Low density of defect states in hydrogenated amorphous carbon thin films grown by plasma-enhanced chemical vapor deposition

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(Received 6 March 2000; accepted for publication 25 October 2000)

The density of electronic defect states in most forms of amorphous carbon deposited at room temperature is found so far to be very high ($10^{18}-10^{22}$ spins cm^{-3}). In this letter, we demonstrate that the radio-frequency plasma-enhanced chemical vapor deposited hydrogenated amorphous carbon (a-C:H) thin film exhibits the lowest spin density of the order of $10^{16}\ cm^{-3}$, investigated by using electron spin resonance (ESR) spectroscopy, a very promising reproducible result comparable with high-quality a-Si:H. In addition, the optical gap of a-C:H has been tailored between a wide range, 1.8–3.1 eV. The ESR spectra of all the films reveal a single Lorentzian line whose linewidth ΔH_{pp} varies strongly with the optical gap. Also, there is a strong dependence of spin density on the optical gap, and we show that this dependency is a direct result of structural changes due to sp^3/sp^2 carbon bonding network. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1335548]

Much interest has been shown in the use of tetrahedral amorphous carbon (ta-C), deposited by filtered cathodic arc, in the fabrication of electronic devices.[1,2] However, limited success was achieved in producing devices with properties that might make its use in electronic applications commercially viable. This lack of success may, in part, be due to the high density of defect states in the amorphous carbon. The spin densities of ta-C, and indeed in most forms of amorphous carbon (a-C, a-C:H, DLC, etc.), films deposited at room temperature (RT) are found to be very high ($10^{18}-10^{22}\ cm^{-3}$),[3–17] as compared to those found in device-quality a-Si:H ($10^{16}\ cm^{-3}$).[18] As a result, there have been concerted efforts to reduce the defect density in amorphous carbon by various means.

In this letter, we report the electron spin resonance (ESR) investigation of the density of electronic defect states of the PECVD deposited a-C:H thin films. We find that the quality of the films is significantly improved with the ESR spin density in the order of $10^{16}\ cm^{-3}$, which is comparable with high-quality a-Si:H, a promising result prompts future prospects of a-C:H as an electronic material.

Quartz (ESR grade) and crystalline silicon substrates were used for the deposition of carbon thin films. The carbon films were deposited in a 13.56 MHz rf-powered PECVD system, at RT, with CH_4 as the source gas, in a clean room setup. For the films studied here, the chamber pressure was 10 Pa, the flow rate of CH_4 and H_2 were 30 sccm each, all optimized,[19,20] and the rf power (P_{rf}) was the variable. The films were deposited to a thickness of about 0.6–0.7 μm. All the films exhibit excellent adherence to both the substrates.

The UV–visible spectral transmittance and reflectance measurements were performed (on quartz) in the range of 350–1150 nm to derive the Tauc optical gap (E_{Tauc}) for amorphous semiconductors. The ESR measurements were performed (on quartz) at the X band (9.5 GHz) with 100 kHz field modulation and a nonsaturating incident microwave power of 0.04 mW at 4.2 K.[21] The absolute N_s in these films was obtained by measuring the sample against a Mn^{2+} standard. The set of films discussed here were also studied (on Si) for their structure, bonding, and composition by various standard spectroscopic techniques.[19,20] The films are found to be sp^3 rich (>80%) and free from contamination (such as O or N). The estimated H concentration was about 30% and found to decrease with increasing P_{rf}.[19,20]

Most of the spectra are best fitted with a single Lorentzian curve. The g values obtained from the ESR spectra of all the films are found to be around 2.0030 ($\pm$0.0003) with slight variations across the films.[7–9] Particularly, a slight tendency to larger values for the films deposited with P_{rf} below 100 W (polymer-like films with wide E_{Tauc}) suggests the existence of both sp^3 ($g=2.003$) and sp^2 ($g=2.0027$) coordinated carbon dangling bonds.[9] On the other hand, the ESR linewidth (ΔH_{pp}) and spin density (N_s) are varied over a wide range between 3–10 G and $10^{16}-10^{19}\ cm^{-3}$, which are slightly narrow and significantly low (at least by 1–2 orders) compared with many other reports,[1–17] respectively. The details are discussed in Figs. 1–3.

