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DENSITY OF STATES STUDY IN SPUTTERED a-Si:H : EFFECT OF IMPURITIES AND H RELATED DEFECTS

P. Viktorovitch*, G. Moddel, J. Blake, S. Oguz, R.L. Weisfield and W. Paul

Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

Abstract.- We observe two regimes in the variation of gap size (E_{04}) and density of states (DOS) as a function of H-content (c_H) in sputtered a-Si:H. In the first regime, an increase in c_H from 5 to 17% is accompanied by an exponential functional decrease of the DOS near midgap, which varies also directly with E_{04} over a wide range of preparation conditions. In the second regime, additional incorporation of H beyond 17% fails to further decrease the DOS (with c_H and E_{04}), which shows a saturation with scatter. This behavior is interpreted in terms of H-induced and residual impurity related defects. Variation of the DOS in the lower half of the gap, responsible for hole trapping, is observed *via* the hole mobility-lifetime product, which exhibits a dramatic drop with impurity incorporation (P,O) and deteriorates for increasing c_H in the second regime.

Introduction.- A study of the change in the overall density of states (DOS) *versus* H-content (c_H) in a-Si:H produced by sputtering reveals two distinct regimes in the variation of the DOS, which are interpreted in terms of H-induced and impurity-related defects. The c_H is obtained from the integrated intensity of the Si-H wag mode vibrational absorption band.¹ Additional information about H-bonding is derived from thermal evolution experiments.² Different types of measurement are used to investigate the DOS distribution: near IR and visible (1.4-2.5 eV) absorption measurements provide information about the valence band edge DOS³ and give a measure of the optical gap E_{04} (the energy at which $\alpha = 10^4 \text{cm}^{-1}$); deeper states are sampled by lower energy absorption measurements (1.1-1.4 eV)⁴ which complete and confirm the determination of the DOS distribution between the midgap and the Fermi level obtained from Schottky diode conductance/capacitance [$G(\omega)/C(\omega)$] measurements *versus* frequency at zero bias;^{5,6} finally, the Schottky device spectral response is applied to give the hole mobility-lifetime product $[(\mu\tau)_p]$ ⁷ from which information is inferred regarding the states in the lower half of the gap responsible for the trapping of holes.

Sample preparation.- a-Si:H was prepared⁸ by rf sputtering of a c-Si target in an Ar-H₂ atmosphere. The incorporation of impurities (P,O) was achieved by introducing phosphine or oxygen to the plasma.

Results.- Figure 1 shows the variation of the DOS near midgap⁹ *versus* c_H . Two distinct regimes are observable. In the first regime an increase in c_H up to about 17% results in an exponential functional decrease in the DOS. In the second regime, additional incorporation of H, beyond 17%, fails to further decrease the DOS, which shows a saturation with scatter. The H evolution spectra for $c_H < 17\%$ and for $c_H > 17\%$ are shown in Fig. 2. The two regimes are also clearly reflected in the variation of the DOS *versus* E_{04} shown in Fig. 3. Intentional incorporation of impurities (P,O) results in a large increase in the DOS magnitude and a significant modification of its distribution near midgap.

The most relevant result to this paper of a detailed study of $(\mu\tau)_p$ published elsewhere⁷ concerns the second regime: it was found that, for a given DOS, $(\mu\tau)_p$ is

* École Centrale de Lyon, ERA CNRS Génie Électronique (no. 661), 36 Route de Dardilly, 69130 Ecully, France.

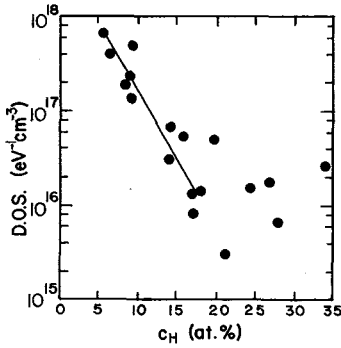


Figure 1: Midgap density of states DOS *versus* c_H . Two distinct regimes are clearly observable corresponding respectively to an exponential decrease of the DOS for $c_H < 17\%$ and to a saturation of the DOS with scatter for $c_H > 17\%$.

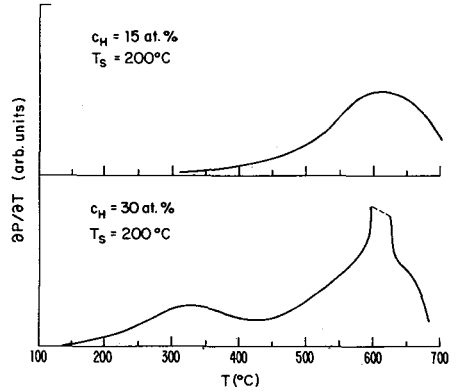


Figure 2: Evolution spectra showing the rate of hydrogen evolution, $\partial P/\partial T$ *versus* T , for a film with $c_H < 17\%$ and one with $c_H > 17\%$, both deposited onto 200°C substrates (T_S).

