Thermal Desorption Spectroscopy of Hydrogen from Amorphous Hydrogenated Silicon

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Received 18 April 1996

Thermal desorption spectroscopy (TDS) based on the mass spectroscopy of thermally evolved hydrogen is used for desorption analysis of amorphous hydrogenated silicon (a-Si:H). Two series of glow discharge chemical vapour deposited a-Si:H were investigated by the TDS method. Constant temperature growth rate enabled to determine temperature regions of hydrogen evolution and its total content in the film. These values are compared with the results of infrared (IR) absorption spectroscopy. The dependence of the H content and the position of the maximum of the evolution curve on deposition conditions, as radio frequency (RF) power used in a standard plasma enhanced chemical vapour deposition (PE CVD) glow discharge, was observed. The RF power was related to a silane flow rate during the deposition. The lower temperature of the evolution peaks and simultaneously the lower H content were observed in the layers prepared under the larger relative RF power conditions (the high silane decomposition efficiency). These results correlate well with light degradation measurements in device quality samples.

The thermal desorption spectroscopy (TDS) is a modern analytical method for organic substances [1]. It can be also used in special cases for analysis of inorganic materials and their chemical binding, *e.g.* to evaluate the content of gas elements or substances in bulk solids or thin solid films, their bonding energy, and the structure of crystalline or amorphous network. In this paper TDS was used for the study of hydrogen in amorphous hydrogenated silicon a-Si:H. The previous papers on this topic used different detection techniques. The first activity in this direction reported the application of total pressure gauge for the hydrogen detection [2], in the later attempts the gas chromatography [3] and the quadrupole mass spectrometer [4, 5] have been used. In this paper we use quadrupole mass spectrometer in a computer-operated apparatus.

Hydrogen can be incorporated in high quality a-Si:H in several configurations. The most of it is bonded in a monohydride form SiH and the remainder in SiH_2 and SiH_3 groups which can be well distinguished by the IR spectroscopy. The existence of hydrogen, its content, bonding and distribution in a-Si:H is proved to be of crucial importance for the device quality a-Si:H [5]. In spite of this fact, many controversies remain in the issue of hydrogen in a-Si:H. Let us take the silicon—hydrogen bonding and hydrogen release from the bonding. According to *Jackson* and *Zhang* [6] H is predominantly bonded in the silicon network in pairs on sites of broken weak Si—Si bonds. In such a way "number density" of approximately 4×10^{21} cm^{-3} can be inserted and removed from the Si network without any impact on electron paramagnetic resonance signal. The reason for this is that after each releasing of the hydrogen atom the Si—Si bond is likely reconstructed. The observed diffusion activation energy of bonded H is about 1.5 eV, for the defect annealing even 1.1 eV although according to calculations it should be at least 2.3 eV.

The associated problem is, how to insert two H atoms instead of a weak Si—Si bond. Calculations of bond distances, angles, and repulsive forces of bonded H atoms, and also NMR measurements indicate that their energetical distance is not closer than 0.2—0.23 eV [6]. Four possible ways of inserting of two hydrogen atoms into silicon network that cannot be distinguished by the IR spectroscopy are illustrated in Fig. 1. Moreover, Si atoms can be in three charge states - neutral, positively and negatively charged. The TDS method can help to study (examine) the concentrations of the H atoms in various configurations. The release rate and corresponding release temperature are proportional to the Si—H bond energy, which differs for different Si—H configurations. Several other models of hydrogen bonding and distribution in amorphous silicon network have been suggested [7—9], but the results are controversial.

