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**Beyond surface nanoindentation: combining static and dynamic nanoindentation to assess intrinsic mechanical properties of Chemical Vapor Deposition amorphous silicon oxide (SiO<sub>x</sub>) and silicon oxycarbide (SiO<sub>x</sub>C<sub>y</sub>) thin films.**

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**Abstract**

Nanoindentation is a well-known technique to assess the mechanical properties of bulk materials and films. Despite that, nanoindentation of thin films is not straightforward, given that the measured properties are composite information from a film/substrate system and

1 depend on the indentation depth. By using dynamic indentation experiments and analytical or  
2 empirical models, we assessed the intrinsic film properties of chemical vapor deposited silicon  
3 oxide ( $\text{SiO}_x$ ) and silicon oxycarbide ( $\text{SiO}_x\text{C}_y$ ) thin films with thicknesses ranging from 60 to  
4 700 nm. In this work, the Bec rheological model and several mixing laws were reviewed.  
5 Measured Young modulus appeared to be affected by the substrate properties more than  
6 hardness: for the thinnest films, moduli were measured at *ca.* 90 GPa whereas intrinsic moduli  
7 were calculated at *ca.* 50 GPa. Using calculated intrinsic film modulus and hardness, it was  
8 possible to establish correlations between these properties, the chemical composition and the  
9 structural organization of the films.

10 **Keywords:** chemical vapor deposition coatings, nanoindentation, models, intrinsic film  
11 properties, silicon oxide, silicon oxycarbide, thin films.

12

## 13 **1. Introduction**

14 The recent development of (multi-)functional nanometric films was made possible by the  
15 evolution of thin film deposition technologies and the flourishing of advanced characterization  
16 techniques [1]. Silicon-oxide-based coatings such as silicon oxides ( $\text{SiO}_x$  [2,3]), silicon  
17 oxycarbides ( $\text{SiO}_x\text{C}_y$  [4]) or silicon oxynitrides ( $\text{SiO}_x\text{N}_y$  [5]) have been studied in detail and  
18 several deposition approaches have been published for high quality dense films, including wet  
19 chemistry-based methods [6] or gas-phase-deposition-based [4,5,7]. The resulting films have  
20 proven themselves attractive as multifunctional materials, like anti-corrosion, anti-reflective or  
21 diffusion barrier coatings. Such films can be applied for the encapsulation of systems for  
22 protection against humidity [8], oxygen, ambient contaminants and mechanical damages [9].  
23 These barrier properties can be correlated with the characteristics of the films (thickness [8],

1 chemical composition [10], network density [11], inter alia), which in turn, can be tuned by  
2 modifying their deposition conditions [10,12].

3 Nanoindentation characterization and the pioneering work of Oliver and Pharr [13] allowed  
4 probing shallow indentation depths and conveniently assessing the Young modulus (E) and  
5 Hardness (H) of heterogeneous materials and films. Still, coated systems characterization by  
6 nanoindentation is not straightforward: substrate properties affect the measured values of E and  
7 H when the elastic and plastic deformations (respectively) are no longer confined within the  
8 film. This substrate contribution is all the more likely to be probed as films become very thin.

9 A first solution to avoid the substrate contribution is to work at shallow indentation depth and  
10 low normal loads, taking advantage of the precision of nanoindentation. Classically, the  
11 substrate contribution is considered negligible when the relative indentation depth ( $h/t$ , i.e. the  
12 indentation depth  $h$  divided by the thickness  $t$  of the film) is below 0.1, based on Bückle's  
13 work [14]. Under this assumption, measured E and H are considered equal to the intrinsic film  
14 modulus and hardness (quoted, respectively,  $E_f$  and  $H_f$ ). This rule has been widely adopted in  
15 nanoindentation studies as it gives satisfying results for systems where the film and the  
16 substrate present relatively similar mechanical properties. However, Bückle 10 % rule can be  
17 too loose or too strict, depending on several factors affecting the elastic and plastic deformation  
18 of the film and the substrate. Among other factors, the ratios  $H_f/E_f$  and  $E_f/E_s$  are to consider  
19 carefully as a low  $H_f/E_f$  value or a substrate significantly stiffer than the film may make the  
20 substrate contribution sensible for  $h/t < 0.1$  [15–17]. The critical value of  $h/t$  below which  $E_f$   
21 and  $H_f$  can no longer be assessed by means of straightforward indentation is complex to predict  
22 as it depends on numerous interacting factors sometimes not easily accessible for thin films.

23 As a consequence, another approach has been developed to access intrinsic properties of films;  
24 this method is based on mathematical modeling of the composite mechanical properties of the

1 film/substrate system. Several models have been proposed to remove, or at least reduce, the  
2 substrate contribution from the measured mechanical properties and thus access the intrinsic  
3 film properties [18]. These approaches are still underused compared to the Bückle's 10 % rule,  
4 as they are comparatively more complex and require mechanical characterization of the film  
5 and/or of the substrate at several indentation depths. Still, determining the intrinsic film  
6 properties is of interest and these model-based methods may be applied in situations where the  
7 Bückle's rule cannot be reasonably used (e.g. for a few nanometer-thin films, multilayer  
8 systems or when investigating superficial phenomena ...).

9 Within this context, in order to assess the intrinsic mechanical properties of amorphous silicon  
10 oxide and silicon oxycarbide thin films processed on silicon Si(100) substrates by thermal  
11 Chemical Vapor Deposition (CVD), the present work deals with the evaluation of the main  
12 published models for the determination of  $E_f$  and  $H_f$ . We compare the obtained values to  $E$  and  
13  $H$  measured by classical static indentation at shallow indentation depths and discuss these  
14 properties with regard to the deposition temperature ( $T_d$ ) of the films, their chemical  
15 composition and structure.

16

## 17 **2. Materials and Methods**

### 18 **2.1. Silicon oxide and oxycarbide films**

19 Two sets of films deposited on 280  $\mu\text{m}$  thick Si(100) substrates (provided by Neyco) are  
20 investigated: "TEOS" films deposited from tetraethyl orthosilicate ( $\text{SiC}_8\text{H}_{20}\text{O}_4$ , TEOS) and  
21 "HMDS" films deposited from a dual-precursor chemistry involving TEOS and  
22 hexamethyldisilazane ( $\text{Si}_2\text{NC}_6\text{H}_{19}$ , HMDS). For both, deposition was performed at deposition  
23 temperatures ( $T_d$ ) ranging from 360°C to 550°C; details can be found in two previous  
24 articles [10,12]. For each set, two subsets are defined, namely as thin and thick films with  $t$  of

1 about 100 nm and superior to 400 nm, respectively, obtained by adjusting the deposition time  
2 under the same process conditions (as summarized in Table 1).

3 Both TEOS and HMDS films are amorphous according to X-ray and electron diffraction  
4 characterizations and the structure and chemical composition of both have been characterized  
5 by Fourier transform infrared spectrometry and Ion Beam Analysis (not shown). Roughness  
6 has been measured using atomic-force microscopy (AFM) (size of image: 1  $\mu\text{m}^2$ ) and  $t$  has  
7 been measured by spectroscopic ellipsometry. All films present a low roughness with a root  
8 mean square roughness parameter lying in the range 0.5 to 5 nm.

