Ion-beam induced hydrogen redistribution in a-Si:H-based triple layer structures

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Abstract. Ion-beam induced hydrogen migration has been studied in triple layer structures, a-Si/a-Si:H/a-Si and SiO₂/a-Si:H/SiO₂. Nuclear reaction analysis has been used for simultaneous irradiation with MeV ions and measurement of hydrogen distribution in the structures. It has been established that there is no hydrogen loss from SiO₂/a-Si:H/SiO₂ structures, but an asymmetric redistribution due to hydrogen penetration into the bottom SiO₂ layer. Hydrogen loss has been observed from the a-Si/a-Si:H/a-Si structures. The inspection of the surface of these samples by means of atomic force microscope has shown that it proceeds by bubble formation and blistering at the inner interface. The observed ion-beam induced selective penetration of hydrogen into the underlying material can be used as a tool for preparation of microcavity and microchannel arrays.

1. Introduction
An impact of ionizing irradiation on the electronic and structural properties of hydrogenated amorphous silicon (a-Si:H) has been observed in recent studies. It has been established that electron irradiation induces structural defects in the films and that the defect creation is not initiated by recombination events, but by energy transfer during collisions [1,2]. The impact of ionizing irradiation on the hydrogen content and on its bonding configuration in a-Si:H has attracted less attention. High energy irradiation may induce hydrogen migration with different consequences. MeV ion-beam induced loss of hydrogen from organic and inorganic materials has often been observed and is usually associated with its out-diffusion through the sample surface into the vacuum environment [3-7]. Studies have reported about hydrogen accumulation near the interfaces [8] and bubble formation inside the films [9]. It has also been shown that hydrogen thermally evolved from a-Si:H film can diffuse into and be retained within the substrate [10].

Irradiation-induced hydrogen release from its bonded sites is related to the electronic excitation of the solid. For MeV ions irradiating sub-micrometer thick films this mechanism prevails the nuclear interaction between the ions and the target atoms. In the present work, MeV ion-beam induced hydrogen redistribution has been studied in a-Si:H, which has been sandwiched between thin hydrogen-free amorphous silicon (a-Si) or SiO₂ layers. It is shown that in these layer stacks ion-beam induced hydrogen migration strongly depends on the interface properties. Moreover, a selective
penetration of hydrogen into the underlying material has been established, which could be used as a tool for microcavity and microchannel engineering.

2. Experimental procedure

Figure 1 shows schematically the configuration of the studied samples. The layer stacks consisted of an a-Si:H layer sandwiched between two hydrogen-free a-Si layers or between two SiO2 layers. The a-Si layers were prepared by DC magnetron sputtering in argon atmosphere at a gas pressure of 6.7 Pa and a power of 250 W applied to a silicon target. The SiO2 layers were deposited by RF magnetron sputtering from a fused silica target using argon/oxygen mixture, at a total pressure of 0.67 Pa and a power of 1000 W. The a-Si:H layer was deposited by plasma enhanced CVD using 10% silane diluted in hydrogen, at a pressure of 133 Pa and a power density of 100 mW/cm². After each deposition run the samples were exposed to air because of using different chambers for the layer deposition. This led to the absorption of the water molecules on the layer surface, which was particularly detectable for SiO2 due to its high sensitivity to humidity. All layers constituting the structure were deposited at room temperature in order to increase the hydrogen concentration in a-Si:H and to reduce as much as possible any asymmetry in the structure properties. The film thicknesses were 100 nm for a-Si and SiO2, and 50 nm for a-Si:H. The substrates were crystalline (100) Si wafers.

Hydrogen concentration has been measured at the 5 MV tandem accelerator of the Forschungszentrum Rossendorf using the following nuclear reaction:

\[ ^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + \gamma (4.43\text{ MeV}) \]

This reaction has a narrow resonance at the energy \( E_{\text{res}} \) of 6.385 MeV. By increasing the energy of \(^{15}\text{N} \) ions above \( E_{\text{res}} \), the ions reach the resonance energy at a certain depth of the sample due to energy loss in the material. Therefore, hydrogen depth profiles can be determined by measuring the yield of the 4.43 MeV \( \gamma \) -rays as function of the energy of the \(^{15}\text{N} \) ions. The \( \gamma \) -rays were detected by a 4” × 4” BGO detector. The \(^{15}\text{N} \) ion beam spot had an area of 2.5 mm². The depth resolution was about 8 nm.

To estimate the effect of the \(^{15}\text{N} \) ion irradiation on hydrogen depth distribution, the measurements were carried out on a different sample spot for each ion energy, i.e. at each specified depth. The ion fluence was varied from \( 6 \times 10^{13} \) to \( 1.7 \times 10^{15} \) ion cm⁻².

