



# Transient thermal conductivity in PECVD SiN<sub>x</sub> at high temperature: the thermal signature of an on-going irreversible modification

M Hadi, S Pailhès, R Debord, A Benamrouche, Emmanuel Drouard, Thomas Gehin, Claude Botella, Jean -Louis Leclercq, P Noe, F Fillot, et al.

## ► To cite this version:

M Hadi, S Pailhès, R Debord, A Benamrouche, Emmanuel Drouard, et al.. Transient thermal conductivity in PECVD SiN<sub>x</sub> at high temperature: the thermal signature of an on-going irreversible modification. *Materialia*, 2022, 26, pp.101574. 10.1016/j.mtla.2022.101574 . hal-03854197

**HAL Id: hal-03854197**

**<https://hal.science/hal-03854197>**

Submitted on 15 Nov 2022

**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.

# Transient thermal conductivity in PECVD SiN<sub>x</sub> at high temperature: the thermal signature of an on-going irreversible modification

M. Hadi, S. Pailhès, R. Debord

*Institut Lumière Matière (ILM), UMR5306 - UCBL - CNRS, 10 rue Ada Byron, 69622, Villeurbanne CEDEX, France*

A. Benamrouche, E. Drouard

*Univ Lyon, Ecole Centrale de Lyon, CNRS, INSA Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, INL, UMR5270, 69130, Ecully, France*

T. Gehin, C. Botella, J.-L. Leclercq

*Univ Lyon, CNRS, INSA Lyon, Ecole Centrale de Lyon, Université Claude Bernard Lyon 1, CPE Lyon, INL, UMR5270, 69130, Ecully, France*

P. Noe, F. Fillot

*Université Grenoble Alpes, CEA, LETI, 38000, Grenoble, France*

V. M. Giordano\*

*Institut Lumière Matière (ILM), UMR5306 - UCBL - CNRS, 10 rue Ada Byron, 69622, Villeurbanne CEDEX, France*

---

## Abstract

PECVD amorphous silicon nitride (a-SiN<sub>x</sub>) films are largely used into the dielectric stacks of integrated circuits, as passivation or capping layers, and are today an important alternative to silicon for integrated nonlinear optical applications, such as waveguides. In such applications, a-SiN<sub>x</sub> presents also the advantage of having a very low thermal conductivity, about 0.7 W/m K at room temperature, which is of relevance, as such films contribute to the thermal balance of the devices, and thus play a role in solving the thermal management problem in microelectronics. The deposition parameters, and more specifically

---

\*Corresponding author

*Email address:* `valentina.giordano@univ-lyon1.fr` (V. M. Giordano)

the deposition temperature, have been found to be critical in determining its physical properties, like density, elastic properties and intrinsic stress, as they influence the microstructure of the amorphous film. In this work, we report the first investigation of the effect of the temperature deposition on the thermal conductivity in amorphous  $\text{SiN}_x$  films of thicknesses between 200 and 500 nm, as measured by thermoreflectance technique up to 773 K. Surprisingly, for all deposition temperatures between 300 and 573 K, thermal conductivity exhibits a steep decrease above 473 K, decreasing by more than 30% down to a minimum around 673 K, before increasing back to values comparable with the room temperature one. This transient behavior, observed only for a first heating of the sample, is associated to an irreversible modification of the thin film, and may be related to a partial desorption of the hydrogen trapped in a- $\text{SiN}_x$  during the deposition.

*Keywords:* thermal conductivity, silicon nitride, PECVD, thin film, thermoreflectance, hydrogen desorption

---

## 1. Introduction

Amorphous silicon nitride (a- $\text{SiN}_x$ , with  $0 < x < 1.33$ ) films have attracted an ever growing interest in recent years thanks to their appealing physical, chemical, structural, optical and electrical properties, which make them suitable for applications in a very large panoply of technologies. Largely used into the dielectric stacks of integrated circuits, as passivation or capping layers [1], and as gate insulators in thin film transistors [2, 3, 4], this material has become today an important alternative to silicon for integrated nonlinear optical applications, such as waveguides [5], and is at the focus of research for photonic architectures in energy harvesting applications [6]. The possibility of tuning its properties, and specifically its band gap, by tuning the nitrogen content makes it a very attractive material with manageable vibrational, electrical and optical properties [7, 8, 9, 10].

Still, the very same variability of these properties represents a technical chal-

15 lenge, as it strongly depends on the growth technique used and the resulting film  
 morphology, texture, and chemical composition, which are not always perfectly  
 mastered. Many are the techniques used for growing amorphous  $\text{SiN}_x$  thin films,  
 which lead to quite different materials, with a large variability in properties such  
 as density, elastic moduli, intrinsic stress and thermal conductivity. Among such  
 20 techniques, the one of choice for the preparation of  $\text{SiN}_x$  for electronic and optic  
 devices is the Plasma Enhanced Chemical Vapor Deposition (PECVD), which  
 has the advantage of growing the material at low temperature. Here as well,  
 however, the choice of the growth parameters, such as the deposition tempera-  
 ture, the radio-frequency, and the plasma pressure, can dramatically affect the  
 25 properties of the deposited film [11, 12]. Such large variability comes not only  
 from the morphology or the exact Si:N ratio, but as well from an often un-  
 controlled content of hydrogen, which is bounded to both Si and N. Indeed, it  
 has been reported that hydrogen is almost always present and its content and  
 relative amount of the two types of bonds significantly affect the structural, elec-  
 30 trical and mechanical properties of the thin film [13, 14, 15]. A panoramic of the  
 different physical properties of  $\text{SiN}_x$ , depending on the growth technique, can  
 be found in two recent reviews from Kaloyeros et al. [16, 17]. Here it is possible  
 to appreciate the advantage of the PECVD method over the others, concerning  
 thermal applications of  $\text{SiN}_x$ . Indeed, PECVD a- $\text{SiN}_x$  has been reported to  
 35 present a very low thermal conductivity, about 0.7 W/m K at room tempera-  
 ture [18], which is of relevance, as such films contribute to the thermal balance  
 of the electronic devices, and thus play a role in solving the thermal manage-  
 ment problem in microelectronics. This value has been reported for thicknesses  
 larger than 100 nm, and represents the smallest thermal conductivity among  
 40 all possible growing techniques for such thicknesses, the values being almost the  
 double for the Atmospheric Pressure Chemical Vapor Deposition (APCVD) and  
 the Chemical Vapor Deposition at 1173 K [17, 18], and going up to 13 W/mK  
 in Low Pressure Chemical Deposited  $\text{SiN}_x$  [19, 20, 21, 22]. Such a difference  
 has been partially explained by a larger presence of voids, or micro-pores, in the  
 45 microstructure of PECVD  $\text{SiN}_x$  with respect to the other growing techniques.

Still, it is expected that hydrogen content and exact stoichiometry play a role as well.

