly visible in the 2700–3200 cm⁻¹ wavenumber region. The interference pattern has been fitted to obtain the IR refractive index and thickness using the analytical expression given by Gielen *et al.*¹⁸ and Swanepoel³⁹ method for some selected films deposited under low Ar/C₂H₂ gas flow ratios. The main aim of using the IR absorption technique in this work is to have better insight in the C—H_x stretching absorption bands. For this purpose the background subtracted spectrum of absorption peaks is fitted. In this procedure the absorption peaks are fitted for different possible C—H_x modes, where each contribution is represented by a Gaussian function.

All the C—H_x vibration frequencies in the wavenumber region 2800–3200 cm⁻¹ are listed in Table I, according to Ristein *et al.*⁴⁰ A commonly encountered problem while assigning sp^3 CH modes is its overlap with sp^3 CH₂ asymmetric mode at 2920 cm⁻¹. Distinguishing between the two modes was quite essential for this work. Based on the literature data available on polymers, the ratio of the asymmetric/symmetric sp^3 CH₂ mode is ~1.63, which was used here to

resolve the band attributions for the hard films.^{40,41} However, a clear distinction among sp^2 CH aromatic and olefinic was not possible for some films.

The deconvoluted IR spectra are also used for the estimation of hydrogen content. Although the procedure is ambiguous and could lead to large errors, the results are confirmed by comparing with elastic recoil detection analysis (ERDA) measurements. Note that the integrated intensities of IR stretching absorption bands are proportional to the number of bonds under consideration.^{5,42,43} The relation used to calculate an estimate of the hydrogen concentration $[H]$ is

$$[H] = A_s(\text{CH}_x) \int \frac{\alpha(k)}{k} dk, \quad (2)$$

where $\alpha(k)$ is the absorption coefficient at wavenumber k and $A_s(\text{CH}_x)$ is the absorption cross section (also called proportionality constant). $A_s(\text{CH}_x)$ is inversely proportional to the oscillator strength. The choice of the right cross section does not have a widely accepted consensus. Estimation of the absolute hydrogen density from the IR spectroscopy strongly depends on the chosen proportionality constant. Two main schools of thought can be found in literature: first where the same proportionality constant was used for all sp^y CH_x (x and $y=1,2,3$),^{5,43} and second where different values have been recommended for every bonding type.⁴⁴ The second argument has a strong physical basis; i.e., for hydrocarbon gases, the absorption cross sections per bond for the CH_x bonds show different values for each band group. Several C—H bonds exhibit symmetric and asymmetric vibrations simultaneously. Only one vibration is used for each bond: asymmetric one for the sp^3 and symmetric one for sp^2 bands.²⁰

The hardness measurements have been performed using a nanoindenter (MTS-XP) where indentations were made using a Berkovich indenter. The load-displacement curves are recorded under load controlled mode, where loads were chosen such that the maximum indentation depth was restricted only up to 10% of the film thickness. The load-displacement response typically shows an elastic-plastic loading followed by an elastic unloading resulting into a hysteresis. Based on Oliver and Pharr⁴⁵ method, the unloading data are used to determine the hardness of the films. Following Gielen *et al.*,⁴ the hardness was normalized to that of Si(100) hardness, i.e., 11.5 GPa.⁴⁶ For the bluntness of the indenter tip no corrections were made.

III. RESULTS

As mentioned earlier, all depositions were performed at a fixed temperature of 250 °C (active substrate temperature control)¹⁷ and at a gas pressure of 35 Pa. In Ref. 17, it is established that a substrate temperature as high as 250 °C is optimum for a-C:H growth to provide films with enhanced tribological properties deposited in an ETP-CVD. Figure 3(a) demonstrates the same trend for the conditions under reduced $\text{Ar}/\text{C}_2\text{H}_2$ gas flow ratio showing enhanced refractive index (2.5 at 633 nm) at 250 °C. The choice of gas pressure is also obvious from Fig. 3(b), where under similar gas flow conditions the refractive index is highest at 35 Pa. Moreover,

FIG. 3. (Color online) Refractive index and deposition rate for different (a) substrate temperatures and (b) chamber pressures at a fixed $\text{Ar}/\text{C}_2\text{H}_2$ flow ratio.

the deposition rate increased with increasing pressure and decreasing temperature. Note that under the chosen conditions (substrate temperature of 250 °C and pressure of 35 Pa) the deposition rate is relatively high, i.e., ~20 nm/s.

