Hydrogen Diffusion and Trapping in Micro-Nanocrystalline Silicon
L. Lusson, P. Elkaim, A. Correia, D. Ballutaud

To cite this version:

HAL Id: jpa-00249372
https://hal.archives-ouvertes.fr/jpa-00249372
Submitted on 1 Jan 1995

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Hydrogen Diffusion and Trapping in Micro-Nanocrystalline Silicon

L. Lusson, P. Elkaim, A. Correia and D. Ballutaud

Laboratoire de Physique des Solides de Bellevue, CNRS, 1 place Aristide Briand, 92195 Meudon cedex, France

(Received 20 January 1995, accepted 3 May 1995)

Résumé. — Des expériences d’exodiffusion sont réalisées sur des échantillons de silicium déposés en couches minces par pulvérisation cathodique, cristallisés par recuit thermique et post-hydrogénés (deutérés). L’analyse des spectres d’exodiffusion et des profils de diffusion obtenus par spectrométrie de masse d’ions secondaires permet de conclure à la présence de cavités suffisamment larges pour contenir de l’hydrogène sous forme moléculaire, à la présence d’hydrogène faiblement lié situé dans des micro-cavités ainsi qu’à celle d’hydrogène piégé aux joints de grains. Ces résultats sont corrélés aux microstructures des couches analysées par Microscopie Electronique en Transmission, microstructures qui dépendent des conditions de dépôt des couches initiales de silicium amorphes.

Abstract. — Effusion experiments and Secondary Ion Mass Spectrometry (SIMS) profiling are performed on post-hydrogenated (deuterated) micro-nanocrystallized silicon films obtained by thermal annealing of amorphous sputtered layers. The analysis of the effusion spectra and SIMS profiles allows to evidence the existence of cavities containing molecular hydrogen, the presence of weakly bonded hydrogen in small clusters and hydrogen trapped at grain boundaries. These results are analysed with regard to the microstructure of the crystallized layers studied by Transmission Electron Microscopy. This microstructure depends on the conditions of deposition of the original amorphous layers.

1. Introduction

Due to a higher mobility, polysilicon thin film transistors are expected to replace their amorphous counterparts in some electronics devices [1]. During the last few years, many studies have been developed to understand deposition mechanisms leading to microcrystalline silicon. The production of microcrystalline films by glow-discharge plasma deposition has been extensively studied and several mechanisms have been proposed: hydrogen enhanced surface diffusion [2], weak bond etching by hydrogen [3], and sub-surface chemical annealing. In the last few years, several groups have reported microcrystalline silicon growth by reactive magnetron sputtering [4]. However, good quality microcrystalline silicon films have been obtained
before [5] by the deposition of hydrogenated silicon in the amorphous phase and subsequent crystallization by thermal annealing or rapid thermal annealing. While the incorporation of hydrogen during amorphous silicon growth has been shown to improve the electronic properties of the films, the presence of hydrogen in the original amorphous layer may compromise the quality of the microcrystallized material. Compared with chemical vapour deposition or glow-discharge, sputtering is a deposition technique allowing to control more accurately the rate of hydrogen introduced in the layer [6] and presents some interest from this point of view. Furthermore, post-hydrogenation by atomic hydrogen is well known to passivate intra- and inter-grain defects in polycrystalline silicon, such as grain and sub-grain boundaries [7], dislocations and dangling bonds, and thus to improve the electronic properties of the material [8]. The problem is to know which defect is passivated by hydrogen [9].

In this paper, in order to study the configurations and stability of hydrogen bonding in microcrystalline silicon, we report results of effusion experiments performed on post-hydrogenated (deuterated) small grain (< 250 Å) micro-nanocrystalline silicon obtained by thermal crystallization of amorphous sputtered films. The post-hydrogenation (deuteration) of the microcrystallized samples was performed using hydrogen plasma annealing, and the deuterium solubility was provided by Secondary Ion Mass Spectrometry (SIMS). The grain size and crystallization quality were analysed by Transmission Electron Microscopy (TEM). A quick description of the experimental approach is given. The effects of the presence of hydrogen in the original amorphous layer and the use of a magnetron cathode are studied. The results are compared with those obtained previously on monocrystalline silicon [10]. The role of hydrogen in the crystallization process and the nature of the different bonding configurations are discussed.