Several reports exist in the literature on the room temperature thermal conductivity of PECVD  $\text{SiN}_x$ , with values largely scattered between  $\sim 0.45$  and 4.5 W/mK, a consequence of the different deposition parameters used in the different works, often not mentioned apart from the temperature [23, 24, 25]. Recently, Braun *et al.* have pointed to the hydrogen content as the critical parameter behind such variability. They have reported an exhaustive study of the effect of hydrogen content on the room temperature thermal conductivity of PECVD  $\text{SiN}_x$  deposited at 673 K. By annealing the films at different temperatures above 923 K, in order to gradually release hydrogen, the authors show that thermal conductivity is essentially determined by the hydrogen content, which is responsible for the increase of the average inter-atomic bond lengths and thus a decrease of the density. More specifically, after releasing all hydrogen at the highest annealing temperature, the thermal conductivity increases by a factor as large as 2.5 independently on the actual Si-N composition. Concerning the temperature dependence of the thermal conductivity, the most complete study to our knowledge is the one of Lee et al. [18], who investigated it in PECVD  $\text{SiN}_x$  for a deposition temperature of 573 K, gas pressure of 1.8 Torr and RF power of 16W. They have reported a thermal conductivity increasing from  $\sim 0.45$  to  $\sim 0.7$  W/mK for thicknesses between 20 and 100 nm, and then stabilizing for thicker samples. This behavior was ascribed to an effect of the interface thermal resistance, whose importance, stronger for thinner films, would become negligible for films thicker than 100 nm. The reported values, indeed, were obtained neglecting all interface contributions. As such, the increase with the thickness would only be apparent, an artefact of the analysis. Similarly, the observed increase of the thermal conductivity with temperature between 78 and 400 K could be overestimated, as it included the interface thermal resistance, which is expected to decrease with temperature.

While the work from Braun *et al.* has helped in understanding the large variability of results in the literature, and has pointed to the hydrogen content

as the key parameter determining the room temperature value for the thermal conductivity, it cannot fully account for the large scattering of reported values over an order of magnitude. It appears then that other systematic studies still  
80 need to be performed in order to get an exhaustive understanding of the thermal properties of PECVD  $\text{SiN}_x$  and their dependence on the growth conditions. The technological interest of such study is evident for engineering optimized stackings in microelectronics and for controlling the thermal balance in many applications. Indeed, the zoology of different results for different, not neces-  
85 sarily known, growth conditions hinders any understanding of the dependence of this quantity on the growth parameters. Moreover, the investigation of its temperature dependence, as a function of the growing parameters, is critical for applications where high temperatures are typically needed.

In this work, we present an exhaustive investigation of the temperature de-  
90 pendence of the thermal conductivity of PECVD  $\text{SiN}_x$  between 300 and 773 K, as a function of the deposition temperature, chosen between 298 and 573 K, keeping all other growth parameters fixed. As we will show, a linear dependence of the room temperature thermal conductivity with the deposition temperature is found, which can be ascribed to an increase of the elastic moduli at a high de-  
95 position temperature. Surprisingly, for all deposition temperatures, the thermal conductivity exhibits a steep decrease with temperature above 473 K, featuring a minimum around 673 K, before increasing back to values comparable to those at room temperature. As we will show, this behavior, observed only the first time the sample is heated, is associated to an irreversible modification of the  
100 thin film, and may be related to a partial desorption of the hydrogen trapped in a- $\text{SiN}_x$  during the deposition. The article is organized as follows: in section 2 we give experimental details on sample preparation, measurement techniques and analysis method, in section 3 we present our experimental results, and in section 4 a discussion on the microscopic origin of the observed behavior is  
105 provided. Conclusions and perspectives are given in section 5.

## 2. Experimental Methods

Amorphous  $\text{SiN}_x$  materials have been deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) on Silicon substrate using a 200 mm OXFORD Plasmalab 80+ PECVD system.  $\text{SiH}_4$  4% in He,  $\text{NH}_3$ , Ar and  $\text{N}_2$  were used as reactive gases plasma mixture. Plasma gases were adjusted with  $\text{SiH}_4/\text{He} = 80$  sccm, Ar = 200 sccm,  $\text{NH}_3 = 10$  sccm and  $\text{N}_2 = 600$  sccm. 13.56MHz RF power was held at 70 W under a pressure of 1.2 Torr. Temperature of deposition was varied from 298 K to 573 K. Pre-conditioning of the deposition chamber was operated during 5 minutes before each introduction of sample.

A first set of samples was deposited at 573 K, with three  $\text{SiN}_x$  thicknesses: 200, 292 and 501 nm. This last thickness was also deposited on  $\text{SiO}_2$  substrate, in order to establish the independence of the thermal transport measurements on the kind of substrate. A second set was deposited at substrate temperatures of 298 K, 323 K, 373 K, 473 K, 523 K, and 573 K and thickness of 300 nm. Layers of  $\sim 14$  and  $\sim 30$  nm were also deposited in the same conditions for density measurements by X ray reflectivity (XRR). Samples were then characterized by FTIR spectroscopy to identify the presence of oxygen and hydrogen, as well as the evolution of chemical bonds with deposition temperature. Experimental details and spectra for XRR and FTIR characterization are reported in the Supplementary Material.

Thermal conductivity was measured using the thermoreflectance technique [26, 27] with the commercial apparatus TF-LFA from Linseis. The pump laser had a pulse width of 8 ns, a wavelength of 1040 nm and an energy of 2.6 mJ, while the probe laser was continuous, and had a wavelength of 523 nm and 3.8  $\mu\text{W}$  power. The signal was collected in time by a Si-PIN-Photodiode with an aquisition rate of 2.5 GHz. Samples were coated with a 5 nm thick Cr layer, as a diffusion barrier, and a 100 nm thick Au layer, which was impulsively heated by the pump laser. The time relaxation of its temperature was deduced from the time evolution of its temperature-dependent reflectivity, as measured using the probe laser. High temperature measurements were performed under

Argon atmosphere, in a furnace chamber with optical aperture, able to go up to 773 K. The thermorefectance signal was collected at temperature steps of 50 K, after the time needed for temperature stabilization. For each sample and temperature, we collected 8 thermorefectance signals, changing the position on the sample, in order to get rid of eventual inhomogeneities and increase our statistics.

The signal has been fitted using the Cahill model adapted to time domain measurements[27], which takes into account the temperature-dependent contribution to temperature relaxation from all the layers in the stacking, here Au, Cr, SiN<sub>x</sub> and Si. The only unknown parameter in the fitting procedure is the thermal conductivity of SiN<sub>x</sub>. It is worth remembering that the total thermal resistance of the stacking corresponds to a series of thermal resistances:

$$R_{tot} = R_{Au} + R_{Au-Cr} + R_{Cr-SiN_x} + R_{SiN_x} + R_{SiN_x-Si} + R_{Si} \quad (1)$$

Where  $R_{A-B}$  is the thermal resistance at the interface between A and B. In our program, we fit an effective thermal conductivity [28] for SiN<sub>x</sub> which includes all the interface thermal contributions:

$$k_{meas} = \frac{d_{SiN_x}}{R_{SiN_x,eff}} \quad (2)$$

with

$$R_{SiN_x,eff} = R_{SiN_x} + R_{IF} = \frac{d_{SiN_x}}{k_{SiN_x}} + R_{IF} \quad (3)$$

and  $d$  the SiN<sub>x</sub> layer thickness. By fitting our measured values of  $\frac{d_{SiN_x}}{k_{meas}}$  as a function of the SiN<sub>x</sub> thickness, we can get from the slope the real SiN<sub>x</sub> thermal conductivity and from the intercept the interfacial thermal resistance. This latter resulted to be between  $2$  and  $6 \times 10^{-8} \text{m}^2\text{K/W}$ , in good agreement with what reported by Lee et al. [18]. Within our error bar, we can consider its temperature dependence negligible. More details on the fitting model and procedure, and the slope method for the extraction of the thermal conductivity are reported in the Supplementary Material.