9 TEOS films are partially hydrated silicon oxides ( $\text{SiO}_x$ ), with their network hydration  
10 decreasing as  $T_d$  increases from 400 to 550°C, and subsequently their hydrogen content  
11 decreasing from 8 to 5 at.%) [12]. HMDS films have tunable chemical composition depending  
12 on  $T_d$ : they consist of silicon oxycarbides ( $\text{SiO}_x\text{C}_y$ ) containing  $\text{CH}_3$  moieties (with hydrogen  
13 content between 8 and 17 at.%) at low  $T_d$  (i.e. below 500°C) and they evolve to silicon oxides  
14 at higher temperature of 500 and 550°C (with constant hydrogen content of about. 7 at.%) [10].  
15 Because of this compositional evolution, for every film set, the increase of  $T_d$  results in the  
16 increase of the network cross-linking. This network densification is beneficial to the barrier  
17 properties illustrated by the decrease of the etching rate of the films when immersed in an acidic  
18 solution following the P-etch protocol [10,12].

## 19 2.2. Mechanical characterization methods

20 Mechanical properties (*i.e.* Young modulus and hardness) were characterized by  
21 nanoindentation using an UltraNanoIndenter apparatus from CSM Instruments (Anton Paar)  
22 with a modified Berkovich diamond indenter. The displacement of the indenter is measured  
23 relatively to a spherical reference, located apart from the indenter, through a differential  
24 capacitive sensor, thus allowing to consider the thermal drift. Two kinds of experiments were

1 carried out: static to measure the apparent Young modulus and hardness (E and H, respectively)  
2 of the film/substrate systems and dynamic nanoindentation to determine the intrinsic Young  
3 modulus and hardness of the films ( $E_f$  and  $H_f$ , respectively).

4 During static nanoindentation experiment, a gradually increasing normal force was applied up  
5 to a maximum value of 0.5 mN. This maximal load was maintained for 30 s, after which the  
6 force was gradually decreased to 0 mN. The loading and unloading rates were set to  
7  $1 \text{ mN}\cdot\text{min}^{-1}$ . E and H were calculated from load vs. depth curves using the Oliver and Pharr  
8 method [13]. Each sample was probed with this method on a minimum of 5 different locations  
9 on the sample surface. Before each sample characterization an indentation on fused silica  
10 standard has been performed to control the tip shape and calibration. This characterization  
11 allows an important accuracy for the measurements, with a systematic error of *ca.* 3 %.  
12 Systematic error has been evaluated by static nanoindentation on fused silica standards at  
13 30 mN, with 10 distinct locations probed. E was experimentally found equal to  $71.3 \pm 0.7 \text{ GPa}$   
14 (with a certified Young modulus of  $73.3 \pm 0.3 \text{ GPa}$ ). The bare Si(100) substrate was also  
15 characterized in the same way, in order to assess substrate Young modulus and hardness ( $E_s$   
16 and  $H_s$ ). These were found equal to  $172 \pm 4 \text{ GPa}$  and  $15.3 \pm 0.4 \text{ GPa}$ , respectively. As shown  
17 in Figure 1, only one value of h is probed at a time by static indentation.

18 Dynamic nanoindentation experiments were carried out by operating the apparatus in the so-  
19 called Linear Sinus Loading mode. In this mode, a gradually increasing normal force with  
20 oscillations was applied until a maximum load (between 10 and 30 mN depending on t). This  
21 load was maintained for 30 s, then gradually decreased to 0 mN without oscillations. The  
22 loading rate was set at  $3 \text{ mN}\cdot\text{min}^{-1}$ , oscillation amplitude and frequency were set respectively  
23 at 0.5 mN and 12 Hz, and the unloading rate was set at  $30 \text{ mN}\cdot\text{min}^{-1}$ . Each sample was probed  
24 at 3 different locations, at least. The oscillating load allows to access local load and unload  
25 curves at several h which were exploited with the Oliver and Pharr method, allowing to

1 calculate local values of Young modulus and hardness for each value of  $h$  probed, as  
2 schematized in Figure 1. From these local values, experimental curves of  $E$  (or  $H$ ) vs.  $h/t$  are  
3 obtained. These curves will be used as experimental input for the determination of  $E_f$  (or  $H_f$ )  
4 with the mathematical models, as explained below.

5 For disambiguation purposes, dynamic indentation local values of Young modulus and  
6 hardness are noted  $E(h)$  and  $H(h)$ , respectively, as opposed to static indentation  $E$  and  $H$ . In  
7 order to prevent biases due to tip defects and surface roughness, any data obtained for  
8  $h < 50$  nm were systematically discarded. This 50 nm threshold was experimentally set using  
9 fused silica standards.

10 As shown in Figure 1, whether assessed by static or dynamic indentation, the values of the  
11 film/substrate system Young modulus and hardness range between  $E_f$  and  $E_s$ , and  $H_f$  and  $H_s$ ,  
12 respectively.

13

### 14 2.3. Determination of the intrinsic film mechanical properties

15 Several models have been proposed to remove substrate contribution during the indentation of  
16 films. Most of these models were developed and verified on controlled systems for which both  
17 films and substrates had known mechanical properties (Au/Si [19], Al/glass, Al/sapphire,  
18 Al/Si [20], Ni/Cu [21], TiO<sub>2</sub>/Ti<sub>6</sub>Al<sub>4</sub>V alloy [22] etc.). Only few authors have tested models  
19 outside ideal conditions and on systems comparable to the present ones, both in terms of  
20 thickness range or chemical composition [23,24]. For this reason, we proof-checked various  
21 models from the literature in order to select the most suitable ones. By fitting the models with  
22 experimental  $E(h)$  vs.  $h/t$  (or  $H(h)$  vs.  $h/t$ ) curves,  $E_f$  and  $H_f$  can be determined among other  
23 output model parameters. The fitting process of the model to the experimental curves of  
24  $E(h)$  vs.  $h/t$  (or  $H(h)$  vs.  $h/t$ ) is based on the reduction of  $\chi^2_m$  by the optimization of the values



1 of the model output parameters.  $\chi^2_m$  is defined as the mean value of  $\chi^2$ , as shown by Equations 1  
 2 and 2 (respectively for the Young modulus and the hardness).

$$\chi^2_m = \frac{1}{N} \sum_{i=1}^N \chi^2(h_i) = \frac{1}{N} \sum_{i=1}^N \frac{(E_{exp}(h_i) - E_{mod}(h_i))^2}{E_{mod}(h_i)} \quad (1)$$

3

$$\chi^2_m = \frac{1}{N} \sum_{i=1}^N \chi^2(h_i) = \frac{1}{N} \sum_{i=1}^N \frac{(H_{exp}(h_i) - H_{mod}(h_i))^2}{H_{mod}(h_i)} \quad (2)$$

4

5 where  $h_i$  is the local probed indentation depth ( $h_1$  is the minimal indentation depth allowing  
 6 measurement without biases and it is superior to 50 nm,  $h_N$  is the maximal indentation depth),  
 7  $E_{exp}(h_i)$  (or  $H_{exp}(h_i)$ ), the value of  $E(h)$  (or  $H(h)$ ) experimentally measured at  $h_i$  and  $E_{mod}(h_i)$  (or  
 8  $H_{mod}(h_i)$ ), the value of  $E(h)$  (or  $H(h)$ ) calculated with the model selected at  $h_i$ .

9 The determination of the  $E_f$  and  $H_f$  implies two hypotheses. The first hypothesis is that films  
 10 deposited under the same conditions present identical chemical composition and structural  
 11 organization. As a consequence, thin films and thick films should present identical  $E_f$  and  $H_f$ .

12 The second hypothesis assumes that each sample consists of a homogeneous film with constant  
 13  $E_f$  and  $H_f$  throughout the indentation depth. This hypothesis is supported by previous studies  
 14 that revealed the bulk of the TEOS and HMDS films present homogeneous chemical  
 15 composition and structural organization without noticeable porosity nor visible cavities[10,12].

