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Thermal desorption study on possible hydrogen sources and diffusion barriers in CMOS technology

Jacopo Remondina¹, Alain Portavoce¹, Maxime Bertoglio¹, Guillaume Roland^{1,2}, Frédéric Lorut², Yannick Le Friec², Daniel Benoit², Magali Putero^{1*}

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Keywords: Hydrogen, Thermal desorption spectroscopy, CMOS, Nitride, Oxide

Abstract

Hydrogen passivation of silicon dangling bonds is a key requirement in the realization of reliable CMOS devices. The creation of a hydrogen reservoir in the device near the silicon may be a solution supporting constant passivation during the life-cycle of the device. In this work, we used thermal desorption spectroscopy to evaluate the amount of hydrogen stored in undoped silicon glass (USG) deposited using SiH_4 (USG- SiH_4) or tetraethyl orthosilicate (USG-TEOS), and silicon (carbon) nitrides, typical dielectrics used in CMOS technology. The goal of the study is to determine if these materials can be used as hydrogen source or diffusion barrier. Our results suggest that USG- SiH_4 can act as an efficient source of hydrogen, while Si nitrides can act as reliable diffusion barrier.

1. Introduction

Si-based complementary-metal-oxide-semiconductor (CMOS) technology is used to produce low power consumption and high noise resistance [1,2] microelectronic transistors for all kind of applications, from the more popular/mainstream (PC, smartphone, wearable, IoT, etc) to the more dedicated/demanding ones (industrial applications, automotive, biological, etc) [3,4].

However, Si device performances are directly influenced by the number of defects present in the active region of the device. Indeed, despite the use of ultra-pure Si wafers, some intrinsic defects were shown to compromise device performances, such as vacancies and related extended defects (dislocations, interfaces...) [5]. These defects are known to alter the energy band scheme, introducing localized states [6] that can negatively influence the properties of a wide range of devices. One of the proposed and implemented solutions consists in saturating Si dangling bonds using hydrogen (H) [7] (or deuterium [8]). Usually, Si dangling bond saturation by H is performed during growth, exposing the material to a H-rich atmosphere [9]. However, this technique cannot be used for all applications, depending on device fabrication process, and the passivated region needs to be encapsulated by an H diffusion barrier for device reliability.

A second technique would consist in including in the surrounding materials an environment supporting H passivation during the entire life-time of the device [10]. In this work, we used thermal desorption spectroscopy (TDS) to investigate the possibility of using typical CMOS-compatible dielectrics (two Si oxides and two Si nitrides) as H source or H diffusion barrier for such application.

2. Materials and methods

The materials were investigated in the form of thin films. Deposition was performed on cleaned Si(001) wafers in PECVD reactors. Two 940 nm thick Si dioxides layers were investigated for possible H sources: both are undoped silicon glass (USG) either deposited at 275°C using silane gas as precursor (USG-SiH₄), or deposited at 380°C using tetraethoxysilane (USG-TEOS). Nitrogen was used as carrier gas. The two materials expected to act as H diffusion barrier were a 40 nm-thick SiCN layer deposited at 350°C and a 600 nm-thick Si₃N₄ layer deposited at 380°C. Two types of samples were produced, as the nitride layers were deposited either on a cleaned Si wafer or a possible H source layer (Si₃N₄/USG-SiH₄ and SiCN/USG-SiH₄ samples).

After deposition, the samples were placed on a 1 cm diameter PBN furnace and loaded in an ultrahigh vacuum (UHV) system equipped with an Ametek LC-D quadrupole mass spectrometer, allowing TDS measurements to be performed (see SI). The samples were introduced in the UHV chamber (< 10⁻¹⁰ mbar) through an introduction chamber (base vacuum of 10⁻⁷ mbar). The sample temperature was measured and controlled via an Eurotherm controller thanks to a thermocouple placed close to the sample on the PBN furnace. The samples experienced an isochronal annealing of 4°C.min⁻¹ during mass spectrometry.

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A full desorption spectrum comprising masses up to 45.7 Dalton was first recorded during sample annealing and compared to a same full spectrum recorded in same conditions in the UHV setup without any sample (see Fig.S2 in SI), allowing to select the masses of interest. Fig.1a presents the TDS measurements of the selected masses performed on the USG-SiH₄ layer. CO₂ and H₂O are regularly detected in vacuum chambers during heating due to the degassing of parts coming from atmosphere, such as the sample holder in our case. They are used as references in Fig. 1a, as their desorption trends are identical with or without sample in the chamber and were found to be similar to all the detected molecules beside H, nitrogen (N) and oxygen (O) related molecules. Indeed, only H₁, H₂, N₂, and O₂ molecules show desorption peaks (Fig.1a) compared to their base line measured in the UHV chamber free of sample (Fig. S2). H and N molecules were expected to leave the Si oxide layers in addition to O₂ as they are part of their fabrication process. One can note that H₂O desorption shows no peak, it is similar to the H₂O desorption base line recorded without sample in the setup. Consequently, the H desorption peak appears to be independent of the H₂O molecule dissociation and corresponds to H contained in the bulk of the layer. Besides all the desorption peaks appear at the same temperature, around 300 °C, which is close to USG-SiH₄ deposition temperature (275 °C). Same observations were made on the different samples. Thus, further discussions will only focus on molecular H desorption, relative to the present subject of interest.