### 160 **3. Results**

#### *3.1. Sample Characterization*

In order to study the dependence of the thermal transport properties on deposition temperature, we have prepared a set of samples deposited on silicon at different temperatures  $T_{dep}$  between 298 and 573 K, for which, from literature,  
165 it is expected that both film microstructure and local chemical structure will be different.

Indeed, at low deposition temperatures, the incoming free radicals will have less mobility and will be essentially stuck where they arrive on the surface, with no optimization of their position, leading to a fractal-like network with many  
170 embedded micro-voids [29, 30]. Increasing deposition temperature, the larger mobility allows a more packed arrangement, leading to higher densities, and indeed linearly increasing densities going from 1.8 to 2.9 g/cm<sup>3</sup> were reported for deposition temperatures between 373 and 573 K [30].

In Fig.S1 we report our experimental density, measured by XRR as a function  
175 of deposition temperature. Only a very weak increase is observed, by 4%, suggesting that in our growth conditions the microporosity is very weakly affected by the deposition temperature.

Our FTIR characterization revealed the presence of hydrogen bounded to both Si and N for deposition temperatures larger than 323 K, and oxygen incorporated in the film at all deposition temperatures, also bound to Si and N.  
180 Increasing deposition temperature leads to a reduction of the oxygen content and an increase of the Si-N bonds, in agreement with previous reports [31]. Instead, we could not quantify any change in the hydrogen content (See Supplementary Material).

#### 185 *3.2. Thermal conductivity study*

We first measured the thermal conductivity of the as-grown films upon annealing up to 773 K (“first annealing”). After cooling to room temperature, the measure was repeated following the same thermal protocol (“second annealing”). In Fig. 1 we report some representative thermoreflectance spectra

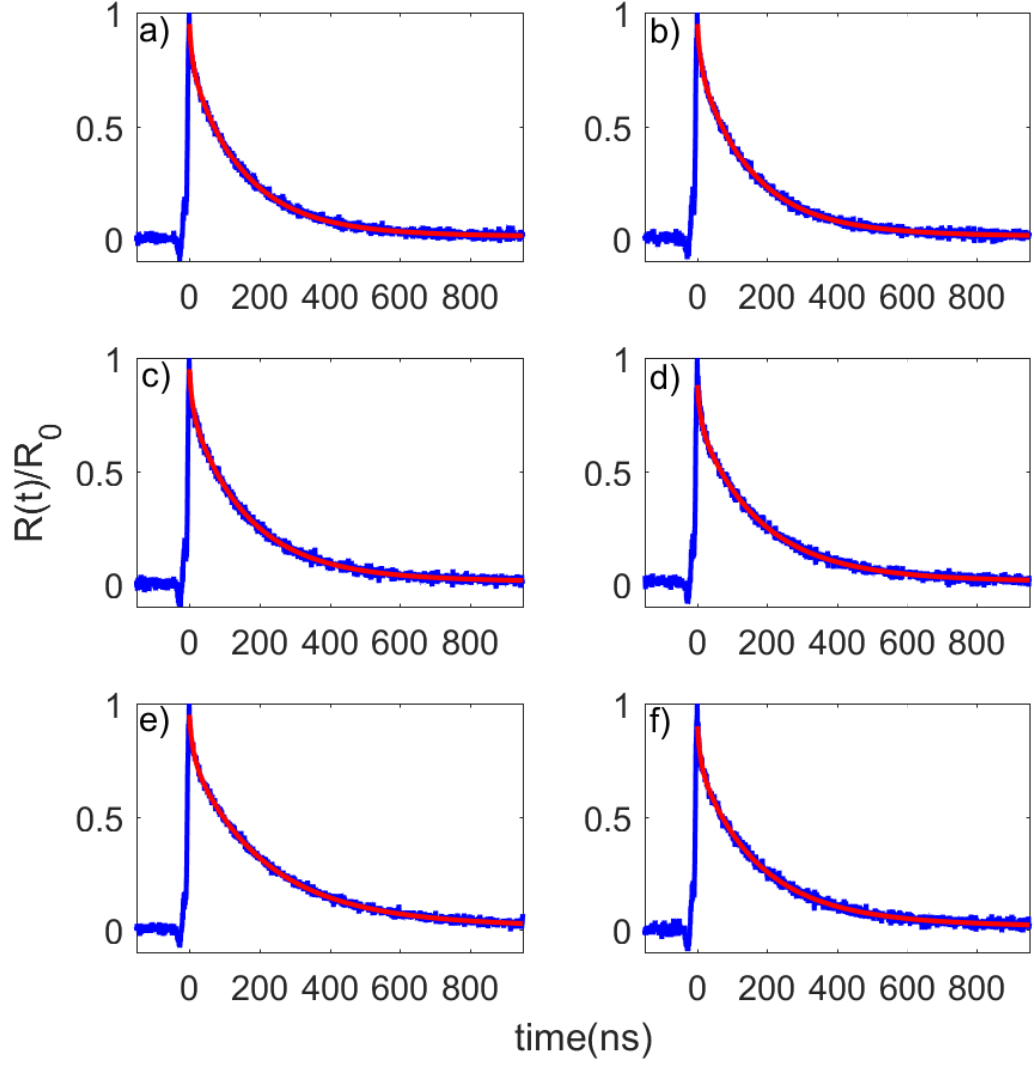


Figure 1: Thermoreflectance signal measured upon heating on a 292 nm thick  $\text{SiN}_x$  sample deposited on silicon at a deposition temperature of 573 K. The signal, in blue, is reported after subtraction of the electronic noise and normalization to 1. The red curve is the fit result, performed using the Cahill method as described in the Supplementary Material. The temperature of the measurement is 298 (a), 373 (b), 473 (c), 573 (d), 673 (e) and 773 K (f).

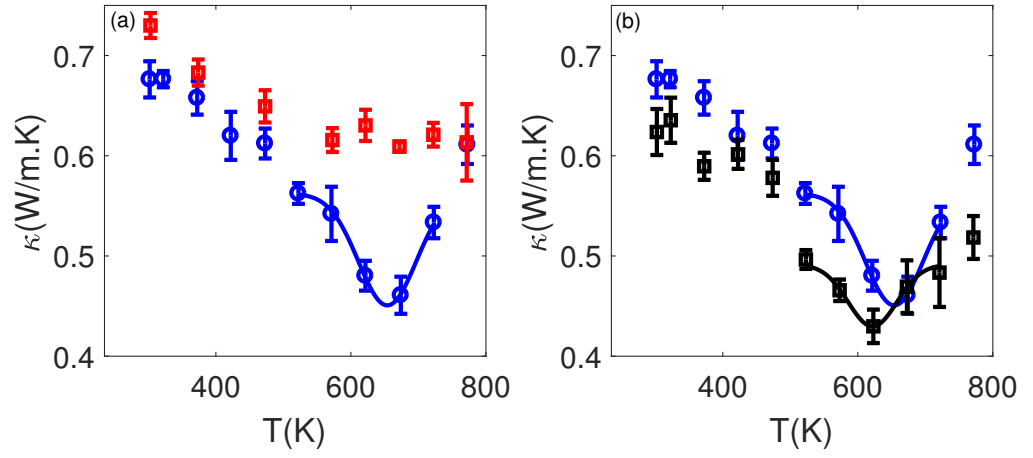


Figure 2: Temperature dependence of the thermal conductivity in a  $\text{SiN}_x$  thin film. (a): Thermal conductivity ( $\kappa$ ) of a 292 nm thick  $\text{SiN}_x$  sample deposited on Si, reported as a function of temperature ( $T$ ) during the very first heating ramp on the as-grown sample (blue circles) and during a second heating ramp run after the very first one (red squares). (b) Thermal conductivity on 501 nm thick  $\text{SiN}_x$  deposited on Si (blue circles) and  $\text{SiO}_2$  (black filled squares), reported as a function of temperature during the very first heating ramp. All error bars correspond to the standard deviation of the distribution of values obtained from 8 different measurements at each temperature.