16 However, it neglects the presence of surface modifications formed by hydration or  
 17 contamination due to atmospheric exposure [25]. Such a superficial 10 nm-thick layer  
 18 containing 4 at.% of carbon has been previously observed for 120 nm-thick-TEOS-like  
 19 samples [12]. Due to higher hydration and to the presence of organic moieties [25–28], this  
 20 superficial layer is expected to present lower Young modulus and hardness. Nevertheless, it

1 could be overlooked due to its thinness compared to the values of  $t$  (from 63 to 713 nm, as  
2 shown in Table 1) and because, as previously mentioned, only the data obtained for  $h \geq 50$  nm  
3 are considered.

4

### 5 **3. Results and discussion**

#### 6 **3.1. Static indentation results**

7 E and H were measured by static indentation experiments for TEOS and HMDS samples. The  
8 obtained values are displayed in Table 2 and the graphical representations of these results are  
9 plotted in Figure 2 and Figure 3 for TEOS films and in Figure 4 for HMDS films.

10 As expected, E is systematically higher for thin than for thick films, due to the higher influence  
11 of the silicon substrate ( $E_s$  has been found equal to 172 GPa). The values of E for thin films lie  
12 between 1.4 times (for TEOS films deposited at 500°C) to 3.1 times higher (for HMDS films  
13 deposited at 500°C) than the values found for corresponding thick films. Similarly, most of the  
14 hardness values of thin films are superior to those of the thick ones. One exception is for TEOS  
15 films deposited at  $T_d = 400^\circ\text{C}$ : the thick film presents a value of H that is significantly higher  
16 than the one found for the corresponding thin film and also higher than the values measured  
17 for the rest of the thick films. Also, as expected, H values vary less than E values between thin  
18 and thick films (with thin films hardness *ca.* 1.3 times higher to equivalent thick films hardness)  
19 due to the smaller contribution of the substrate on hardness than on Young modulus.

20 The presence of hydrated and organic moieties is known to generally decrease the value of E  
21 and H for silicon oxide materials. Classically, silicon oxides have E and H ranging,  
22 respectively, from 73 to 20 GPa and from 8 to 5 GPa depending on the level of  
23 hydration [25,26,28]. Silicon-oxide-based materials containing organic moieties can be found  
24 with E between 20 and 3 GPa and H between 3 and 0.2 GPa depending on the content of

1 organic carbon [11,27,29]. Considering these expected  $E_f$  and  $H_f$  values and the known  $E_s$  and  
2  $H_s$  values, TEOS and HMDS films may present a  $H_f/E_f$  ratio of about 0.1-0.3 and a  $E_f/E_s$  ratio  
3 in the range of 0.4 to 0.1 and 0.1 to 0.01, respectively. Therefore, the substrate contribution can  
4 be assumed limited for the thick films as  $h/t \leq 0.2$  [15–17] and it is possible to consider that E  
5 and H measured for thick films are good estimations of  $E_f$  and  $H_f$ .

6 As shown in Table 2, thick films present values of E and H in good agreement with the expected  
7 values of the literature discussed previously. TEOS thick films show higher values of E and H  
8 than HMDS thick films, attributed to lower hydration and the absence of  $\text{CH}_3$  moieties  
9 (contrary to HMDS films with  $T_d < 500^\circ\text{C}$ ) [10,12].

10 TEOS values of E and H seem to increase slightly with the increase of  $T_d$ , with exception of  
11 the values found for TEOS-400°C-525nm, which presents surprisingly high values of E and H  
12 ( $62 \pm 2$  GPa and  $7.2 \pm 0.4$  GPa, respectively). This evolution may be related to the dehydration  
13 and the increasing network cross-linking of the TEOS films with the increase of  $T_d$  as  
14 previously reported by Diallo et al. [12] and by Ponton et al. for similar films [3].

15 For HMDS thick films, neither E nor H show a clear evolution as a function of  $T_d$  and both  
16 seem to fluctuate around 32 and 2.4 GPa, respectively. This absence of a correlation between  
17 E (and H) and  $T_d$  was not expected, considering the increasing network cross-linking of HMDS  
18 films with the increase of  $T_d$  and the fact that the chemical composition of these films switches  
19 from  $\text{SiO}_x\text{C}_y$  with  $\text{CH}_3$  moieties to  $\text{SiO}_x$  between 450 and 500°C [10].

20 Indeed, as a first approximation, we assumed that  $E \approx E_f$  and  $H \approx H_f$  for thick films.  
21 Nevertheless, it is possible that substrate contribution varies with sufficient magnitude,  
22 especially for the HMDS films, making the comparison of E and H as functions of  $T_d$  inaccurate  
23 and preventing the observation of any trend, as  $h/t$  ranges from 9.4 to 19.2 % for TEOS thick  
24 films and from 14.9 to 20.6 % for HMDS thick films. Therefore, a more reliable analysis may

1 be possible by using intrinsic  $E_f$  and  $H_f$  values obtained by modeling, especially for the thin  
2 films.

### 3 3.2. Initial selection of models

4 Several models have been proposed for the indentation of films. Two model sets can be  
5 identified: the analytical rheological models (with Bec model [19] as the only rheological  
6 model) and the empirical models (with every other model listed in Table 3). Analytical  
7 rheological models, are built on the physical modeling of the system with elementary  
8 rheological elements (i.e. springs, etc.). Empirical models are based on mixing laws:  
9 mathematical functions designed empirically to fit the considered data.

10 Four among the nine reviewed models were originally designed for indenters with disciform  
11 contact area: (i.e. flat cylindrical punch, sphere or cone tip): the Bec, the Song-Pharr, the  
12 Perriot-Barthel and the Kovalev. These models use “a”, the radius of the indenter, as an input  
13 variable. In order to adapt these models to the modified Berkovitch tip used in this study, we  
14 express “a” as a function of “h”, as shown in Equation 3.

$$a = h \sqrt{\frac{24.5}{\pi}} \quad (3)$$

15

16 This expression allows to simulate the radius of an indenter with a projected disciform contact  
17 area equal to the projected contact area of the modified Berkovitch indenter at a given  
18 indentation depth “h”.

19

1 Table 3 List of the considered models

Model	Output parameters	Model equations	Reference
Bec	$E_f$	$\frac{1}{E(h)} = \frac{2a}{1+\frac{2t}{\pi a}} \left( \frac{t}{\pi a^2 E_f} + \frac{1}{2a E_s} \right)$ with $a = h \sqrt{\frac{24.5}{\pi}}$	[19,30]
Song-Pharr (Modified Gao)	$E_f, \nu_f$	$\frac{1}{E(a)} = \frac{(1 - \nu_s)(1 - \nu_f)}{1 - (1 - I_1(a))\nu_f - I_1(a)\nu_s} \left( \frac{1 - I_0(a)}{(1 - \nu_s)E_s} + \frac{I_0(a)}{(1 - \nu_f)E_f} \right)$ with $I_0(a) = \frac{2}{\pi} \text{Arctan} \left( \frac{t}{a} \right) + \frac{1}{2\pi(1-\nu)} \left[ (1 - 2\nu) \frac{t}{a} \ln \left( \frac{1+(\frac{t}{a})^2}{(\frac{t}{a})^2} \right) - \frac{t}{a} \frac{1}{1+(\frac{t}{a})^2} \right]$ , $I_1(a) = \frac{2}{\pi} \text{Arctan} \left( \frac{t}{a} \right) + \frac{t}{\pi a} \ln \left( \frac{1+(\frac{t}{a})^2}{(\frac{t}{a})^2} \right)$ and $a = h \sqrt{\frac{24.5}{\pi}}$	[24,31]
Saha-Nix (Modified King)	$E_f, \nu_f, \alpha$	$\frac{1}{E(h)} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_f^2}{E_f} \left( 1 - \exp \left( -\frac{\alpha(t-h)}{\sqrt{A_p(h)}} \right) \right) + \frac{1 - \nu_s^2}{E_s} \exp \left( -\frac{\alpha(t-h)}{\sqrt{A_p(h)}} \right)$ with $A_p(h) = 24.5 h^2$ for a modified Berkovitch indenter	[20,32]
Martyniuk	$E_f, A, C$ $H_f, B, D$	$E(h) = E_s \left( \frac{E_f}{E_s} \right)^{L(h)}$ with $L(h) = \frac{1}{1+A(\frac{h}{t})^C}$ $H(h) = H_s \left( \frac{H_f}{H_s} \right)^{M(h)}$ with $M(h) = \frac{1}{1+B(\frac{h}{t})^D}$	[23]
Korsunsky	$H_f, k$	$H(h) = H_s + \frac{H_f - H_s}{1 + k \left( \frac{h}{t} \right)^2}$	[21,33]
Modified Korsunsky	$H_f, \beta_0, X$	$H(h) = H_s + \frac{H_f - H_s}{1 + \left( \frac{h}{\beta_0 t} \right)^X}$	[34]

