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Continuous-wave and pulsed electron-nuclear double-resonance study of paramagnetic defects in amorphous hydrogenated silicon-carbon alloy

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Alloying amorphous hydrogenated silicon with carbon, although increasing the optical band gap, results in a dramatic increase in the number of paramagnetic defects and subsequent deterioration of optoelectronic properties. Electron-nuclear double-resonance and electron spin resonance studies of ^{13}C-enriched materials provide a picture of how unpaired electrons, silicon atoms, and carbon atoms relate to each other in the alloys. We report the observation of weak hyperfine interactions originating from ^{13}C and ^{29}Si nuclei which are about two bond lengths away from the unpaired electrons. The absence of stronger interactions between unpaired electrons and ^{13}C nuclei indicates that carbon dangling bonds do not exist, even in materials with a high level of paramagnetic defects. We suggest a model involving dangling-bond migration and carbon-double-bond formation to explain these results.

The main reason for alloying amorphous hydrogenated silicon (*a*-Si:H) with carbon is to prepare wide-band-gap materials for microelectronic applications.[1,2] The optical band gap of amorphous hydrogenated silicon-carbon alloy (*a*-SiC:H) increases rapidly with carbon incorporation.[3] However, the number of paramagnetic defects in *a*-SiC:H also increases dramatically with carbon incorporation, leading to an increase in the gap states and the deterioration of optoelectronic properties.[4–8] In *a*-Si:H, these defects have been identified as undercoordinated silicon dangling bonds,[9] and efforts have been made to reduce the dangling-bond density by improving deposition techniques.[10] The nature and origin of defects in *a*-SiC:H are not as well known. Questions such as whether the paramagnetic defects are silicon- or carbon-associated dangling bonds and how carbon alloying affects these dangling bonds are still unanswered. Further research on these subjects will not only provide a deeper insight about the material structure, but may also suggest better ways of improving the material performance.

This work reports the observation of hyperfine interations between electronic and nuclear spins which leads to a picture of how unpaired electrons, hydrogen atoms, silicon atoms, and carbon atoms relate to each other in *a*-SiC:H. Using continuous-wave (cw) and pulsed electron-nuclear double-resonance (ENDOR) and electron spin resonance (ESR) spectroscopies, and ^{13}C enrichment, we are able to distinguish weak hyperfine interactions of unpaired electrons with either ^{13}C or ^{29}Si nuclei. Our results indicate that only silicon dangling bonds exist in *a*-SiC:H. The closest carbon atoms observed are about two bond lengths away from the unpaired electrons. Finally, we propose a mechanism that explains the absence of carbon dangling bonds.

Materials with and without ^{13}C enrichment (*a*-Si^{13}C:H) and *a*-SiC:H) are prepared in a plasma-enriched chemical-vapor deposition system described previously.[11] Source gases used in this study are silane (SiH_4) and methane (either $^{13}CH_4$ with 99% ^{13}C enrichment or CH_4 with 1.1% ^{13}C) with flow rates fixed at 6 and 12 cubic centimeter per minute at STP, respectively. The plasmas are generated by applying 20 W of power at 13.56 MHz. Depositions proceed simultaneously on Corning 7059 glass and aluminum substrates at a pressure of 200 mTorr and a substrate temperature of 240 °C. These conditions have been optimized for preparing good quality *a*-Si:H with a hydrogen content of about 10 at. %.

The optical absorption spectra are recorded with a Perkin Elmer 330 spectrophotometer for the films deposited on glass. The absorption coefficient α is calculated by normalizing with film thickness, which is derived from the interference fringes in the nonabsorbing or weakly absorbing region (> 1000 nm).[12,13] The optical band gap (E_{04}) is reported as the energy where $\alpha = 10^4$ cm^{-1}. Both *a*-Si^{13}C:H and *a*-SiC:H films have an optical band gap of 2.2 eV, higher than the value of typical *a*-Si:H films.

Films deposited on aluminum are removed from the substrates by etching with dilute hydrochloric acid, yielding material for ENDOR and ESR studies. Pulsed or cw ENDOR experiments are performed on locally built spectrometers operating in the *X* band (microwave frequency at 9 GHz) or in the *Q* band (35 GHz). A Mims sequence consisting of microwave and radio frequency pulses is applied for the pulsed experiments.[14] Matching the radio frequency with a nuclear resonance frequency causes changes in the spin-echo amplitude and the detection of ENDOR signals at frequencies of $|\nu \pm A/2|$, where ν is the nuclear Larmor frequency and A is the hyperfine constant. ESR experiments are performed at room temperature with a Varian *X*-band spectrometer. Both *a*-Si^{13}C:H and *a*-SiC:H samples have a spin density on the order of 10^{18} cm^{-3} calibrated by α,α'-diphenyl-β-

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picrylhydrazyl.[15]

The cw proton ENDOR signal of ^{13}C-enriched *a*-SiC:H is a smooth peak centered at the proton Larmor frequency (Fig. 1). Its shape undoubtedly reflects a distribution of hyperfine couplings with maximal values of at least the breadth of the wings, namely, the hyperfine constant, $A \sim 6$ MHz; it is similar to those reported earlier for *a*-Si:H.[16,17] Although the origins of these signals are still controversial, it is generally believed that they are caused by the distinct distributed and clustered hydrogen environments in *a*-Si:H. The distributed and clustered hydrogen phases were also observed for *a*-SiC:H, and more hydrogens were found to be incorporated into the clustered phase upon carbon alloying.[6] Compared to the ENDOR spectrum of *a*-Si:H, the broader and stronger unsplit signal of our sample is more likely to originate from the clustered hydrogens.