190 after subtraction of the electronic noise, together with their fit. The spectra  
 have been collected upon heating on a 292 nm thick  $\text{SiN}_x$  sample deposited on  
 silicon at a deposition temperature of 573 K. In Fig. 3(a) we report the tem-  
 perature dependence of the effective thermal conductivity for the same sam-  
 ple, as representative for all measured thicknesses, the overall behavior be-  
 195 ing similar among all the films. As shown in the Supplementary Material,  
 the thermal conductivity extracted using the slope method only slightly dif-  
 fers from the effective one for a thickness of 292 nm, reported here, which  
 can thus be used as a reference for our discussion. First of all, our room  
 temperature values,  $k_{300K} = 0.63 \pm 0.03 \text{ W.m}^{-1}\text{K}^{-1}$  (on the as-grown) and  
 200  $k_{300K} = 0.70 \pm 0.03 \text{ W.m}^{-1}\text{K}^{-1}$  (after the first annealing ramp), are consistent  
 with the  $\sim 0.7 \text{ W.m}^{-1}\text{K}^{-1}$  reported by Lee [18] on a 252 nm PECVD  $\text{SiN}_x$  film  
 deposited at the same temperature, with  $\rho = 2.2 \text{ g/cm}^3$ . On the other hand,  
 Lee reports an increasing thermal conductivity with temperature, which slightly  
 flattens above 400 K, matching the usual behaviour observed in amorphous ma-  
 205 terials [32]. In our sample, we can at least say that above 300 K, we don't  
 observe an increase in thermal conductivity, but a surprising decrease with tem-  
 perature. On the first heating ramp,  $\kappa(T)$  decreases linearly upon heating from  
 300 K to 450 K and then drops abruptly down to a minimum of  $\sim 0.45 \text{ W/mK}$   
 at 673 K, before increasing again. This behavior is very specific to the first  
 210 heating ramp indicating that it results from an irreversible modification of our  
 sample. Upon a second annealing,  $\kappa(T)$  exhibits a linear decrease up to  $\sim 450 \text{ K}$   
 following almost the same slope as for the first heating ramp and then saturates  
 at higher temperature. This latter behavior of  $\kappa(T)$  is then reproducible if the  
 sample is annealed again.

215 The presence of this minimum is quite intriguing. A first possibility is that  
 it is an artefact due to a non-correct account for thermal interface resistance.  
 To rule out this hypothesis, we have deposited the same sample on a  $\text{SiO}_2$   
 substrate, in order to have different interfaces at play, as well as a different  
 contribution from the substrate to the total thermal relaxation. Due to the  
 220 different stacking, a thicker  $\text{SiN}_x$  layer is needed for a reliable extraction of

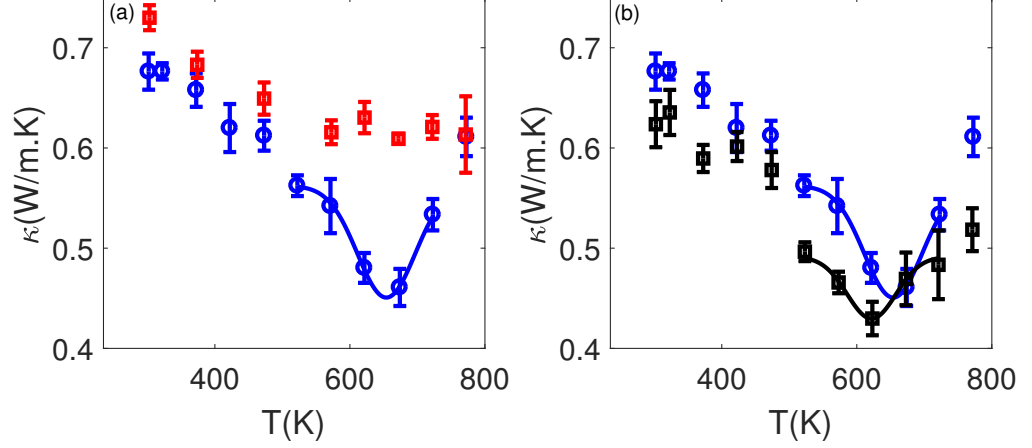


Figure 3: Room temperature thermal conductivity ( $\kappa_{300K}$ ) of  $\text{SiN}_x$  on Si grown by PECVD as a function of the deposition temperature ( $T_{dep}$ ). The error bars correspond to the standard deviation of the distribution of values obtained from 8 different measurements at each temperature. The solid black line is a linear fit.

its thermal conductivity. We report in Fig. 1 (b) the measurement of  $\kappa(T)$  on 501 nm thick samples deposited on Si and  $\text{SiO}_2$ . If for  $\text{SiN}_x$  on  $\text{SiO}_2$  the absolute value is slightly smaller, the same temperature dependence is reproduced, with a slight downshift of the minimum position, which is found at 623 K.

Once assessed that the peculiar temperature dependence is real and an intrinsic property of our PECVD  $\text{SiN}_x$ , it is interesting to see how it depends on the deposition temperature. We first report in Fig. 3 the measured room temperature thermal conductivity ( $\kappa_{300K}$ ) as a function of the deposition temperature ( $T_{dep}$ ).  $\kappa_{300K}$  increases with deposition temperature with a linear rate of change of  $0.27 \pm 0.02 \text{ W/m.K}^2$ . Despite this, the global temperature dependence during the first annealing is found to be the same in all samples, independently on the deposition temperature, as can be observed in Fig. 4 (a), where we report  $\kappa(T)$  in all samples during the first annealing (data have been vertically shifted for optical convenience). The same curves are reported in Fig. 4 (b) after normalization to the respective room temperature value.

It may be seen that in all samples  $\kappa(T)$  undergoes a first linear decrease in

the 300 K - 450 K temperature range followed by a drop, a minimum and an increase at higher temperatures. The slope of the first linear decrease is found to increase with the deposition temperature by a factor as large as  $\sim 50\%$  at the highest deposition temperature, going from  $-0.39(9)$  mW/ m K<sup>2</sup> at  $T_{dep} =$   
240 298 K to  $-0.61(4)$  mW/m K<sup>2</sup> at  $T_{dep} = 573$  K. Then, starting from  $\sim 500$  K, a steeper decrease leads to the minimum before increasing almost up to the room temperature value. The position of the minimum weakly increases with deposition temperature from  $\sim 600$  K at  $T_{dep} = 298$  K to  $\sim 654$  K at  $T_{dep} =$   
245 573 K, keeping its depth essentially the same for all samples (see Fig. 4 (b)). In all cases the minimum disappears for further annealings.

