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Hard graphitelike hydrogenated amorphous carbon with distinct infrared absorption spectra in the $C-H_x$ stretching region is reported. These spectra are characterized by two separated peaks corresponding predominantly to sp^3 CH and sp^2 CH stretching modes and reveal a distinct absence of endgroups (sp^2 CH_2 and sp^3 CH_3). The relatively dense films ($\sim$2.1 g/cm^3) have low hydrogen content ($\sim$20%), high refractive index ($\sim$2.4 at 3 μm), nanohardness exceeding 16 GPa, and a characteristic optical dispersion relation. These films are deposited at growth rates >15 nm/s, in the absence of high-energy ion bombardment, indicating the importance of the specific Ar$-C_2H_2$ chemistry of the remote plasma used. © 2008 American Institute of Physics.
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The properties of diamondlike hydrogenated amorphous carbon (a-C:H) films can be adjusted over a wide range by manipulating the sp^3, sp^2, and sp^1 hybridized carbon and hydrogen content [H] in the film through variation of processing conditions.[1] In general, the optical properties such as refractive index (n) and optical bandgap are linked with the a-C:H quality and indicate better cross-linking, higher density, and higher sp^3 C–C content with increasing refractive index. The latter property strongly correlates with enhanced mechanical properties such as the nanohardness (H_a).[1,2] Conventionally, good quality films in terms of nanohardness are deposited using sources with high-energy carbon and hydrocarbon ions ($\sim$100 eV/C) bombarding the substrate, in line with explanations based on the so-called subplantation model of Robertson *et al.*[1] Nevertheless, a high growth rate without compromising the film quality has been a scientific and technological challenge where expanding thermal plasma-chemical vapor deposition (ETP-CVD) technique has emerged as a promising method.[3,4] This technique belongs to the class of remote plasma processing and exhibits a high growth rate >10 nm/s, contrastingly large compared to other ion bombardment based techniques with a maximum growth rate of typically a few nm/s. In recent years, ETP-CVD in Ar$-C_2H_2$ mixtures has shown the ability to grow good quality films, with a moderate hardness of up to 13 GPa, in the absence of energetic ions bombarding the growing film surface.[2,4]

Here, we report on a hard graphitelike a-C:H which possesses a characteristic infrared (IR) absorption spectrum in the $C-H_x$ stretching region and a distinct optical dispersion relation in the photon energy region of 1.24–5 eV. A relatively high a-C:H film density ($\sim$2.1 g/cm^3), a low hydrogen content ($\sim$20%), a high IR refractive index ($n_{IR} \sim$2.4 at 3 μm), and a nanohardness exceeding 16 GPa suggest that the material is a distinct form of well cross-linked graphitelike a-C:H.

Films are deposited utilizing the ETP-CVD technique at a low chamber pressure of 35 Pa. The plasma is generated in a thermal plasma source at (arc current in the range of 50–90 A and voltages in the range of 40–60 V) subatmospheric pressure in argon. The argon plasma (around 10% ionization degree) flows through a 4 mm diameter and 24 mm long arc channel and expands through a nozzle into a low pressure (remote) chamber where acetylene is introduced downstream by means of an injection ring. Distinct from previous work, relatively low Ar/C_2H_2 gas flow ratios were used in this study.[2,4–6] The downstream plasma is characterized by a low electron temperature ($\sim$0.3 eV) due to the expansion, which leads to an ion-driven chemistry and a low substrate bias.[2–6] All films were deposited at a fixed temperature of 250 °C by active substrate temperature control.

Detailed studies clarifying the argon ion induced plasma chemistry have been taken up by our group at several occasions.[4–7] In particular, Benedikt *et al.* using threshold ionization mass spectrometry and cavity ring down spectroscopy has shown that resonantly stabilized C_3H_x ($x=0,1$), radicals are the most abundant radicals at the substrate level.[5] In this study, it was impossible to differentiate between the linear and cyclic forms of these radicals. Independent molecular dynamics calculations revealed that these radicals have sticking probabilities which, together with the determined fluxes, strongly suggest that they contribute significantly to the growth of moderately hard a-C:H films.[7] Moreover, these studies revealed that the tricarbon radical concentration scales with the refractive index at 633 nm, which indirectly correlates with the film density.[5] For the work presented here, which has lead to the graphitelike a-C:H, we have tailored the ETP-CVD chemistry to conditions which favor C_3H_x ($x=0,1$), production as well as suppress the atomic hydrogen flux at the film surface. An Ar/C_2H_2 gas flow ratio of approximately 2 at an arc current of 75 A and an arc voltage of 50 V revealed the best film properties.

