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Wide wavelength-range optical studies of hydrogenated amorphous carbon films: from 700 nm to 10 μm

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Abstract

Hydrogenated amorphous carbon (a-C:H) films were deposited on double-side polished germanium substrates by RF plasma-assisted chemical vapour deposition method using benzene as a precursor, and their optical properties were investigated in the wavelength range from 700 nm to 10 μm . In particular, we used a dispersion-function-based non-linear regression to fit the reflectance in the range from 700 to 1800 nm and the baselines of the infrared transmittance in the range from 1000 to 5000 cm^{-1} , respectively. Optical constants determined in both ranges, together with their respective thickness values, showed overall consistency. As a function of self-bias, we found that the refractive index increased while the band gap decreased, which was indicative of film densification and increase of sp^2 -bonded carbons. Detailed information on the self-bias-dependent evolution of microscopic bonding structure in a-C:H films was revealed via the quantitative vibration-absorption spectra in the mid-infrared region, which was obtained after taking Urbach-tail-like electronic absorption into consideration. More specifically, it was found that as self-bias was increased hydrogen content decreased, olefinic sp^2 -bonding decreased while aromatic sp^2 -bonding increased, and more carbon bonding was distorted due to increased cross-linking. Maximum sp^2 -bonding was observed between -300 and -400 V of self-bias. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The potential of hydrogenated amorphous carbon (a-C:H) films for optical coatings stems from their excellent optical and mechanical properties [1]. In addition to their chemical inertness and high hardness, their infrared transparency and resistance to moisture-penetration make them ideal for infrared coatings, in particular. Moreover, due to a wide variation of their

optical properties, it is probably possible to fabricate antireflection coatings for any particular infrared sensors or windows using a-C:H films [2]. However, it is now well known that the ability of carbon to form different bonding configuration is responsible for the wide range of properties of amorphous carbon films. In particular, the ratio of sp^3/sp^2 is often cited as the controlling factor for both the optical and the mechanical properties [3,4]. Therefore, investigation of deposition-condition-dependent evolution of microscopic bonding and concomitant variation of optical properties is a prerequisite for design and fabrication of custom-designed antireflection coatings.

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Due to sensitivity of infrared to carbon–hydrogen and carbon–carbon bonding, infrared spectroscopy has been widely used for structural investigation of a-C:H films [3–8]. In particular, the insensitivity of carbon–hydrogen vibration to their surroundings has rendered the identification of different carbon hybridisation feasible from the mid-infrared absorption spectra. However, until recently most infrared studies of a-C:H films have been qualitative and even in few exceptions, the contribution of electronic transition to the mid-infrared absorption has not been explicitly considered. The major hindrance to the quantitative analysis of infrared absorption has been the difficulty in baseline determination, which becomes harder as thicker films are used to enhance the absorption features. In spite of successful baseline determination with an approximate transmission equation in few cases, the applicability of the same approximation for much thicker films is unclear [6,9]. Moreover, the dispersion of refractive index in mid-infrared range, which has to be taken into consideration to optimise antireflection conditions for a particular wavelength, has not been discussed in those cases.

In this study, we have simultaneously determined the absorption due to electron transition and the dispersion of refractive index in mid-infrared range via dispersion-based non-linear regression fit of baselines to the transmission equation, and those fitted baselines have been used to determine vibration-absorption spectra. Reflectance spectra of the same films in the range from 700 to 1800 nm have also been analysed using another form of dispersion function, and the results have been compared to those of infrared analyses to check their consistency. It has been particularly interesting to note that the broad electronic absorption tail is extended all the way down to mid-infrared range. As far as we know, this is the first systematic study of the electronic absorption tail in this energy range.

2. Experiment and data analysis

A series of a-C:H films were deposited on double-side polished germanium substrates by the RF plasma-assisted chemical vapour deposition method using benzene as a precursor. Germanium substrates were placed on the water-cooled cathode, where

13.56 MHz RF power was delivered through the impedance matching network. All films were deposited at the pressure of 10 mTorr, and the RF power was adjusted to vary the self-bias systematically from –100 to –700 V. In this study, rather thick films (3–5 μm) were investigated.

For all samples, reflectance and infrared transmittance were measured in two different wavelength ranges, respectively. The reflectance was measured in the wavelength range 700–1800 nm with a resolution of 2 nm using a Perkin-Elmer Lambda 14 spectrophotometer. The infrared transmittance was measured between 1000 and 5000 cm^{-1} with a resolution of 4 cm^{-1} using a Perkin-Elmer 900 FTIR spectrometer and averaged over 64 scans.