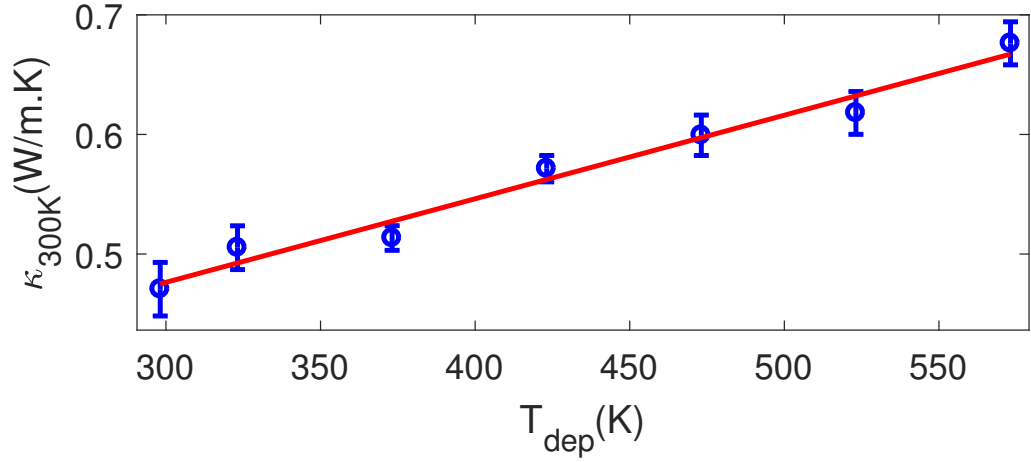


Figure 4: Temperature dependence of the thermal conductivity of SiN<sub>x</sub> thin films for different deposition temperatures. (a) Thermal conductivity ( $\kappa(T)$ ) as a function of temperature ( $T$ ) during the very first heating ramp of samples deposited on Si at different temperatures. The deposition temperature is indicated next to each curve. Dashed lines follow the linear decrease in the first temperature range, solid lines mark the shape of the minimum (b) The same curves in (a) are here reported after normalization to the room temperature value. The color/symbol legend is the same as in (a). The error bars correspond to the standard deviation of the distribution of values obtained from 8 different measurements at each temperature.

Our results indicate that the presence of the minimum do not depend on the microstructure of our PECVD SiN<sub>x</sub>, nor the specific density and elastic

constants, which depend on the deposition temperature. It is the result of an irreversible process which is thermally activated at about the same temperature for all samples, around 500 K. The question arises whether the measured values at each temperature are equilibrium values or whether they would evolve, if given time enough. In other words: once we are in the minimum, does the system need additional thermal energy to get out of it, or does it indefinitely remain there? In order to answer this question, we have heated a  $\text{SiN}_x$  sample grown at  $T_{dep} = 573$  K up to the position of the minimum, 673 K, and we have followed the time evolution of its thermal conductivity at 20 min time steps. We report these data in Fig. 5. It may be seen that thermal conductivity increases in time, relaxing back to the equilibrium value, which corresponds to the one which can be found during a second annealing. 100 minutes are needed for the full relaxation, and then the thermal conductivity remains constant for the next 300 minutes, indicating that no other process is active at this temperature. The relaxation time constant can be estimated by fitting the data to an exponential function, and it results in  $\tau = 70 \pm 10$  min. It is worth noticing here that the existence of kinetics active on the 20 minutes time scale may explain the little modifications of the minimum shape and position through the different samples, as we did not use the same thermalization time in all samples.

#### 4. Discussion

First of all, we shall comment on the dependence of the room temperature thermal conductivity on the deposition temperature. The observed increase can be due to a smaller porosity of  $\text{SiN}_x$  when deposited at higher temperatures, as reported in the literature [29, 30], so that we can model our material as effectively composed of  $\text{SiN}_x$  and micropores [29]. The effective medium theory allows to estimate the expected thermal conductivity of a porous medium from the zeros of the function

$$(1 - x) \frac{k_1 - k_e}{k_1 + 2k_e} + x \frac{k_2 - k_e}{k_2 + 2k_e} = 0 \quad (4)$$

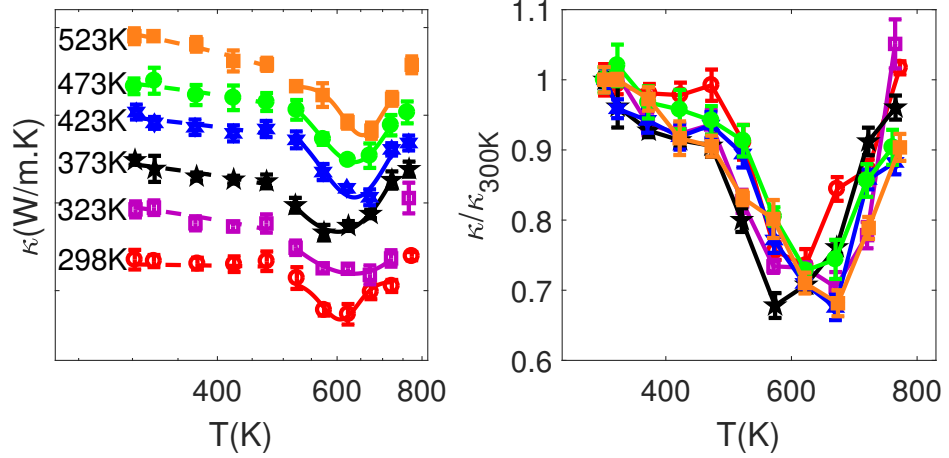


Figure 5: Time evolution of the thermal conductivity of a  $\text{SiN}_x$  thin film at high temperature. The measured thermal conductivity of  $\text{SiN}_x$  on Si grown by PECVD at 523K heated to 673K as a function of time. The red line is the fit of the data to an exponential function. The error bars correspond to the standard deviation of the distribution of values obtained from 8 different measurements at each temperature.

where  $k_1, k_2, k_e$  and  $x$  are the thermal conductivity of non porous  $\text{SiN}_x$ , pores and the effective thermal conductivity of the porous medium respectively and  $x$  is the pores volume fraction [33]. As we don't know the thermal conductivity of an equivalent non-porous  $\text{SiN}_x$ , we use  $k_1 = 0.7$  W/mK for estimating how much porosity should change for giving the observed thermal conductivities. For pores, we take  $k_2 = 0$ . Using the measured thermal conductivity values at room temperature, we obtain pores volume fractions ranging from 3% up to 24% from the highest to the lowest deposition temperature. Such a large change in porosity is however not compatible with the measured weak density change, which is at most 4%. This could be explained by the limitations of the model, which does not take into account the additional thermal resistance introduced by the  $\text{SiN}_x$ -pore interfaces. Still such a strong difference in the porosity estimated from density and from thermal conductivity points to another origin for the large change in this latter.