The evolution of the optical parameters and deposition rate with changing gas flows is summarized in Fig. 4. The results of varying argon gas flow for a fixed C_2H_2 gas flow are presented in Fig. 4(a), as a function of $\text{Ar}/\text{C}_2\text{H}_2$ flow ratio. The refractive index is highest for a $\text{Ar}/\text{C}_2\text{H}_2$ flow

FIG. 4. (Color online) General trend of optical parameters and deposition rate as a function of varying (a) Ar gas flow in the arc and (b) C_2H_2 flow in the deposition chamber.

FIG. 5. (Color online) The E_{04} optical bandgap as a function of film refractive index (at 633.3 nm).

ratio of 2 (i.e., $n=2.5$). A similar trend has been obtained for the extinction coefficient as well. The trend of refractive index suggests that the deposited films have high mass density under low argon flows. On the other hand, the deposition rate and E_{04} optical bandgap decreased at low argon gas flows (due to transformed polymeric sp^3 CH to more graphitic sp^2 bonds) suggesting an increase in sp^2 hybridized carbon fraction in the films. As established for ETP-CVD, high refractive index and low optical bandgap indicate enhanced tribological properties. This indicates an enhanced material quality at an Ar/ C_2H_2 flow ratio of 2.

For further insight a series with changing C_2H_2 gas flow is also performed, keeping the argon gas flow fixed at a low value. The results for optical parameters along with deposition rates are summarized in Fig. 4(b). The refractive index saturates at a value of ~ 2.5 up to an Ar/ C_2H_2 gas flow ratio of 6, after which a slow decrease is observed. A similar trend has been observed for the extinction coefficient as well. These results point out an increase in mass density under high C_2H_2 flows (low Ar/ C_2H_2 gas flow ratios). The optical bandgap under these conditions decreased with the increase in C_2H_2 flow (decrease in Ar/ C_2H_2 gas flow ratio) suggesting increased fraction of sp^2 hybridized carbon in the films. The deposition rate was also constantly increasing with the increasing C_2H_2 gas flow (decreasing Ar/ C_2H_2 gas flow ratio). Note that the hard graphitelike a-C:H is deposited under an Ar/ C_2H_2 gas flow ratio of 2.

In line with the previous reports on ETP produced a-C:H materials, the established trend of a decrease in the E_{04} optical bandgap with increasing refractive index is proved to be true under these conditions as well. The results are summarized in Fig. 5, where an optical bandgap as low as 0.98 ± 0.02 eV has been calculated for the material deposited under low Ar/ C_2H_2 gas flow ratio. The association of low bandgaps to enhanced nanohardness is demonstrated with the help of Fig. 6, which shows that a high hardness was measured for the films grown under reduced Ar/ C_2H_2 gas flow ratios. Based on previous findings a refractive index around 2.5 (at 633 nm) and optical bandgap around 1 eV clearly reflect that the chemistry generated in the ETP-CVD is favorable for C_3H_x ($x=1,2$) production. This point will be discussed later.

The refractive index is known to relate directly to material density.¹ Figure 7 shows the dependence of mass density

FIG. 6. (Color online) a-C:H hardness as a function of refractive index. Inset (left): a broad CH stretching mode for soft polymerlike a-C:H. Inset (right): unique sharp individual peaks pointing out the unique feature for graphitelike a-C:H.

[measured by Rutherford backscattering spectroscopy (RBS)] as a function of the IR refractive index (at 3 μm) for the different types of carbon materials deposited by ETP-CVD. As expected, the dependence is almost linear and can be used to estimate the material density from the IR refractive index. Moreover, the measured nanohardness is also demonstrated in terms of IR refractive index (see Fig. 6). High nanohardness was measured for the films with high IR refractive index. The maximum IR refractive index of 2.37 (corresponding to $n \sim 2.5$ at 633 nm) is measured for the films with nanohardness of 16 GPa. We have recently categorized these films as a novel form of carbon thin film material.³⁴ These films are also characterized by a very low optical bandgap of ~ 1 eV, as compared to the bandgap of the soft films of ~ 2.5 eV ($n_{\text{IR}}=1.55$ and nanohardness ~ 4 GPa). Another obvious difference between the two films is observed in terms of C—H_x stretching vibrations (2700–3200 cm^{-1}) using FTIR. A broad IR spectrum, typical for a-C:H films, was measured for the soft films, while a completely different one, with two sharp narrow bands, for the hard films. This feature and its evolution will be discussed later in detail.

