SPIN EQUILIBRATION IN HYDROGEN DEPLETED AMORPHOUS SILICON †

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Equilibration of the spin density in hydrogenated amorphous silicon (a-Si:H) following thermal quenching was measured in as-deposited and hydrogen-depleted specimens. The behavior in the depleted specimens was comparable to that for as-deposited specimens: the thermal activation energy for the equilibration time is 1.6 eV, and equilibration times are approximately proportional to the spin density. A hydrogen-mediated model for equilibration is presented.

1. INTRODUCTION

The dream of defect research in a-Si:H is surely to achieve a unified description of three major defect phenomena: (i) The origin of defects in deposition processes, (ii) The metastable increase in density which occur with illumination, carrier injection, and thermal quenching, and (iii) The changes in density which occur when hydrogen is removed or replaced from the material.

The metastabilities of a-Si:H in its as-deposited state have been extensively studied in the last fifteen years. Relatively recently it has become clear that “equilibration” — that is, the return to a state of relative thermal equilibrium following illumination, thermal quenching, etc. — shows features which are well correlated with certain aspects of hydrogen diffusion.1–4 The obvious inference from these correlations is that hydrogen mediates the defect phenomena listed above.

It is reasonable to ask whether these hydrogen-mediated models are fertile — that is, whether they can predict phenomena which were unknown when the models were formulated. Defect phenomena in hydrogen-depleted a-Si:H may provide this test. In recent work5,6 we have shown that the equilibrium spin density and its temperature-dependence in hydrogen-depleted a-Si:H were predicted by a relatively simple “hydrogen-deficit” model, which assumes that the equilibrium state of varying samples of a-Si:H can be predicted essentially from knowledge only of the number of unoccupied (or deficient) hydrogen bonding sites in the material.

Here we shall present our measurements of spin equilibration in hydrogen-depleted a-Si:H. The measurements extend the range of previous work on equilibration in as-deposited specimens of widely varying quality. We find that equilibration in hydrogen-depleted a-Si:H broadly supports the principal conclusions obtained in the earlier work. Equilibration times at constant temperature are proportional to the spin density of the material. Equilibration times for a given specimen are thermally activated with an activation energy of 1.6 eV. We present a model for hydrogen-mediated equilibration which predicts these features.

2. MEASUREMENTS

We prepared a thickness series of a-Si:H specimens using plasma decomposition of pure silane gas and a substrate temperature of 250°C (13.56 MHz excitation frequency, Plasma Technology, Inc. “Plasmalab” reactor.) For the as-deposited specimens we found an interfacial spin density of 2 × 10¹² cm⁻³ and a bulk density of 1.0 × 10¹⁷ cm⁻³ at 500 K. Two groups of specimens were then annealed at 500 and 550°C; this treatment is known to evolve hydrogen from a-Si:H. At various

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Decay of excess spin density following fast cooling to the indicated temperature from an elevated temperature (300°C as-deposited, 500°C hydrogen-depleted).

Times in the treatment the specimens were cooled to room temperature, and the spin density measured. We found that the 2.2 μm thickness specimen had a reasonably homogeneous spin density following about 50 hours of annealing. We discuss the equilibration measurements done for the as-deposited and depleted specimens of this thickness here. Further details are presented elsewhere.

In Fig. 1 we have shown as the upper section the decays of the excess spin density obtained by quenching the specimen temperature from 300°C to the indicated temperatures. The excess spin density ΔN_s(t) was defined as ΔN_s(t) = N_s(t) - N_s(t_{max}), where t_{max} was the longest time shown on the figure. The data shown are the normalized values ΔN_s(t)/ΔN_s(0), where the value of the spin density at 300°C in equilibrium was used to estimate ΔN_s(0).

Spin densities were measured by quenching the specimen temperature to room-temperature, conducting the density measurement, and returning to the indicated annealing temperature. This procedure agreed well with in situ spin density measurements when both were possible. In the lower section of the figure we show the decay of the excess spin density in the hydrogen-depleted specimen (500°C series) following quenching from 500°C. These quenching treatments were reversible, and we checked reproducibility of the data in several cases.

The spin density at the longest times shown were used to estimate an equilibrium spin density as a function of temperature. These data are presented in Fig. 2. Note that the spin density is thermally activated. The activation energy for the undepleted specimen was about 0.30 eV, which is comparable to other reports in undepleted specimens with spin densities up to about 10^{17} cm^{-3}. The hydrogen-depleted specimens show a reduced activation energy; this effect was predicted by a hydrogen-deficit model, as described in more detail elsewhere.

An equilibration time can be defined from the relation ΔN_s(t) = e^{-1}ΔN_s(0). Previous discussion of equilibration has also addressed the “stretched-exponential” form for ΔN_s(t); we have not addressed this aspect of the decays. In Fig. 3 we present some measurements of the equilibration time as a function of reciprocal temperature 1000/T; the activation energy obtained from these measurements was 1.6 eV.

These measurements can be compared with previous work on equilibration in as-deposited specimens of
3. EQUILIBRATION MODEL

In this section we present a short calculation of the equilibration time $\tau_e$ based on the assumption that equilibration is mediated by a small density $n$ of energetically excited, mobile hydrogen atoms; these are presumably hydrogen atoms occupying unbounded or interstitial sites in the amorphous silicon network. We discuss the observations that $\tau_e$ is proportional to the spin density, and that $\tau_e$ and the diffusion constant have related thermal activation energies and other properties.