EXPERIMENTAL

The apparatus (Fig. 2) consists of the desorption chamber of small dimensions provided with the heated sample holder connected through a gate valve to the

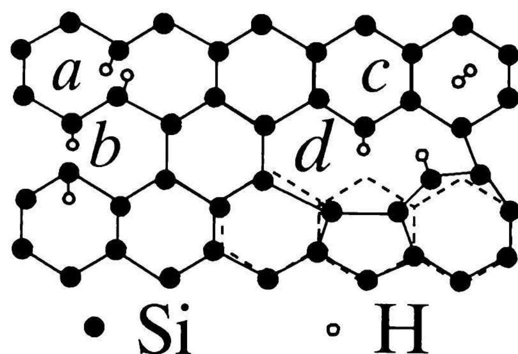

Fig. 1. Four possible ways of inserting two H atoms into silicon network. *a* – two H atoms inserted into the Si—Si bond, *b* – formation of an H_2^* complex, *c* – formation of molecular H_2, *d* – larger scale relaxation involving the second and the third nearest neighbours [6].

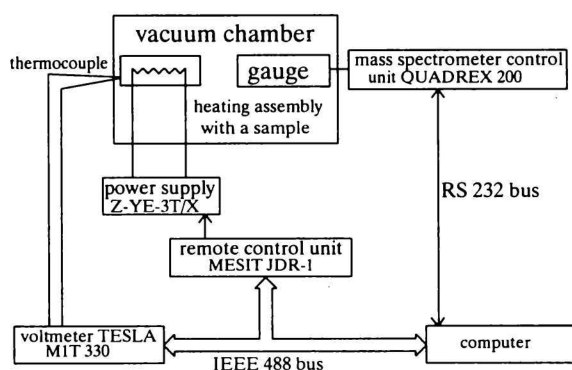

Fig. 2. Block diagram of the apparatus for temperature control and data acquisition of the thermal desorption spectroscopy (TDS) method.

vacuum pumping unit AV-63 equipped with the mass spectrometer (Leybold-Quadrex 200) and the cool trap. The apparatus is controlled by a computer. The computer temperature control actuates the D/A unit with power output (Mesit Z-YE-3T/X), the temperature of the sample is measured by the Fe—constantan thermocouple and the A/D converter (Tesla M1T 330) forming feedback for the control loop. All these instruments are connected to the computer by the IEEE 488 bus. The mass spectrometer Quadrex 200 is connected to the computer by the RS 232 bus. The Quadrex 200 built-in software enables to operate in 9 display modes, of which the table mode is the most convenient one, because it simultaneously gives values of 6 chosen adjustable mass numbers. The computer collects all the data, *i.e.* the temperature, time, and preselected partial pressures of chosen elements into the data array and gives their time evolution on the screen display in both graphical and numerical forms. The sample is inserted into the desorption chamber, pumped to the base pressure of 10^{-4} Pa, and after that the temperature starts to rise forming a linear temperature ramp. The hydrogen is evolved gradually at temperatures in excess of 200 °C expressing several typical peaks. After completing the desorption cycle at about 700 °C the calibration dose of molecular hydrogen is injected into the desorption chamber, while the data collecting continues. The resulting data are then plotted against the time, integrated and calibrated for absolute and relative content calculation in mole %.

The described apparatus enables the measurement of the desorption spectra of preselected gases with the absolute sensitivity better than 1 mm^3 . The temperature controller operates with the linear temperature rise and adjustable sweep rate is from 0 to 50 °C per min with the maximum achievable temperature about 700 °C.

The IR spectra were measured by the Perkin—Elmer 1720 Fourier IR spectrometer and the H total content ϕ was calculated by the standard method from 630 cm^{-1} absorption peak described *e.g.* in [10].

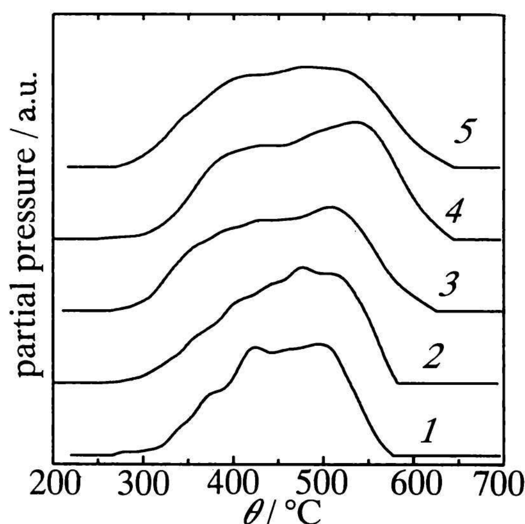

Fig. 3. Dependence of the evolution curve shape on the temperature sweep rate. *1.* 10 °C min^{-1}, *2.* 15 °C min^{-1}, *3.* 20 °C min^{-1}, *4.* 25 °C min^{-1}, *5.* 30 °C min^{-1}.

