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HYDROGEN EVOLUTION FROM PLASMA-DEPOSITED AMORPHOUS SILICON FILMS

W. Beyer and H. Wagner

Institut für Grenzflächenforschung und Vakuumphysik, Kernforschungsanlage Jülich, D-5170 Jülich, F.R.G.

Abstract.— The results of a systematic study of hydrogen evolution from glow-discharge a-Si:H films are presented. The influence of doping, film thickness and substrate temperature is discussed. Two evolution processes can be discerned: A low temperature effusion attributed to the release of H₂ through voids or cracks from polysilane-like intergrain material and an evolution at high temperatures from compact a-Si:H material, dominated by atomic diffusion of hydrogen. Addition of diborane leads to a pronounced shift of the evolution peaks of both processes to lower temperatures and to a change of the hydrogen content.

Introduction.— For a characterization of a-Si:H films the knowledge of the hydrogen content and of the bonding states of hydrogen is highly desirable. Information on both can be obtained from hydrogen evolution experiments (1,2). By comparison with infrared absorption (2) and nuclear reaction (2,3) measurements it is known that heating silicon films to $T > 800^{\circ}\text{C}$ leads to a rather quantitative removal of hydrogen. Therefore, evolution measurements can be used for the determination of the absolute hydrogen content. Furthermore, such measurements yield spectra of the hydrogen evolution rate as a function of temperature, giving information on the Si-H bonding states, modified possibly by hydrogen diffusion effects (4).

In this work, hydrogen evolution measurements are used to study the influence of substrate temperature, film thickness and of doping by phosphine and diborane on hydrogen content and hydrogen bonding in glow-discharge a-Si:H films.

Experimental.— The films were grown in an inductively coupled rf glow-discharge system using pure silane, silane-phosphine and silane-diborane mixtures. The deposition parameters were: pressure: 0.4 mbar, flow rate: 6 sccm, rf power: $< 5\text{ W}$, growth rate: $\sim 1.5\text{ Å/s}$. As substrates we used sapphire, crystalline silicon and fused silica platelets. The results presented in this paper were obtained entirely on sapphire and crystalline silicon substrates since it was found that fused silica acts as a hydrogen sink between 500 and 650°C and, consequently, as a hydrogen source at temperatures above 700°C , thus changing the evolution spectra considerably. Minor modifications of the evolution curves near 450°C were also observed in case of sapphire and crystalline silicon substrates due to blistering effects as described by Shanks and Ley (5). For the hydrogen evolution, the films were inserted into a quartz tube evacuated by a turbomolecular pump and heated to 1000°C at a rate of 20 K/min . The base pressure prior to hydrogen evolution was less than 10^{-7} mbar. The hydrogen partial pressure (H₂) was monitored by means of a quadrupole mass analyzer. At a constant pumping speed it is directly proportional to the hydrogen evolution rate. The apparatus was calibrated by admitting a well known flow of H₂ through a calibrated leak.

Results and Discussion.— Typical evolution spectra are shown in Figs. 1a and 1b for films prepared at substrate temperatures $T = 25^{\circ}\text{C}$ and $T = 300^{\circ}\text{C}$, respectively. Plotted is the hydrogen evolution rate $\frac{dN_{\text{H}}}{dt}$, i.e. the number of hydrogen atoms released per unit film volume and unit time, as a function of temperature. In Fig. 1a, the evolution rate is given on a logarithmic, in Fig. 1b on a linear scale. The re-

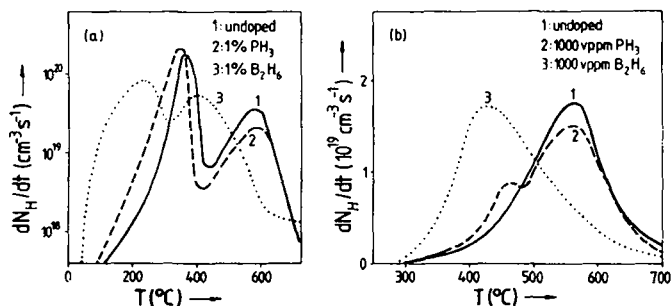


Fig. 1 : Hydrogen evolution rate as a function of temperature for undoped and doped a-Si:H films prepared at the substrate temperatures (a) $T_s = 25^{\circ}\text{C}$ (film thickness $d \sim 0.6 \mu\text{m}$) and (b) $T_s = 300^{\circ}\text{C}$ ($d \sim 0.8 \mu\text{m}$).

