

## HYDROGEN AND DEUTERIUM INCORPORATION IN GLOW DISCHARGE AMORPHOUS SILICON

K.M.H. MAESSEN, M.J.M. PRUPPERS, F.H.P.M. HABRAKEN,  
J. BEZEMER, and W.F. van der WEG.

Technical Physics Department, State University Utrecht, P.O. Box 80.000,  
3508 TA Utrecht, The Netherlands

The incorporation of hydrogen in glow discharge a-Si:H is investigated with an isotope method. During deposition D<sub>2</sub> or H<sub>2</sub> is added to the silane. Although for low silane flow the incorporation of deuterium is affected by isotope exchange this process plays a minor role for high silane flow. At these gas flows it is estimated that the hydrogen in the a-Si:H layer for our conditions originates for 70% from SiH<sub>x</sub> compounds.

### INTRODUCTION

As a part of a systematic investigation of the influence of deposition parameters on the properties of the a-Si:H films the origin of hydrogen in the layer is studied. Hydrogen is not only present in the plasma as H<sub>2</sub> addition to silane but also as a product of the decomposition of silane. To distinguish between the hydrogen incorporated from SiH<sub>x</sub> compounds and from pure H<sub>2</sub> present in the plasma, the added H<sub>2</sub> is replaced by D<sub>2</sub>. Similar experiments were performed earlier by Yatsurugi et al. [1]. It will be shown that for the interpretation of the experimental results, it is necessary that care should be taken of isotope exchange in the gas phase.

### DEPOSITION

The samples are prepared in a capacitively coupled radiofrequent (rf) glow discharge reactor [2]. The frequency of the rf power source is 13.56 MHz and the substrate temperature is 250°C. The ratio between the flows of silane and the added H<sub>2</sub> or D<sub>2</sub> in the gas mixture is always kept constant at 2/3.

In order to separate the influence of the gas pressure, the rf power and the incoming gas flow three series of samples are deposited. The first series is deposited at a fixed rf power of 20 W and a gas flow of 10 sccm SiH<sub>4</sub> whereas the gas pressure is varied between 18 and 45 Pa. The second series consists of samples prepared at constant gas pressure of 30 Pa and constant gas flow of 10 sccm SiH<sub>4</sub> while the rf power is varied between 5 and 30 W. In the last series the samples are grown at a pressure of 30 Pa and an rf power of 20 W while the gas flow is changed from 1 to 20 sccm silane.

## ANALYSIS

The geometrical thickness of the samples is determined by optical reflection and transmission experiments [3]. The hydrogen concentration is measured by nuclear reaction analysis (NRA) using the reaction  ${}^1\text{H}({}^{15}\text{N}, \alpha\gamma){}^{12}\text{C}$  [4]. Depth profiling using this reaction results in a measure for the film thickness. The ratio between the incorporated hydrogen and deuterium is determined by elastic recoil detection (ERD) [5]. Details of the NRA and ERD set up will be given in ref. [6].

## RESULTS AND DISCUSSION

## 1. Pressure dependence

The deposition rate (measured optically) turns out to be linearly dependent on the gas pressure during deposition. By comparing the geometrical thickness with the thickness information from the NRA analysis it appears that the silicon atomic density of all samples is equal, independent of  $\text{D}_2$  or  $\text{H}_2$  addition, and gas pressure. For that matter the rf power and gas flow do not influence the density either.

## 2. rf power variation

The deposition rate as a function of the rf power for films deposited with  $\text{H}_2$  or  $\text{D}_2$  added to silane is presented in fig. 1. From this figure it is clear that the deposition rate steeply increases with rf power. This is to be expected since an increasing rf power will obviously produce more  $\text{SiH}_x$  radicals in the glow discharge. It is also observed that the deposition rate for samples grown with  $\text{D}_2$  is consistently 25% higher than for samples deposited with  $\text{H}_2$ . As a possible explanation for this effect we suggest a contribution of the  $\text{D}_2$  emission to the dissociation of silane (photo CVD).  $\text{D}_2$  molecules excited in the glow discharge emit a relatively large amount of vacuum-uv radiation compared with  $\text{H}_2$ . We anticipate a significant contribution of this radiation to the decomposition of silane.