2. Experimental

Undoped amorphous silicon was deposited by radiofrequency (RF) plasma sputtering on a highly resistive silicon substrate, using a monocrystalline undoped silicon target and a pure argon or (argon + 15% hydrogen) mixture to produce a-Si or a-Si:H respectively. The substrate temperature was ruled at 250 °C, the power density of the RF plasma was 2 W cm⁻² and the pressure 5 x 10⁻³ mbar. The deposited layers were 1 μm thick. Some layers were deposited in a reactor using a simple cathode, others with a magnetron cathode, i. e. with minimization of the damages to the growing films due to the bombardment of secondary electrons, thanks to the magnetic confinement of the charged particles. The microcrystalline films were prepared by thermal crystallization of the amorphous layers which were submitted to a linear heating rate of 20 K min⁻¹ from room temperature to 800 °C.

The post-deuteration of the microcrystalline samples was performed in a deuterium RF plasma reactor; the plasma exposure conditions were set to 15 min, 120 °C, a pressure of 1 mbar and a power density of 0.12 W cm⁻². Deuterium concentration profiles were obtained by SIMS measurements with a CAMECA IMS4F apparatus. The primary ion was Cs⁺ and the absolute concentrations were reached by calibration with deuterium implanted reference samples and by using a profilometer to measure the abrasion depths.

The effusion spectra [11] were measured by a quadrupole mass spectrometer coupled to an evacuated quartz tube (10⁻¹⁰ mbar) which contained the deuterated samples submitted to a linear rate heating of 20 K min⁻¹ between room temperature and 1000 °C. The effusion set-up was an open one [11], and the pumping speed was ruled so that the deuterium partial pressure measured by the mass spectrometer was proportional to the deuterium flow outgassing from the sample.

Plan-view Transmission Electron Microscopy (TEM) was carried out on a 200 kV JEOL 2000FX fitted with a small gap pole piece for High Resolution Electron Microscopy (optical
resolution: 0.28 nm; \( d_{111} \) in silicon: 0.314 nm). For plan-view examination, thin foils were prepared by chemical etching: the deposited film was protected by varnish, then the opposite side i.e. the substrate was etched by an \( \text{HNO}_3;\text{CH}_3\text{COOH};\text{HF} \) aqueous solution [12]. For the cross section imaging of the layer, several samples were stuck together, and the thinning was carried out by ion milling.

The effusion experiments were performed on the following groups of samples:

- deuterated microcrystalline silicon samples \( \mu c(\text{a-Si}:\text{H}) \) and \( \mu c(\text{a-Si}:\text{H}_m) \), obtained by crystallization of sputtered hydrogenated amorphous silicon (a-Si:H) or sputtered hydrogenated amorphous silicon using a magnetron cathode (a-Si:Hm), then deuterated in a RF plasma.

- deuterated microcrystalline silicon samples \( \mu c(\text{a-Si}) \) and \( \mu c(\text{a-Si}_m) \), obtained by similar crystallization of non-hydrogenated sputtered amorphous silicon (a-Si) or sputtered amorphous silicon using a magnetron cathode (a-Si_m), then deuterated in a RF plasma.

The deuterium profiles were analysed by SIMS before the effusion run.

3. Results

3.1. Effusion Results and SIMS Profiles Analysis. — Figure 1 reports the deuterium effusion spectra provided by the two samples labelled \( \mu c(\text{a-Si}:\text{H}) \) and \( \mu c(\text{a-Si}:\text{H}_m) \) preliminarily submitted to a post-deuteration for 15 min at 120 °C. It reveals two low temperature overlapping peaks at respectively 370 and 520 °C, and for the post-deuterated \( \mu c(\text{a-Si}:\text{H}) \) sample, the emergence of an important peak at nearly 800 °C. This one is still visible but much less
important for $\mu c(a\text{-}Si\text{:}H_m)$. The effusion spectra of these two microcrystalline samples are different from those observed previously in amorphous silicon layers where three main peaks are generally observed at about 400, 600 and 700 °C. These ones correspond respectively to weak bonded hydrogen (deuterium) in clusters, strong bonded hydrogen embedded in the amorphous structure and hydrogen outgassing during crystallization [11]. In the post-deuterated microcrystalline silicon, the peaks at 600 and 700 °C have disappeared. A new peak is observed at 520 °C, similar to the one previously observed in post-deuterated monocrystalline silicon (Fig. 2) [10]. In this case, the peaks at 370 – 400 °C were attributed to the effusion of high concentration deuterium trapped on defects due to plasma damage near the surface, and when the monocrystalline silicon was doped, to the effusion of deuterium trapped on dopant to form deuterium-dopant complexes. The effusion peak at 520 °C was attributed to neutral deuterium isolated in the silicon structure [10].