The evolution of IR transmission spectrum in the stretching region with changing deposition conditions is depicted in Fig. 8(a). At low Ar/ C_2H_2 gas flow ratio (also corresponds to high n) distinct from high Ar/ C_2H_2 ratio, an enhanced absorption is obvious from IR spectrum, as the fringes disap-

FIG. 7. (Color online) Mass density as a function of IR refractive index for soft polymerlike, moderate hard, and hard graphitelike a-C:H films.

FIG. 8. (Color online) (a) FTIR spectrum characterizing three distinct (soft polymerlike, moderately hard, and graphitelike a-C:H) ETP-CVD films grown under three different gas flow ratios. (b) Refractive index and extinction coefficient as a function of wavelength for three distinct films (soft polymerlike, moderately hard, and graphitelike a-C:H) grown under three different gas flow ratios.

pear in the region of strong absorptions. The extrapolation of the curve for the film deposited at $\text{Ar}/\text{C}_2\text{H}_2=2$ (the hard graphitelike material) toward high wavenumber crosses the abscissa at 7805 cm^{-1} corresponding to 0.97 eV , which is close to the measured E_{04} bandgap (0.98 eV) from SE. This reduced bandgap observed in this photon energy region for the hard graphitelike material is unique. Moreover, at high $\text{Ar}/\text{C}_2\text{H}_2$ gas flow ratios corresponding to low to moderately high refractive index, the films are characterized by the well known spectrum for a-C:H films, as expected.

Another peculiar feature for the hard graphitelike material is the optical dispersion relation presented in terms of n - k versus photon energy [see Fig. 8(b)]. A steep nature for the solid curves especially in the range 1.25 – 2.5 eV for the extinction coefficients and 2.5 – 5 eV for the refractive indices was obtained under these conditions only. Note that E_{04} bandgap is calculated using these extinction coefficient values and the steep nature for extinction coefficient accounts for the low optical bandgap. These exceptionally low optical bandgaps along with unique optical dispersion relation have been reported earlier and are associated with graphitic phases in the film.⁴⁷ Distinct from our conditions, in this study the films are grown under elevated ion bombardment as well as high substrate temperatures, conditions favorable for grow-

FIG. 9. (Color online) C—H_x stretching vibration IR spectrum as a function of decreasing $\text{Ar}/\text{C}_2\text{H}_2$ flow ratio.

ing sp^2 graphitic clusters. The results are substantiated on the basis of the theoretical explanation of Robertson,¹ who also suggested that the strong graphitization and low optical bandgap in the film relate to an increased sp^2 graphitic phase. However, as mentioned earlier, any physical phenomenon of such kind is discarded under our deposition conditions and the enhanced sp^2 graphitic phase in our films was obtained via a purely chemical route only.

To study the stoichiometry of the films, the C—H_x stretching region has been exploited. In Fig. 9, the evolution of IR absorption spectra in the C—H_x stretching region (2700 – 3200 cm^{-1}) as obtained using FTIR spectroscopy is shown for films that were deposited under tailored $\text{Ar}/\text{C}_2\text{H}_2$ flow conditions. The spectra evolve from a broad and merged single absorption band for soft polymerlike a-C:H to a distinct narrow double absorption band for the hard graphitelike a-C:H. In this regard, Gielen *et al.*¹⁸ related the broadening to increased hardness and refractive index, and a similar effect is revealed in Fig. 9. Interestingly, the absorption features under the low $\text{Ar}/\text{C}_2\text{H}_2$ flow ratio (of 2), probably related to dispersed H in the film, are similar to the IR absorption spectra reported by Weiler *et al.*⁴⁸ for ultrahard ta-C:H and by Dischler *et al.*⁴³ for soft polymerlike a-C:H. These results were obtained under high energy ion bombardment and due to annealing, respectively. Since the resembling spectra in Refs. 43 and 48 show sharp peaks at different wavenumbers, induced by physical effects, only a qualitative comparison can be made with our ETP-CVD material. We performed depositions under even reduced $\text{Ar}/\text{C}_2\text{H}_2$ flow conditions but material proved to possess inferior properties in terms of surface roughness, hardness, and no C—H_x absorption could be resolved (probably due to a very low H concentration in the film). This suggests that under these conditions the presence of atomic hydrogen at the substrate level is greatly reduced, probably due to its diffusion in the background gas and further recombination at the reactor wall.^{49,50}

