



## Direct evidence of porosity in carbon-rich hydrogenated amorphous silicon carbide films

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M. Hitchcock (both of Oak Ridge National Laboratories) for assistance in carrying out the tritium experiments. This work was supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

<sup>1</sup>E. Schram and R. Lombaert, *Organic Scintillation Detectors* (Elsevier, Amsterdam, 1963).

<sup>2</sup>D. Clark, *Nucl. Instrum. Meth.* **117**, 295 (1974).

<sup>3</sup>Present applications of RL lighting include emergency exit lights in commercial aircraft, and luminous instrumentation (such as watch dials and sunsights). Many other potential applications for long-term, steady-state, nonelectric light sources can be envisioned, particularly involving remote locations where electricity is not readily available, or emergency systems that must function reliably during electric power failure. An application of current interest is for landing lights at remote runways. Note that the low-energy betas from tritium are effectively attenuated by thin layers of mate-

rials (the attenuation length is less than  $1\ \mu\text{m}$  in both the organic and glass components), so that tritium lights, such as the ones we have demonstrated, emit no appreciable quantities of radiation to the external environment.

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<sup>11</sup>J. A. Tompkins (private communication).

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## Direct evidence of porosity in carbon-rich hydrogenated amorphous silicon carbide films

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Infrared absorption spectroscopy was used to study the oxidation of hydrogenated amorphous silicon carbide ( $a\text{-Si:C:H}$ ) films prepared by the glow-discharge decomposition of gaseous mixtures of silane and methane. It has been found that carbon-rich samples incorporate oxygen when exposed to air, as detected by an increased absorption of the Si-O-Si stretching vibration band. The analysis of the infrared spectra of samples annealed in air at room temperature and at  $200\ ^\circ\text{C}$  indicates that, except for their oxidation rate, no appreciable difference exists in the mechanisms of oxygen incorporation in the films at the two temperatures. The oxidation kinetics suggests an open porous structure for these carbon-rich films. On the contrary, samples having a low carbon content appear to oxidize on the surface only, in a way similar to amorphous silicon.

In the past few years considerable attention has been devoted to the study of the optoelectronic properties of hydrogenated amorphous silicon carbide ( $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ ) films. This interest originates, on one hand, from the present and potential industrial applications of these alloys and, on the other hand, from the related need of a deeper understanding of the fundamental properties of tetrahedrally bonded amorphous semiconductors.<sup>1,2</sup> Since the pioneer publication by Anderson and Spear,<sup>3</sup> much work has been done on the establishment of the optical and electrical properties of  $a\text{-Si}_{1-x}\text{C}_x\text{:H}$  alloys as a function of composition.<sup>4-9</sup> The studies reveal that for  $x$  values in the 0.5-0.7 range, peculiar changes occur in the optoelectronic properties of the films.<sup>2</sup> These variations have been related to modifications in the bonding configuration, namely, changes in the hybridization state of the carbon atoms.<sup>9,10</sup> Moreover, other evidences indicate that the number of silicon-carbon bonds reaches a maximum for  $x$  between 0.6 and 0.7.<sup>2,9</sup>

It is reasonable to expect that the changes occurring at

the atomic scale should be reflected in the structure of the material. To our knowledge, however, only a few works<sup>9,11,12</sup> consider problems such as, for instance, the presence of carbon-induced voids in the films. Combining data of density measurements and the optical theory for void-substance composites, Menna *et al.*,<sup>11</sup> concluded that the incorporation of carbon into the network results in a very large void fraction. Mui *et al.*<sup>9</sup> found that the fitting of optical data with the complex dielectric function gives a maximum in the void fraction for  $x \cong 0.4$ . Beyer *et al.*<sup>12</sup> studied the hydrogen evolution in samples containing different amounts of carbon. These authors found two peaks in the hydrogen effusion curve occurring at low and high temperatures, respectively. The hydrogen evolved at low temperatures is associated with the presence of voids producing a material with poor electronic properties.

In this communication, we report a study on the evolution of the infrared (IR) spectra of samples having different carbon contents. It has been found that samples possessing a

low carbon content present stable IR spectra, even after a long exposure to oxidizing atmospheres. On the contrary, samples having a high carbon content incorporate oxygen when exposed to air. This experimental finding is interpreted in terms of a carbon-induced open porous network. The oxidation kinetics of  $\alpha\text{-Si}_{1-x}\text{C}_x\text{H}$  samples, isothermally annealed at 200 °C in air, has been determined for carbon-rich material.