Puchi-Cabrera	$H_f, k, m$	$H(h) = H_s + (H_f - H_s)e^{-k\left(\frac{h}{t}\right)^m}$	[18]
Perriot-Barthel	$E_f, x_0, n$	$E(a) = E_s + \frac{E_f - E_s}{1 + \left(x_0 \frac{t}{a}\right)^n}$ with $a = h \sqrt{\frac{24.5}{\pi}}$	[35]
Kovalev	$E_f, \lambda, \tau$	$E(a) = E_f + \frac{E_s - E_f}{1 + \exp\left(-\lambda \frac{E_s - E_f \frac{a}{t} - \tau}{E_f \tau}\right)}$ with $a = h \sqrt{\frac{24.5}{\pi}}$	[36]

E(h) or E(a): the measured Young modulus (GPa); H(h) or H(a), the measured hardness (GPa)

Input constants: t: film thickness (nm);  $E_s$ : intrinsic measured Si(100) substrate Young modulus (172 GPa);  $H_s$ : intrinsic measured Si(100) substrate hardness (15.3 GPa);  $\nu_s$ : Poisson ratio of the Si(100) silicon (0.25 [19,20])

Input variables: a: radius of the indenter (flat cylindrical punch for Bec and Song-Pharr, sphere tip for Kovalev) (nm); h: the indentation depth of the indenter (nm);  $A_p(h)$ : projected area of the indenter ( $\text{nm}^2$ )

Output parameters:  $E_f$ : intrinsic Young modulus of the film (GPa);  $H_f$ : intrinsic hardness of the film (GPa);  $\nu_f$ : Poisson ratio of the film;  $\alpha, A, C, B, D, k, \beta_0, X, m, x'_0, n, \lambda$  and  $\tau$ : fitting parameters

1 TEOS-550°C-713 nm has been selected as the reference sample for the identification of the  
 2 most suitable models, as it was probed by static nanoindentation at the lowest relative  
 3 indentation depth ( $h/t = 9.4 \pm 0.1 \%$ , cf. Table 2), within the boundaries of Bückle 10 % rule.  
 4 With this low  $h/t$  value, the substrate contribution on  $E$  and  $H$  is as low as possible. As a  
 5 consequence, models are selected only by meeting the following criteria:  $E_f$  and  $H_f$  must be  
 6 found close to  $E$  and  $H$  (reliability criterion), respectively, and  $\chi^2_m$  must be as low as possible  
 7 (fitting criterion). Every model from Table 3 has been used for TEOS-550-713 nm and the  
 8 calculated values of  $E_f$ ,  $H_f$  and  $\chi^2_m$  are displayed in Table 4.

9 Most of the models met both reliability and fitting criteria and were selected. Bec [19,30] and  
 10 Song-Pharr [24,37] models present values of  $\chi^2_m$  higher than the other models. This can be  
 11 explained as these model use few (or no) output parameters and possess a lower degree of  
 12 latitude to fit the experimental  $E(h)$  vs.  $h/t$  and  $H(h)$  vs.  $h/t$  curves. Thus, these models are not  
 13 discarded. Finally, only two models were discarded: Kovalev model [36], because it gives an  
 14 abnormal value of  $E_f$  despite an excellent fit and Saha-Nix model [20,32] as it is unusable for  
 15  $h/t > 1$  (due to the exponential terms it contains), a situation that is likely to be encountered in  
 16 thin films. The seven selected models are listed in Table 5.

17 Table 5 Summary of the models selected using TEOS-550°C-713 nm reference sample

Models for $E_f$ calculation	Models for $H_f$ calculation
Perriot-Barthel [35] Bec [19,30] Song-Pharr [24,31]	Martyniuk [23] Korsunsky [21,33] Modified Korsunsky [34] Puchi-Cabrera [18]

18  
 19 **3.3. Models validation with thick TEOS samples**

20 The selected models from Table 5 have been tested with the rest of the thick TEOS samples.  
 21 The resulting  $E_f$  and  $H_f$  are compared with static indentation values of  $E$  and  $H$  in Figure 2a  
 22 and Figure 2b.

1 As shown by Figure 2a, static indentation  $E$  is systematically found superior to  $E_f$  values, due  
2 to the higher value of  $E_s$ . It can be observed that the difference between  $E$  and  $E_f$  is minimal at  
3  $550^\circ\text{C}$  (*i.e.*, for the sample with the lowest value of  $h/t$ ) which confirms that  
4 TEOS- $550^\circ\text{C}$ -713 nm was an accurate choice for reference sample. Every model can be  
5 considered reliable as they give similar values of  $E_f$ .

6 Figure 2b systematically reveals that  $H_f \approx 1.3H$ , probably due to a more limited substrate  
7 contribution to the hardness measured by static indentation (with  $h/t < 20\%$ ). Finding  $H_f > H$   
8 is surprising as substrate contribution was expected to increase the measured hardness (as  
9  $H_s = 15.3$  GPa). The lower values found for  $H$  than  $H_f$  may originate from several sources:  
10 models misestimating the substrate contribution on  $H$ , mainly sinus measurement inaccuracy  
11 for  $H$  or possible contribution of a thin soft surface alteration layer that models would neglect.  
12 As models systematically give  $H_f > H$ , the overestimation of substrate contribution seems  
13 unlikely. The source of the higher  $H_f$  values remains an open question but models can be  
14 considered reliable: they consistently give values of  $E_f$  and  $H_f$  which are close to  $E$  and  $H$   
15 values, in good agreement with literature values, while at the same time  $E_f$  and  $H_f$  present a  
16 similar evolution with  $T_d$  to  $E$  and  $H$ .

#### 17 3.4. Models selection for thin films

18 When tested for thin films, most of the seven models shown in Table 5 fail to find consistent  
19 values of  $E_f$  or  $H_f$ , leading to extremely low or null values (not shown). Only three models (the  
20 Bec [19], Song-Pharr [24,31] and Korsunsky [21,33] models) provide consistent values of  $E_f$   
21 or  $H_f$  (*i.e.* close to the one found for the corresponding thick films and in good agreement with  
22 literature for similar silica glass [25,26,28]) as shown in Figure 3a and b for TEOS samples,  
23 Figure 4a and b for HMDS samples.