The deconvolution of the IR absorption spectra, which were normalized on the film thickness, gives more insight into the presence of different C—H_x stretching modes in terms of hybridization and bond configuration, as shown in Fig. 10. The plausible C—H_x stretching modes are given in Table I. The results of deconvolution for the soft polymerlike film [$\text{Ar}/\text{C}_2\text{H}_2$ flow ratio of 42, $n_{\text{IR}} \sim 1.75$, and $H_a \sim 4\text{ GPa}$;

FIG. 10. (Color online) Deconvolution of FTIR spectra in the C—H_x stretching region (a) for soft polymerlike ETP-CVD film under relatively high gas flow ratio (Ar/C₂H₂:42.5), (b) for moderately hard ETP-CVD films (Ar/C₂H₂:6.7), and (c) for the hard graphitelike a-C:H (Ar/C₂H₂:2).

see Fig. 10(a)] and moderately hard film [Ar/C₂H₂ flow ratio of 6.7, $n_{\text{IR}} \sim 2.1$, and $H_a \sim 13$ GPa; see Fig. 10(b)] indicate a range of C—H_x stretching modes with significant contributions from end groups (such as CH₃ and CH₂ along with CH, as assigned in Fig. 10). In contrast, the hardest film [see Fig. 10(c)] showed a clear reduction in absorption of the CH_x end groups (namely sp^2 CH₂ and sp^3 CH₃), a major contribution of sp^3 CH and sp^3 CH₂ around 2900 cm⁻¹, and a sp^2 CH mode in the 3000–3040 cm⁻¹ region. As stated in Table I, aromatic and olefinic sp^2 CH lie in the same band region; thus a clear distinction among these two contributions is difficult. The sp^2 CH mode in the 3000–3040 cm⁻¹ was tentatively assigned to an aromatic unit in our previous work.³⁴ However, it could be argued that, due to the improved cross-linking of the hard graphitelike carbon material, it is more likely that this mode is olefinic.

The evolution of end-group concentrations extracted using IR spectra with increasing Ar/C₂H₂ gas flow ratio is shown in Fig. 11(a). Relative increase in the end groups such as sp^3 CH₃ and sp^2 CH₂ is obvious, indicating an increase in hydrogen concentration. The deconvoluted spectra are also used to obtain the hydrogen content of the films. A detailed discussion on hydrogen concentration calculation for ETP-CVD produced a-C:H was undertaken by Gielen *et al.*¹⁸ previously. In that work the plausibility of different methods, which could be implemented, and their comparison are also discussed. In the present work a wide range, in terms of film as well as plasma chemistry, is covered. Assuming one proportionality constant $A_s(\text{CH}_x)$ value [cf. Eq. (2)] for the whole range of carbon materials results in ambiguous trends. However, in the case of hydrogenated amorphous silicon (a-Si:H), the implementation of one proportionality constant for a range of different a-Si:H materials was demonstrated.⁵¹ In this work, for comparison purposes, both methods mentioned earlier have been used. The first, based on Jacob⁵/Dischler *et al.*,⁴³ using only a single value of proportionality constant for every C—H_x stretching band. The second based on Tanaka

FIG. 11. (Color online) (a) Evolution of bond contributions absent in the graphitelike a-C:H films as a function of Ar/C₂H₂ gas flow ratio. (b) The hydrogen concentration as a function of Ar/C₂H₂ gas flow ratio.

et al.,⁴⁴ where different proportionality constants have been used for different bond types. For the first method we used $A_s(\text{CH}_x) = 1 \times 10^{21}$ at./cm² (cf. Ref. 32), whereas for the second method we used values from Ref. 44, $A_s(\text{CH}_3) = 3.65 \times 10^{20}$ at./cm², $A_s(\text{CH}_2) = 3.85 \times 10^{20}$ at./cm², and $A_s(\text{CH}) = 3.85 \times 10^{21}$ at./cm². As shown in Fig. 11(b), the estimated bonded hydrogen content from the IR fits indicates a clear trend of reduction with decreasing Ar/C₂H₂ gas flow ratio, which is unexpectedly low for the hard graphitelike a-C:H material. Moreover, the values obtained using a fixed $A_s(\text{CH}_x)$ were relatively higher than the one based on different proportionality constants, which is in line to what was previously reported.¹⁸

The result of a high refractive index and low hydrogen concentration under low Ar/C₂H₂ flow ratio from IR measurements agrees well with mass density and hydrogen content measurements performed using RBS and ERDA, respectively. These measurements revealed a relatively high density (2.0 g/cm³) and a remarkable low hydrogen content of about 22% for the hard graphitelike a-C:H material. The uniqueness of this material is clearly illustrated by placing it in the ternary phase diagram of sp^2 - sp^3 -[H] for carbon films¹ (see Fig. 12). Note that the material is grown under the absence of ion bombardment via a purely chemical route.