To determine the optical constants and the thickness of each a-C:H film, we fitted the measured reflectance and the infrared transmittance to the reflectance and the transmittance equations for the system of single film on a substrate, in which the multiple reflection of light inside the film was considered as coherent while that inside the substrate was considered incoherent. Moreover, we parameterized the photon-energy-dependent variation of optical constants via two types of dispersion models for each measurement range. First, in the wavelength range 700–1800 nm, we used the 5-parameter dispersion model introduced by Forouhi and Bloomer [10], which is popular for amorphous carbon films. Second, in the mid-infrared range, we used four-parameter dispersion model introduced by Stenzel, in which the slowly varying refractive index was parameterized as $n(E) = n_0 + AE^2$, and the absorption coefficient was parameterized as $\alpha(E) = \alpha_0 \exp(E/E_0)$ [11]. Note that, this exponential form of absorption, known as Urbach tail, is observed in virtually all amorphous semiconductors. It is worth while to emphasise that both electronic transitions and vibrations contribute to the absorption in the mid-infrared range, and, therefore, without a proper handling of electronic contributions, a quantitative analysis of microscopic bonding from infrared absorption spectra would not be possible. In this study, absorption due to electronic transitions in the mid-infrared range was determined by fitting the infrared transmittance to the transmittance equation using the above parameterization in the vibration-free range, and the baseline corresponding to the determined electronic absorption was used to separate the absorption due to vibrations.

The actual determination of the dispersion parameters, together with the thickness, was carried out by non-linear regression. In particular, we used the Levenberg–Marquardt algorithm to minimise the difference between the measured and the fitted spectra [12].

3. Results and discussions

The typical measured reflectance is presented in Fig. 1(a) together with the best-fit curve, and the typical infrared transmittance and the best-fit baseline are also presented in Fig. 1(b). Note the excellent agreement between the measured infrared transmittance and the fitted baseline in the regions 1800–2800 cm^{-1} and above 3500 cm^{-1} . It was the great advantage of our baseline-determination procedure that the thickness, the refractive index, and the absorption coefficient were determined through this procedure. These were compared to those determined by reflectance fitting to confirm the validity of the fitted baseline.

In Fig. 2, the refractive index and extinction coefficient determined from the reflectance and the infrared transmittance are compared. The thickness corresponding to the reflectance (d_R) and the infrared transmittance (d_{IT}) are also listed. The observation

Fig. 1. Reflectance and infrared transmittance of a-C:H film deposited at the self-bias of 400 V. The best-fit curve to reflectance was obtained by using the Forouhi-and-Bloomer dispersion model (a), and that to the baseline of infrared transmittance was produced by using the Stenzel dispersion model (b).

Fig. 2. The photon-energy-dependent variation of the optical constants of a-C:H films: (a) refractive index and (b) absorption coefficient. High- and low-energy segment is the fitting result to the reflectance and to the infrared-transmittance baseline, respectively. Note that the mid-infrared absorption in (b) is only electronic contribution.

that for all the samples investigated, d_R and d_{IT} agree within error-bar, and the refractive index are consistent across the two measurement range strongly confirms the validity of our baseline-determination procedure. There is also consistency in the absorption coefficient across the two measurement ranges, and consequently, the electronic contribution to the mid-infrared range absorption is significant in some a-C:H films. Moreover, it is interesting to note the slope change in the photon-energy dependence of the absorption coefficients between two measurement ranges, which implies that the different electron-transition mechanism is at work in each energy range. Also, the broad Urbach tail indicates a large tail width of the localised states due to disorder.

Fig. 3. Two main vibration-absorption bands of a-C:H films in mid-infrared range. For the identification of each marked feature, please see the text.

The fitted baselines were used in calculating vibration absorption spectra following Lambert–Beer's law [9]. Since the electronic part of the absorption was explicitly included in computing the baselines, both the interference effect and the electronic contribution were eliminated from the absorption spectra. Therefore, the spectra presented in Fig. 3 are the true absorption spectra of the vibration modes, which warrant quantitative analysis. All samples show two main absorption bands, one around 3000 cm^{-1} and another below 1800 cm^{-1} , which can be assigned to the various carbon–hydrogen stretching vibrations and the carbon–hydrogen bending and the carbon skeletal vibrations, respectively, [2,3,9,13]. The film deposited at the self-bias of -100 V shows many sharp features and, consequently, the relevant vibration modes are easily identified. The first two peaks at 1032 and 1076 cm^{-1} are $\text{sp}^3\text{ CH}_2$ (peak a) and $\text{sp}^3\text{ CH}_3$ (peak b) modes respectively [7,8], and the tiny peak at 1112 cm^{-1} corresponds to olefinic $\text{sp}^2\text{ CH}_2$ mode (peak c) [3]. Interestingly, $\text{sp}^3\text{ C–C}$ mode (peak d) at 1160 cm^{-1} is observed [7], and another mode corresponding to $\text{sp}^3\text{ CH}_2$ (peak e) is observed at 1185 cm^{-1} . Two kinks at ~ 1245 and 1280 cm^{-1} are assigned to mixed $\text{sp}^2/\text{sp}^3\text{ C–C}$ (peak f) and olefinic $\text{sp}^2\text{ CH}$ mode (peak g) [3], respectively. The peak at 1300 cm^{-1} is another mixed sp^2/sp^3

