Direct Experimental Evidence for Molecular Hydrogen in Amorphous Si:H

H. v. Löhneysen and H. J. Schink
Zweites Physikalisches Institut der Rheinisch-Westfälischen Technischen Hochschule,
D-5100 Aachen, West Germany

and

W. Beyer
Institut für Grenzflächenforschung und Vakuumphysik der Kernforschungsanlage Jülich,
D-5170 Jülich, West Germany

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Molecular hydrogen in amorphous Si:H films prepared by glow discharge is detected calorimetrically at low temperatures from the heat release associated with the ortho-to-para conversion. The H_2 concentration is much higher in samples prepared at 250 °C (6.4×10^{19} cm^{-3}) than in those prepared at room temperature (2.4×10^{18} cm^{-3}). These results support a recent model of ^1H nuclear spin relaxation via interaction with H_2 molecules in *a*-Si:H and, in addition, give new insight into the structure of *a*-Si:H.

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Despite the technological importance of amorphous Si:H, many unsolved problems still remain with regard to the structural and electronic properties. Recently, proton NMR measurements have been employed in order to elucidate the spatial distribution of H in *a*-Si:H.[1,2] A particularly interesting feature is the observation of a minimum in the longitudinal ("spin-lattice") relaxation time T_1 as a function of temperature around 30 K.[12] Originally[2] it was proposed that this minimum arises from disorder modes, i.e., low-energy tunneling states common to amorphous solids,[3] involving the motion of hydrogen between two equilibrium positions. While the density of these excitations in tetrahedrally bonded amorphous semiconductors is about an order of magnitude smaller than in vitreous silica,[4,5] presumably because of the overconstrained rigid network of *a*-Si and *a*-Ge, it is possible that hydrogen-rich *a*-Si:H samples support these excitations,[5] as in this case the network is much less rigid.

An alternative explanation[6] of the T_1 minimum has been proposed, namely that the proton spin relaxation is due to a few *o*-H_2 molecules whose spins are relaxed rapidly by modulation of the intramolecular dipolar interaction due to rotational motion. Relaxation of the remaining majority of nuclear spins occurs by spin diffusion to these molecules. The observation of an increase of T_1 after prolonged waiting at low temperatures is in agreement with this model.[7] In order to test this model, a direct determination of the H_2 content of *a*-Si:H with different preparation and annealing temperatures would be highly desirable. Unfortunately optical detection of H_2 molecules is difficult because only about 1% of the hydrogen in *a*-Si:H is estimated[6] to be molecular. Furthermore, H_2 could not be detected by NMR measurements.[7] We therefore chose to detect H_2 calorimetrically by means of the ortho-to-para conversion. In our experiment, the sample is coupled weakly to a cold source and the heat release associated with the *o-p* conversion causes a temperature difference between sample and cold source which can be easily measured.

The *a*-Si:H samples were prepared by rf glow discharge (anode grounded) of undiluted SiH_4 at a pressure of 0.4 mbar and a flow rate of 6 cm^3 (at STP) min^{-1}; rf power was ≈4 W (capacitively coupled), and the growth rate was 1.5 Å/s. Sample masses were ≈10 mg. The samples were grown on single-crystalline Si plates (polished to optical flatness for sample 1 and unpolished for sample 2). They were attached together with the substrate to a calorimeter[8] which was thermally coupled by nylon threads to the mixing chamber of a dilution refrigerator.

The minimum temperatures $T_{\rm min}$ of the calorimeter obtained with the samples are listed in Table I (further details about the samples are also given there). They are appreciably higher than the temperature $T_{\rm mc}$ of the mixing chamber which was always kept at ≈30 mK, and also higher than $T_{\rm min}$ for the empty calorimeter (ec) as measured in two independent runs, hinting at a considerable heat release $\dot{Q}$ within the *a*-Si:H samples which strongly depends on the deposition (T_s) and annealing temperatures (T_a), see Table I. The observation that $T_{\rm min} > T_{\rm mc}$ already for the empty calorimeter can of course be attributed to parasitic heat inputs $\dot{Q}_p$ of the

TABLE I. Sample characterization and experimental results for *a*-Si:H (the symbols are explained in the main text).