sults for undoped films (curve 1) agree well with published data from other laboratories (1-4): In case of $T_s = 25^{\circ}\text{C}$ two evolution peaks are observed, one at 370°C (LT) and another between 550 and 600°C (HT). At $T_s = 300^{\circ}\text{C}$, only the HT peak near 550°C remains. Curves 2 and 3 show the results for doping by addition of phosphine and diborane, respectively. While the influence of phosphorus doping is found to be weak, boron doping leads to rather drastic changes of the evolution spectra. Both the LT and HT peaks are shifted by approximately 150°C to lower temperatures. The hydrogen concentration is also influenced.

Changes in the hydrogen evolution peaks are present down to diborane concentrations as low as 10 ppm as demonstrated in Fig.2 for $T_s = 300^{\circ}\text{C}$ films (film thickness $0.4 - 0.55 \mu\text{m}$). For $10 \text{ ppm B}_2\text{H}_6$ a shift of $30 - 40^{\circ}\text{C}$ is observed (curve 2) — compared to undoped material. In the doping range $10^2 - 10^4 \text{ ppm}$, the evolution maximum lies close to 400°C . The hydrogen content C_H which is obtained from the area under the curves rises from 14 at.% for the undoped sample to 20 at.% for lightly doped films ($10 - 100 \text{ ppm}$) and decreases to below 10 at.% for 1% B_2H_6 .

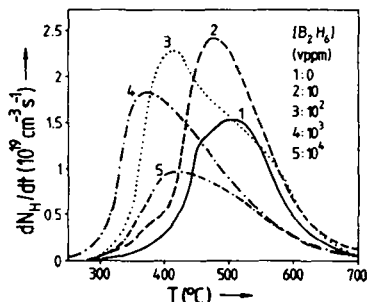


Fig. 2 : Hydrogen evolution rate as a function of temperature for a-Si:H films ($T_s = 300^{\circ}\text{C}$) doped with diborane at various concentrations.

Generally, three processes may determine the rate of the hydrogen evolution: (a) the Si-H dissociation leading to a release of atomic or molecular hydrogen, (b) the diffusion of hydrogen to the surface and (c) the surface recombination of atomic hydrogen. An easy discrimination whether the evolution rate is diffusion-limited or not is the measurement of the thickness dependence (4). Results are shown in Fig.3. For a series of undoped and boron-doped a-Si:H films, the peak position T_M (Fig.3a) and the atomic ratio N_H/N_{Si} (Fig.3b) of hydrogen to silicon atoms in the film (assuming the crystalline Si density of $5 \times 10^{22} \text{ cm}^{-3}$) are plotted as a function of film thickness d . Clearly, for the high temperature peaks of undoped a-Si:H films (curves 1(HT) and 2(HT)) the evolution is found to be diffusion-limited, in agreement with others (4). The same was found to be true for phosphorus doping and, in case of boron doping, for the substrate temperatures $T_s = 25^{\circ}\text{C}$ (curve 3(HT)) and $T_s = 100^{\circ}\text{C}$ (curve 4(HT)). We note, however, that there is no unequivocal correlation between film thickness and T_M . A decreasing substrate temperature leads to a higher T_M , addition of B_2H_6 on the other hand to a lower T_M at the same film thickness. These results point against a unique diffusion constant of hydrogen in amorphous silicon. Apparently, hydrogen diffusion is enhanced by boron doping. For boron-doped films prepared at $T_s = 300^{\circ}\text{C}$ (curve 5(HT)), only a weak thickness dependence of T_M is observed. Practically no thickness dependence is found for the LT peaks of undoped films (curve 1(LT)), boron-doped samples (curve 3(LT)) and phosphorus-doped films. Inspection of the hydrogen content (Fig.3b) shows that apart from

