

Brief Reports

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Amorphous deuterated-hydrogenated carbon thin-film infrared absorption spectrum

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(Received 8 February 1983)

We have grown amorphous deuterated-hydrogenated carbon thin films by plasma deposition of deuterated acetylene. The infrared absorption spectra of these thin films consist of C-H and C-D stretching bands and CH₂, CHD, and CD₂ bending bands. The luminescence spectra show weak periodic sidebands with the same period as those of amorphous hydrogenated carbon.

Infrared absorption has become a standard measurement for amorphous hydrogenated silicon (*a*-Si:H) and carbon (*a*-C:H) thin films because of its relatively easy observation and interpretation. One of the first such studies was by Brodsky, Cardona, and Cuomo on *a*-Si:H and amorphous deuterated silicon (*a*-Si:D).¹ They observed and identified the Si-H and Si-D stretching bands at 2095 and 1510 cm⁻¹, respectively; they noted that the ratio of these two frequencies 2095/1510 = 1.39 is almost equal to the square root of the ratio of the masses of D to H. They also reported the Si-H and Si-D bending bands at 895 and 650 cm⁻¹, respectively; again they noted that 895/650 = 1.38. Further confirmation of these results and assignments came from Knights, Lucovsky, and Nemanich.²

The infrared absorption spectra of *a*-Si-C:H and *a*-Si-C:D alloys were first reported by Wieder, Cardona, and Guarnieri, who observed the C-H stretching band at 2920 cm⁻¹ but did not see the C-D stretching band.³ They also suggested that the C-H and C-D bending bands were at 1250 and 890 cm⁻¹, respectively. Sussman and Ogden⁴ also looked at *a*-Si-C:H and identified C-H stretching bands at 2900 cm⁻¹, bending bands at 1440, 1360, and 1250 cm⁻¹, and wagging bands at 1020 and 950 cm⁻¹.

Recently, we observed in *a*-C:H the C-H stretching and bending modes at 2900 and 1450 cm⁻¹, respectively.⁵ We also reported periodic oscillations in the luminescence spectra of *a*-C:H with a period of approximately 1460 cm⁻¹. We now report the infrared absorption and luminescence spectra of *a*-C:(D,H) thin films.

Anderson⁶ and, more recently, Myerson and Smith⁷ have grown *a*-C:H alloys from plasma deposition of acetylene (C₂H₂). We have used both C₂H₂ or C₂D₂ as our feedstock in a capacitively coupled plasma reactor following the design of Knights.⁸ The operating conditions for film growth using either C₂H₂ or C₂D₂ were the following: substrate temperature ~300°C, pressure = 0.35 Torr, flow rate ≈ 0.4 sccm; and polished Si and quartz substrates were mounted on the anode. The C₂D₂ gas was described as 99% deuterated and was purchased from two different suppliers, KOR Inc. and Isotope Labeling Corp. The infrared absorption spectra for both *a*-C:H and *a*-C:(D,H) thin films are shown in Fig. 1.

We suggest the following interpretation for the *a*-

C:(D,H) infrared absorption spectrum. First, the pair of lines at 2240 and 2150 cm⁻¹ are the D-C-D symmetric and antisymmetric stretching bands. Calculating the ratio of the H-C-H stretching-band frequencies to the D-C-D stretching-band frequencies gives 2960/2240 = 1.32 and 2900/2150 = 1.35. These ratios are in good agreement with the ratio of their reduced masses, 1.36. Further confirmation of this assignment comes from the fact that these two bands are the most intense in their respective spectra. The observation of a pair of lines means that CD₂ local clusters must be present in significant numbers.

The single line at 2950 cm⁻¹ must be the C-H stretching band. If we estimate that the relative H and D concentrations are proportional to their stretching-band integrated intensities, then we get 1.44 D atoms for each H atom. Either the C₂D₂ feedstock was not nearly as deuterated as claimed or there is a tremendous preferential incorporation of H over D in our thin films. The observation of a single C-H stretching band means that the H is primarily in CH and/or CHD local clusters.

In order to identify the bending bands observed in the *a*-

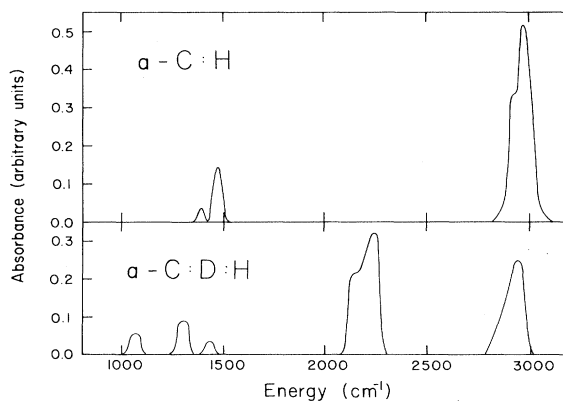


FIG. 1. Infrared absorption spectra of *a*-C:H and *a*-C:(D,H) thin films.

C:(D,H) spectrum it is useful to compare them to those observed in hydrogenated, singly deuterated, and double deuterated 1,1-dichloroethylene (CH_2CCl_2 , CHDCCl_2 , and CD_2CCl_2). In CH_2CCl_2 , the CH_2 bending band is at 1400 cm^{-1} ; in CHDCCl_2 , the CHD bending band is at 1280 cm^{-1} ; and in CD_2CCl_2 , the CD_2 bending band is at 1039 cm^{-1} .⁹ We therefore identify the bands at 1430, 1300, and 1065 cm^{-1} as bending bands from CH_2 , CHD, and CD_2 local clusters, respectively. Further confirmation of these assignments comes from the ratio of the CH_2 bending frequency to the CD_2 bending frequency, $1430/1065 = 1.34$.

Finally, we measured the photoluminescence spectra of α -C:(D,H) photoexcited with laser photons with energies between 1.94 and 2.10 eV. We observed the same periodic sidebands with the same period ($\sim 1460\text{ cm}^{-1}$) as observed in the α -C:H spectra, but their intensity relative to the back-

ground luminescence was significantly less than in the α -C:H spectra. If the deuterated sample was 100% deuterated, then the period of the sidebands should have decreased by 25% if they were due to the emission of CD_2 bending quanta. In our case with both H and D present, one might expect two sets of sidebands or one set of shifted sidebands, if the sidebands are due to bending quanta. The absence of either of these possibilities suggests that these sidebands are not due to bending quanta. However, further work is needed to settle this question.

ACKNOWLEDGMENT

We wish to acknowledge the financial support of the University of Missouri Improved Research Quality Grant.

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