Sample	T_s (°C)	T_a (°C)	C_{H} (at.%)	N_s (10^{17} cm^{-3})	t (h)	T_{min} (mK)	$\dot{Q}$ (10^{-10} W)	n_{H_2} (10^{19} cm^{-3})
ec run 1	···	···	···	···	30	71	0.34	···
ec run 2	···	···	···	···	30	74	0.38	···
1*a*	25	···	35[a]	37[b]	30	96	0.79	0.24
1*b*	25	210[c]	35[a]	1.7[b]	30	97	0.81	0.29
2*a*	250	···	16[a]	2.6[b]	30	261	11.1	6.4
2*a*	250	···	16[a]	2.6[b]	56	232	8.1	6.4
2*a*	250	···	16[a]	2.6[b]	126	189	4.8	6.4
2*b*	250	400[c]	14[a]	3.7[b]	30	360	25.6	17.7

[a] From H evolution studies.

[b] From ESR measurements.

[c] Annealing was done for 10 min in argon.

order of 40 pW.[9] Keeping the *a*-Si:H samples at low temperatures (≤ 4.2 K) for considerable times t results in a decrease of T_{min} and hence of $\dot{Q}$ (see Table I, where t denotes the time elapsed after the first introduction of liquid nitrogen into the refrigerator).

We suggest that the heat current $\dot{Q}-\dot{Q}_p$ is due to conversion of o-H$_2$ to p-H$_2$ in the *a*-Si:H samples, i.e., $\dot{Q}-\dot{Q}_p = q\,dN_0/dt$ where $q = 2.35\times10^{-21}$ J is the energy difference between o and p states of the H$_2$ molecule[10] and N_0 is the number of o-H$_2$ molecules in the sample. A possible time-dependent heat leak due to slowly relaxing tunneling states[11] is estimated to be several orders of magnitude smaller even if all the excess specific heat observed in *a*-Si:H[5] is attributed to tunneling states.

The heat current $\dot{Q}$ from the calorimeter to the mixing chamber (see Table I) is calculated from

$$\dot{Q} = \int_{T_{\mathrm{mc}}}^{T_{\mathrm{min}}} K(T)\,dT,$$

where $K(T)$ is the thermal conductance of the weak link. $K(T)$ can be experimentally determined from the thermal relaxation time $\tau_{\mathrm{th}} = C/K$ where C is the heat capacity of the empty calorimeter. We find $K = aT^n$ with $a = (9.5\pm1)\times10^{-8}$ W/cm$\cdot$K^{n+1} and $n = 1.6\pm0.1$, in good agreement with K for nylon as determined from direct thermal conductivity measurements.[12]

In the following we will first discuss possible o-H$_2$ to p-H$_2$ conversion mechanisms in *a*-Si:H as can be inferred from the time dependence of $\dot{Q}$ or dN_0/dt, and thereafter the dependence of the H$_2$ content on deposition and annealing temperatures and the implications for the structure of *a*-Si:H. The time dependence of dN_0/dt as determined with sample 2*a* is shown in Fig. 1. The experimental data are compatible with either a catalytic conversion (first-order reaction), i.e., $dN_0/dt = -\tau^{-1}N_0(0)\exp(-t/\tau)$ with $\tau = 105$ h (this would yield a straight line in Fig. 1), or with an autocatalytic conversion, i.e.,

$$dN_0/dt = -N_0(0)kx_0^2(1+x_0kt)^{-2}$$

with $k = 0.010$ h^{-1} (cf. solid line in Fig. 1). Here x_0 denotes the molar fraction of o-H$_2$ in H$_2$. Note that the decay of dN_0/dt cannot be represented by an autocatalytic conversion with $k = 0.019$ h^{-1} which occurs in solid H$_2$[10,13] and which would yield the dashed line in Fig. 1.

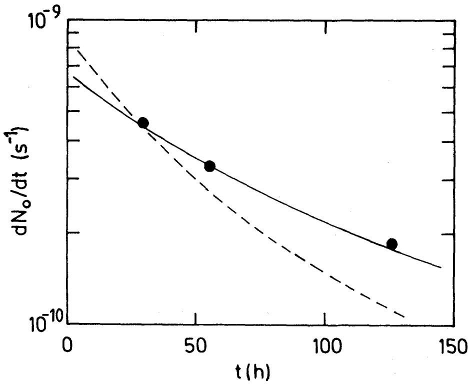

FIG. 1. Conversion rate dN_0/dt of the o-H$_2$ molecules (as determined from the heat leak of sample 2*a*) as function of time t. Solid line indicates dN_0/dt for autocatalytic conversion with $k = 0.010$ h^{-1}, dashed line is for $k = 0.019$ h^{-1}.