As we have seen, the chemical structure evolves with the deposition temper-



ature: oxygen content decreases and Si-N bonds increase.  $\text{SiN}_x$  being a dielectric, the main heat carriers are the atomic vibrations, whose quasi-particle is the phonon. Not only the interfaces can scatter phonons, but also the atomic defects in the Si-N network, such as oxygen and hydrogen bonds. Decreasing  
 295 their content means decreasing scattering from defects, leading thus to larger thermal conductivities. Moreover, the Si-N bond content increasing with deposition temperature, the elastic constants are expected to increase as well, due to the higher rigidity of this bond, and indeed an increase of the Young modulus by a factor of 2 has been reported in literature for deposition temperatures  
 300 between 373 and 573 K [30]. From the kinetic theory for a phonon gas, the thermal conductivity reads  $k_T = \frac{1}{3}C_v v l$ , with  $C_v$  the specific heat,  $v$  the sound velocity and  $l$  the phonon mean free path. Considering that the longitudinal and transverse velocities are given by  $v_{L/T} = \sqrt{M_{L/T}/\rho}$  with  $M_{L/T}$  the longitudinal and shear elastic modulus and  $\rho$  the mass density, we expect the thermal  
 305 conductivity to increase with the square root of the elastic moduli. A rough estimation using the Young moduli reported in the literature gives a change of the thermal conductivity by a factor of  $\sim 50\%$  between 373 and 573 K, which well corresponds to the observed increase.

Second, we shall comment on the unusual decrease with temperature of the  
 310 thermal conductivity, independent on the deposition conditions. As mentioned, this is opposite to what is usually observed in amorphous materials, where thermal conductivity at high temperature increases due to the increase of the specific heat, while the phonon mean free path is almost constant at its minimum value. It is in fact a very weak decrease, as the slope of the thermal conductivity is in  
 315 the  $0.4\text{-}0.6 \cdot 10^{-3} \text{ W/mK}^2$  range for an absolute value of about  $0.7 \text{ W/mK}$ . A similar behavior was previously reported on CVD amorphous  $\text{Si}_3\text{N}_4$ , and explained as the result of a relevant interfacial thermal resistance, three orders of magnitude larger than in our case, and of its temperature dependence. The intrinsic thermal conductivity was shown to weakly increase with temperature [34]. In  
 320 our case, the interfacial thermal resistance is quite small and its temperature dependence negligible within our experimental uncertainty. Indeed, as mentioned

and as shown in the Supplementary Material, the intrinsic thermal conductivity is not very different from the effective one as measured on the 292 nm thick film. Still, the slope of the initial decrease is reduced in the intrinsic thermal conductivity, leading to an almost constant value with temperature prior to the decrease leading to the minimum.

We come finally to the presence of a minimum in the thermal conductivity during the first annealing, at  $\sim 673$  K, which disappears in the second annealing ramp in all samples, independent on deposition temperature and substrate. A possible origin of this behavior is that our amorphous  $\text{SiN}_x$  starts crystallizing at high temperature. However, the crystallization temperature in PECVD  $\text{SiN}_x$  has been reported to be much larger,  $\sim 1148$  K [35]. Moreover, even if some incipient crystallization were present, this should lead to an increase of the thermal conductivity, being the one of the crystalline phase about 26 W/mK [17]. A second possibility is the activation of a temperature induced structural relaxation. The higher temperature induces higher atomic mobility, which can lead to slight atomic rearrangements, responsible for the evolution of elastic and thermal properties. This is expected to have a role for temperatures larger than the deposition temperature, thus we would expect the steep decrease of the minimum to appear at lower temperatures for lower deposition temperatures. This is however not the case. Moreover, in case of structural relaxation, we would expect a monotonic and asymptotic behavior, from the unrelaxed to the more relaxed state, while here we face a steep decrease followed by a similarly steep increase back to an unperturbed value.

In fact, the observed phenomenology resembles to a temporary thermally induced perturbation of our system: thermal transport is progressively hindered by some temperature-activated mechanism and then comes back to the unperturbed behavior when the mechanism is over. Being this phenomenon independent on deposition temperature, we cannot expect it to be related to the presence of oxygen nor the amount of Si-N bonds, which depend both on this latter. On the other hand, we also know that there is hydrogen in our sample, both bound to Si and N, and under a non-bonded molecular form, trapped

within the porous structure [36], and we could not see important differences  
 among samples deposited at different temperatures. In order to see whether  
 355 hydrogen could be responsible for the minimum in the thermal conductivity,  
 we have measured the FTIR spectrum of our  $\text{SiN}_x$  deposited at 573 K before  
 and after the annealing, but we could find indication of only a very slight de-  
 crease of the Si-H and N-H bonds content (see Supplementary Material). Still,  
 FTIR is sensitive only to bounded hydrogen, so that we cannot rule out an  
 360 effect of molecular  $\text{H}_2$ . Detecting small quantities of molecular hydrogen in  
 thin films is not trivial. The typical H-content in PECVD SiN is about  $1.7 \cdot 10^{22}$   
 atoms/ $\text{cm}^3$  [37], of which only a few percent will be under the form of molecular  
 hydrogen [36], *i.e.* about  $10^{20}$  atoms/ $\text{cm}^3$ . This amount has remained elusive to  
 our tentative Raman measurements. More advanced techniques are necessary to  
 365 detect it in thin films, such as effusivity measurements [36], time of flight elastic  
 recoil detection analysis [38] or a self-consistent analysis of the light element  
 NRA data combined with an RBS analysis for heavy elements [39].

An exhaustive study of the hydrogen effusivity as a function of temperature  
 in PECVD  $\text{SiN}_x$  deposited at 673 K with different stoichiometries has been re-  
 370 cently reported by Jafari et al.[36]. It is found that, starting from 673 K, the  
 thermal energy is enough to break first the N-H bond and then, above  $\sim 973$  K,  
 the more energetic Si-H bond, so that all hydrogen diffuses out of the sample  
 between 673 and 1273 K. Interestingly, for N-rich compositions, a small peak  
 appears in the hydrogen effusivity, with a maximum between 650 K and 670 K  
 375 depending on the N content, accounting for about the 2-5% of the total hy-  
 drogen effusivity signal. This peak has been ascribed to the premature release  
 of hydrogen from surface desorption of  $\text{H}_2$  molecules. The correspondence of  
 the temperature range, as well as the similar peak shape points to the diffusion  
 and release of molecular hydrogen as the cause of the observed minimum in the  
 380 thermal conductivity. The  $\text{SiN}_x$  matrix with freely moving  $\text{H}_2$  can be assim-  
 ilated to the case of a superionic material, where some atoms are characterized  
 by a liquid-like mobility. In these latter, the active ions movement may en-  
 hance phonon scattering, due to disorder and anharmonicity, as reported in the

high temperature super-ionic phase of  $\text{CuCrSe}_2$  [40]. We may expect a similar  
 385 phenomenology here. In our case the large  $\text{H}_2$  mobility is limited to the temperature - or time at a given temperature - range within which all the molecular hydrogen diffuses out of the sample, thus the perturbation on thermal transport disappears once all the molecular hydrogen has left, being an irreversible process. The peak shape can be understood as due to a scattering probability  
 390 proportional to the amount of mobile  $\text{H}_2$ . The fact that we find a similar shape, and more specifically depth, of the minimum throughout all samples may indicate that the quantity of mobile  $\text{H}_2$  is quite insensitive on the deposition temperature, or that there is a saturation effect.