In Fig. 1, the evolution of IR absorption spectra in the $C-H_x$ stretching region (2800–3100 cm^{-1}) as obtained using Fourier transformed IR (FTIR) spectroscopy is shown for
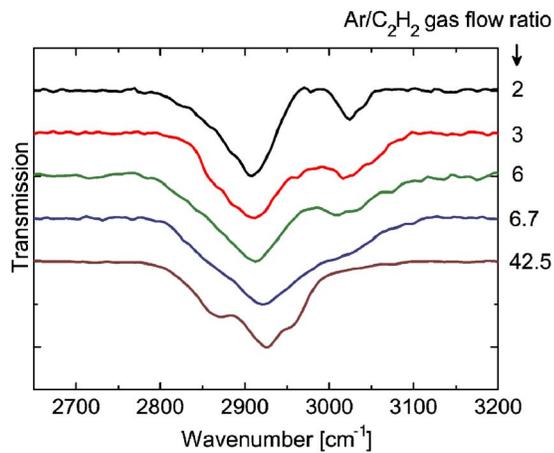

FIG. 1. (Color online) $C-H_x$ stretching vibration IR spectrum as a function of decreasing Ar/C_2H_2 flow ratio. Unique sharp features appear for the lowest flow ratio.

FIG. 3. (Color online) The ETP-CVD graphitelike a-C:H material placed in a ternary phase diagram of sp^2-sp^3-[H] for carbon (see Ref. 1). DLCH, PLCH, and GLCH stands for diamond-, polymer- and graphitelike hydrogenated carbon, respectively.

films that were deposited under tailored Ar/C_2H_2 flow conditions.[2,4] The spectra evolve from a broad spectrum for moderately hard a-C:H to a distinct narrow bimodal spectrum for the graphitelike a-C:H.[2,4,8] Interestingly, the absorption features under low Ar/C_2H_2 flow ratio are qualitatively similar to the IR absorption spectra reported by Weiler *et al.* for ultrahard tetrahedral hydrogenated carbon (ta-C:H) and to Dischler *et al.* for soft polymerlike a-C:H, these results were obtained under high-energy ion bombardment and due to annealing, respectively.[9,10] The similarity might be due to the relatively low hydrogen content in all three cases.

The measured nanohardness as obtained from the nanoindentation measurements is shown as function of the IR refractive index in Fig. 2.[2,11] As depicted in Fig. 2, higher refractive index, i.e., higher material density leads to higher nanohardness, in line with previous results.[1,2,4] These results agree with mass density and hydrogen content measurements using Rutherford backscattering spectroscopy and elastic recoil detection analysis, respectively, and which revealed a relatively high density of 2.1 g/cm^3 and a remarkable low hydrogen content of about 20%. Positioning this material in the "ternary phase diagram" of sp^2-sp^3-[H] for carbon films

clearly illustrates the peculiarity of the material (Fig. 3).[1]