C–C mode (peak h), and the shoulder at $\sim 1326\text{ cm}^{-1}$ is another $\text{sp}^3\text{ CH}_3$ mode (peak i) [3]. The peak at 1370 cm^{-1} is clearly $\text{sp}^3\text{ CH}$ mode (peak j), and one at 1497 cm^{-1} is one more $\text{sp}^3\text{ CH}_3$ mode (peak k) [9]. Unlike other features we discussed so far, the peak at $\sim 1450\text{ cm}^{-1}$ (peak l) cannot be assigned to a single mode since there are three known modes around this region: aromatic $\text{sp}^2\text{ CH}$ at 1445 cm^{-1} , and olefinic $\text{sp}^2\text{ CH}_2$ and $\text{sp}^3\text{ CH}_2$ at 1450 cm^{-1} [9]. However, the absorption bands at higher energy imply that probably the latter two have the dominant contribution. There is a strong peak corresponding to olefinic $\text{sp}^2\text{ C=C}$ mode (peak m) at 1600 cm^{-1} [3], while aromatic $\text{sp}^2\text{ C=C}$ mode (peak n) at $\sim 1580\text{ cm}^{-1}$ [3] appears only as a shoulder. Also in the stretching-absorption band, olefinic $\text{sp}^2\text{ CH}$ (3000 cm^{-1} , peak o) and olefinic $\text{sp}^2\text{ CH}_2$ (3020 cm^{-1} , peak p) modes form a peak, while the weak shoulder at $\sim 3050\text{ cm}^{-1}$ corresponds to aromatic $\text{sp}^2\text{ CH}$ mode (peak q) [13]. Strong peak around 2920 cm^{-1} (peak r) in the stretching band is attributed to $\text{sp}^3\text{ CH}_2$ and $\text{sp}^3\text{ CH}$ modes since corresponding bending modes are observed for both [9]. The shoulder at $\sim 2870\text{ cm}^{-1}$ is assigned to $\text{sp}^3\text{ CH}_3$ mode (peak s), and barely discernable feature at $\sim 2960\text{ cm}^{-1}$ is also assigned to $\text{sp}^3\text{ CH}_3$ mode (peak t) to account the well-known doublet [13]. Similarly, $\text{sp}^3\text{ CH}_2$ stretching vibration has a doublet, and another peak at $\sim 2850\text{ cm}^{-1}$ (peak u) [13] that corresponds to the one at 2920 cm^{-1} can explain the long tail in the low-energy side. Finally, the peak at 3300 cm^{-1} is assigned to $\text{sp}^1\text{ CH}$ stretching mode (peak v) [3].

Apart from the film deposited at -100 V , all the other films deposited at the higher self-bias share common features in their absorption spectra. First of all, many sharp features assigned to $\text{sp}^3\text{ CH}_3$ and $\text{sp}^3\text{ CH}_2$ bending modes disappear, and the peak at $\sim 1450\text{ cm}^{-1}$ becomes smaller while the peak at 1370 cm^{-1} persists. This observation indicates that as self-bias is increased mono-hydride $\text{sp}^3\text{ C}$ becomes dominant over di- and tri-hydride $\text{sp}^3\text{ C}$. We also find that the absorption bands assigned to mixed $\text{sp}^2/\text{sp}^3\text{ C–C}$ vibration become stronger and wider. Together with a dominance of mono-hydride $\text{sp}^3\text{ C}$, this indicates that cross-linking of carbon network is promoted at higher self-bias. Another common feature is the broad and strong absorption band due to $\text{sp}^2\text{ C=C}$ skeletal vibration. However, the downshift of this band from

$\sim 1600\text{ cm}^{-1}$ to $\sim 1580\text{ cm}^{-1}$ shows that more aromatic $\text{sp}^2\text{C}=\text{C}$ bonding are formed at higher self-bias. We also find the common features from the stretching band of the films deposited at higher self-bias: two peaks at ~ 3300 and 2920 cm^{-1} , two shoulders at ~ 2850 and 3000 cm^{-1} , and long high-energy side tail. Note the disappearance of features assigned to sp^3CH_3 and the weakening of olefinic sp^2C -related features, which confirm our aforementioned observations. However, the shoulder at $\sim 2850\text{ cm}^{-1}$ indicates that di-hydride sp^3C is still present and, therefore, contributes to the peaks at ~ 1450 and 2920 cm^{-1} .