**Figure 1.** Schematic view of \(^{15}\text{N} \) ion irradiation of the a-Si/a-Si:H/a-Si and SiO2/a-Si:H/SiO2 layer stacks.

**Figure 2.** Hydrogen depth profiles in the a-Si/ a-Si:H/a-Si and SiO2/a-Si:H/SiO2 layer stacks irradiated with the ion fluence of \( 6x10^{13} \) ion/cm².
3. Experimental results and discussion

Compilation of the NRA measurements carried out with different $^{15}\text{N}$ ion energies provides a hydrogen depth profile for the entire structure. It is assumed that the hydrogen distribution measured with the lowest ion fluence of $6 \times 10^{13}$ ion/cm$^2$ is characteristic for the as-prepared structures. Figure 2 shows the initial hydrogen distribution in SiO$_2$/a-Si:H/SiO$_2$ and a-Si/a-Si:H/a-Si samples. Note that the hydrogen depth distribution in the as-deposited a-Si:H is uniform [11] and in the triple layer structure studied here it should appear as a 50 nm wide bar in the middle of the layer stack. The Gaussian form and hydrogen spreading outside the a-Si:H layer (beyond the 100 - 150 nm region) is related to the unavoidable ion straggling effect. Near the interfaces there is a difference between the hydrogen concentrations in the sputtered SiO$_2$ and a-Si layers. This difference is related to a higher water molecule absorption by the open SiO$_2$ lattice structure, as compared to a-Si. The effect is most evident in the region close to the top surface of the sandwich structures and reflects the sensitivity of the former to the air humidity. Hydrogen on the surface is not stable and its concentration decreases strongly with the irradiation.

It has been presumed that if there is any ion-beam induced hydrogen loss from a-Si:H film it should proceed through both - outer and inner - interfaces, because of the symmetric structure and the seemingly similar properties of the interfaces. Therefore, it has been expected that the increase in ion fluence would lead to a gradual decrease in the hydrogen concentration inside the a-Si:H layer and a corresponding symmetric increase in the regions outside a-Si:H, close to the interfaces. Instead, a different behaviour has been established for the outer and inner interfaces. Figure 3 shows the variation in the hydrogen concentration with increasing ion fluence at different depths in the triple layer structures. The amount of hydrogen measured outside the a-Si:H layer is partially related to the

![Figure 3](image-url)

**Figure 3.** Effect of $^{15}\text{N}$ ion fluence on the hydrogen concentration in a-Si/a-Si:H/a-Si and SiO$_2$/a-Si:H/SiO$_2$ layer stacks: a) in the middle of the a-Si:H layer; b) around the outer interface; c) around the inner interface.
straggling effect, but the trends are associated with the actual changes in the hydrogen concentrations and reflect its irradiation-induced dynamics.

Figure 3 (a) shows the impact of the ion fluence on the hydrogen concentration in the middle of the a-Si:H layer. As expected, the MeV $^{15}$N$^{+}$ irradiation leads to an essential gradual decrease in the hydrogen concentration inside the a-Si:H layer, i.e. there is irradiation-induced hydrogen out-diffusion from a-Si:H. Figure 3 (b) shows the impact of ion fluence on the hydrogen concentration at the outer interface, from the side of the top layers (depth point 80 nm). At both interfaces, a-Si/a-Si:H and SiO$_2$/a-Si:H, the hydrogen concentration is stable and does not change under the irradiation. A higher concentration of hydrogen at the SiO$_2$/a-Si:H interface is related to the water contaminated SiO$_2$. Thus, it can be suggested that hydrogen does not penetrate from a-Si:H layer into the top layers. Figure 3 (c) shows the impact of ion fluence on hydrogen concentration at the inner interface, from the side of the bottom layers (depth point 170 nm). There is a well detectable increase in the hydrogen concentration for the a-Si:H/SiO$_2$ interface, whereas for a-Si:H/a-Si interface the hydrogen concentration remains constant.

![Figure 4](image_url)

**Figure 4.** Effect of $^{15}$N ion fluence on the hydrogen content in the entire in a-Si/a-Si:H/ a-Si and SiO$_2$/a-Si:H/SiO$_2$ layer stacks.

Figure 4 shows the irradiation induced changes in the hydrogen amount for the whole structures. The amount of hydrogen has been determined by the integration of the depth profiles over the entire thickness of the layer stack. This estimation takes into account all hydrogen, including the water molecules absorbed on the surface. In the SiO$_2$/a-Si:H/SiO$_2$ samples the hydrogen concentration decreases after the first measurements and then remains stable. The initial decrease is related to the hydrogen desorption from the water molecules adsorbed on the sample surface. Bearing in mind the data presented in figure 3 this suggests that hydrogen loss only proceeds from the a-Si:H layer and not from the whole sample. In the a-Si/a-Si:H/a-Si samples hydrogen concentration decreases continuously, which suggests that hydrogen leaves the sample and not only the a-Si:H layer.