RESULTS AND DISCUSSION

A. Fig. 3 shows the evolution curves of a-Si:H prepared by decomposition of silane in microwave ECR plasma in our laboratory. The layer was 2 μm thick with the area of about 0.5 cm^2. The reproducibility of the method was checked by comparing the total hydrogen content measured on an identical material giving the values from 12 to 14 mole %.

As it is obvious from Fig. 3, hydrogen is evolved from a-Si:H in the temperature range from 300 up to 700 °C. It could be incorporated in various configurations mentioned above. It might evolve in two or three energy steps and the largest energy controls the evolution process. At first atoms from $Si{=}H_2$ configuration are released, as confirmed by IR spectroscopy of partially heated samples and concomitant decrease of

Table 1. Preparation Conditions of Power P and Relative Power P_r Series

Sample	P/W	Q/(cm^3 min^{-1})	P_r/(W/(cm^3 min^{-1}))	x(H)/mole % IR	x(H)/mole % TDS	θ_{max}/°C
1275-5	64			14.8	17.8	525
1276-5	32			10.7	11.5	499
1277-5	16			5.7	5.7	473
1278-5	8			4.3	5.5	464
1279-5	4			4.5	4.8	478
1280-5	128			12.6	13.2	514
1285-5	32	78	0.41	10.4	9.0	496
1286-5	30	40	0.75	4.3	4.6	494
1287-4	26	20	1.3	3.7	4.4	492
1288-5	20	10	2	4.4	4.7	478
1289-4	15	5	3	4.3	4.8	476
1290-4	9	2.5	3.6	4.5	4.2	467
1291-5	32	78	0.41	7.2	8.8	488

Q – the silane flow rate, IR resp. TDS – H content measured by IR spectroscopy resp. TDS, θ_{max} – the temperature of the maximum of the TDS curve.

the absorption peak situated at $\tilde{\nu} = 2090$ cm^{-1}. This configuration is present mainly in the interconnected voids, so released H can easily diffuse to the sample surface at temperatures slightly in excess of 300 °C. The observed resulting position of the evolution peak at 400 °C is then independent on the thickness of the film [4]. According to the low transport energy in the interconnected void model the evolution is controlled by the surface energy barrier. At about 400 °C the void structure collapses and rather compact material is reconstructed [5]. The most of remaining hydrogen is now bonded in H_2^* configurations in platelet clusters according to Fig. 1*a,b,d*. The rest is in single pairs (Fig. 1*c*) or single Si—H configuration dispersed in the bulk. The evolution from such configurations is controlled by the trap limited diffusion [6], so the position of the second evolution maximum moves to a higher temperature with the increasing thickness or temperature sweep rate. In the experiment, some other phenomena occurred. If there is an internal stress in the films and the temperature sweep rate is high, hydrogen accumulates in the voids and is subsequently released explosively. This phenomenon was observed with some samples, usually of inferior quality as a burst-like evolution of remaining hydrogen with the collapse of the layer. *Roch* and *Delgado* [1] observed in their GD films a sharp evolution peak at 500—520 °C. Also recrystallization was observed, but at much higher temperatures. Some of our MW ECR CVD samples and the samples delivered by *Stuchlík et al.* [11] show a sharp evolution peak at 590 °C, most probably indicating the recrystallization. The possible presence of oxygen is not considered to have an effect according to high stability of the silicon—oxygen bonding.