An exponential decrease of N_0 would suggest that the o-p conversion occurs on isolated H_2 molecules. It is unlikely that electron spins catalyze the conversion because dN_0/dt for samples 1a and 1b is almost equal while the spin densities differ by more than an order of magnitude (see Table I). This change in spin density upon annealing would have to be canceled by a large increase of the H_2 concentration which is hard to believe because a-Si:H is permeable to H_2 when deposited at room temperature and annealed below ≈200 °C.[14] Another (speculative) possibility is that the conversion takes place via exchange with atomic hydrogen which is present at rather large densities in a-Si:H. More likely, however, is an autocatalytic conversion which can occur in a-Si:H if H_2 molecules agglomerate in microvoids. Indeed, these are known to exist in a-Si:H prepared under various conditions.[15,16] Independent evidence for such a conversion mechanism comes from the proton-spin relaxation study of Carlos and Taylor[7] who showed that the T_1 minimum around 30 K increases linearly with time. This is expected if o-H_2 molecules which autocatalytically convert to p-H_2 serve as relaxation centers. From these measurements $k = 0.010$ h^{-1} is inferred in very good agreement with our value. The difference from the k value observed in bulk solid H_2 can be attributed to three factors: First, the average coordination number of H_2 clusters in voids can be considerably reduced when many "surface" molecules are present, with respect to the coordination number 12 for bulk solid H_2. This, of course, leads to a decrease of the conversion rate. Second, the conversion rate in solid H_2 is strongly dependent on the lattice constant.[17] Third, the phonon spectrum is shifted to lower frequencies for small clusters as compared to bulk solids; this is also expected to decrease the conversion rate.[18]

For an estimate of the H_2 content n_{H_2}, we assume the same conversion constant k for all a-Si:H samples. We obtain (using $\rho = 1.5$ g/cm^3 for sample 1 and 2.1 g/cm^3 for sample 2[19]) $n_{H_2} = 2.4 \times 10^{18}$ cm^{-3} for sample 1 and 6.4×10^{19} cm^{-3} for sample 2, i.e., the fraction of hydrogen in molecular form (with respect to the total hydrogen amount) is only 0.04% for the room-temperature–deposited film, and 1.6% for the film prepared at 250 °C. Note that the n_{H_2} for sample 1 corresponds to only 2×10^{16} H_2 molecules, indicative of the method's sensitivity. The latter percentage compares very well with the 1% estimate of Conradi and Norberg[6] for the amount of H_2 needed to explain the NMR data[2] on an a-Si:H film prepared at elevated temperatures. While n_{H_2} increases by annealing only slightly (within the error margin) for sample 1, there is a strong increase, by a factor of 3, for sample 2 (see Table I). Again, this increase corresponds nicely to the decrease of the T_1 minimum by a factor of about 2 upon annealing of a 33 °C-deposited sample at 450 °C.[7] Our independent determination of the H_2 content in a-Si:H films (as deposited and annealed) therefore lends strong support to the Conradi-Norberg model.

As a final point, we will interpret our data, in particular the striking difference of H_2 content between samples 1 and 2, in terms of a structural model which is based on recent results of hydrogen evolution experiments.[14] These studies indicate for a-Si:H films deposited at $T_s < 150$ °C a relatively open, void-rich structure allowing for rapid diffusion of molecular hydrogen at rather low temperatures. This structure is hardly changed upon moderate annealing ($T_a \lesssim 200$ °C). For higher substrate temperatures, on the other hand, the data suggest the growth of a more compact material not permeable for hydrogen molecules. Accordingly, molecular hydrogen, when incorporated in the film during deposition or when formed by annealing, will effuse readily for low-T_s films while it will be trapped in the material for high-T_s a-Si:H. The evidence for an autocatalytic conversion as discussed above provides support for the hypothesis that voids which can accomodate H_2 clusters are present even in high-quality a-Si:H prepared at elevated temperatures.

In conclusion, we have provided independent evidence for the presence of molecular hydrogen in a-Si:H, which was previously only indirectly inferred from NMR measurements. We predict that the proton-spin-lattice relaxation time in room-temperature–deposited samples should exhibit no minimum near 30 K because of the very small H_2 concentration. The dependence of the H_2 concentration on deposition and annealing temperatures supports current structural models of a-Si:H.

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