To construct the model we use the "hydrogen deficit" picture we have described elsewhere. The spin density is attributed to unoccupied sites of the dilute phase of hydrogen found in NMR. However, in this model spin densities are normally small compared to the density of unoccupied sites in a clustered phase; these latter "C-sites" do not contribute to the spin density or to the mid-gap defect density because they have a "negative hydrogen correlation energy" property.

The rate equation for the spin density $N_s$ may be written:

$$\frac{dN_s}{dt} = (N_D - N_s)e - nbN_s \ ,$$  \hfill (1)

where $N_D$ is the density of dilute-phase sites ($D$-sites) and $n$ is the density of mobile hydrogen atoms. $e$ is the emission rate for hydrogen from an occupied $D$-site, and $b$ is the capture rate of a $D$-site. We shall neglect throughout this discussion the potentially important effects of the distribution of emission times for the hydrogen bonding sites.

When equilibration is complete, the spin-density and interstitial densities are related by the steady-state solution of (1):

$$N_{s,e} = N_D \frac{e}{e + nb} \ .$$  \hfill (2)

We now reach a crucial issue. After the spin density and the interstitial density have equilibrated, there is no experimental evidence for further time-dependence in $N_{s,e}$. We conclude, using eq. (2) that $n$ itself is also time-independent following equilibration. This result is
most easily justified if \( n \) equilibrates with the \( C \)-phase more rapidly than \( n \) equilibrates with the \( D \)-phase (and \( N_s \)). We also know from examination of the equilibrium solutions to this model\(^5\) that the equilibrium values for both \( n \) and \( N_s \) are primarily determined by the density of unbonded sites in the \( C \)-phase.

We shall therefore neglect the time-dependence of \( n \) in solving (1), assuming instead that it has already attained its final equilibrium value prior to equilibration of \( N_s \). We rewrite (1) in terms of the deviation \( \Delta N_s(t) \equiv N_s(t) - N_{s,e} \):

\[
\frac{d\Delta N_s(t)}{dt} = -(e + nb)\Delta N_s(t) \quad .
\]

To further evaluate this expression, we note that the density of spins \( N_s \) is much less than the density \( N_D \sim 2 \times 10^{21} \text{cm}^{-3} \) of dilute phase sites. Inspection of equation (2) above then yields \( nb \gg e \).

To treat the relationship of equilibration and diffusion, we note that the capture rate \( b \) of a spin for an interstitial hydrogen is surely diffusion limited: \( b = 4\pi D_i r_D \).\(^\text{7,8}\) Here \( D_i \) is an interstitial diffusion coefficient and \( r_D \) is the capture radius of the spin. Diffusion limitation must be used to describe capture when the "mean free path" of hydrogen motion is less than or comparable to the capture radius. Using this expression we obtain:

\[
\frac{d\Delta N_s(t)}{dt} = -(4\pi r_D)n D_i \Delta N_s(t) \quad .
\]

Since \( nD_i \) is plausibly proportional to the hydrogen diffusion coefficient \( D_H \), this equation is very similar to the phenomenological relation originally suggested by Kakalios, et al.\(^1,2\)

\[
\frac{d\Delta N_s(t)}{dt} \propto -D_H(t)\Delta N_s(t) \quad ,
\]

where the hydrogen diffusion coefficient \( D_H(t) \) is known to be "dispersive" or time-dependent.\(^1\) Equation (5) was proposed to rationalize the stretched exponential form for equilibration, and for the similarity of the activation energies of \( D_H \) and the equilibration time. However, we have only been able to establish equation (5) under the condition that the time-dependence of \( D_H(t) \) is attributed solely to time-dependence of \( D_i \); we have treated \( n \) as a constant. Other models do not make this assumption.

We next address equilibration for materials with varying spin density. We use the hydrogen chemical potential \( \mu_H \) to describe the equilibrium values of \( N_s \) and \( n \). In particular we assume that \( \mu_H \) lies below \( \xi_i \), the energy level associated with interstitial hydrogen, and that \( \mu_H \) lies above \( \xi_D \), the energy level associated with dilute phase hydrogen. Then we can write the densities \( N_{s,e} \) and \( n \) using Boltzmann statistics as:

\[
N_{s,e} = N_D \exp(-{\mu_H - \xi_D}/k_BT) \quad ,
\]

\[
n = n_i \exp(-{\xi_i - \mu_H}/k_BT) \quad ,
\]

where \( n_i \) is the effective density of interstitial sites. Multiplying these expressions yields a "mass-action" expression:

\[
n N_{s,e} = n_i N_D e^{-({\xi_i - \xi_s})/k_BT} \quad .
\]

We obtain by substitution:

\[
\frac{d\Delta N_s(t)}{dt} = -\frac{bn_i N_D e^{-({\xi_i - \xi_s})/k_BT}}{N_{s,e}} \Delta N_s(t) \quad .
\]

Inspection of this equation shows that equilibration is proportional to \( N_{s,e}^{-1} \).

4. REFERENCES