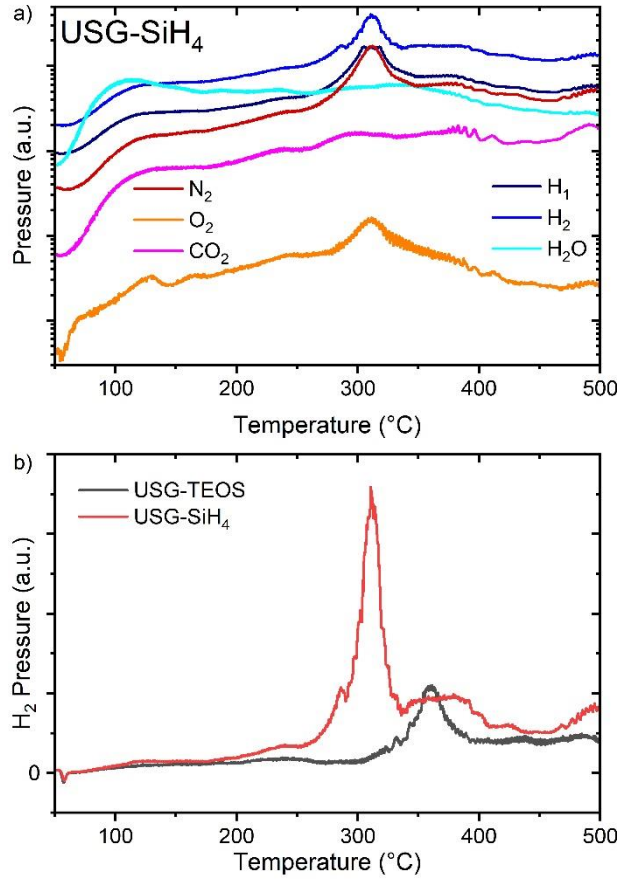


Figure 1: TDS measurements performed during $4\text{ }^{\circ}\text{C min}^{-1}$ ramp annealing of a 940 nm-thick layer of USG-SiH₄: a) for different masses and b) for H₂ mass, compared with USG-TEOS film.

Fig. 1b presents the desorption spectra recorded on both oxide layers USG-SiH₄ and USG-TEOS, after subtraction of the chamber background signal and normalization according to the sample surface area size. H is observed to desorb from both layers, but the main desorption peaks occur at different temperatures: $T \sim 310\text{ }^{\circ}\text{C}$ from USG-SiH₄ and $T \sim 360\text{ }^{\circ}\text{C}$ from USG-TEOS. The H content of the USG-SiH₄ film is found to be significantly higher. The difference of H content of the two films may be related to their respective growth temperatures, as the USG-SiH₄ layer was grown at lower temperature ($275\text{ }^{\circ}\text{C}$).

Fig. 2a presents the H₂ desorption spectra recorded from the Si₃N₄ layer compared to that of USG-SiH₄. Two desorption peaks are detected around $T = 310\text{ }^{\circ}\text{C}$ and $T = 375\text{ }^{\circ}\text{C}$. The H amount leaving this layer is noticeably smaller than from the USG-SiH₄ layer (red solid line) but similar to that of the USG-TEOS layer. Furthermore, the desorption spectra recorded if the USG-SiH₄ layer is capped with the Si₃N₄ layer is similar to that of the single Si₃N₄ layer, meaning that Si₃N₄ is a weak H source but an efficient H diffusion barrier. **Fig. 2b** presents the H₂ desorption spectra recorded on the SiCN layer and on the USG-SiH₄ layer capped with SiCN compared to that of USG-SiH₄ alone. H desorption from SiCN is weaker than from USG-TEOS and Si₃N₄, and thus, SiCN cannot be considered as an efficient source of H. However, despite that more H is found to leave the SiCN/USG-SiH₄ sample than from the single SiCN layer, the amount detected in this case being similar to that detected from the Si₃N₄/USG-SiH₄ sample, the SiCN layer can also be considered as an efficient H diffusion barrier. In particular, the thickness of the SiCN layer is more than one order of magnitude smaller than that of the Si₃N₄ layer.