1 Since every model meets the curve fitting criterion (whether or not they failed to find consistent  
2 values of  $E_f$  or  $H_f$ ), the cause of the failure cannot be a poor fitting of the experimental data.  
3 An explanation may be the higher level of extrapolation required for thin films: as data obtained  
4 for  $h < 50$  nm are systematically discarded, the minimal  $h/t$  probed for thin films is of about  
5 0.6 (for thick films, it was between 0.09 and 0.2). Only the models with the lowest number of  
6 fitting parameters could find consistent values of  $E_f$  (Bec and Song-Pharr models) and  $H_f$   
7 (Korsunsky model), proving a robustness superior to models with a higher degree of latitude,  
8 which is in good agreement with the literature [18]. As an indication of reliability and  
9 robustness, these three models have been shown in recent articles [38–40] to characterize  
10 efficiently various systems, including coated systems with films of thicknesses similar to the  
11 TEOS and HMDS films of the present work.

12 More interestingly,  $E_f$  values calculated for thin and thick films deposited at identical  $T_d$  are  
13 found consistent and in good correlation with the values of  $E$  obtained for the thicker films.

14 As previously noted, calculated values of  $E_f$  are found systematically slightly lower than  $E$  for  
15 thick (with  $E_f \leq E \leq 1.5E_f$ ) and lower than  $E$  for thin films (with  $1.4E_f \leq E \leq 2.1E_f$ ) due to the  
16 more or less negligible substrate contribution on system elastic strain.  $H_f$  and  $H$  values are in  
17 close agreement for thick (with  $H \approx 0.8H_f$ ) and thin films (with  $H \approx 1.1H_f$ ) due to the more  
18 limited substrate contribution (which may explain why  $H \leq H_f$  only for thin films).

19 This demonstrates the efficient removal of substrate contribution by the selected models.  
20 Similar calculated  $H_f$  values are found for both thin and thick films deposited at the same of  
21  $T_d$ , with the exception of TEOS-400°C-525 nm. Both  $E_f$  and  $H_f$  values (for thin and thick films)  
22 increase with  $T_d$ , as expected, considering the previously reported evolution (composition and  
23 cross-linking) of the films [12].

1 A similar comparison between E and  $E_f$  and H and  $H_f$  is carried out for HMDS thick and thin  
2 films and displayed in Figure 4a (for E and  $E_f$ ) and Figure 4b (for H and  $H_f$ ), respectively.

3 As previously observed for TEOS samples, calculated  $E_f$  and  $H_f$  values for HMDS samples are  
4 found close to the static E and H measured for thick films. Due to the smaller substrate  
5 contribution on hardness,  $H_f$  and H are systematically found close for both thin and thick films  
6 (with  $H \approx 0.8H_f$  for thick films and  $0.7H_f \leq H \leq 1.2H_f$  for thin films).

7 Whereas measured E shows no clear behavior as a function of  $T_d$ , both calculated  $E_f$  and  $H_f$   
8 increase with  $T_d$ , similarly to TEOS samples and in a good agreement with the evolution of the  
9 chemical composition of HMDS films.

10 Finally, the E,  $E_f$ , H and  $H_f$  values found for HMDS-500°C-500nm sample must be pointed  
11 out, as they are consistently and inexplicably lower compared to the rest of the values found.

12 In summary, from the initial nine tested models, only the Bec, Song-Pharr and Korsunsky  
13 models allowed a successful assessment of  $E_f$  and  $H_f$  for the silica-based coatings of interest  
14 within this work. Using calculated  $E_f$  and  $H_f$  instead of E and H allowed a more accurate  
15 correlation between the mechanical properties of TEOS and HMDS samples and the evolution  
16 of the chemical composition and structural organization, in better agreement with the literature.  
17 It also leads to an expanded range of films thicknesses that can be accurately evaluated through  
18 nanoindentation, thus allowing reduced chemical vapor deposition time that was  
19 conventionally required for the assessment of film mechanical properties.

20

#### 21 **4. Conclusion**

22 By associating dynamic indentation experiments with analytical or empirical models, more  
23 accurate values of Young modulus and hardness could be calculated for  $\text{SiO}_x$  and  $\text{SiO}_x\text{C}_y$  to

1 SiO<sub>x</sub> samples obtained from TEOS and HMDS+TEOS, respectively. These calculated values  
2 are likely to be closer to the real intrinsic properties of the thin films. Among the nine initially  
3 considered models, three could systematically determine E<sub>f</sub> and H<sub>f</sub> for silicon oxide and silicon  
4 oxycarbide films with t ranging from 60 to 700 nm. These are the Bec and Song-Pharr models  
5 for the determination of E<sub>f</sub> and the Korsunsky model for H<sub>f</sub> calculation.

6 The comparison between measured E and calculated E<sub>f</sub> highlighted that Young modulus is  
7 more likely to be affected by substrate contribution, as generally expected, even for thick films.  
8 For the thinner films (with typical t below 120 nm), the consideration of calculated E<sub>f</sub> instead  
9 of E is essential, given that extremely high and unrealistic values of E were found for the  
10 thinnest films (with values up to 98 ± 3 GPa for TEOS-550°C-95 nm and 95 ± 2 GPa for  
11 HMDS-550°C-103 nm). H and H<sub>f</sub> exhibited smaller differences as a sign of the more limited  
12 substrate influence on hardness.

13 Using E<sub>f</sub> and H<sub>f</sub> instead of E and H makes the correlation with the previously characterized  
14 chemical composition and the structural organization of TEOS and HMDS samples easier: such  
15 a correlation is much more complicated to observe when considering static indentation alone,  
16 as the larger influence of the substrate has a levelling effect on the obtained data [10,12]. The  
17 consistence of the values found for films of very different thicknesses and obtained from  
18 various precursors with expected literature-based values proves the reliability of the method.

19 In conclusion, dynamic indentation associated to models is a promising tool for the precise  
20 study of thin films and superficial events, as it leads to an expanded range of films thicknesses  
21 that can be accurately evaluated through nanoindentation technique. Developing new physics-  
22 based analytical models, like the rheological model proposed by Bec et al., to simulate the  
23 elastoplastic behavior of the film/substrate system with improved accuracy would be of interest  
24 to expand the array of available tools. On the other hand, pushing forward the use of models

1 by characterizing thinner coatings or thin superficial regions of bulk materials, such as the  
2 alteration layer on bulk materials or multi-layered materials [22,39,41], still remains an  
3 interesting challenge for a better understanding of deposition growth and evolution  
4 mechanisms of coated and/or altered systems.

5

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9

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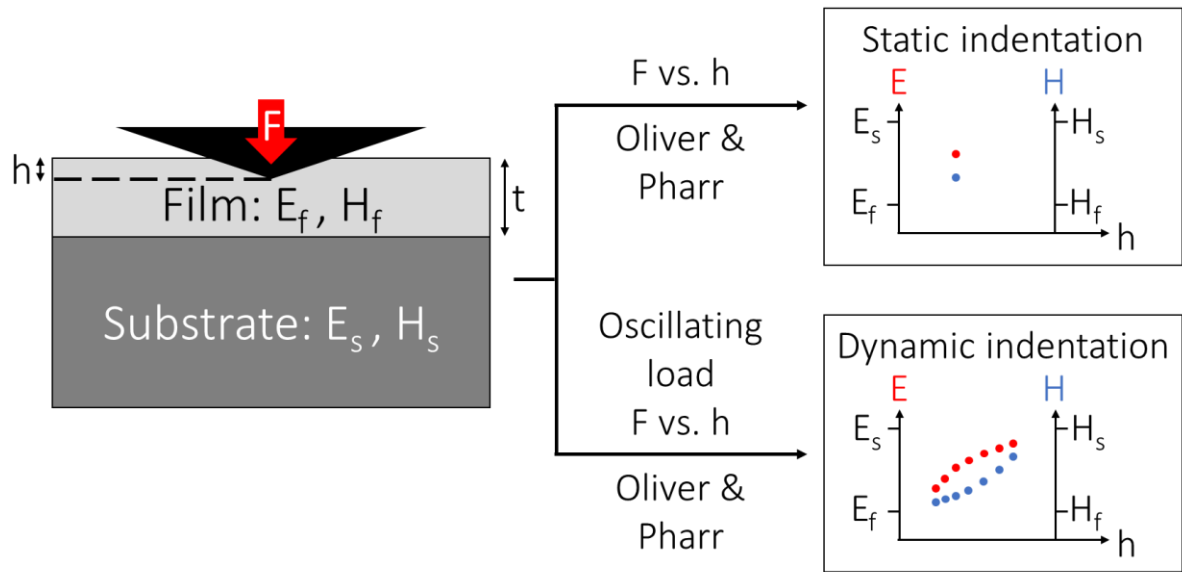
1 **List of Figures**

