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Interstitial molecular hydrogen and deuterium in PECVD and HW amorphous silicon

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Abstract

For many years it has been known that high quality plasma-enhanced chemical vapor deposition (PECVD) hydrogenated amorphous silicon contains small quantities (≤ 100 ppm) of molecular hydrogen in microvoids. More recently it has been demonstrated that there exist major (10–40%) molecular hydrogen populations singly trapped as interstitials in the amorphous equivalents of tetragonal T sites of the a-Si network. Comparative NMR studies have shown that a substantial fractional molecular hydrogen population residing in T sites correlates well with high photovoltaic quality as measured by film's mobility–lifetime product $\eta\mu\tau$. Now our current NMR measurements have turned to ^1H – ^{29}Si double resonance experiments in hot wire amorphous silicon films (HW a-Si:H). Our HW a-Si:H films have been provided by Schropp and Branz and the PECVD films by Paul. The HW films show several resolved proton NMR components at 80 and 300 K. These components include a narrow line arising from molecular hydrogen resident in T-like sites and perhaps also in voids. A second broader line reflects clusters of Si-bonded H. A third superbroad (~ 80 kHz FWHM) line also is present as is a diamagnetically shifted feature. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In hydrogenated amorphous silicon films made either by plasma-enhanced chemical vapor deposition (PECVD) [1] or by hot wire chemical vapor deposition (HWCVD) [2] there are rich arrays of structures for contained hydrogen. These are now known to include substantial populations of molecular hydrogen singly trapped in the amorphous

equivalents of interstitial tetragonal T sites. These T site hydrogen molecules may be the mobile species required to understand the film dynamic responses to photoillumination and to dark anneal. In addition to these hydrogens the HWCVD films also include proton NMR features not seen so far in PECVD films. These include a narrow line arising from trapped H_2 and whose width and shift depend on film orientation in the magnetic field [3], a superbroad proton line some 80 kHz FWHM, and a proton resonance component shifted diamagnetically by 25 ppm [4].

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2. Experimental procedures

Proton, silicon, and deuteron NMR (DMR), have been employed at dc fields between 8.5 and 4.7 T to examine silicon-bonded hydrogen and molecular hydrogen (H_2 , HD, and D_2) in PECVD and HWCVD amorphous silicon films. The PECVD films were prepared in William Paul's laboratories at Harvard. The HWCVD films were provided by Schropp's group at Utrecht and by Branz and Xu at NREL [4].

It has long been known that even high quality PECVD a-Si:H has ≤ 100 ppm molecular hydrogen trapped in microvoids. These H_2 include 'effectively dilute' relaxation center *ortho*- H_2 molecules for which the intermolecular EQQ interaction has been quenched by crystal fields from the internal surfaces of the voids [5]. So then the temperature dependences of the spin-lattice relaxation times T_1 , for various hydrogen components reflect spin diffusional relaxation to these individual relaxation center H_2 .

However, it has now been shown [6] that there also exist 10–40 at.% molecular hydrogen trapped as interstitials in the amorphous equivalents of tetragonal T sites in the a-Si lattice. This large population of molecules also has been shown for D_2 and HD in a-Si:H, D and for D_2 in deuterated single crystal n-type Si [7].

3. Results

First we have examined the deuteron magnetic resonance (DMR) line shape at 80 K in a perdeuterated amorphous silicon film, H579, a-Si:D. With a $90_x-\tau-90_y$ solid echo pulse sequence at a long pulse sequence repetition delay of 1000 s, the line shape from the solid echo at 2τ shows (Fig. 1(a)), the characteristic 66 kHz Si-D doublet from Si-bonded D. There is also a modest central feature which primarily reflects $I = 1$ *para*- D_2 molecules trapped in tetragonal T sites. When the radiofrequency pulse sequence is modified to $90_x-\tau-45_y$ (Fig. 1(b)), the Si-D 66 kHz doublet decreases by a factor of two, so the lower 1b panel is plotted with twice the vertical scale of 1a in order to bring the Si-D doublets back into equality.