Figure 2 presents ENDOR spectra of *a*-SiC:H and *a*-Si^{13}C:H that reveal interactions between unpaired electrons and ^{29}Si or ^{13}C nuclei. Based on measurements of the optical band gap and ESR spin density, we estimate that the carbon content in both samples is 15 at. %. In the unenriched *a*-SiC:H sample, low natural abundance (1.1%) leads to a ^{13}C concentration of less than 0.2 at. %. In Fig. 2(b), only one signal from ^{29}Si, centered at the ^{29}Si Larmor frequency of 2.76 MHz, is observed for the dangling-bond–^{29}Si interaction. In the *a*-Si^{13}C:H sample, due to 99% enrichment, the concentration of ^{13}C is comparable to that of ^{29}Si, and the ENDOR signal from this sample shows overlapping signal from both these nuclei in Fig. 2(a). The difference between spectra (a) and (b) is shown in Fig. 2(c). This signal is centered at the ^{13}C Larmor frequency (3.50 MHz) and originates from the dangling-bond–^{13}C interaction.

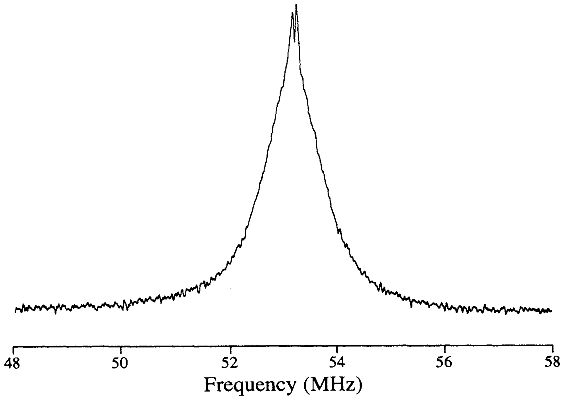


FIG. 1. The continuous-wave proton ENDOR spectrum of *a*-Si^{13}C:H. Experiment is performed in a homebuilt *Q*-band spectrometer at magnetic field, 12 480 G; microwave frequency, 35.03 GHz; microwave power, 1.58 mW; modulation amplitude, 0.2 G; and receiver gain, 320.

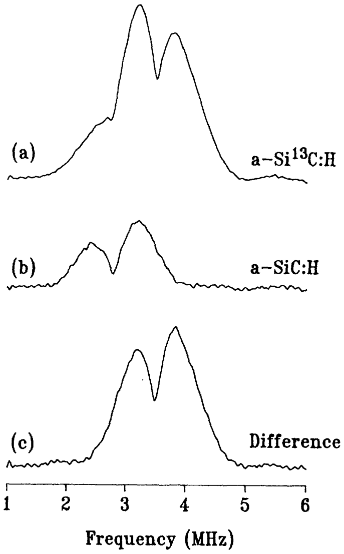


FIG. 2. The pulsed ENDOR spectra of *a*-Si^{13}C:H (a), *a*-Si:H (b), and their difference (c). Experiments are performed in a homebuilt *X*-band spectrometer at a temperature of 77 K, a magnetic field of 3280 G, and a microwave frequency of 9.195 GHz. Spectra are obtained by applying a Mims sequence (Ref. 14) with pulse widths 16, 16, and 16 ns; time between pulses, 400 and 35 132 ns; number of scans, 20; shot repetition time, 2 ms; echo intensity, 17 mV; and gain, 5 mV.

The total breadth of the ^{29}Si ENDOR pattern corresponds to a maximal hyperfine coupling of ca. 2 MHz (0.7 G) and the apparent splitting corresponds to a coupling of 0.82 MHz (0.29 G). These interactions are about two orders of magnitude smaller than the reported values for unpaired electrons localized at ^{29}Si nuclei in *a*-Si:H, 70–75 G for the isotropic hyperfine constant and 15–20 G for the anisotropic hyperfine constant.[9] A theoretical calculation using the extended Hückel theory predicts that the isotropic hyperfine constant for an unpaired electron and the ^{29}Si nucleus two bonds removed is 0.21–13.3 G, and the anisotropic hyperfine constant is 0.1–1.4 G.[18] The observed ^{29}Si couplings fall in these ranges. The total breadth of the ^{13}C ENDOR pattern corresponds to a maximal hyperfine coupling of ca. 2.5 MHz (0.9 G) and the apparent splitting corresponds to a coupling of 0.65 MHz (0.23 G). As the ^{13}C and ^{29}Si couplings for a given unpaired spin density should be roughly equal,[15] we suggest that both the ^{29}Si and ^{13}C signals in Fig. 2(c) originate from the interaction between unpaired electrons and nuclei at least two bond lengths away.