The deconvolution of the IR absorption spectra gives more insight into the presence of different $C-H_x$ stretching modes in terms of hybridization and bond configuration. Results of deconvolution for the moderately hard film (Ar/C_2H_2 flow ratio of 6.7, $n_{IR} \sim 2.2$, $H_a \sim 13$ GPa) indicate a range of $C-H_x$ stretching modes with significant contributions from endgroups [such as CH_3 and CH_2 along with CH; as assigned in Fig. 4(a)].[2,6] In contrast, the hardest film showed a clear reduction in absorption of the CH_x endgroups (namely, sp^2 CH_2 and sp^3 CH_3), a major contribution of sp^3 CH and sp^3 CH_2 around 2900 cm^{-1} [cf. Fig. 4(b)] and a sp^2 CH mode in the 3000–3040 cm^{-1} region, which we tentatively assign to an aromatic unit.[8]
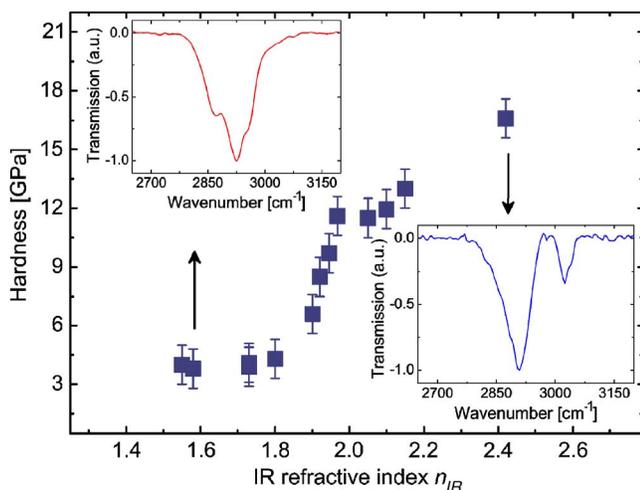

FIG. 2. (Color online) a-C:H hardness as a function of refractive index. Inset (left): a broad CH stretching mode with merged individual contributions. Inset (right): unique sharp individual peaks pointing out the distinctive feature of the deposited layer.
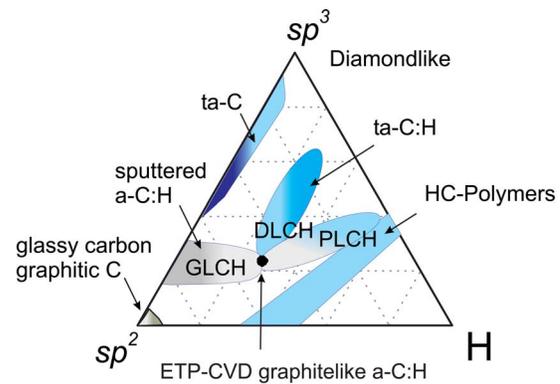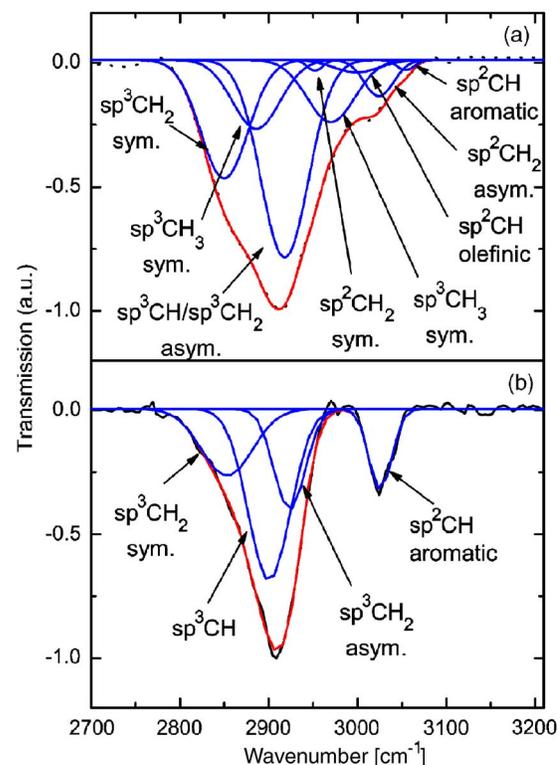