Figure 1 shows the dependence of ΔH_{pp} and N_s as a function of E_{Tauc}. Also shown, the E_{Tauc} as a function of fraction of sp^2 carbon (f_{sp^2}) and E_{Tauc} and E_{04} as a function of P_{rf} as insets of Figs. 1 and 3, respectively, for a quick reference. In brief, E_{Tauc} and E_{04} decreases with the increase of f_{sp^2} and P_{rf}. The behavior, which is very common, was also observed by many others,[3,4,8,9,13,14,22] and can well be explained on similar lines which was discussed in greater detail elsewhere.[20]

It is obvious from Fig. 1 that both the N_s and ΔH_{pp} decreases with increasing E_{Tauc} (decreasing f_{sp^2}). Further, the ΔH_{pp} varies in proportion (approximately) to the N_s except at the N_s being lowest. This contrasts with Ehrhardt *et al.*[14] and comparable with that found in ta-C:H[5] and a-C:H[13] by others. In more detail, the ΔH_{pp} decreases (9.84–7.46 G) with increasing E_{Tauc} (1.95–2.53 eV) below 2.6 eV (above 150 W) and increases (2.98–4.03 G) with

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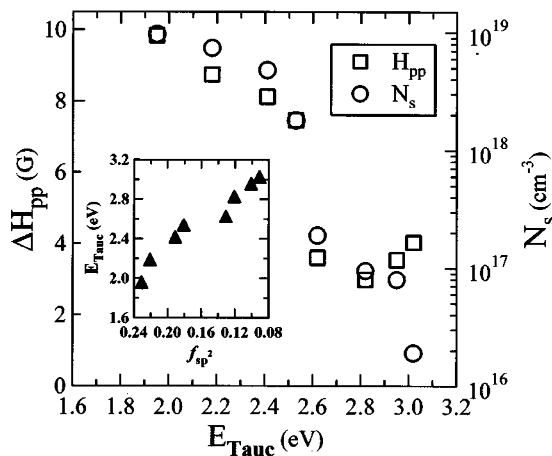

FIG. 1. The linewidth (left) and spin density (right) of rf PECVD grown a-C:H films as a function of optical gap. Inset shows the variation of optical gap with sp^2 fraction (note that the axis is reversed).

further increase of E_{Tauc} (2.82–3.02 eV) above 2.6 eV (below 100 W) followed by a continuous decrease of N_s.

A similar dependence of ΔH_{pp} on optical gap (above 1.9 eV but below 2.6 eV) was found in polymer-like a-C:H films by Schutte *et al.*[11] and they explained, in terms of exchange narrowing, that the spins are no longer localized but are able to tunnel to neighboring clusters. Also, their decrease in ΔH_{pp} was followed by a decrease in N_s. This should explain the decrease of ΔH_{pp} below 2.6 eV in our films as well. On the other hand, based on our observed g value tendency and relatively large H concentration[19,20] bonded to sp^3 site (also Fig. 2) which explains both the decrease of N_s and increase of ΔH_{pp} in the region above 2.6 eV (below 100 W) due to an increase in the hyperfine interaction with the protons. Our observations are consistent with the proposal of Bounouh *et al.*[10] Silva *et al.*[13] also found a similar trend around E_{Tauc} (above 2.6 eV) in their a-C:H films and even suggested that the present analyses may also explain the observed correlation or approximate linearity between N_s and ΔH_{pp}.

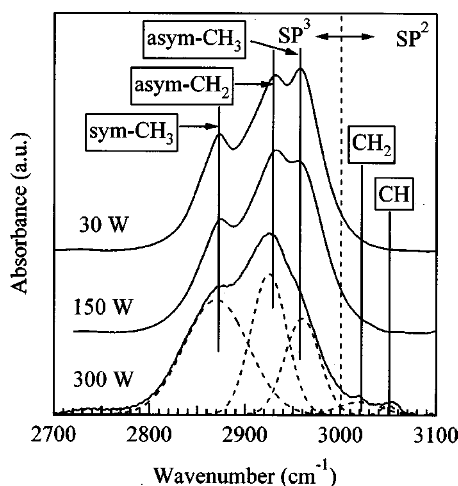

FIG. 2. The IR spectra of representative rf PECVD grown carbon films as a function of rf power. The spectra are deconvoluted (the curves with broken lines) into five significant contributions from various asymmetric (asym) and symmetric (sym)—C–H$_x$ vibration modes represent sp^3 and sp^2 carbon bonding network in the films. The gradual disappearance of 2960 cm^{-1} peak [(asym) sp^3-CH$_3$] and diminishing of others correspond to the sp^3-CH$_x$ vibrations with simultaneous appearance of sp^2-CH$_x$ modes (above 3000 cm^{-1}), with increase of rf power, not only indicate the direct role of structural changes for the increase of spin density as a function of rf power but also the dependence of spin density on the optical gap.

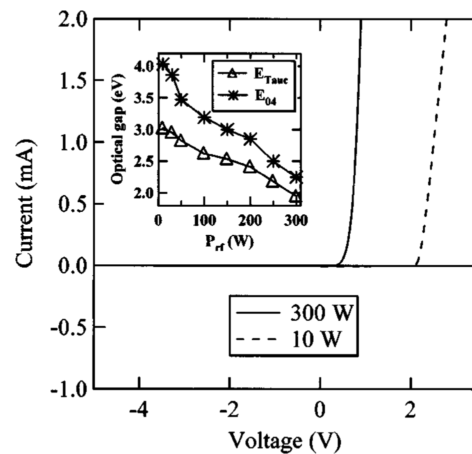

FIG. 3. The $I-V$ characteristics of the a-C:H/n-Si diodes, showing a perfect rectifying behavior. Inset shows the variation of optical gap [E_{Tauc} and E_{04} (the energy value at which the absorption coefficient assumes a value of 10^4 cm^{-1})] with rf power. The difference in the cutoff voltage between the two can well be explained based on the difference in the optical gaps of the two films deposited at different rf powers.