2 Table 1 Deposition temperatures  $T_d$  and thicknesses  $t$  for the investigated samples

3

<b>Set</b>	<b>Sub-set</b>	<b>Sample</b>	<b><math>T_d</math> (°C)</b>	<b><math>t</math> (nm)</b>
TEOS samples	Thin films	TEOS-400°C-98nm	400	98
		TEOS-450°C-102nm	450	102
		TEOS-500°C-128nm	500	128
		TEOS-550°C-95nm	550	95
	Thick films	TEOS-400°C-525nm	400	542
		TEOS-450°C-402nm	450	402
		TEOS-500°C-498nm	500	498
		TEOS-550°C-713nm	550	713
HMDS samples	Thin films	HMDS-400°C-92nm	400	92
		HMDS-450°C-63nm	450	63
		HMDS-500°C-114nm	500	114
		HMDS-550°C-103nm	550	103
	Thick films	HMDS-360°C-703nm	360	703
		HMDS-400°C-525nm	400	525
		HMDS-500°C-500nm	500	500

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2 Figure 1 Illustration of the difference between the results of the static and the dynamic  
 3 indentation (with  $E_f < E_s$  and  $H_f < H_s$ )

4

1 Table 2 Values of E and H measured by static nanoindentation for the investigated samples,  
 2 maximum indentation depth h on film thickness t ratio i.e. relative indentation depth is given  
 3 for each sample

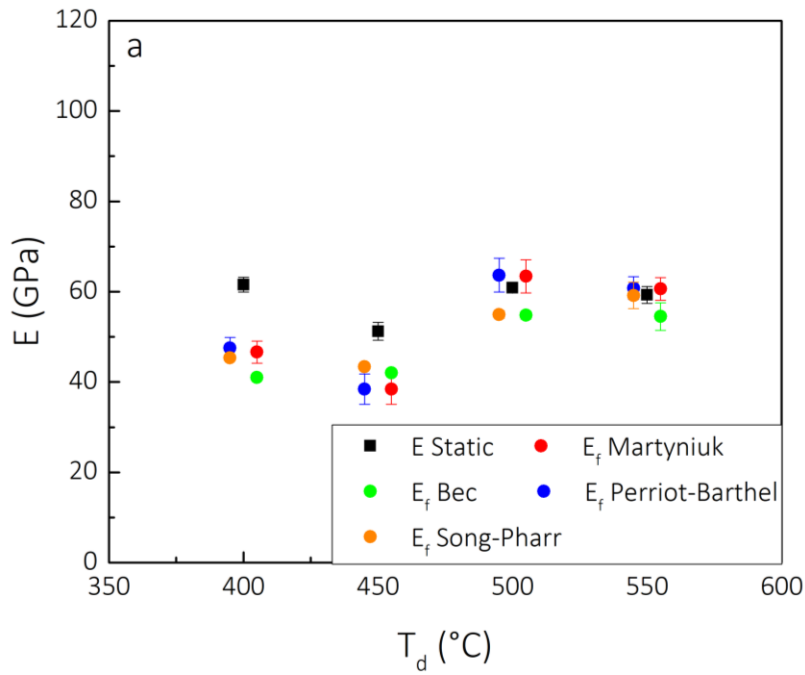
Set	T <sub>d</sub> (°C)	Thin films			Thick films		
		h/t (%)	E (GPa) <sup>a</sup>	H (GPa) <sup>a</sup>	h/t (%)	E (GPa) <sup>a</sup>	H (GPa) <sup>a</sup>
TEOS	400	68.9 ± 2.2	89 ± 3	3.9 ± 0.3	14.4 ± 0.3	62 ± 2	7.2 ± 0.4
	450	61.4 ± 2.0	93 ± 4	4.7 ± 0.3	19.2 ± 0.8	51 ± 2	3.6 ± 0.3
	500	45.6 ± 1.1	87 ± 3	5.7 ± 0.3	13.8 ± 0.3	61 ± 2	4.5 ± 0.3
	550	58.1 ± 1.6	98 ± 3	6.1 ± 0.3	9.4 ± 0.1	59 ± 2	5.0 ± 0.1
HMDS	360	-	-	-	14.9 ± 1.6	20 ± 2	1.8 ± 0.2
	400	72.1 ± 3.7	89 ± 6	4.1 ± 0.4	15.4 ± 0.2	48 ± 0(4)	3.3 ± 0.1
	450	102.9 ± 4.7	105 ± 5	4.1 ± 0.4	-	-	-
	500	57.1 ± 1.8	89 ± 2	4.3 ± 0.3	20.6 ± 0.4	29 ± 1	2.2 ± 0.1
	550	57.6 ± 0.7	95 ± 2	5.2 ± 0.2	-	-	-

For reference, E<sub>s</sub> = 172 GPa and H<sub>s</sub> = 15.3 GPa

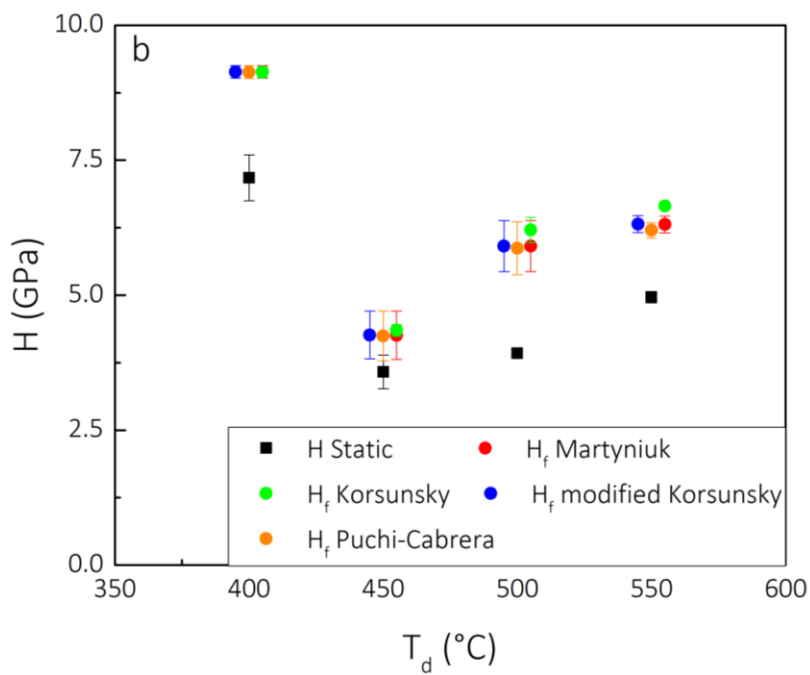
<sup>a</sup> Measured with static indentation at 0.5 mN