FIG. 4. (Color online) Deconvolution of FTIR spectra in the $C-H_x$ stretching region (a) for ETP-CVD film under relatively high gas flow ratio (Ar/C_2H_2:6.7) (b) for the graphitelike a-C:H material (Ar/C_2H_2:2).
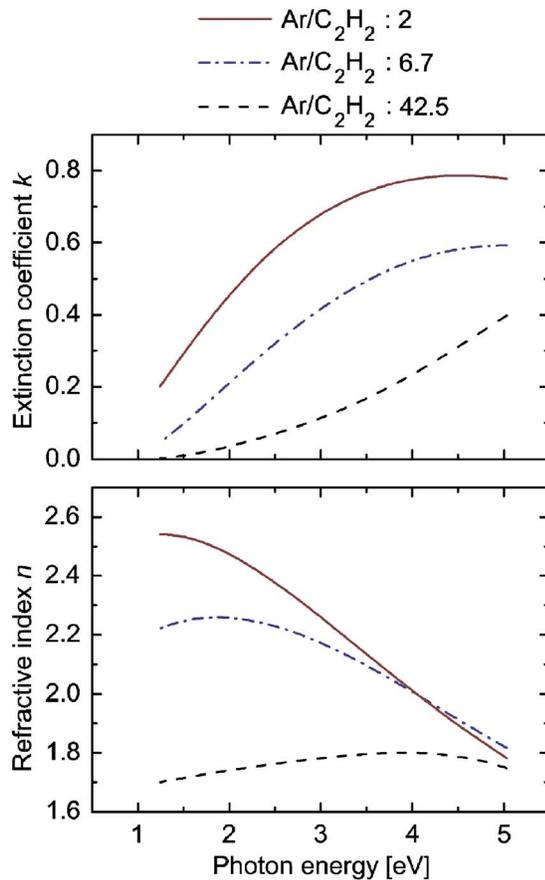
FIG. 5. (Color online) Optical dispersion relation obtained for three different gas flow ratios. The solid curve refers to the graphitelike a-C:H material. The dashed dispersion relation curve is typical for very soft polymerlike films ($n_{IR} < 1.5$) and the dash-dot curve is typical for moderately hard ($n_{IR} \sim 2.2$) films.

Another peculiar feature of the films deposited under low Ar/C$_2$H$_2$ flow conditions is the optical dispersion relation as retrieved from spectroscopic ellipsometry measurements (Fig. 5). The optical model employed consists of a single layer on crystalline silicon with a thin native oxide, no roughness layer being included. A Tauc-Lorentz oscillator model is used to represent the a-C:H dielectric function.[12] A steep nature for the solid curves especially in the region of 1.25–2.5 eV for extinction coefficient (k) and 2.5–5 eV for n were obtained for the graphitelike a-C:H. These films are also characterized by a low bandgap[13] E_{04} $=1.02 \pm 0.02$ eV compared to very soft polymerlike films $E_{04}=2.50 \pm 0.02$ eV ($n_{IR}=1.55 \pm 0.01$), in line with previous results of Gielen *et al.*[6] A similar dispersion relation has been reported by Hong *et al.*,[14] but different from our deposition conditions, their depositions were performed under ion bombardment conditions, suggesting strong graphitization. Following the reasoning of Robertson,[1] they attribute this behavior to the increased sp^2 graphitic clusters, formed due to strong ion bombardment. Note that any physical phenomenon of such kind cannot be part of our explanation. However, as mentioned, we suggest that the specific plasma chemistry characteristic of ETP-CVD under low Ar/C$_2$H$_2$

flow ratio might be favorable for the production of graphitic phase in our films in line with the observed low bandgap E_{04} and the elimination of endgroups.[7,15] Therefore, tentatively, we propose that this graphitelike a-C:H material is well cross-linked, i.e., a form of a-C:H containing graphitic phases which are interconnected by sp^3 C–C bonds. The improved hardness for this graphitelike a-C:H might have a similar cause as the improved mechanical properties of multiwalled nanotubes by incorporation of sp^3 C–C bridging in between the different graphitic nanotubes walls as predicted by Xia *et al.*[16]

In conclusion, a unique form of hard graphitelike a-C:H material with a nanohardness exceeding 16 GPa is deposited at deposition rates exceeding 15 nm/s, utilizing ETP-CVD. The unique plasma chemistry of the ETP-CVD, i.e., a purely chemical deposition method in the absence of high-energy ion bombardment, suggests alternative routes to obtain hard a-C:H under high deposition rate conditions.

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