Concerning the SIMS analysis, the deuterium concentration profile before the effusion process in $\mu c(a\text{-}Si\text{:}H_m)$ exhibits (Fig. 3, Curve b) somewhat of an erfc function, which contrasts with the almost constant deuterium concentration in $\mu c(a\text{-}Si\text{:}H)$ (Fig. 3, Curve a) as well as with the corresponding profile measured on monocrystalline silicon (Fig. 3, Curve e) [13].

We have proceeded then to the same experiment on similarly treated samples except that the original sputtered amorphous silicon layers were deposited using pure argon instead of an (argon + deuterium) mixture. These two samples were labelled $\mu c(a\text{-}Si)$ and $\mu c(a\text{-}Si_m)$. Figure 4 shows the effusion spectra of these post-deuterated samples. The striking feature is the absence of the above mentioned important peak at 800 °C. The structures at lower temperature (370 - 520 °C) are similar to the corresponding ones observed for $\mu c(a\text{-}Si\text{:}H)$ and $\mu c(a\text{-}Si\text{:}H_m)$ (Fig. 1).
Fig. 3. — SIMS deuteration concentration profiles in post-deuterated micro (nano)-crystalline silicon obtained by crystallization of (a-Si:H) (Curve a); (a-Si:H_m) (Curve b); (a-Si) (Curve c) and (a-Sim) (Curve d). For comparison, the deuterium concentration profile in monocrystalline undoped silicon deuterated with the same conditions is also reported (Curve e).

Fig. 4. — Effusion spectra of post-deuterated micro (nano)-crystalline silicon obtained by crystallization of (a-Si) (Curve a) and (a-Sim) (Curve b).
Table I. — $\mu c(a\text{-Si}:H_m)$ SAD Pattern Indexation.

<table>
<thead>
<tr>
<th>Ring</th>
<th>$d_{\text{sat}}$ (Å)</th>
<th>$d_{\text{sat}}$ (Å)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Experimental</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.22</td>
<td>2.22</td>
<td>211</td>
</tr>
<tr>
<td>2</td>
<td>1.36</td>
<td>1.36</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>1.11</td>
<td>1.14</td>
<td>422</td>
</tr>
<tr>
<td>4</td>
<td>0.96</td>
<td>0.95</td>
<td>440</td>
</tr>
<tr>
<td>5</td>
<td>0.86</td>
<td>0.87</td>
<td>620</td>
</tr>
</tbody>
</table>

Table II. — $\mu c(a\text{-Si}_m)$ SAD Pattern Indexation.

<table>
<thead>
<tr>
<th>Ring</th>
<th>$d_{\text{sat}}$ (Å)</th>
<th>$d_{\text{sat}}$ (Å)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Experimental</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.84</td>
<td>4.00</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>2.22</td>
<td>2.29</td>
<td>211</td>
</tr>
<tr>
<td>3</td>
<td>1.36</td>
<td>1.40</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>1.25</td>
<td>1.22</td>
<td>331</td>
</tr>
</tbody>
</table>

Concerning the SIMS analysis, the deuterium concentration before effusion process in $\mu c(a\text{-Si})$ and $\mu c(a\text{-Si}:H)$ is higher than in respectively $\mu c(a\text{-Si}_m)$ and $\mu c(a\text{-Si}:H_m)$ (Fig. 3, Curves a, b, c and d).

3.2. TEM Results. — The TEM plan-view of the $\mu c(a\text{-Si}:H_m)$ (Fig. 5a) shows a disorganized structure with nano-grains. This result is confirmed by the Selected Area Diffraction (SAD) pattern (Fig. 5b). The radii of the circular SAD pattern have been indexed and found to correspond to the d-spacing of silicon (Tab. I). A high resolution microscopy plan-view has been performed on this sample (Fig. 6), exhibiting an average grain area of 60 nm², the interplanar distance $d_{111}$ of silicon (3.14 Å) and also cavities. Observations on the cross-section view (Figs. 7a, b) are in good agreement with the previous ones. Figure 7a indicates that the layer is about 1 μm thick, result confirming the value obtained by SIMS (Fig. 3). A magnification (Fig. 7b) allows us to observe the same disorganized structure as shown in Figure 5a. The SAD pattern performed on this cross-section view is similar to the one of Figure 5b and its indexation gives the d-spacing of the silicon too.