Besides the disappearance of the sp^1CH stretching-mode peak at 3300 cm^{-1} , the stretching band shows overall reduction and shape change, which we attribute to the decrease of hydrogen content and the microscopic structural change, respectively. To investigate the microscopic structural change further, we decomposed the stretching band into the multiple Gaussian components. As presented in Fig. 4(a), we decomposed the stretching band of the sample deposited at -100 V into the seven Gaussian components. The four Gaussian components below 2960 cm^{-1} correspond to sp^3C , and remaining three Gaussian components above 3000 cm^{-1} correspond to olefinic and aromatic sp^2C (see the above discussion for the

Fig. 4. Typical multi-Gaussian deconvolution of stretching mode absorption band of a-C:H films. The stretching bands of the films deposited at the self-bias of 100 (a) and 400 V (b) are decomposed into seven and four Gaussian components, respectively.

detailed identification of each component). However, we used only four Gaussian components at ~ 2850 , 2920 , 3000 , and 3500 cm^{-1} to decompose the stretching band of the other films: two each below and above 2960 cm^{-1} , respectively. The two components around 2870 and 2960 cm^{-1} were not included because sp^3CH_3 seemed absent, and the component around 3020 cm^{-1} were not included since the two olefinic components were not well resolved. Nevertheless, the deconvolution was excellent as presented in Fig. 4(b), and we were able to separate the contribution of sp^3 (~ 2850 and 2920 cm^{-1}), olefinic sp^2 ($\sim 3000\text{ cm}^{-1}$), and aromatic sp^2 ($\sim 3050\text{ cm}^{-1}$) C to the stretching bend intensity.

The deconvolution results were summarised in Fig. 5, together with refractive index and E_{04} gap, as a function of self-bias. Note that with increasing self-bias, E_{04} gap decreased monotonically. Similarly, both the total C–H stretching intensity and the ratio

Fig. 5. Self-bias-dependent variation of (a) refractive indexes at 800 and 2500 nm, E_{04} gap; (b) total area of stretching mode absorption band, the ratio of sp^3 and sp^2 stretching-band area, and the ratio of olefinic and aromatic sp^2 stretching-band area.

olefinic sp^2 /aromatic sp^2 decreased as a function of self-bias, while the refractive index showed opposite behaviour. Above 400 V, the ratio sp^3/sp^2 also decreased with increasing self-bias. However, there was a significant increase of sp^3/sp^2 between the bias of 100 and 300 V. The increase of the refractive index, concomitant with decreasing C–H stretching total intensity, can be easily attributed to density increase. As less hydrogen was incorporated, the carbon network became more cross-linked, and consequently, there was less micro-void. It is very interesting to note that the E_{04} gap decreased between the bias of 100 and 400 V, while the ratio sp^3/sp^2 increased. This observation clearly shows that E_{04} gap is not a good indicator for sp^3/sp^2 ratio, and conversely, that E_{04} gap is not determined by sp^3/sp^2 ratio. However, the clear correlation between the ratio olefinic sp^2 /aromatic sp^2 and the E_{04} gap is a strong evidence that the band gap in a-C:H films are controlled by aromatic sp^2 C. More specifically, the observed development of aromatic sp^2 C=C absorption band with increasing self-bias indicates that the clustering of aromatic sp^2 C was responsible for E_{04} gap decrease.

4. Conclusion

We have demonstrated that the dispersion-function-based non-linear regression is a very powerful tool for the analysis of optical spectra in a wide wavelength range. In particular, we analysed the reflectance and the infrared transmittance of a-C:H films, and determined the refractive index and the electronic absorption coefficient from 700 nm to 10 μ m; the slightly decreasing refractive index and the broad absorption tail were found. As far as we know, the electronic absorption edge of a-C:H films was never measured down to this low energy range.

After removing the contribution from the interference and the electronic absorption, we obtained the quantitative vibration-absorption spectra of a-C:H films, and from which we found the following self-bias dependence of the microscopic structural variation. At -100 V, a large amount of hydrogen was incorporated, and consequently, a polymeric film that contained mono-, di-, and tri-hydride sp^3 C together with a great deal of mono- and di-hydride olefinic sp^2 C was formed. When the self-bias was increased to

300 V, a less amount of hydrogen were incorporated, and, therefore, instead of chain-like sp^2 bonding, more cross-linked sp^3 and sp^2 bonding were formed. As a result of that, we observed the increase in the refractive index, the big drop in the E_{04} gap, and the dominance of mono-hydride sp^3 C. At 400 V, in spite of large reduction in hydrogen content, there was no significant change in the sp^3/sp^2 ratio. However, we found the increase both in the fraction of aromatic sp^2 C and in the refractive index, and consequently, concluded that more aromatic sp^2 -bonded carbons were clustered. Therefore, we attribute the observed reduction in the E_{04} gap to the clustering of aromatic sp^2 C. The similar variation observed at even higher self-biases can be also attributed to the increase of aromatic bonded sp^2 C, and their clustering.

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