Figure 5 shows the hydrogen depth profiles in both kinds of structures before and after the irradiation with highest fluence of 1.7x10$^{15}$ ion/cm$^2$. It is seen that the ion-beam induced variation in the hydrogen distribution is asymmetric and takes place mainly in the middle of the a-Si:H layer and in the regions close to the inner interface. Final hydrogen depth distribution depends on the underlying layers. In the SiO$_2$/a-Si:H/SiO$_2$ structures hydrogen leaves a-Si:H layer by penetrating into the bottom SiO$_2$ layer. In the a-Si/a-Si:H/a-Si structures there is a decrease in the hydrogen concentration in the region at the inner interface. Specific for latter structures is the appearance of blisters (figure 6). The measurement of the depth of the exfoliated blisters using AFM gives the value of 150 nm, i.e. the sum of a-Si and a-Si:H thicknesses (figure 7). Thus, it can be suggested that the irradiation of a-Si/a-Si:H/a-Si leads to hydrogen accumulation and bubble formation at the inner interface. The hydrogen loss in these structures is associated with the delamination of the a-Si:H layer.
The obtained results suggest that hydrogen leaves thin a-Si:H layer in both kinds of structures through the inner interface, either by blistering and delamination, or by diffusion into the bottom layer. The hydrogen loss through the surface might also proceed, but it seems to have a minor contribution, as there is not any essential ion-beam induced change in the hydrogen concentration in the top layers and at the outer interface. The irradiation-induced decrease in the hydrogen concentration should be considered as related to the diffusion of the liberated hydrogen atoms. Hydrogen diffusion in amorphous silicon is a complex phenomenon. It strongly depends on the structure of the amorphous network, which defines the hydrogen transport path and the hydrogen chemical potential [12-14]. Since the release of hydrogen from the bonded sites is the same throughout the a-Si:H layer, the observed asymmetric redistribution of hydrogen should be ascribed to a difference in the structural properties of the inner and outer interfaces. Although the layer stacks seemed to be symmetric there might be a hidden asymmetry due to the reverse sequences of the argon/oxygen and silane/hydrogen plasma. Actually, the initial stage of the top layer deposition is associated with the ion bombardment of a-Si:H and may lead to an increase in the density of the structural defects at the outer interface. It results in a local increase in the energy difference between the hydrogen transport path and the
hydrogen chemical potential. Due to the exponential dependence of the diffusion coefficient on this energy parameter even a small increase of the latter can lead to a considerable decrease in the hydrogen transport at the outer interface. Thus, the main stream of the liberated hydrogen atoms is through the inner interface.

The following hydrogen migration depends on the material properties of the bottom layer and is selective regarding the a-Si and SiO$_2$ layers. This fact could be used as a tool for microcavity and microchannel engineering. An approach for the preparation of a microchannel array is schematically shown in figure 8. A structure consisting of a-Si:H, a-Si and SiO$_2$ layers can be prepared with appropriate dimensions using conventional photolithographic methods (figure 8a). Under the impact of the MeV ions the part of a-Si:H layer on SiO$_2$ layer remains intact, due to the hydrogen penetration into the bottom layer. Hydrogen accumulation and bubbles formation proceeds on the inner a-Si:H/a-Si interface (figure 8b). Further irradiation leads to the delamination of a-Si:H layer in the region over the a-Si layer (figure 8c). Note, the delaminated parts remain buckled due to the compressive stress in a-Si:H. The delamination process might be controlled by ion fluence and hydrogen concentration in the as-prepared a-Si:H. Buckling process might also depend on the thickness ratio of the layers, as well as on the mechanical stress in a-Si:H.

![Figure 8](image-url)
4. Conclusion
It is shown that a MeV ion beam induces hydrogen diffusion in the a-Si/a-Si:H/a-Si and SiO2/a-Si:H/SiO2 samples, which is sensitive to the interface properties. Hydrogen loss from the samples proceeds mainly through the inner interface. Depending on the material below the a-Si:H layer, there is either hydrogen diffusion through the interface or bubble formation and a-Si:H layer delamination.

Acknowledgments
This study was carried out with the support of AIM - Center for Application of Ion Beams to Materials Research under RITA Contract No. 025646, and of Institute of Solid State Physics, Bulgarian Academy of Sciences, Contract No BK9-2.

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