

## RF-power-controlled young's modulus of plasma-polymerized organosilicon films

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Mechanical properties of thin films are of great importance with respect to applications such as protective coatings to improve wear resistance or possibly lubrication. Therefore thin films of quite different mechanical properties are required. Multicomponent materials such as composites require functional films that are embedded among components to improve their compatibility, for example fiber reinforced plastics (FRP) combine the high strength of rigid reinforcements with the high toughness of a flexible matrix. The fibers must be coated by a thin film (interlayer) to form a strong but tough link between the fiber and the polymer matrix. The Young's modulus and thickness of the interlayer are among the main parameters influencing composite performance [1]. Model calculations even suggest controlling the composite strength and toughness by varying the interlayer modulus [2]. Although it is not yet fully known which coating material is most suitable for a specific composite system, ductile or flexible films of the modulus value close to that of polymer matrix are expected to fulfil the demands [3]. Glass fibers (GF; 73 GPa) are often (90%) used as reinforcements in polyester resin (3.5 GPa). Therefore, an organosilicon polymer film of a modulus ranging from 3.5 to 73 GPa is required as a "model" material that could be tested as a compatible interlayer in GF/polyester composite in order to control composite performance [4].

Experimental data drawn from the literature indicate that thin films of variable moduli can be deposited even by the same monomer using plasma technologies (Table I). Prepared materials such as a-Si:H [5], a-SiN:H [6], or a-SiO<sub>2</sub>:H [6] are too stiff. Hydrogenated amorphous carbon (a-C:H) was prepared with a slightly lower modulus [5, 7], but an organosilicon material (a-SiCO:H) can be stiff [8] or even soft [3, 9]. Thin and ultrathin organosilicon films of controlled mechanical properties with the Young's modulus as low as that of the polymer matrix were the aim of this study.

Plasma-polymerized (PP) films of vinyltriethoxysilane (VTES) were prepared by plasma-enhanced chemical vapor deposition (PE CVD) using an RF (13.56 MHz) helical coupling plasma system [4] work-

ing as continuous plasma or pulsed plasma. An RF power of tens or hundreds of watts is generally used to deposit PP-films, however the material is highly cross-linked and therefore too stiff. In our study we have reduced the power using pulsed plasma in order to decrease the degree of cross-linking of plasma polymer, which could result in material of lower Young's modulus. The effective power ( $W_{\text{eff}}$ ) of pulsed plasma can be controlled by changing the ratio of the time when plasma is switched on ( $t_{\text{on}}$ ) to the time when plasma is switched off ( $t_{\text{off}}$ ),  $W_{\text{eff}} = W_{\text{total}} \times t_{\text{on}} / (t_{\text{on}} + t_{\text{off}})$ , where  $W_{\text{total}} = 50$  W.

PP-VTES films were deposited on silicon (1 0 0) wafers at an effective power of 0.05, 5.0, and 25 W using pulsed plasma with  $t_{\text{on}} = 1$  ms (0.45 sccm, 0.02 mbar). Even lower power (<0.05 W) was applied but the deposition rate was very low (<1 nm min<sup>-1</sup>) and the deposition time increased. Continuous plasma was used for deposition of a film at an RF power of 50 W. However, as the plasma volume in the glass tube varied with the power applied, the power density was estimated approximately.

The Young's modulus and the hardness of the films were determined [10] from load-displacement curves (loading and unloading rate was in range 3–20  $\mu\text{N s}^{-1}$  with a minimum load of 1  $\mu\text{N}$  and the hold time was 60 s) obtained using a Hysitron Triboscope attached to a DI Dimension 3100 AFM and equipped with a three-sided pyramid Berkovich indenter. Between 9 and 15 indentations were made on each sample to a penetration depth of 30%. The elastic modulus,  $E$ , was estimated by averaging the values measured up to 10% of the film thickness, where the measurements are not influenced by the substrate [11]. The Poisson's ratio used was 0.3. The film thickness was measured by a Profilometer Talystep (Taylor-Hobson) using a defined scratch in the layer as deep as the substrate.