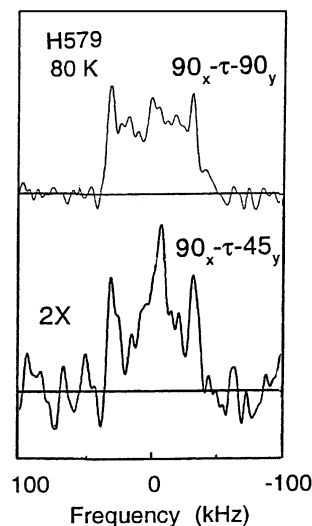


Fig. 1. The use of a $90_x-\tau-45_y$ solid echo sequence selects the signal arising from $I = 2$ *ortho*- D_2 molecules. The repetition interval pulse delay for both sequences is 1000 s.

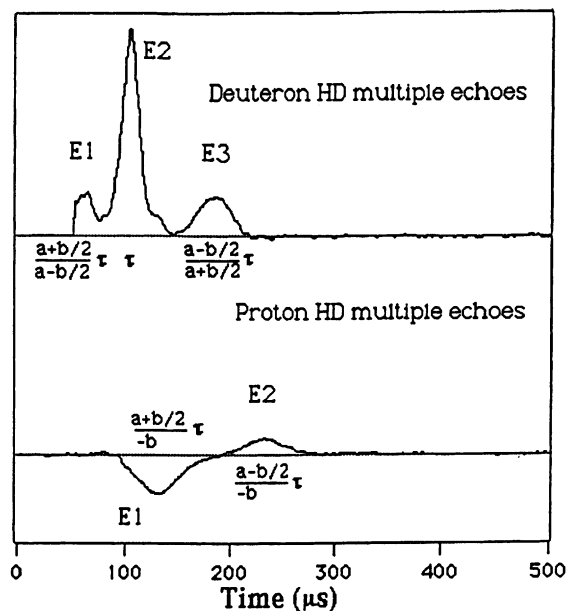


Fig. 2. (a) Deuteron HD multiple echoes generated by a $90_x^D-\tau-90_y^D$ pulse sequence and (b) proton HD multiple echoes created by the corresponding three pulse coherence transferring sequence: $90_x^D-\tau-90_y^D-t_w-90_y^H$ for film H541 at 20 K. Here t_w is the pulse width of the second deuteron pulse and $\tau = 100 \mu\text{s}$ for both of the pulse sequences.

In Fig. 1(b) then one now sees an enhanced narrow central feature arising from T-site-trapped $I = 2$ *ortho*-D₂ molecules. The *ortho*-D₂ have a longer spin–lattice relaxation time T_1 than the *p*-D₂, but in a fully relaxed situation one expects the central *ortho*-D₂ signal to be five times larger than that from *p*-D₂.

Next we examine HD multiple echoes in a high quality PECVD a-Si:D, H film H541 at 20 K. Here molecular HD trapped in interstitial T sites manifests itself in DMR by molecule-specific HD deuteron multiple echoes (Fig. 2(a)), generated from a $90_x^D - \tau - 90_y^D$ rf pulse sequence, and also by proton HD multiple echoes created by a three pulse coherence transfer sequence $90_x^D - \tau - 90_y^D - t_w - 90_y^H$. The occurrence times for the proton HD echoes depend on τ and on the specific indicated combinations of the molecular parameters a and b [8].

Now the proton HD multiple echoes decrease with increasing τ at a rate which reflects primarily