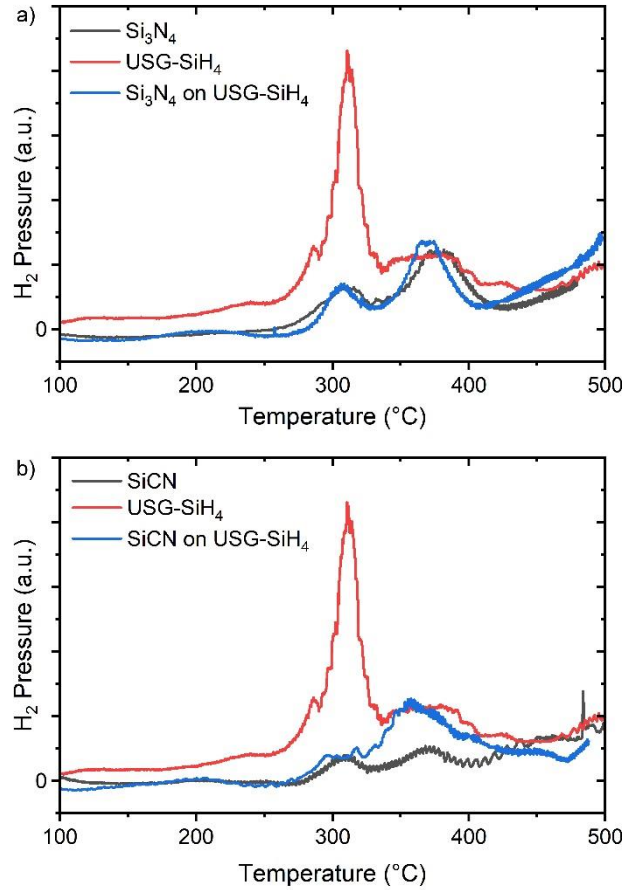


Figure 2: (a) H_2 desorption spectra recorded on the Si_3N_4 layer (black line) and the $Si_3N_4/USG-SiH_4$ sample (blue line) compared to the $USG-SiH_4$ layer desorption (red line), and (b) H_2 desorption spectra recorded on the $SiCN$ layer (black line) and the $SiCN/USG-SiH_4$ sample (blue line) compared to the $USG-SiH_4$ layer desorption (red line).

H desorption from H-passivated Si(001) substrates was studied as an attempt to pseudo-quantify the H amount detected in our experiments. The Si substrates were passivated with H by staying 1 minute in a 5% HF solution. In this case, a single monolayer (ML) of H covers the Si surface [11]. The desorption signal being normalized to the surface area size of the samples, this ML was used as the H amount unit. Table 1 presents the results of the conversion of desorption peak areas to H MLs.

Sample	Peak #	Area (a.u.)	H_2 MLs	H_2 MLs
H-passivated Si		1.39*	1*	
USG-SiH ₄	1	12.19	8.8	14±0.5
	2	7.49	5.4	
USG-TEOS	1	0.65	0.5	4.5±0.5
	2	5.36	3.9	
SiN	1	2.53	1.8	6.5±0.5
	2	6.34	4.6	
USG-SiH ₄ +SiN	1	1.92	1.4	6.0±0.5
	2	6.18	4.4	
SiCN	1	1.91	1.4	3.5±0.5
	2	2.72	2.0	
USG-SiH ₄ +SiCN	1	1.44	1.0	6.0±0.5
	2	6.72	4.8	

Table 1: TDS peak areas measured on the TDS spectra converted into H ML units using the desorption amount detected from H-passivated Si(001) substrates as reference*. The error on the ML detection was estimate to be 0.5 ML.

4. Conclusions

Two Si oxides (USG-SiH₄ and USG-TEOS) and two Si nitrides (Si₃N₄ and SiCN) commonly used in the CMOS technology were investigated as possible source of H or possible H diffusion barriers using TDS measurements. USG-SiH₄ was found to be the larger source of H, releasing about 3 times more H than USG-TEOS. Si₃N₄ and SiCN can be considered as effective H diffusion barriers. However, Si₃N₄ was found more effective for blocking H coming from an underneath layer, but was found to release more H from its bulk.

CRedit authorship contribution statement

J. Remondina: Investigation, Validation, Formal analysis, Data Curation, Visualization, Writing-Original Draft. **A. Portavoce:** Conceptualization, Methodology, Writing – Original Draft and review& editing, Supervision, Project Administration, Funding acquisition. **M. Bertoglio, G. Roland:** Investigation. **F. Lorut:** Project administration. **Y. Le Friec:** Resources. **D. Benoit:** Resources, Methodology, Writing – review& editing. **M. Putero:** Conceptualization, Methodology, Writing – review& editing, Supervision, Project Administration, Funding acquisition.