As mentioned above, the N_s decreases strongly with increasing E_{Tauc} (hydrogen rich and low f_{sp^2}). A similar behavior was observed by many others;[3,4,8,9,11–14] whereas a few others observed opposite.[5] However, not much analyses was made by any of those authors. The dependency may be considered linear, in a broad manner, considering all the points, however, a close look at the data points indicates a slight deviation from linearity. The films deposited with P_{rf} below 100 W reveal a sharp decrease in N_s (about an order) with gradual increase in E_{Tauc} (2.62–3.02 eV) as the P_{rf} decreases from 100 to 10 W. However, the change in the order of increasing N_s was observed to be relatively less (less than an order) for the samples deposited with P_{rf} above 150 W despite a relatively sharp and large decrease in the E_{Tauc} (2.53–1.95 eV) with increasing P_{rf} up to 300 W. And, also, there seems to be something important and interesting happening within a narrow range of 100–150 W because the N_s varies almost by an order, although the variation in E_{Tauc} is negligibly small ($2.62-2.53=0.1$ eV), which attracts further investigation. This region can be considered as a transition region ($2.5-2.6\pm0.05$ eV) for the films converting from the soft, polymer-like carbon with wide optical gaps ($>2.6\pm0.05$ eV) and low spin densities ($10^{16}-10^{17}$ cm^{-3}) to hard, diamond-like carbon with relatively narrow optical gaps ($<2.5\pm0.05$ eV) and high spin densities ($10^{18}-10^{19}$ cm^{-3}).

These results indicate increasing disorder and breaking of bonds in the films as a result of higher ion energy bombardment with larger P_{rf}, thereby either simultaneous increase of dangling bonds as there is little hydrogen available or attached to the carbon bonds to passivate or increase of π electron oriented sp^2 carbon double bonding. The analysis was well supported by the IR spectra (Fig. 2), where it was observed that the sp^3-C–H$_x$ vibration modes were diminished with simultaneous enhancement of sp^2-C–H$_x$ modes, significant for the films deposited with P_{rf} above 150 W, not only indicate the role of structural changes caused due to sp^3/sp^2 carbon bonding (also see insets of Figs. 1 and 3) for

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the increase of N_s with increasing P_{rf} but also demonstrate the sudden rise in N_s in the transition region (P_{rf} 100–150 W corresponding to E_{Tauc} 2.6–2.5 eV). Further, a more striking feature of these results is that the N_s obtained for the film deposited with 10 W is about $2\times10^{16}\,cm^{-3}$, the lowest N_s for the film deposited at RT by PECVD, which is comparable to high-quality a-Si:H and a quite promising reproducible result for future device applications.

It is worth mentioning here that unlike in the case of a-Si where the defect dangling states are passivated by the incorporation of hydrogen, carbon does not undergo the same completely due to its structural complexity—because hydrogen also plays an important role in determining the bonding network of the films. Moreover, sometimes, excess H_2 has adverse effects on the properties of carbon films in the sense that at smaller concentrations hydrogen appears to passivate the dangling bonds and increase the sp^3 carbon bonding, however, at larger concentrations sp^2 carbon bonding is preferably increased due to etching out of carbon by excess hydrogen (and/or larger P_{rf}) as is the case seen when we increased the hydrogen flow rate from 0 to 200 sccm.[19] It should be noted here that some (optimum) amount of hydrogen is essential and this would be in addition to the source gas, as it plays a crucial role in terms of structural changes[19,20] which in turn affect the properties such as N_s.

Finally, to realize the practical importance of these films, the films deposited on n-Si are subjected to the current–voltage ($I-V$) characteristics upon making proper front/back metal ohmic contacts.[23] Note that the intrinsic (undoped) a-C:H known to be weakly p type.[23] The $I-V$ characteristics shown in Fig. 3 clearly reveal a perfect rectifying nature of the a-C:H/n-Si diodes. The difference in the cutoff voltage between the two can well be explained based on the difference in the optical gaps of the two films deposited at different rf powers. A more detailed analysis can be obtained from the capacitance–voltage measurements and work on these lines is in progress.

In summary, we have investigated the density of electronic defect states in rf PECVD grown amorphous carbon films and obtained high-quality films with the spin density in the order of $10^{16}\,cm^{-3}$ for the film deposited with 10 W, at room temperature, a very promising result which is reproducible and comparable with device quality a-Si:H. There is a strong dependence of ESR spin density and linewidth on the optical gap and also exists a correlation between the former two. The results merit possible technological importance of these films for device application.

This work was supported by the Japan Society for the Promotion of Science under the program ''Research for the Future.''

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