The $\mu c(a\text{-Si}_m)$ sample TEM plan-view (Fig. 8a) exhibits a different structure from the previous one. We observe a larger grain area but also defects inside some grains which are microtwins. The radii of the SAD pattern rings have been indexed and give the d-spacing of silicon (Tab. II). The SAD pattern (Fig. 8b) shows that the grains are larger, result in good agreement with the TEM observations. It is observed on the high resolution TEM view grains with an area of 600 nm² average (Fig. 9), one order of magnitude higher than in the $\mu c(a\text{-Si}:H_m)$ sample (Fig. 6). It exhibits also the interplanar distance corresponding to {111} silicon planes i.e 3.14 Å. Contrary to the $\mu c(a\text{-Si}:H_m)$ sample, TEM views do not evidence cavities.
4. Discussion

From the comparison between the data of the different samples, it is possible to advance some conclusion concerning the behaviour of hydrogen during the crystallization mechanism. It seems that in the originally hydrogenated amorphous films, it exists small clusters of hydrogen in microvoids, where some amount of molecular hydrogen has been already evidenced in sput-
Cavities lead to the growth of larger clusters during the thermal crystallization and bring about the formation of large cavities in the resulting nanocrystalline material. The existence of these cavities in the case of \( \mu c(a\text{-Si:H}) \) and \( \mu c(a\text{-Si:H}_m) \) would explain the very different response to post-deuteration: a higher concentration of deuterium in the microcrystalline layers, a very stable configuration of deuterium responsible for the high temperature peak of the effusion spectra. The high temperature needed to desorb these deuterium species suggests that molecular deuterium is formed in the above mentioned cavities during the post-deuteration. The deuterium molecule has to dissociate before the out-diffusion process may occur, which explains the high effusion temperature observed. This deuterium molecule trapping in cavities is less pronounced when a magnetron cathode is used to deposit the original amorphous silicon layer.
We propose the following interpretation of the origin of the two overlapping peaks between 370 and 520 °C by comparison with the similar ones observed for deuterated monocrystalline silicon (Fig. 2) [10]. The effusion peak at 400 °C is due to high concentration deuterium trapped in plasma damaged surface regions, or in damaged regions at grain boundaries, the 520 °C one is likely to be due to deuterium “quenched” in the grain, as proposed in monocrystalline silicon.

The different microstructures of the samples analysed by TEM are coherent with the relative importance of the different effusion peaks and SIMS profiles. The TEM view performed on μc(a-Si:H_{m}) (Fig. 6) confirms the existence of cavities which are not seen on the TEM view of μc(a-Si_{m}) (Fig. 9). During the crystallization process, the presence of hydrogen in the initial amorphous silicon layer induces, in the nanocrystalline structure, cavities large enough to trap molecular deuterium during post-deuteration. In this case, the crystallites are smaller and disorganized regions are detected by TEM (Fig. 5). The absence of cavities corresponds to the absence of the effusion peak at 800 °C (Figs. 1 and 4). The use of a magnetron cathode during the amorphous layer deposition decreases the density of cavities and defects in the resulting
nanocrystalline silicon, as it is shown by the decreasing of the 800 °C effusion peak in this case (Fig. 1) and by a lower deuterium solubility (Fig. 3).

In conclusion, the structure of the nanocrystalline silicon film depends on the conditions of deposition of the silicon amorphous layer. Introducing hydrogen in the initial sputtered amorphous layer promotes, during thermal crystallization, the formation of cavities large enough to trap molecular deuterium. These cavities are detected by TEM. The second effect of the presence of hydrogen in the amorphous layer is to lead to smaller grains in the thermally crystallized silicon. In this case, the use of a magnetron cathode during the deposition process seems to improve the nanocrystalline film quality.
Moiré fringes

\[ d_{111}(\text{Si}) = 3.14 \, \text{Å} \]

Fig. 9. — High resolution microscopy plan-view of \( \mu c(a-\text{Si}_m) \).

References