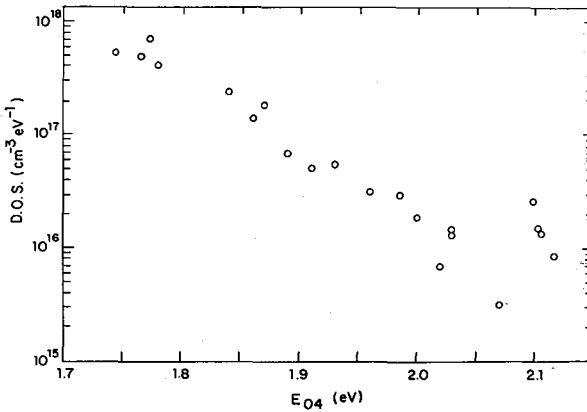


Figure 3: Midgap density of states DOS *versus* E_{04} , the energy where $\alpha = 10^4 \text{ cm}^{-1}$. The two regimes in the characteristic DOS (c_H) are also in evidence here.

lowest for the highest c_H and decreases with impurity content, at any c_H . Typical results illustrating this are given in Table 1.

sample number	SIS 140	SIS 183 II	SIS 174 III	SIS 174 I	SIS 197 IV	SIS 197 III
midgap DOS ($\text{cm}^{-3}\text{eV}^{-1}$)	7×10^{15}	9×10^{15}	3×10^{16}	2×10^{17}	5×10^{17}	1.5×10^{18}
$c_H (\%) = \frac{100 N_H}{N_H + N_{Si}}$	28.5	17.1	21	20.2	9.4	9.6
impurity incorporation (partial pressures of phosphine or oxygen)	-	-	-	$P_{PH_3} = 6 \times 10^{-7} T$	-	$P_O = 10^{-5} T$
$(\mu T)_p$ ($\text{cm}^2 \text{V}^{-1}$)	5.5×10^{-10}	2.5×10^{-9}	4.7×10^{-10}	9×10^{-12}	1.5×10^{-10}	1.3×10^{-11}

Table I: Results obtained on some typical samples illustrating the change in the midgap DOS and $(\mu T)_p$ with c_H (in the second regime) and with impurity incorporation (details regarding the errors in the determination of various parameters are given in references 5 and 10).

Discussion. First regime: the midgap DOS is far larger than that determined ($10^{12} - 10^{13} \text{cm}^{-3} \text{eV}^{-1}$) from extrapolation of the band tails to midgap using the measured slope of the exponential absorption tail,³ not unexpectedly, since the former is presumably caused by defects and the latter by disorder in the completely-coordinated network. Nevertheless the midgap DOS varies directly and decreases exponentially with E_{04} over a wide range of deposition conditions, indicating the simultaneous actions of H of removal of gap states and shifting of band edge states. Evidently the low DOS required for photovoltaic applications can be achieved only at the expense of an increased gap size (although the relationship $\text{DOS} - E_{04}$ may depend on the details of preparation).

Second regime: the increase in the DOS with impurity incorporation indicates that the saturation of the DOS with c_H may be associated with residual impurities whose presence is revealed when most of the dangling bond-related states are compensated by H-incorporation. The failure to further decrease the DOS for c_H larger than 17% can be caused also by H-induced defects. This second interpretation seems to be confirmed by H-evolution measurements: the evolution spectra show that at most 17% of H can go to tightly bound sites and evolve at temperatures higher than 450°C. Any additional H goes into more weakly bound sites and evolves at about 300°C. Therefore we suggest that: (i) only the tightly bound H reduces the midgap DOS; (ii) once these sites are saturated, the additional incorporation of H either has no effect and saturation in the DOS is due to impurities, or H actually induces new defect states. A combination of the two may also occur.

The onset of the second regime coincides with the c_H where other properties are known to undergo a transition. The conductivity shows a scatter in both the preexponential factor and the activation energy for high c_H .¹¹ The photoconductivity magnitude also shows a scatter.¹² The photoluminescence exhibits a second peak near 0.9 eV besides the usual peak at about 1.3 eV, and the photoconductivity spectrum exhibits an enlarged shoulder near 1.2 eV; the material is then similar to a doped material.¹³

The behavior of $(\mu T)_p$ summarized in Table I shows that the incorporation of impurities or an excess H beyond 17% affects the states responsible for hole trapping in the lower half of the gap⁵ more than midgap states: the sample with an excess H

of about 11% ($c_H = 28.5\%$: first column of Table I) has about the same midgap DOS as the sample with $c_H = 17.1\%$ (second column), whereas its $(\mu\tau)_p$ is significantly smaller. The incorporation of impurities (third to sixth column) also reduces $(\mu\tau)_p$ more dramatically than it increases the midgap DOS.

It is uncertain whether residual impurities or excess H are primarily responsible for the behavior observed in the second regime. Given the similar consequences of incorporation of impurities and excess H, it is plausible that they both catalyze the same type of defects which affect the gap state distribution.

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