B. Two series of PE CVD samples were investigated by the TDS and IR method. The deposition conditions were following [11]: the pressure of SiH_4 was 3.5 Pa and the deposition temperature $\theta_D = 400$ °C. The variable parameter was the RF power in the first series

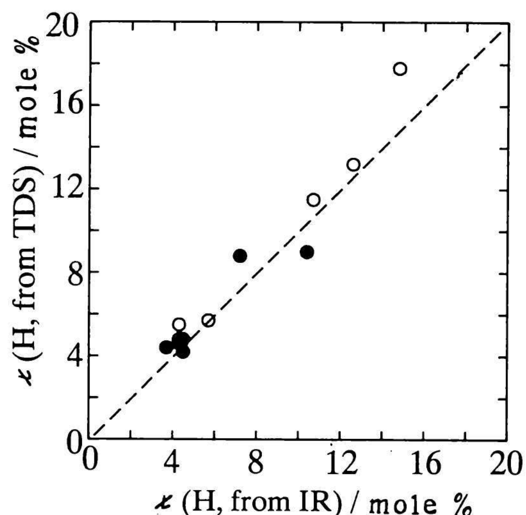

Fig. 4. Comparison of H content measured by IR spectroscopy and TDS. ○ Series 1, ● series 2.

and the RF power related to the flow rate of SiH_4 in the second series. The resulting parameter was the relative power $P_r = P/Q$, where P is the RF power and Q is the silane flow rate. After P adjusting Q was varied so that the measured partial pressure of H atoms was constant, so P_r is proportional to the efficiency of the silane decomposition. Dissociated H pressure was measured by the mass spectrometer during the deposition process.

The dependence of hydrogen content on the RF power for the first series and on the relative power for the second one is in Table 1. The total hydrogen content assessed by IR spectroscopy is in good agreement with that of TDS measurements, as it is obvious from Fig. 4. TDS spectra of the first (power) series are in Fig. 5. The character of the spectra varies only slightly, although the hydrogen content rises with RF power significantly (Fig. 6). There is apparent the

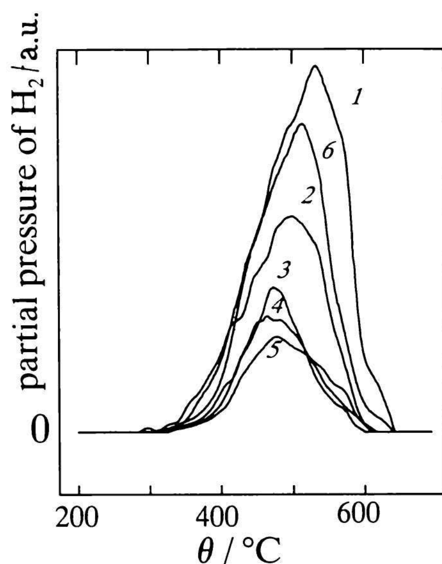

Fig. 5. Evolution spectra of the RF power series according to Table 1. Total content of H (x(H)/mole %): *1.* (1275-5) 17.8 %, *2.* (1276-5) 11.5 %, *3.* (1277-5) 5.7 %, *4.* (1278-5) 5.5 %, *5.* (1279-5) 4.8 %, *6.* (1280-5) 13.2 %.

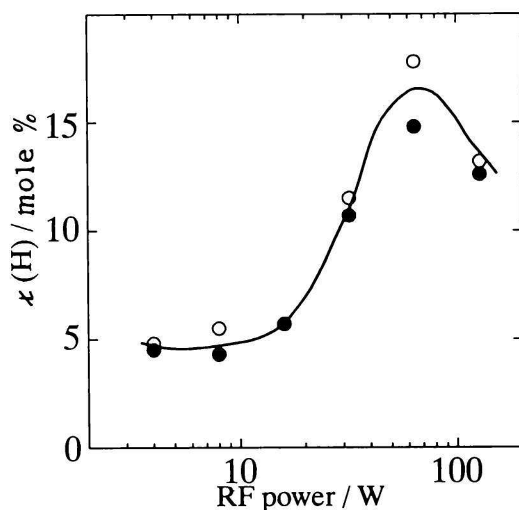

Fig. 6. H content dependence measured either by IR spectroscopy or TDS on the RF power introduced into plasma during the deposition. ○ TDS , ● IR.