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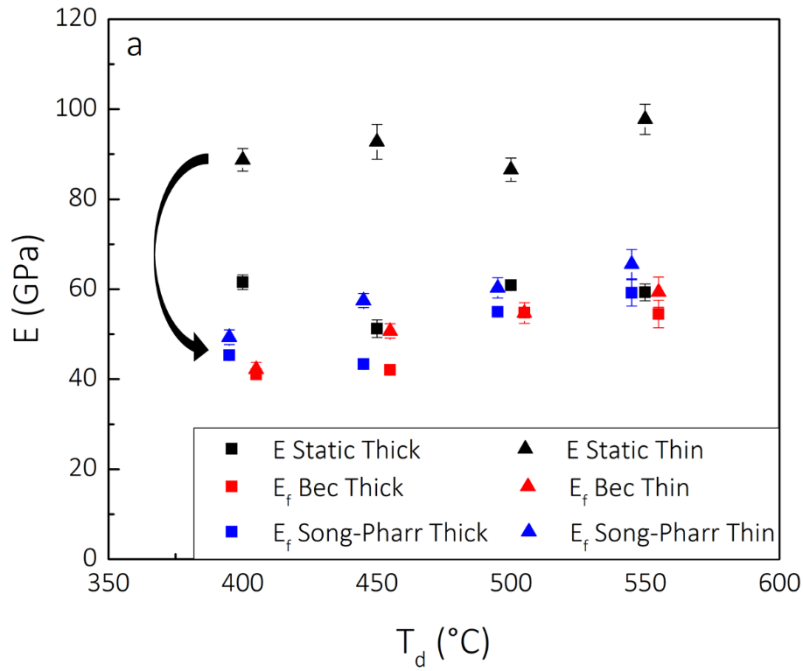
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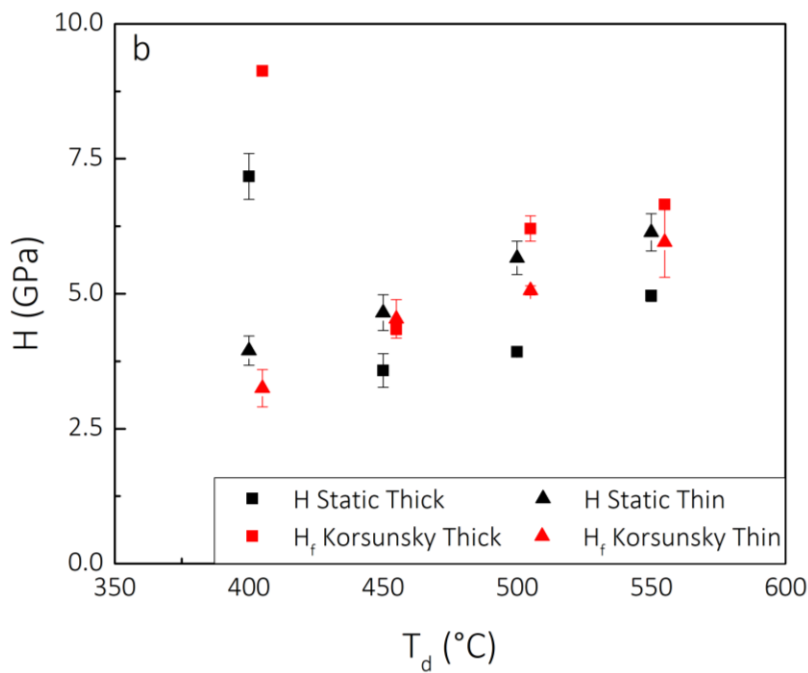
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3 Figure 2 Variation of (a) experimental  $E$  and calculated  $E_f$  and (b) experimental  $H$  and  
 4 calculated  $H_f$  along  $T_d$  for thick TEOS samples (for clarification, data calculated with Perriot-  
 5 Barthel, Song-Pharr and modified Korsunsky models have been shifted by  $-5^\circ\text{C}$  and data  
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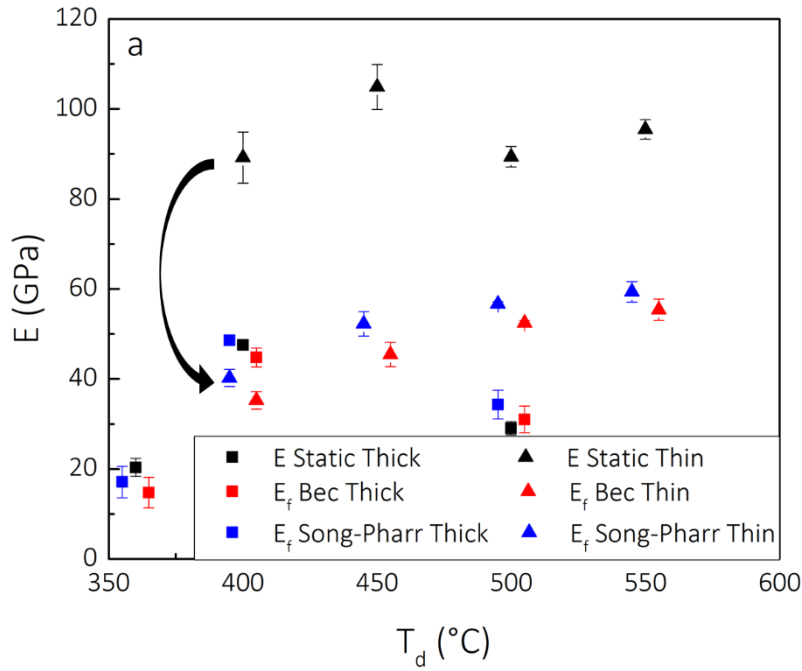
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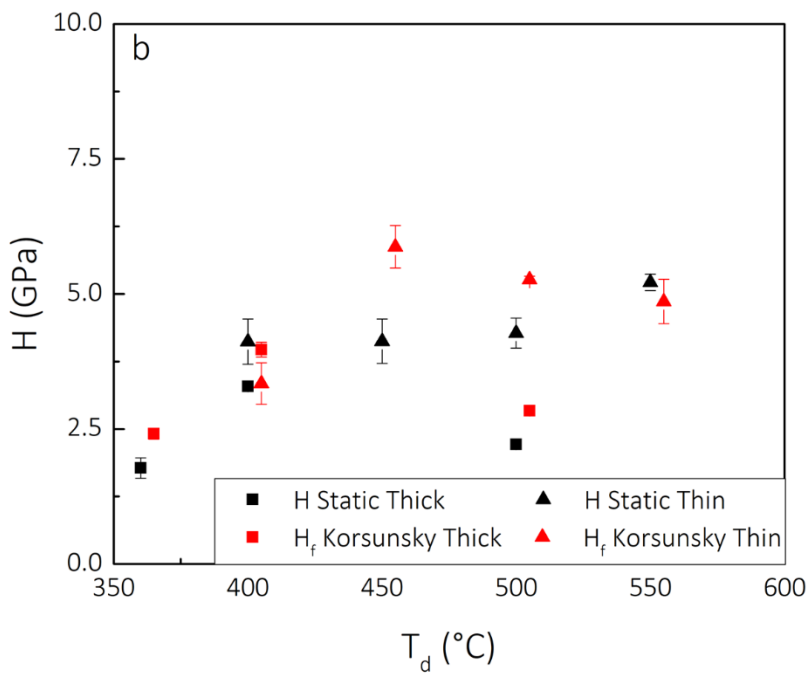
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3 Figure 3 Comparison of (a) experimental E with model calculated  $E_f$  and (b) experimental H  
 4 with model calculated  $H_f$  for TEOS samples versus  $T_d$  (for clarification, data calculated with  
 5 Song-Pharr model have been shifted by  $-5^\circ\text{C}$  and data calculated with Bec and Korsunsky  
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3 Figure 4 Comparison of (a) experimental E with model calculated  $E_f$  and (b) experimental H  
 4 with model calculated  $H_f$  for HMDS samples versus  $T_d$  (for clarification, data calculated with  
 5 Song-Pharr model have been shifted by  $-5^\circ\text{C}$  and data calculated with Bec and Korsunsky  
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1 Table 3 List of the considered models