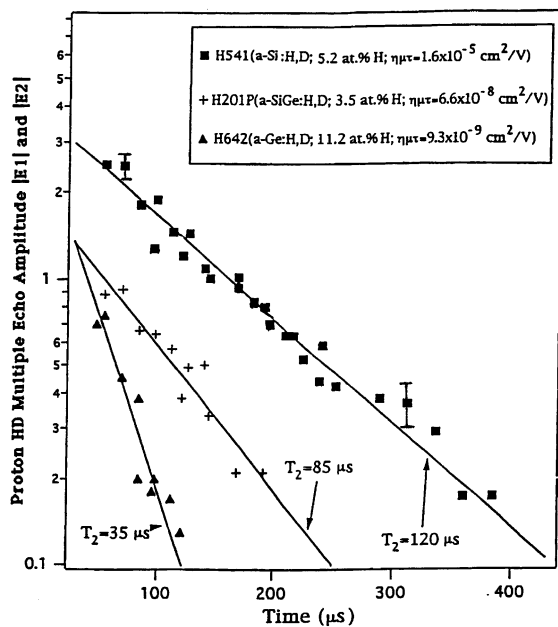


Fig. 3. Plots of the proton HD multiple echo amplitude $|E1|$ and $|E2|$ as a function of the time between the proton pulse and the positions they occur. The differences in T_2 reflect the differences of hydrogen clustering around HD molecules in each film.

the proton clustering around the HD-occupied T sites. This clustering in turn depends upon the photovoltaic quality of the film, as indicated by its mobility–lifetime product $\eta\mu\tau$. In Fig. 3 one sees that the proton HD multiple echoes live longer for a-Si:D, H film H541 with $\eta\mu\tau = 1.6 \times 10^{-5} \text{ cm}^2/\text{V}$, although the H541 5.2 at.% H concentration is larger than the 3.5 at.% H for a-SiGe:D, H film H201, with a poor mobility-lifetime product $\eta\mu\tau = 6.6 \times 10^{-8} \text{ cm}^2/\text{V}$. Good quality films have less hydrogen clustering near HD-occupied T sites.

Next we have turned to proton NMR and to ^1H – ^{29}Si double resonance studies in hot wire HWCVD films provided by Schropp (our S45) and by Branz and Xu (our B42). Because of different preparation conditions [4], film B42 contains about 6% of the H content of film S45. Nevertheless both films show at least four reproducible and resolved HW a-Si:H proton NMR components visible in Figs. 4 and 5. Both films have a sharp narrow central line [3] here powder-averaged to $\sim 3 \text{ kHz}$ FWHM. This component will be shown to include the T-site-trapped molecular H_2 observed [6] in standard high quality PECVD films.

Both films also show in the Fourier transform (FT) of free induction decay (FID) transients following a $1.9 \mu\text{s}$ $\pi/2$ proton pulse, a characteristic superbroad line with $\text{FWHM} \geq 80 \text{ kHz}$. This resonance component damps so quickly that it is

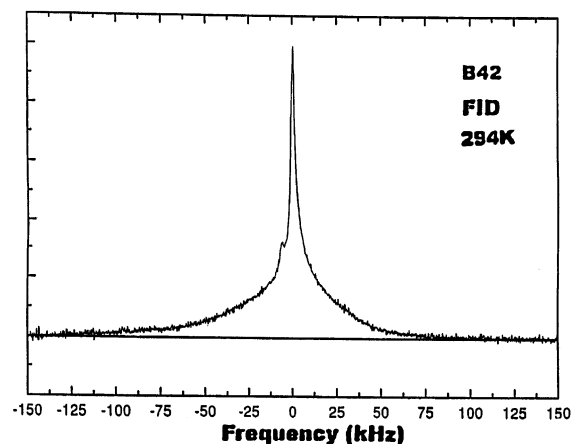


Fig. 4. Room temperature proton spectrum in HW a-Si:H film B42 from transform of 400 summed free induction decays following $\pi/2$ pulses.

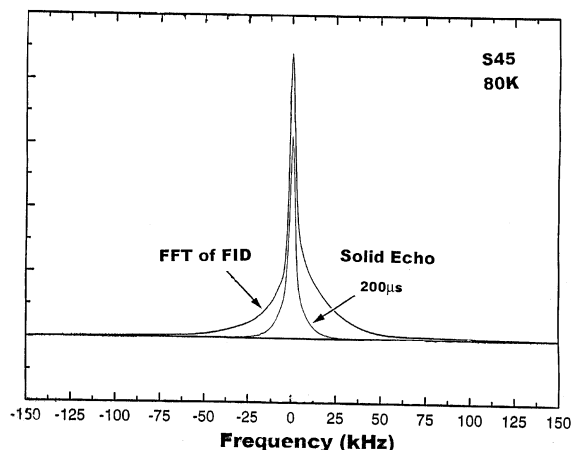


Fig. 5. 80 K proton spectra in HW a-Si:H film S45. The FID spectrum is from 400 summed decays following $\pi/2$ pulses. The solid echo spectrum is the transform of the summed echo in 400 two pulse sequences with pulse separation $\tau = 200 \mu\text{s}$.