The samples were prepared by the rf decomposition of  $\text{SiH}_4 + \text{CH}_4$  and deposited onto crystalline Si and Corning 7059 glass substrates for IR and visible spectroscopy, respectively. The deposition system is a parallel plate, capacitively coupled reactor and the deposition conditions were: pressure of 50 Pa, substrate temperature of 260 °C, rf power of 2.5 W, and total gas flow rate of 10 sccm. Typical film thickness is 500 nm. In order to obtain samples with different carbon contents the composition of the gaseous mixture parameter  $y = [\text{CH}_4]/([\text{SiH}_4] + [\text{CH}_4])$  was varied between 0 and 0.87. Although no direct determination of the carbon content in the film was made, the existence of an abundant bibliography correlating the optical band gap and the refractive index to the carbon content of the alloy, allows an estimation of the value of  $x$ .<sup>2,3,5,7-9</sup> The carbon content of the samples grown with a gaseous mixture  $y = 0.87$  was estimated to be  $x = 0.45 \pm 0.05$ , which corresponds to the highest carbon content among the studied samples.

The IR spectra of the samples were measured immediately after the deposition and after six months of exposure to air at room temperature. Significant variations of the IR spectra were observed only in the films having the highest carbon content. Subtracting the IR absorption spectrum taken on as-deposited samples from the spectrum taken after a six months exposure to air, a new spectrum (hereafter referred to as the differential absorbance) is obtained, which highlights the changes in the absorption bands. Note that increments in the absorbance are proportional to increments in the absorption coefficient.<sup>13</sup>

Figure 1 shows the IR differential absorbance spectrum of a carbon-rich sample obtained after six month room-temperature exposure to air. It is within the 300–1500  $\text{cm}^{-1}$  energy range that the major changes in absorption occur.

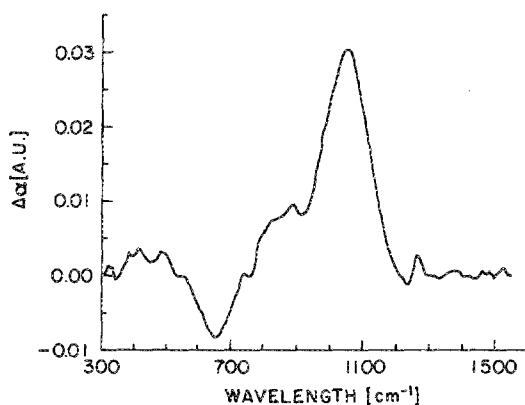


FIG. 1. Differential absorbance spectrum for a sample deposited under  $y = \text{CH}_4/[\text{CH}_4 + \text{SiH}_4] = 0.87$  conditions. The curve was obtained subtracting the absorbance spectrum obtained immediately after sample deposition from the one obtained after a six-months exposure to air at room temperature.

Samples having a smaller carbon content ( $y < 0.7$ ) do not present any particular feature in their differential spectra, an indication of the material stability.

Although the evolution occurs spontaneously at room temperature, a rather long period is needed to detect a significant variation on the IR spectrum. To circumvent this difficulty and speed up the oxidation process, a series of isothermal annealings at 200 °C in air was performed. In such a way, the nature of the kinetics of the evolution process could be studied in a shorter period. Under these new conditions no aging effects were detected in the low carbon content samples either.

Figure 2 shows the differential absorption spectra resulting from the oxidation of a sample deposited under  $y = 0.87$  conditions, following the procedure indicated above. The different spectra correspond to different exposition times as explained in the figure caption. Note that the main features of these spectra do not differ substantially from the spectrum shown in Fig. 1, suggesting the same evolution mechanisms. Next, an analysis of the evolution features observed in the IR spectra is presented.

The strong absorption band in the differential spectra at 1030  $\text{cm}^{-1}$  has been assigned to the antisymmetric stretching mode of the Si-O-Si bridge in siloxane compounds.<sup>14</sup> However, the corresponding mode of the Si-O-C group also appears in this energy region,<sup>14</sup> so that a contribution of this mode cannot be ruled out. The absorption peak appearing at 420  $\text{cm}^{-1}$  has been attributed by some authors to the bending of Si-O-Si bridge.<sup>15</sup> Other publications attribute this mode to a mixing of the rocking and bending modes of the same bridge.<sup>16,17</sup> Note that both peaks increase strongly with annealing time.

As Fig. 1 shows, two bands peaking at 1270  $\text{cm}^{-1}$  (positive absorption) and 650  $\text{cm}^{-1}$  (negative absorption) appear in the differential spectra. The 1270  $\text{cm}^{-1}$  band is normally not found in the amorphous silica IR spectra. However, a band between 1250 and 1275  $\text{cm}^{-1}$  is always present in organosilicon compounds and, according to Bellamy,<sup>14</sup> it can be associated to the symmetric methyl deformation in these compounds. Moreover, by comparing the spectra of the silane-alkane molecules, Wieder *et al.*<sup>4</sup> con-

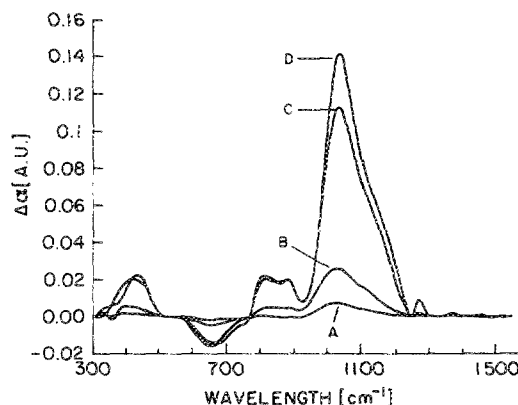


FIG. 2. Evolution with time of the differential absorbance spectra of samples grown under  $y = 0.87$  conditions (same as Fig. 1). The different spectra correspond to the following annealing times at 200 °C: A = 25 min, B = 115 min, C = 3900 min, and D = 16 500 min.

clude that the  $650\text{ cm}^{-1}$  band can be associated to the Si-C stretching mode. The occurrence in this energy region of negative values in the differential absorbance spectra of Figs. 1 and 2, are interpreted as due to the formation of Si-O-Si and Si-O-C complexes in detriment of the Si-C bonds.