The interactions between unpaired electrons and nearer nuclei, such as ^{29}Si dangling bond, give rise to signals with larger hyperfine splittings. These signals cannot be observed with currently available radio-frequency components. Using ESR, the hyperfine doublet for the ^{29}Si dangling bonds has been successfully distinguished from the central signal for the ^{28}Si dangling bonds in *a*-Si:H.[9] Considering the nuclear concentrations in our ^{13}C-enriched sample, it is equally to be expected that another hyperfine doublet for any ^{13}C dangling bonds would be seen in the ESR spectra. However, the observed spectra shown in Fig. 3 are virtually identical for both samples, except that the central peak of the *a*-Si^{13}C:H sample is slightly broadened (less than 1 G). The obvious explanation for the absence of such ^{13}C-split signal is that there are essentially no "carbon dangling bonds"; that is, there

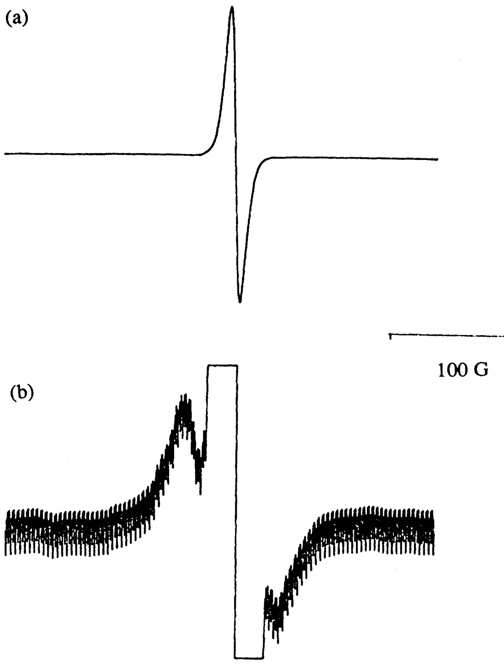
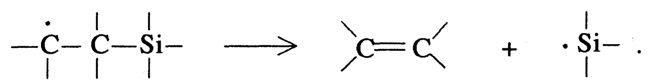


FIG. 3. The ESR spectrum of a-Si^{13}C:H averaged over 100 scans shows an intense central peak (a) and two weak ^{29}Si satellites when enlarged 100 times (b). Experiments are performed at room temperature with a Varian X-band spectrometer at magnetic field 3395 G; microwave frequency, 9.521 GHz; microwave power, 1 mW; modulation amplitude, 1 G.

are no unpaired electrons associated directly with carbon atoms. The ESR signals of these materials, therefore, originate solely from silicon dangling bonds. Neither do we observe in ESR or ENDOR the hyperfine interaction between unpaired electrons and "back-bonded" ^{13}C nuclei, which were suspected to cause the broadened ESR spectrum of another ^{13}C-enriched sample.[19] Thus, in the present experiments, the observed carbon atoms closest to the unpaired electron are two bond lengths away.

To explain the absence of carbon dangling bonds in a-SiC:H, we propose a mechanism that has been discovered for mechanically degraded polymers.[20–22] This mechanism involves migration of unpaired electrons and formation of carbon double bonds. We suggest that a similar reaction might occur during the growth of a-SiC:H as follows:



$$-\overset{\bullet}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{Si}}- \longrightarrow \;>C=C<\; + \;\cdot\overset{|}{\underset{|}{Si}}- . \qquad (1)$$

This reaction breaks one carbon-silicon bond but forms a carbon-carbon unsaturated bond. Of particular interest is that this reaction relaxes the stresses in the silicon network caused by carbon alloying. The substitution of some lattice sites by much smaller carbon atoms inevitably distorts both bond lengths and bond angles from the normal tetrahedral structure. The above reconstruction helps to release this excess strain by breaking the connection between silicon and carbon. The result is a much relaxed network with the dangling bonds moving from carbon to nearby silicon and the formation of carbon double bonds. In the near surface region, similar reconstruction may lead to $C=O$ bonds when exposed to the atmosphere. This model explains not only the absence of carbon dangling bonds, but also the high level of unsaturated carbon bondings in a-SiC:H observed by nuclear magnetic resonance even at low carbon content.[6] We speculate that this reaction occurs spontaneously during film growth or in contact with oxygen. Further experimental confirmation of this model is suggested.

In conclusion, this work provides a clearer picture of how unpaired electrons, silicon atoms, and carbon atoms relate to each other in a-SiC:H. The weak hyperfine interactions observed by ENDOR show the existence of carbon atoms two bond lengths away from the unpaired electrons. The absence of a ^{13}C hyperfine splitting in ESR spectra of the ^{13}C-enriched sample, on the other hand, indicates the absence of carbon dangling bonds, even though the material in this study has a relatively high spin density. These results can be explained by the proposed model involving dangling-bond migration and carbon-double-bond formation.

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