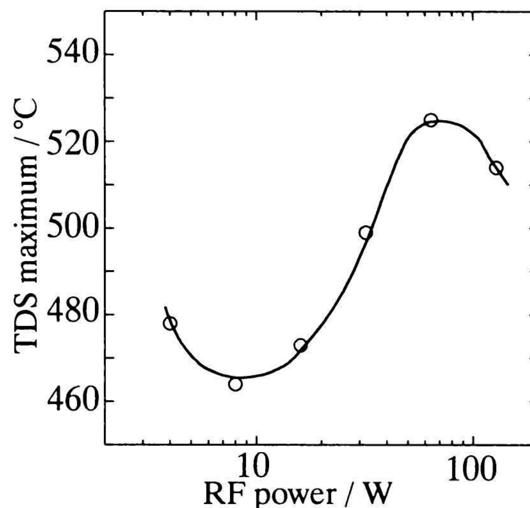

Fig. 7. Position of the TDS maximum in dependence on the RF power introduced into plasma during the deposition.

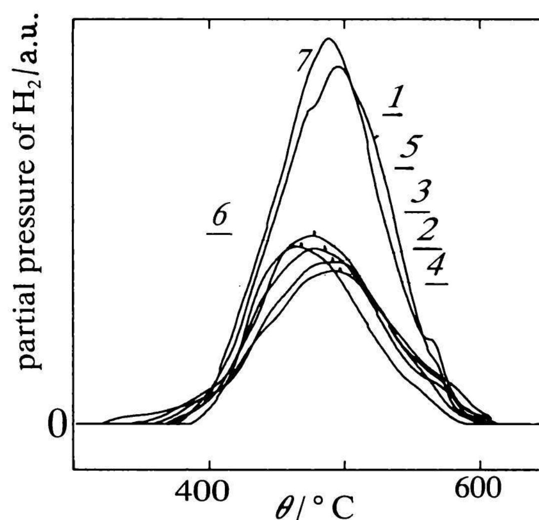

Fig. 8. Evolution spectra of the relative RF power series. Total content of H (x(H)/mole %): *1.* (1285e) 9 %, *2.* (1286e) 4.6 %, *3.* (1287d) 4.4 %, *4.* (1288e) 4.7 %, *5.* (1289d) 4.8 %, *6.* (1290d) 4.2 %, *7.* (1291e) 8.8 %.

peak shift to a higher temperature while rising H content and RF power (Fig. 7). This may be explained so that the higher content of H in the sample causes the higher concentration of the platelet hydrogen clusters. Released hydrogen leaves more dangling bonds that form traps for diffusing hydrogen. It is rather surprising, but current experience shows that better structured a-Si:H has the evolution maximum at the lower temperature. The degradation experiments on the same samples [12] confirm the correlation between the temperature of the evolution maximum position and stability against the Staebler—Wronski effect, the lower the maximum temperature, the better stability.

The hydrogen content increases with the RF power (Fig. 6). This may be caused by the increase of H concentration in plasma during the deposition and its rising average energy. Consequently hydrogen atoms have energy enough to penetrate into deeper sites in the layer to break weak bonds and to be trapped there [9]. But for the RF power still larger the total hydrogen content decreases again and this effect is not satisfactorily explained. It was found that excessive hydrogen content causes increased susceptibility to the Staebler—Wronski effect even if the initial density of dangling bond is lower.