possible nucleation effects ($d \leq 0.3 \mu\text{m}$) the hydrogen concentration generally is film thickness independent. The only exception is the HT peak of boron-doped samples ($T = 300^\circ\text{C}$, curve 5(HT)) where $N_{\text{H}}/N_{\text{Si}}$ decreases rapidly with increasing d . This behaviour, together with the weak thickness dependence of T_{M} , points to the presence of internal surfaces in boron-doped films for $T = 300^\circ\text{C}$. In this case, $N_{\text{H}}/N_{\text{Si}}$ decreases rapidly with increasing d . This behaviour, together with the weak thickness dependence of T_{M} , points to the presence of internal surfaces in boron-doped films for $T = 300^\circ\text{C}$. In this case, hydrogen diffuses to these surfaces and leaves the film through a network of voids or through cracks. The diffusion length, therefore, will be shorter than for compact a-Si films and the evolution peak will lie at lower temperature. The thickness dependence of the hydrogen concentration is explained by effusion of hydrogen during the deposition process. Indeed, we observed that a boron-doped film of $d \sim 0.25 \mu\text{m}$, deposited at $T = 300^\circ\text{C}$, lost almost half of its hydrogen content of $\sim 20 \text{ at.}\%$ when annealed for one hour at 300°C whereas little was changed by the same treatment of undoped films. Clearly, the hydrogen effusion during deposition at $T = 300^\circ\text{C}$ for boron-doped films, the presence of voids in this material and the enhanced hydrogen diffusion are interconnected, the enhanced hydrogen diffusion due to boron-doping, most likely, being the primary effect.

According to these results, the HT evolution process in a-Si:H films apparently involves rather generally hydrogen diffusion. The diffusing species is atomic hydrogen. Confirmation for this assignment comes from an experiment (using sputtered films) where the deuterium and hydrogen evolution from a sandwich structure of two a-Si:H films embedding a a-Si:D film was monitored (W.Beyer, H.Wagner, to be published): Deuterium was found to evolve to a high degree as HD as is expected for atomic diffusion of deuterium. This result points against the possibility of a volume diffusion of molecular hydrogen (deuterium) with a higher diffusion constant than for atomic H (D) diffusion, as has been proposed by Oguz and Paesler (6).

In agreement with others (2,4,6,7) we attribute the LT effusion peak to the release of molecular hydrogen. This is supported by energetic considerations: The energy required for a rupture of Si-H bonds can partially be regained in case of H_2 release by a concomitant formation of Si-Si and H-H bonds. For the release of atomic hydrogen, on the other hand, only an energy gain from Si-Si reconstruction is possible whereas the H_2 formation is delayed and takes place at the film surface. This explains why the latter evolution process proceeds at relatively high temperatures only. The influence of doping on the LT peak, presumably, is connected with these energy gain mechanisms since infrared absorption measurements do not show any difference in the spectra up to doping levels of 1% compared to undoped films. Apparently, the presence of diborane leads to a structurally different material where the Si-Si bond reconstruction is eased. We believe that the hydrogen set free in the LT evolution leaves the film not by volume diffusion but through the way of internal surfaces (voids) or cracks which are either present in the films from the deposition process or which are formed during hydrogen evolution. Therefore, no thickness dependence of the LT evolution peak is expected. The result that films showing a LT evolution peak