Declaration of Competing Interest

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Acknowledgements

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Supplementary information

Figure **S1**

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CRedit author statement

Jacopo Remondina: Investigation, Validation, Formal analysis, Data Curation, Visualization, Writing-Original Draft. Alain Portavoce: Conceptualization, Methodology, Writing – Original Draft and review& editing, Supervision, Project Administration, Funding acquisition. Maxime Bertoglio: Investigation, Methodology. Guillaume Roland: Investigation, Formal analysis. Frédéric Lorut: Project administration. Yannick Le Fric: Resources, Material deposition. Daniel Benoit: Resources, Material deposition, Methodology, Writing – review& editing. Magali Putero: Conceptualization, Methodology, Writing – review& editing, Supervision, Project Administration, Funding acquisition.

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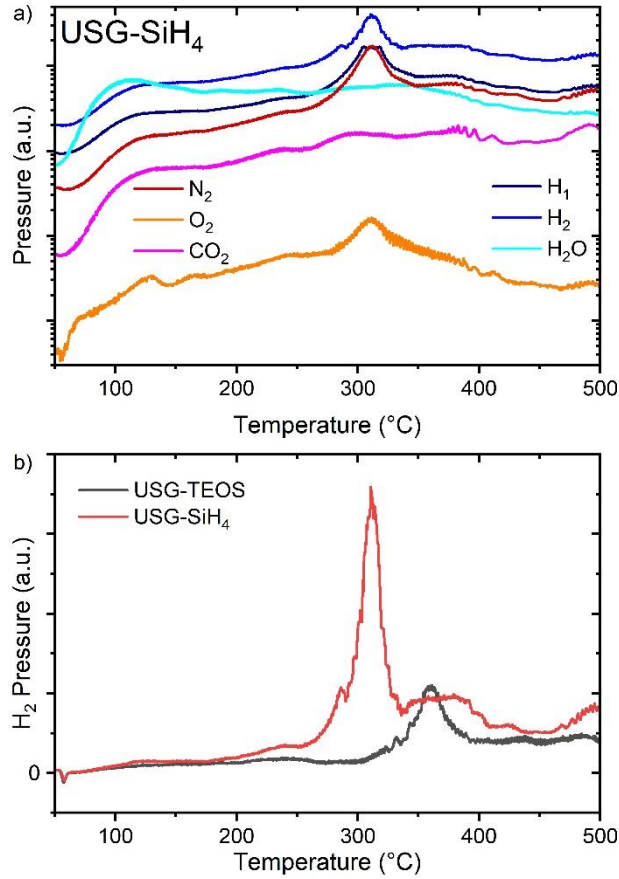


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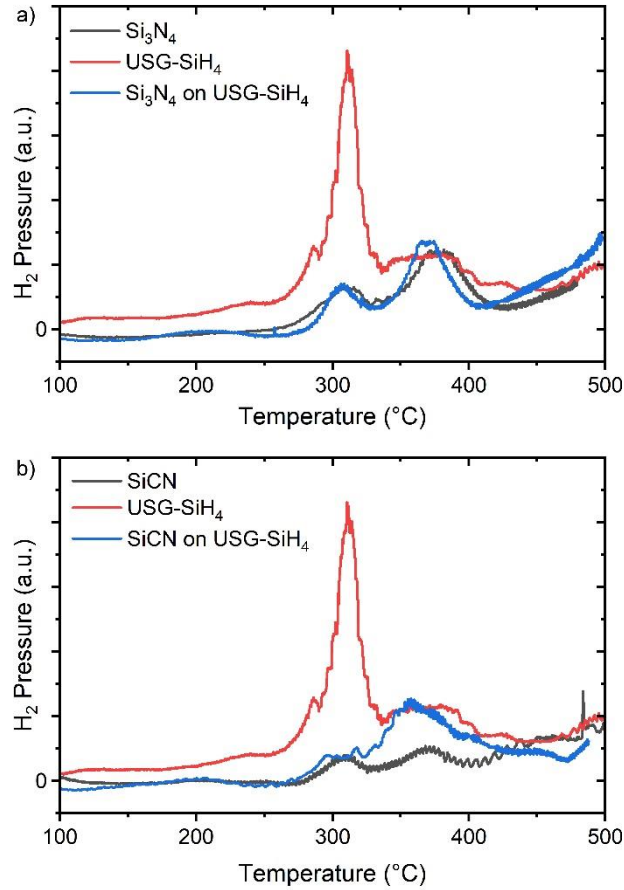


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Supplementary information

Figure **S1**

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