C. The evolution spectra of the second (relative RF power) series (Fig. 8) become narrower and the shoul-

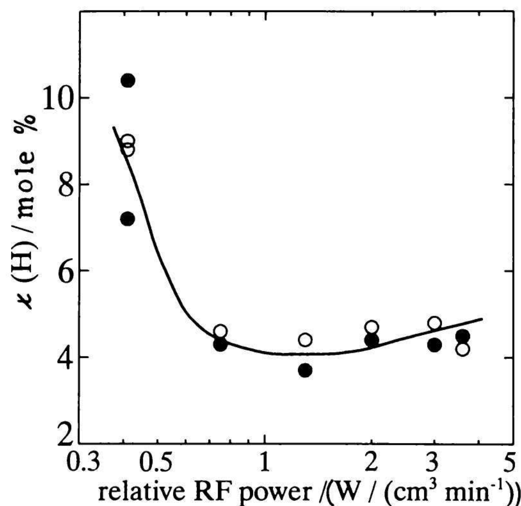

Fig. 9. Dependence of H content on the relative RF power for the second series. o TDS, • IR.

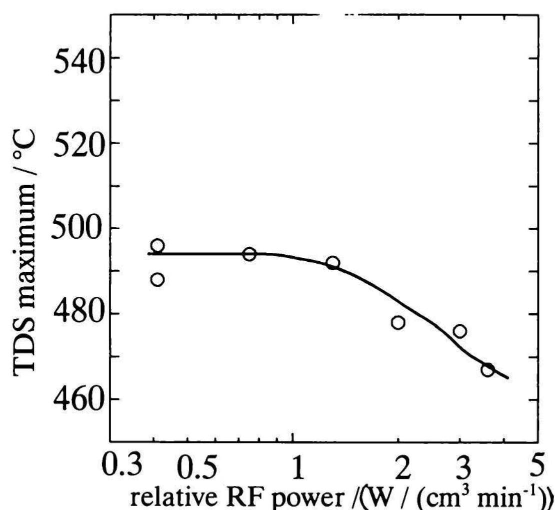

Fig. 10. Position of the TDS maximum against the relative RF power introduced into plasma during the deposition.

der at about 580 °C occurs. In some cases not shown here even a sharp evolution peak was observed. Resulting Fig. 9 gives nearly the same hydrogen content of 4—5 mole % with the exception of the samples prepared under the lowest relative RF power. A different mechanism of the layer growth may affect this fact namely when the deposition rate is too high, the resulting incorporation of SiH_n radicals occurs because surface reactions are not completed before new radicals have been absorbed. The total H content then increases, too. On the other hand, the samples exhibit a slight shift of the evolution maximum to a lower temperature with increasing P_r (Fig. 10), so the samples prepared at the large relative RF power, but with the small RF power and the small flow rate of silane (high efficiency of the silane decomposition), had a structure with the lower amount of built-in voids. It is soon to decide which parameter has the dominating influence in our case.

CONCLUSION

Models for hydrogen bonding and transport in a-Si:H presented in [6—8], are examined. The thermal desorption spectroscopy as a new analytical tool was developed and used for the quantitative evaluation of the hydrogen bonding and concentration in a-Si:H thin films with the result that materials with the mass as small as 10^{-5} g could be analyzed with the sensitivity of about 1 mm^3 H_2 at the normal conditions.

A series of MW ECR CVD samples was measured by this method and the influence of the varying temperature sweep rate on the high temperature evolution peak shift was observed.

Two series of GD CVD samples were analyzed by the TDS method. The total hydrogen contents calculated from the TDS and IR spectra were compared. Detailed observation of TDS was performed. The dependence of the high temperature peak shift on the deposition RF power and on the relative RF power was observed. This shift correlates well with the sample quality investigated by the light degradation measurements [12] at the same series. The lower temperature of the evolution peak indicates the higher stability against light degradation. As a result, the total RF power is not a significant quality parameter for PE CVD a-Si:H, but it depends on the relative RF power, P_r. Decreasing of the flow rate Q while the H concentration in plasma remains constant results in the higher degree of silane decomposition. The layer quality then increases.

Acknowledgements. We would like to thank Dr. J. Stuchlík for the preparation of the samples and Dr. O. Zmeškal for the technical help with data collection.

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Translated by F. Schauer

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