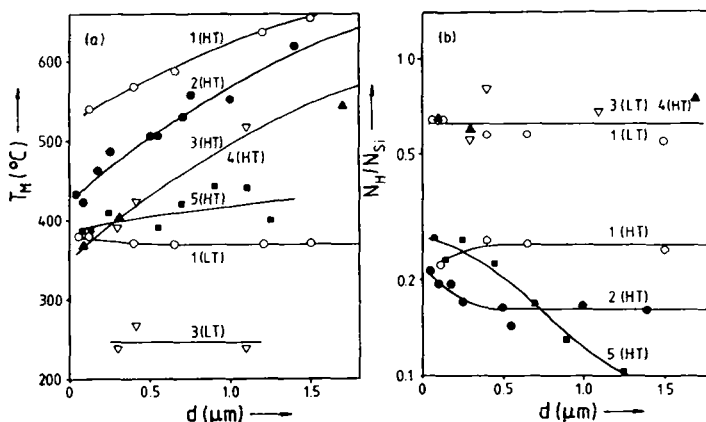


Fig. 3 : (a) Position of the evolution peak T_{M} and (b) hydrogen content as a function of film thickness for differently prepared a-Si:H films. Curve (1): undoped $T = 25^\circ\text{C}$, (2): undoped $T = 300^\circ\text{C}$, (3): 1% B_2H_6 $T = 25^\circ\text{C}$, (4): 1% B_2H_6 $T = 100^\circ\text{C}$ and (5): 1% B_2H_6 $T = 300^\circ\text{C}$. HT and LT refer to high and low temperature evolution peaks, respectively.

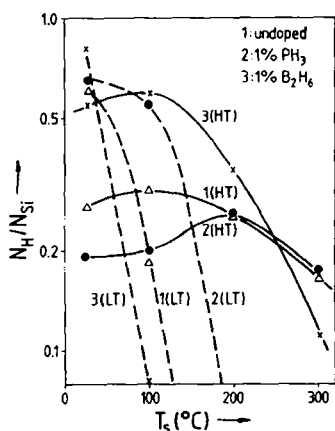


Fig. 4 : Hydrogen content as a function of substrate temperature ($d \sim 0.5 \mu\text{m}$).

also have a HT peak which is thickness dependent points to a two-phase material (8): From a compact phase hydrogen evolves by atomic diffusion leading to the HT peak whereas an intergrain phase releases hydrogen as H_2 resulting in the LT peak. Presumably, the grain size of the compact phase grows subsequently to the LT evolution due to collapsing voids. The presence of a thickness dependence of T_M requires a grain size larger than the film thickness.

This concept of a two-phase material is also supported by the results of Fig.4. Here, the amount of hydrogen evolved under the HT and LT peaks is shown as a function of substrate temperature T_s for undoped (curve 1), phosphorus-doped (curve 2) and boron-doped (curve 3) samples. The hydrogen content related to the LT maximum (dashed curves) is found to decrease rather sharply with increasing T_s so that for $T_s \sim 200^\circ\text{C}$ no LT maximum could be distinguished. The amount of hydrogen evolving under the HT peak (full lines), on the other hand, shows a much weaker dependence on substrate temperature, in particular for undoped and P-doped samples. These

results point to the formation of the compact phase at any substrate temperature whereas the intergrain material grows at low T_s only. Still, both phases seem to relate to the same Si-H species in the plasma. Preliminary results from the investigation of films prepared from $\text{SiH}_4\text{-D}_2$ mixtures show almost the same ratio of D/H for both LT and HT peaks. Conceivably, the high hydrogen content in the intergrain phase is due either to polymerization effects leading to hydrogen-rich polysilanes or due to a sponge-like structure, richly covered with hydrogen. The influence of boron doping, however, is not fully understood. The result that for $T_s = 25^\circ\text{C}$ the hydrogen content in boron-doped films is higher than in undoped films shows that either the presence of diborane promotes the formation of hydrogen-rich Si-H species in the plasma or that boron acts as a nucleation or polymerization center leading to an incorporation of such species in the films. On the other hand, these Si-H groups are rather unstable since an increase of T_s leads to a more rapid decrease of the hydrogen content in case of boron doping than for undoped samples.

Unquestionably, these effects will have considerable impact on the electronic properties of a-Si:H films. Aiming for a low-defect material suitable e.g. for solar energy conversion, polysilane-like intergrain areas as well as voids are certainly undesirable. In agreement, we observed for films with a pronounced LT hydrogen evolution peak a very low photoconductivity only and practically no influence of phosphorus and boron incorporation on the electrical conductivity. For the films shown in Fig.4, the highest photoconductivity indicative of a low density of recombination centers was found for undoped and phosphorus-doped material prepared at $T_s = 200\text{--}300^\circ\text{C}$.

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