IV. DISCUSSION AND CONCLUSIONS

It is interesting to summarize all the results obtained with respect to the effects generated by lowering the Ar/C₂H₂ gas flow ratio. Categorically, the evolutions observed in terms of n - k optical dispersion relation indicate material properties changing from soft polymerlike films to hard graphitelike a-C:H. The evolution of IR spectra also displays films with large hydrogen content (polymeric) to high absorbing, low hydrogen content (graphitelike). From these results we could also conclude a clear hydrogen re-

FIG. 12. (Color online) The ETP a-C:H hard graphitelike films positioning in ternary phase diagram of sp^2 - sp^3 -[H] (adapted after Ref. 1).

removal from the films evolving from hydrogen content around 50% to the one with around 22%. In literature the phenomena of hydrogen removal and graphitization are always associated with energetic ion bombardment or high substrate temperature.^{52,53} These effects often result into enhanced tribological properties. As demonstrated previously, in ETP-CVD the ion energy is very low (<2 eV) and the substrate temperature was also relatively low (250 °C); therefore such physical processes are discarded for our films. In our case such mechanisms are purely induced by the specific plasma chemistry of ETP-CVD in Ar- C_2H_2 mixtures, especially by reducing Ar/ C_2H_2 gas flow ratio. This transforms the film chemistry from polymeric sp^3 CH hybridized to sp^2 graphitic clusters and, at the same time, induces hydrogen removal from the film. These corroborated effects determine the increase in refractive index and decrease in optical bandgap.

With high hydrogen concentration, high end-group concentration, and high bandgap the carbon chains are terminated and the interconnection via sp^2 bonding is low. Such films are polymerlike. They are created under an ETP-CVD Ar- C_2H_2 chemistry strongly influenced by primary species such as C, C_2 , C_2H , and CH. Atomic hydrogen is the main by-product under these conditions, abundant at the substrate level and consequently is highly incorporated in these films, which are rich in CH_3 and CH_2 bonding. By lowering Ar/ C_2H_2 gas flow ratio, a different plasma chemistry develops in the downstream plasma, which is dominated by C_3H_x radicals.²⁸ Moreover, it might be that under these conditions the atomic hydrogen diffuses in the background gas and recombines at the reactor wall.^{49,50} Consequently, the low atomic hydrogen concentration in the downstream plasma at substrate level leads to lower hydrogen concentration in the films.

Finally, under Ar/ C_2H_2 gas flow ratio of 2, the IR stretching region shows the disappearance of end groups. The trend of reduced end-group concentration along with the very low hydrogen content indicates enhanced C—C interconnecting bonds, and the fact that the C—H bonds in the film changed from CH_3 and CH_2 to CH. This is confirmed by the measured high mass density and high nanohardness. In addition, the raised concentration of sp^2 hybridized carbon promotes better cross-linking between the carbon chains.

By looking at the continuous decrease in hydrogen content and good cross-linked hard films, we suggest that the gas residence time in the ETP expansion has increased by reducing the Ar/ C_2H_2 gas flow ratio. Under these conditions due to high acetylene loading films are created by C_3H_x ($x=0,1$) radicals and, simultaneously, there is enough time for hydrogen to escape from the expanding plasma. This induces a distinct plasma chemistry, which needs further investigations. Particularly, distinction between the high and low flow conditions on issues such as C_2H_2 depletion, hydrogen removal, background chemistry, and polymerization will be investigated.

In conclusion, a range of films from soft polymerlike to hard graphitelike a-C:H films were deposited using the ETP-CVD technique in an Ar- C_2H_2 mixture. Hardness of about 16 GPa has been measured for the graphitelike films grown at deposition rates exceeding 15 nm/s. These films show significantly reduced amount of end groups, which indicates hydrogen removal and better cross-linking (similar to fullerenelike carbon material) achieved purely via a chemical route. This unique material opens up opportunities for applications where annealing and high energy ion bombardment could damage sensitive substrates (e.g., plastics), where high deposition rates are critical but also where no biasing of the substrate can be provided.

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