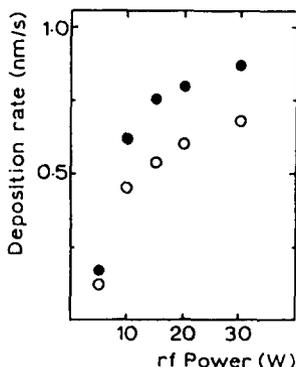


FIGURE 1  
Deposition rate if  $\text{H}_2$  (o) or  $\text{D}_2$  (●) is added to silane as a function of rf power

### 3. variation of the gas flow

The influence of the gas flow ( $\text{SiH}_4 + \text{D}_2$ ) on the deposition parameters is presented in fig. 2, where the abscissa is the  $\text{SiH}_4$  flow since this is the relevant gas. After an increase of the deposition rate with gas flow, apparently a saturation effect sets in around a gas flow of 10 sccm  $\text{SiH}_4$ . For low  $\text{SiH}_4$  flow ( $< 10$  sccm) a  $\text{SiH}_4$  depletion of the gas occurs due to deposition on the substrate and the other exposed surfaces in the reaction chamber. At  $\text{SiH}_4$  flows above 10 sccm, the silane input is sufficiently fast to compensate for the withdrawal of  $\text{SiH}_4$  by the deposition. As a consequence the deposition rate saturates.

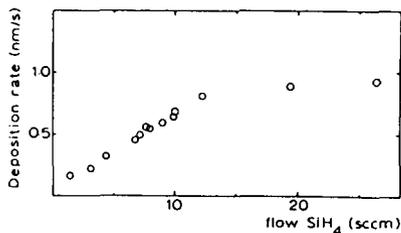


FIGURE 2  
Deposition rate versus gas flow  
(40 vol. %  $\text{SiH}_4$  and 60 vol. %  $\text{H}_2$   
or  $\text{D}_2$ )

The sum and the ratio of the hydrogen and deuterium concentrations in the films versus gas flow are illustrated in fig. 3. For  $\text{SiH}_4$  flows beyond 8 sccm  $[\text{H}] + [\text{D}]$  appears to be independent of the gas flow at a value of  $21 \pm 1$  at.-%.

The deuterium in the layer can originate from the  $\text{D}_2$  gas directly, or, through an isotope exchange process, from  $\text{SiH}_x\text{D}_y$ . It is very likely that in the plasma exchange reactions occur in which a part of the hydrogen atoms in silane is replaced by deuterium. The contribution of the isotope exchange can be estimated by determining the concentrations of hydrogen and deuterium in the layer as a function of gas flow. From fig. 3 it can be seen that the  $[\text{H}]$  to  $[\text{D}]$  ratio initially increases and reaches a saturation value. In the saturation region ( $> 10$  sccm  $\text{SiH}_4$ ) the available time for isotope exchange reduces to a low value. Consequently, for large gas flow, the deuterium is mainly deposited from the gas directly. Reducing the silane flow will

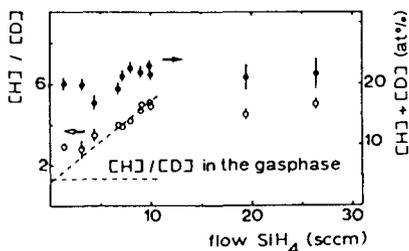


FIGURE 3  
 $[\text{H}] + [\text{D}]$  (●) and  $[\text{H}]/[\text{D}]$  (○)  
versus gas flow (40 vol. %  $\text{SiH}_4$   
and 60% vol. %  $\text{H}_2$  or  $\text{D}_2$ )

lead to an increased isotope exchange which results in a decrease of the [H] to [D] ratio. In the limit of total isotope exchange, hence for zero flow, the [H] to [D] ratio should reach the value of [H]/[D] in the gas, which is 4/3. Extrapolation of the [H]/[D] data between 5 and 10 sccm leads to a value of  $1.2 \pm 0.5$  at zero flow, which is very close to the expected total exchange value i.e. the gas phase ratio. The deviation from this line for small silane flow is interpreted as follows. By the depletion of the gas mixture due to the disappearance of the silane through deposition the isotope exchange time is limited. This results in a higher [H] to [D] ratio than expected from the extrapolation.

We conclude from the saturation behaviour in fig. 3, that the incorporation of deuterium from the gas directly amounts to 3.6 at.%. If we assume the incorporation rate to be proportional to the gas fractions it could be estimated that nearly 30% of the incorporated H or D originates from hydrogen species ( $H, H_2, D, D_2$ ) not bound to silicon.

Yatsurugi et al. [1] observed a [H] to [D] ratio close to the ratio in the gas for high rf power (60 W). They attribute this to the total decomposition of silane in Si and H and suppose that H originates from the gas directly. However from our experiments we conclude that most of the hydrogen is incorporated as  $SiH_x$  compounds (70%). If we assume an increased isotope exchange for increasing rf power, which is likely to occur due to the higher dissociation rate in the plasma, the measurements of Yatsurugi et al. [1] can be explained by isotope exchange processes.

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