Following the considerations above, it is clear that oxygen atoms are incorporated in the exposed material. The kinetics of this oxidation process was established through the analysis of the integrated area of the  $1030\text{ cm}^{-1}$  absorption band. Although the strength of the Si-O-Si oscillator is unknown, the evolution with time of the silicon-oxygen bond density is proportional to the area under this absorption band. Figure 3 shows, for a carbon-rich  $a\text{-Si}_{1-x}\text{C}_x\text{:H}$  sample, the logarithm of the integrated silicon-oxygen absorption band versus the logarithm of the exposure time. Within the studied time interval, the process of oxygen incorporation in the carbon-rich samples does not saturate. The experimental points fall on a straight line with a slope of approximately 0.6. This value is close to the slope of 0.5 expected for a diffusion-limited process in solids.

These experimental findings suggest that in the carbon-rich samples a porous maze allows the oxygen to penetrate into the bulk of the material. We suggest that the presence of a large fraction of the  $(\text{CH}_3)$  precursor radical may be the origin of this porous network in the methane-based silicon carbide layer formation. In carbon-rich samples the incorporation of a large amount of this radical, giving rise to Si- $\text{CH}_3$  complexes at the surface,<sup>1</sup> induces the formation of voids and thus the porous material. In the low carbon content samples, conversely, a thin oxide barrier is probably formed at the surface<sup>18</sup> preventing any further oxidation.

The band appearing in this differential absorbance spectra in the  $790\text{--}900\text{ cm}^{-1}$  range has not been analyzed yet. There is some difficulty in establishing a clear-cut origin for this increased absorption because contributions of different complexes may appear in this spectral region. The band may be decomposed in three Gaussians centered at  $800$ ,  $825$ , and  $880\text{ cm}^{-1}$ , respectively. Among the vibrational modes occurring at these energies we may cite the methyl rocking mode in open chain materials and methyl silanes which are localized at around  $800\text{ cm}^{-1}$ .<sup>14</sup> The Si-C stretch vibration associated to an OSiCH<sub>3</sub> end group<sup>14</sup> generates a band in the  $840\text{--}850\text{ cm}^{-1}$  wave number range. Of dubious origin, the peak detected at  $870\text{ cm}^{-1}$  in Figs. 1 and 2 is often found in SiO.<sup>19</sup> Features similar to those observed in the  $790\text{--}820\text{ cm}^{-1}$  range are observed in oxygen-doped amorphous silicon.<sup>20</sup> Other vibration modes, such as the scissor and bending of SiH<sub>2</sub> and  $(\text{SiH}_2)_n$ , are generally found around  $890$ <sup>21</sup> and  $860\text{ cm}^{-1}$ .<sup>22</sup> It is important to stress at this point that all the structures observed in the  $790\text{--}900\text{ cm}^{-1}$  range may evolve as a consequence of either the formation of new species or the modification of the environment due to the incorporation of oxygen.

In conclusion, we studied the oxidation of  $a\text{-Si}_{1-x}\text{C}_x\text{:H}$  films by means of IR differential spectroscopy. We observed that samples having a low carbon content ( $x < 0.4$ ) do not display the Si-O-Si absorption band, even when annealed at  $200^\circ\text{C}$  in air. On the contrary, samples with a higher carbon content ( $x > 0.45$ ) oxidize spontaneously in air at room tem-

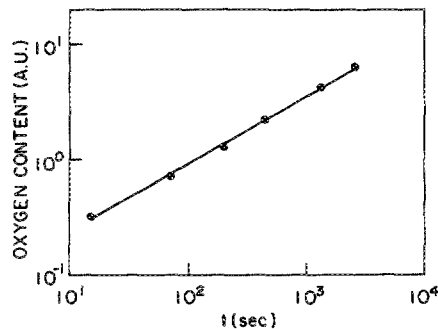


FIG. 3. Oxygen content, in arbitrary units, of annealed material vs time, for samples with  $x \approx 45$  at. % carbon content. The full line corresponds to a linear regression of the experimental points.

perature. Similar effects are found when these samples are annealed in air at  $200^\circ\text{C}$ . The oxygen incorporation has been shown to be nearly proportional to the square root of the exposure time, an experimental indication of a gas diffusion-limited process in solids. We attribute these effects to the existence of a connected void network.

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