Model	Output parameters	Model equations	Reference
Bec	$E_f$	$\frac{1}{E(h)} = \frac{2a}{1+\frac{2t}{\pi a}} \left( \frac{t}{\pi a^2 E_f} + \frac{1}{2a E_s} \right)$ with $a = h \sqrt{\frac{24.5}{\pi}}$	[19]
Song-Pharr (Modified Gao)	$E_f, \nu_f$	$\frac{1}{E(a)} = \frac{(1-\nu_s)(1-\nu_f)}{1-(1-I_1(a))\nu_f - I_1(a)\nu_s} \left( \frac{1-I_0(a)}{(1-\nu_s)E_s} + \frac{I_0(a)}{(1-\nu_f)E_f} \right)$ with $I_0(a) = \frac{2}{\pi} \text{Arctan} \left( \frac{t}{a} \right) + \frac{1}{2\pi(1-\nu)} \left[ (1-2\nu) \frac{t}{a} \ln \left( \frac{1+(\frac{t}{a})^2}{(\frac{t}{a})^2} \right) - \frac{t}{a} \frac{1+(\frac{t}{a})^2}{1+(\frac{t}{a})^2} \right]$ , $I_1(a) = \frac{2}{\pi} \text{Arctan} \left( \frac{t}{a} \right) + \frac{t}{\pi a} \ln \left( \frac{1+(\frac{t}{a})^2}{(\frac{t}{a})^2} \right)$ and $a = h \sqrt{\frac{24.5}{\pi}}$	[24,31]
Saha-Nix (Modified King)	$E_f, \nu_f, \alpha$	$\frac{1}{E(h)} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu_f^2}{E_f} \left( 1 - \exp \left( -\frac{\alpha(t-h)}{\sqrt{A_p(h)}} \right) \right) + \frac{1-\nu_s^2}{E_s} \exp \left( -\frac{\alpha(t-h)}{\sqrt{A_p(h)}} \right)$ with $A_p(h) = 24.5 h^2$ for a modified Berkovitch indenter	[20,32]
Martyniuk	$E_f, A, C$ $H_f, B, D$	$E(h) = E_s \left( \frac{E_f}{E_s} \right)^{L(h)}$ with $L(h) = \frac{1}{1+A(\frac{h}{t})^C}$ $H(h) = H_s \left( \frac{H_f}{H_s} \right)^{M(h)}$ with $M(h) = \frac{1}{1+B(\frac{h}{t})^D}$	[23]
Korsunsky	$H_f, k$	$H(h) = H_s + \frac{H_f - H_s}{1 + k \left( \frac{h}{t} \right)^2}$	[21,33]
Modified Korsunsky	$H_f, \beta_0, X$	$H(h) = H_s + \frac{H_f - H_s}{1 + \left( \frac{h}{\beta_0 t} \right)^X}$	[34]

Puchi-Cabrera	$H_f, k, m$	$H(h) = H_s + (H_f - H_s)e^{-k\left(\frac{h}{t}\right)^m}$	[18]
Perriot-Barthel	$E_f, x_0, n$	$E(a) = E_s + \frac{E_f - E_s}{1 + \left(x_0 \frac{t}{a}\right)^n}$ with $a = h \sqrt{\frac{24.5}{\pi}}$	[35]
Kovalev	$E_f, \lambda, \tau$	$E(a) = E_f + \frac{E_s - E_f}{1 + \exp\left(-\lambda \frac{E_s - E_f a}{E_f t - \tau}\right)}$ with $a = h \sqrt{\frac{24.5}{\pi}}$	[36]

E(h) or E(a): the measured Young modulus (GPa); H(h) or H(a), the measured hardness (GPa)

Input constants: t: film thickness (nm);  $E_s$ : intrinsic measured Si(100) substrate Young modulus (172 GPa);  $H_s$ : intrinsic measured Si(100) substrate hardness (15.3 GPa);  $\nu_s$ : Poisson ratio of the Si(100) silicon (0.25 [19,20])

Input variables: a: radius of the indenter (flat cylindrical punch for Bec and Song-Pharr, sphere tip for Kovalev) (nm); h: the indentation depth of the indenter (nm);  $A_p(h)$ : projected area of the indenter ( $\text{nm}^2$ )

Output parameters:  $E_f$ : intrinsic Young modulus of the film (GPa);  $H_f$ : intrinsic hardness of the film (GPa);  $\nu_f$ : Poisson ratio of the film;  $\alpha, A, C, B, D, k, \beta_0, X, m, x'_0, n, \lambda$  and  $\tau$ : fitting parameters

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- 1 Table 4 Summary of the calculated values of  $E_f$  and,  $H_f$ , and  $\chi^2_m$  found with every model for  
 2 TEOS-550°C-713 nm thick reference sample

Model	Output parameters <sup>a</sup>	$E_f$ (GPa) $\chi^2_m$ (MPa)	$H_f$ (GPa) $\chi^2_m$ (MPa)
Static indentation		$59 \pm 2^b$	$5.0 \pm 0.1^b$
Bec	$E_f$	$55 \pm 3$ $220 \pm 140$	
Song-Pharr	$E_f, \nu_f$	$59 \pm 3$ $260 \pm 150$	
Saha-Nix	$E_f, \nu_f, \alpha$	$71 \pm 5$ $130 \pm 80$	
Martyniuk	$E_f, A, C$	$61 \pm 3$	$6.3 \pm 0.2$
	$H_f, B, D$	$28 \pm 5$	$1.7 \pm 0.3$
Korsunsky	$H_f, k$		$6.7 \pm 0.0(4)$
			$2.2 \pm 0.3$
Modified Korsunsky	$H_f, \beta_0, X$		$6.3 \pm 0.2$
			$1.7 \pm 0.3$
Puchi-Cabrera	$H_f, k, m$		$6.2 \pm 0.1$
			$1.6 \pm 0.2$
Perriot-Barthel	$E_f, x_0, n$	$61 \pm 3$	
		$28 \pm 5$	
Kovalev	$E_f, \lambda, \tau$	$0.4 \pm 0.1$	
		$30 \pm 9$	

<sup>a</sup>  $E_s, H_s$  and  $\nu_s$  are input constants:  $E_s = 172$  GPa,  $H_s = 15.3$  GPa and  $\nu_s = 0.25$  [19,20]

<sup>b</sup> Experimental value, measured with  $h/t = 9.4 \pm 0.1$  %

3

1 Table 5 Summary of the selected models for both  $E_f$  and  $H_f$  calculation of the tested films

<b>Models for <math>E_f</math> calculation</b>	<b>Models for <math>H_f</math> calculation</b>
Perriot-Barthel [35] Bec [19,30] Song-Pharr [24,31]	Martyniuk [23] Korsunsky [21,33] Modified Korsunsky [34] Puchi-Cabrera [18]

2

1 **Figures and table captions**

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3 indentation (with  $E_f < E_s$  and  $H_f < H_s$ )

4 Figure 2: Variation of (a) experimental E and calculated  $E_f$  and (b) experimental H and  
5 calculated  $H_f$  along  $T_d$  for thick TEOS samples (for clarification, data calculated with Perriot-  
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10 Song-Pharr model have been shifted by  $-5^\circ\text{C}$  and data calculated with Bec and Korsunsky  
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12 Figure 4: Comparison of (a) experimental E with model calculated  $E_f$  and (b) experimental H  
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16 Table 1: Deposition temperatures  $T_d$  and thicknesses t for the investigated samples

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