## 5. Conclusions

395 We have here reported an exhaustive investigation of the thermal conductivity of PECVD  $\text{SiN}_x$  thin films as a function of the deposition temperature, all other growing parameters being kept constants. A strong variation of the room temperature value, of a factor of almost 2, is found as a function of the deposition temperature, likely related to the increase of the Si-N bonds content,  
 400 and thus a larger rigidity of the amorphous network at higher deposition temperature. Our data can explain the panoply of results on thermal conductivity reported in the literature, measured on samples grown in different conditions, and can help in aiming the best deposition temperature for the foreseen application, on the basis of the needed thermal properties. Moreover, we find that,  
 405 independently on the deposition temperature, the effective thermal conductivity weakly decreases with temperature, apparently at odds with other reports [18]. This decrease is in fact reduced even more once the interfacial thermal resistance is properly taken into account, leading to an almost temperature independent thermal conductivity below 500 K. Indeed, we have observed the onset of an irreversible process at  $\sim 500$  K, leading to a minimum of the thermal conductivity  
 410 at about 673 K, before it increases back to the unperturbed value. This peculiar behavior does not depend on the deposition temperature, indicating that poros-

ity, Si-N bonds and oxygen bonds are not responsible for it. Instead, we can explain it as due to a premature release of molecular hydrogen, whose diffusiv-  
415 ity is temperature-activated at about the same temperatures [36]. The shape of the minimum and its irreversibility can be understood in terms of an enhanced phonon scattering from mobile  $H_2$ , which is proportional to the content of this latter. Once all the mobile  $H_2$  molecules have left the sample, the process is over and the thermal conductivity comes back to the unperturbed value. Our  
420 results assess the stability of the temperature window in which the phenomenon takes place, and the important effect on the thermal conductivity, which decreases by 30%, together with its relatively long time constant ( $\sim 20$  minutes ). As reported in Braun *et al.* [15], for higher temperatures, such as Si-H and N-H bonds break down and all hydrogen diffuses out of the sample, an irreversible  
425 absolute modification of the thermal conductivity takes place once these point defects have been annihilated. We could thus expect, increasing temperature, a transient behavior even more pronounced than in the present study, as the amount of mobile hydrogen is larger. Our findings indicate that in order to use  $SiN_x$  in electronic or optic applications, when application temperature is larger  
430 than 500 K, a preliminary annealing up to 723 K is fundamental for assuring its thermal stability. For application temperatures larger than 723 K, much higher annealing temperatures will be needed to get rid of all the bound hydrogen. This means as well that, in high temperature applications, it is not possible to tailor the thermal conductivity by tuning the hydrogen content, as suggested  
435 in Ref. [15], because this would introduce transient mechanisms leading to a time evolution of thermal properties. Finally, we stress here the high sensitivity demonstrated by PECVD  $SiN_x$  thermal conductivity with respect to mobile hydrogen, which can open the way to its use to monitor hydrogen diffusion, and possibly to the application of PECVD  $SiN_x$  as membranes for hydrogen  
440 stocking and release.

## 6. Acknowledgements

The authors are grateful to D. Cahill for the fruitful discussions. Funding: this work was supported by the Idex Lyon Scientific Breakthrough program [IPPON project] and the Agence National de la Recherche [MAPS-ANR-20-CE05-0046].

## References

## References

- [1] D. Benoit, J. Regolini, P. Morin, Hydrogen desorption and diffusion in pecvd silicon nitride. application to passivation of cmos active pixel sensors, Microelectronic Engineering 84 (2007) 2169.
- [2] M. Duffy, W. Kern, Preparation, properties and applications of chemically vapor deposited silicon nitride films, RCA Review 31 (4) (1970) 742–753.
- [3] A. Sinha, H. Levinstein, T. Smith, G. Quintana, S. Haszko, Reactive plasma deposited si-n films for mos-lsi passivation, Journal of the Electrochemical Society 125 (4) (1978) 601.
- [4] S. Hasegawa, Y. Amano, T. Inokuma, Y. Kurata, Relationship between the stress and bonding properties of amorphous sin x: H films, Journal of applied physics 72 (12) (1992) 5676–5681.
- [5] L. Wang, W. Xie, D. V. Thourhout, Y. Zhang, H. Yu, S. Wang, Nonlinear silicon nitride waveguides based on a pecvd deposition platform, Opt. Express 26 (2018) 9645.
- [6] A. F. Braña, H. Gupta, R. K. Bommali, P. Srivastava, S. Ghosh, R. P. Casero, Enhancing efficiency of c-si solar cell by coating nano structured silicon rich silicon nitride films, Thin Solid Films 662 (2018) 21–26. doi: 10.1016/j.tsf.2018.06.043.

- [7] N. Ibaraki, H. Fritzsche, Properties of amorphous semiconducting a- s i: H  
a- si n x: H multilayer films and of a- si n x: H alloys, *Physical Review B*  
30 (10) (1984) 5791.
- [8] A. Lowe, M. Powell, S. Elliott, The electronic properties of plasma-  
470 deposited films of hydrogenated amorphous  $\text{sin}_x$  ( $0 \leq x \leq 1.2$ ), *Journal*  
of applied physics 59 (4) (1986) 1251–1258.
- [9] S. Hasegawa, M. Matsuda, Y. Kurata, Si-h and n-h vibrational properties  
in glow-discharge amorphous  $\text{sin}_x$ : H films ( $0 \leq x \leq 1.55$ ), *Applied physics*  
letters 57 (21) (1990) 2211–2213.
- [10] S. Hasegawa, M. Matsuda, Y. Kurata, Bonding configuration and defects  
475 in amorphous  $\text{sin}_x$ : H films, *Applied physics letters* 58 (7) (1991) 741–743.
- [11] A. Stoffel, A. Kovacs, W. Kronast, B. Müller, Lpcvd against pecvd for  
micromechanical applications, *Journal of Micromechanics and Microengi-*  
neering 6 (1) (1996) 1.
- [12] N. Jehanathan, Thermal stability of plasma enhanced chemical vapor de-  
480 posited silicon nitride thin films, University of Western Australia, 2007.
- [13] S. Bae, D. G. Farber, S. J. Fonash, Characteristics of low-temperature  
silicon nitride ( $\text{sin}_x$ : H) using electron cyclotron resonance plasma, *Solid-*  
State Electronics 44 (8) (2000) 1355–1360.
- [14] M. T. Soh, N. Savvides, C. A. Musca, M. P. Martyniuk, L. Faraone, Local  
485 bonding environment of plasma deposited nitrogen-rich silicon nitride thin  
films, *Journal of applied physics* 97 (9) (2005) 093714.
- [15] J. L. Braun, S. W. King, E. R. Hoglund, M. A. Gharacheh, E. A. Scott,  
A. Giri, J. A. Tomko, J. T. Gaskins, A. Al-kukhun, G. Bhattarai, M. M.  
490 Paquette, G. Chollon, B. Willey, G. A. Antonelli, D. W. Gidley, J. Hwang,  
J. M. Howe, P. E. Hopkins, Hydrogen effects on the thermal conductivity  
of delocalized vibrational modes in amorphous silicon nitride (a-SiNx:h),

Physical Review Materials 5 (3). doi:10.1103/physrevmaterials.5.035604.