difficult to study with two pulse spin echo sequences, even with τ as short as $30 \mu\text{s}$. In Fig. 5 the solid echo transform for $\tau = 20 \mu\text{s}$ shows just the familiar narrow Lorentzian line and the 24 kHz Gaussian from clustered SiH [6]. Both films show, just to the left of the central narrow peak in the FID transforms, a distinguishable proton resonance feature which is diamagnetically shifted to lower frequency by about 5 kHz, or 25 ppm. This feature is not present when we run an empty coil as a control.

Fig. 6 shows that at least some of the T-site-trapped H_2 in a HW a-Si:H film has spin interac-

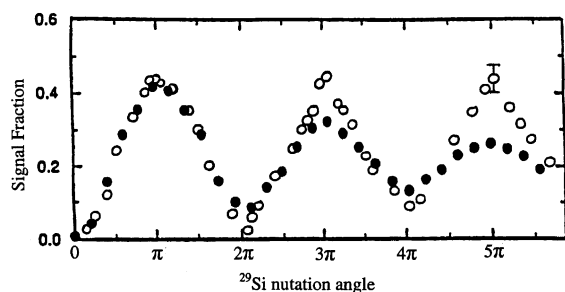


Fig. 6. Proton difference signals at 80 K and $\tau = 400 \mu\text{s}$ induced by various ^{29}Si nutations in films PECVD a-Si:H H538 (open circles) and HW a-Si:H S45 (solid circles).

tions with nearby ^{29}Si similar to those found in high quality PECVD a-Si:H. The abscissa of Fig. 6 is the ^{29}Si nutation angle in a double resonance $^1\text{H}/^{29}\text{Si}$ proton echo experiment. The ordinate is the difference signal at 80 K with and without a ^{29}Si pulse immediately following the last proton pulse. The data points include solid dots, which reflect a proton two pulse solid echo with $\tau = 400 \mu\text{s}$ in HW a-Si:H film S45. The open circles reflect our earlier reported [6] results at 80 K in PECVD a-Si:H H538 where the ^{29}Si pulse followed the third proton pulse in a proton stimulated echo sequence. Both experiments show an approximately 42% response to a ^{29}Si π pulse 5% from clustered Si:H and 38% from near ^{29}Si neighbors to T-site-trapped H_2 [6]. It is to be noted that at $\tau = 400 \mu\text{s}$ the proton echoes are significantly diminished by an envelope T_2 . One cannot improve on this by going to very short τ proton pulse intervals, because it takes about $200 \mu\text{s}$ for the proton precession to reaccumulate in a new shifted local field when a nearby ^{29}Si spin is inverted.

4. Discussion

In HWCVD a-Si:H proton NMR line shapes present a variety of species. The 24 kHz broad Gaussian line is present from clustered Si-H. The ~ 3 kHz Lorentzian line including T-site-trapped molecular H_2 also is present, but there is evidence [3] of co-ordinated geometry of these occupied T sites. We have not yet solved the structural problems presented by the superbroad ≥ 80 kHz line nor by the diamagnetically shifted feature visible in transforms of the free induction decays at room temperature or 80 K.

Additional HWCVD samples are being investigated to resolve the differences in structure compared to PECVD a-Si:H. The measurements include a variety of hole-burning experiments.

5. Conclusion

Interstitial molecular hydrogen is abundantly trapped in the amorphous equivalent of tetragonal

T sites in hot wire PECVD hydrogenated amorphous silicon, just as is the case in non-hot wire films. The exact geometry of these T site assembly remains undetermined. We are examining ways to extend ^1H – ^{29}Si double resonance investigations of HWCVD a-Si:H or to do DMR studies of deuterated HW films, if they can be provided.

Acknowledgements

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