- 495 [16] A. E. Kaloyeros, F. A. Jové, J. Goff, B. Arkles, Silicon nitride and silicon nitride-rich thin film technologies: Trends in deposition techniques and related applications, ECS Journal of Solid State Science and Technology 6 (10) (2017) P691.
- [17] A. E. Kaloyeros, Y. Pan, J. Goff, B. Arkles, Review—silicon nitride and silicon nitride-rich thin film technologies: State-of-the-art processing technologies, properties, and applications, ECS Journal of Solid State Science and Technology 9 (6) (2020) 063006. doi:10.1149/2162-8777/aba447.
- [18] S.-M. Lee, D. G. Cahill, Heat transport in thin dielectric films, Journal of applied physics 81 (6) (1997) 2590–2595.
- 505 [19] X. Zhang, C. P. Grigoropoulos, Thermal conductivity and diffusivity of free-standing silicon nitride thin films, Review of scientific instruments 66 (2) (1995) 1115–1120.
- [20] A. Sikora, H. Ftouni, J. Richard, C. Hébert, D. Eon, F. Omnes, O. Bourgeois, Highly sensitive thermal conductivity measurements of suspended membranes (sin and diamond) using a  $3\omega$ -völklein method, Review of Scientific Instruments 83 (5) (2012) 054902.
- 510 [21] A. Sikora, H. Ftouni, J. Richard, C. Hébert, D. Eon, F. Omnès, O. Bourgeois, Erratum: “highly sensitive thermal conductivity measurements of suspended membranes (sin and diamond) using a  $3\omega$ -völklein method” [rev. sci. instrum. 83, 054902 (2012)], Review of Scientific Instruments 84 (2) (2013) 029901.
- 515 [22] A. Jain, K. E. Goodson, Measurement of the thermal conductivity and heat capacity of freestanding shape memory thin films using the  $3\omega$  method, Journal of Heat Transfer 130 (10).



- 520 [23] Y. Y. Kim, Thermal property evaluation of a silicon nitride thin-film using the dual-wavelength pump-probe technique, *Korean Journal of Materials Research* 29 (9) (2019) 547–552. doi:10.3740/mrsk.2019.29.9.547.
- [24] N. Stojanovic, J. Yun, E. B. K. Washington, J. M. Berg, M. W. Holtz, H. Temkin, Thin-film thermal conductivity measurement using microelec-  
525 trothermal test structures and finite-element-model-based data analysis, *JOURNAL OF MICROELECTROMECHANICAL SYSTEMS* 16 (2007) 1269.
- [25] P. Eriksson, J. Y. Andersson, G. Stemme, Thermal characterization of surface-micromachined silicon nitride membranes for thermal infrared de-  
530 tectors, *JOURNAL OF MICROELECTROMECHANICAL SYSTEMS* 6 (1997) 55.
- [26] C. Yuan, W. M. Waller, M. Kuball, Nanosecond transient thermore-  
flectance method for characterizing anisotropic thermal conductivity, *Review of Scientific Instruments* 90 (11) (2019) 114903.
- 535 [27] D. G. Cahill, Analysis of heat flow in layered structures for time-domain thermoreflectance, *Review of scientific instruments* 75 (12) (2004) 5119–5122.
- [28] J. C. Lambropoulos, M. Jolly, C. Amsden, S. Gilman, M. Sinicropi, D. Di-  
akomihalis, S. Jacobs, Thermal conductivity of dielectric thin films, *Journal*  
540 *of applied physics* 66 (9) (1989) 4230–4242.
- [29] W.-S. Liao, C.-H. Lin, S.-C. Lee, Oxidation of silicon nitride prepared by plasma-enhanced chemical vapor deposition at low temperature, *Applied Physics Letters* 65 (17) (1994) 2229–2231. doi:10.1063/1.112772.
- [30] B. Walmsley, Y. Liu, X. Hu, M. Bush, K. Winchester, M. Martyniuk,  
545 J. Dell, L. Faraone, Effects of deposition temperature on the mechanical and physical properties of silicon nitride thin films, *Journal of applied physics* 98 (4) (2005) 044904.

- [31] M. T. Soh, N. Savvides, C. A. Musca, J. M. Dell, L. Faraone, Chemical structure of low-temperature plasma-deposited silicon nitride thin films, in: J.-C. Chiao, A. J. Hariz, D. N. Jamieson, G. Parish, V. K. Varadan (Eds.), Device and Process Technologies for MEMS, Microelectronics, and Photonics III, SPIE, 2004. doi:10.1117/12.523243.
- 550 [32] M. C. Wingert, J. Zheng, S. Kwon, R. Chen, Thermal transport in amorphous materials: a review, Semiconductor Science and Technology 31 (11) (2016) 113003.
- 555 [33] L. Gong, Y. Wang, X. Cheng, R. Zhang, H. Zhang, A novel effective medium theory for modelling the thermal conductivity of porous materials, International Journal of Heat and Mass Transfer 68 (2014) 295–298. doi:10.1016/j.ijheatmasstransfer.2013.09.043.
- 560 [34] A. Griffin Jr, F. Brotzen, P. Loos, The effective transverse thermal conductivity of amorphous  $\text{Si}_3\text{N}_4$  thin films, Journal of applied physics 76 (7) (1994) 4007–4011.
- [35] N. Jehanathan, M. Saunders, Y. Liu, J. M. Dell, Crystallization and compositional changes in amorphous PECVD  $\text{Si}_x\text{N}_x$  thin films, in: International Conference on Smart Materials and Nanotechnology in Engineering, SPIE, 2007. doi:10.1117/12.779215.
- 565 [36] S. Jafari, J. Hirsch, D. Lausch, M. John, N. Bernhard, S. Meyer, Composition limited hydrogen effusion rate of a-SiNx: H passivation stack, in: AIP Conference Proceedings, Vol. 2147, AIP Publishing LLC, 2019, p. 050004.
- 570 [37] J. Z. Xie, S. P. Murarka, X. S. Guo, W. A. Lanford, Stability of hydrogen in silicon nitride films deposited by low-pressure and plasma enhanced chemical vapor deposition techniques, Journal of Vacuum Science & Technology B: Microelectronics Processing and Phenomena 7 (1989) 150.
- [38] Z. Siketić, I. B. Radović, M. Jakšić, Quantitative analysis of hydrogen in

- 575 thin films using time-of-flight elastic recoil detection analysis, Thin Solid  
Films 518 (2010) 2617–2622.
- [39] W.A.Lanford, M.Parenti, B.J.Nordell, M.M.Paquette, A.N.Caruso,  
M.Mantymäki, J.Hamalainen, M.Ritala, K.B.Klepper, V.Miikkulainen,  
O.Nilsen, W.Tenhaeff, N.Dudney, D.Koh, S.K.Banerjee, E.Mays,  
580 J.Bielefeld, S.W.King, Nuclear reaction analysis for h, li, be, b, c, n, o  
and f with an rbs check, Nuclear Instruments and Methods in Physics Re-  
search Section B: Beam Interactions with Materials and Atoms 371 (2016)  
211–215.
- [40] J. L. Niedziela, D. Bansal, A. F. May, J. Ding, T. Lanigan-Atkins,  
585 G. Ehlers, D. L. Abernathy, A. Said, O. Delaire, Selective breakdown  
of phonon quasiparticles across superionic transition in (*cucrse*)<sub>2</sub>, Nature  
Physics 15 (1) (2018) 73–78. doi:10.1038/s41567-018-0298-2.