Plasma polymers behaved as a true elastic material as was evident from the load-displacement recordings; the plastic energy was approximately zero. Deformation of the film material induced by the indenter at the loading part of measured cycle was almost completely removed after unloading. There is thus

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TABLE I Selected mechanical properties of thin films prepared by plasma techniques

Plasma technique gas-monomer	Thin film	Young's modulus ( $E$ ) (GPa)	Hardness ( $H$ ) (GPa)	$H/E$ ratio	Reference
Sputtering Si target + $H_2/Ar$	a-Si:H	60–100	4–10	0.093	[5]
PE CVD $SiH_4/NH_3$	a-SiN:H	135–145	9–10	0.071	[6]
PE CVD $SiH_4/N_2O$	a-SiO <sub>2</sub> :H	76–94	4–6	0.059	[6]
PE CVD $CH_4$	a-C:H	40–145	5–15	0.115	[5]
PE CVD $C_2H_2/H_2$	a-C:H	41–142	4–15	0.110	[7]
PE CVD $SiC_4H_{12}/O_2$	a-SiCO:H	130–160	14–20	0.112	[8]
PE CVD $Si_2C_6OH_{18}/O_2$	a-SiCO:H	2.1–5.5	–	–	[3]
PE CVD $Si_2C_7H_{20}/O_2$	a-SiCO:H	4.5–8.8	0.4–0.5	0.063	[9]
PE CVD $SiC_8O_3H_{18}$	a-SiCO:H	3.7–11.3	0.7–2.1 (1.2–3.3)	0.185 (0.302)	This paper

TABLE II The Young's modulus and the hardness of PP-VTES films prepared at different power densities under pulsed (p) or continuous (c) plasma

Effective power density ( $W\ cm^{-3}$ )	Film thickness (nm)	Young's modulus (GPa)	Hardness (GPa)	
			$H_{bulk}$	$H_{max}$
$8 \times 10^{-4}$ (p)	112	4.9	1.2	1.7
$8 \times 10^{-4}$ (p)	240	3.7	0.7	1.2
$2 \times 10^{-2}$ (c)	80	6.1	1.6	3.3
$7 \times 10^{-2}$ (p)	180	7.4	1.1	2.0
$7 \times 10^{-2}$ (p)	390	6.8	1.0	2.2
$7 \times 10^{-2}$ (p)	1480	6.6	1.1	2.1
$3 \times 10^{-1}$ (p)	80	11.3	2.1	2.5

practically no visual footprint of the indenter in the film after the measuring cycle. The Young's modulus and the hardness of PP-VTES films prepared at different power densities are summarized in Table II.  $H_{max}$  denotes the maximum value of the hardness at the film surface and  $H_{bulk}$  is a bulk hardness estimated as a mean value of data obtained below 20 nm from the film surface.

The Young's modulus of PP-VTES as a function of the effective power density is shown in Fig. 1. In spite of different film thicknesses, it is evident that the modulus increases with increasing power density from 3.7 to 11.3 GPa. This change represents an enlargement of the modulus by 205%. The values of the modulus determined are close to that of polyester resin (3.5 GPa) and thus the film can be employed as an interlayer for GF/polyester composite. Our films were prepared at a relatively low-power density, and the lower plasma energy therefore seems to be the reason for the reduced elastic modulus. Monomer molecules are more activated and fragmented forming a higher density of free radicals, if the plasma energy increases, and the reactive species results in a highly cross-linked polymer. A cross-linking of material may also be supported by ion bombardment. It has been shown that the ion energy effectively enhances the film packing density

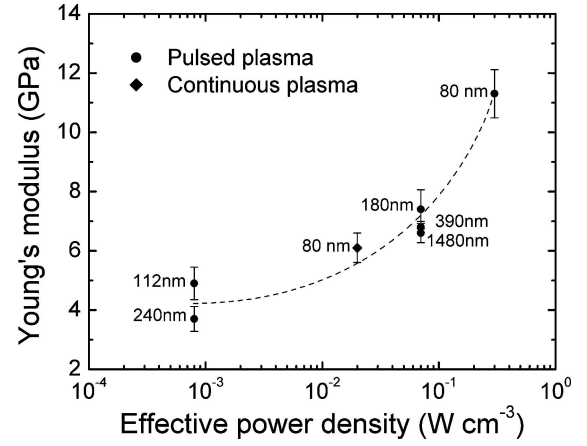


Figure 1 Young's modulus of PP-VTES films as a function of the effective power density.

[12]. It may be surprising that the modulus of the film prepared under continuous plasma corresponds to the dependence (Fig. 1) largely constituted for films prepared under pulsed plasma. However, we can expect that the Young's modulus is really governed by the effective power density and thus through the effective plasma energy. It means that we are able to control the film modulus very simply by changing the power density.

Films of different thickness were deliberately deposited under the same deposition conditions to investigate a variation of elastic modulus. A dependence of the Young's modulus on the film thickness is given in Fig. 2 for two power densities. The Young's modulus decreases slightly with the film thickness for both sets of samples that were prepared at different powers. It is known that the kinetics of film growth changes during thin film deposition [13]. At the beginning of the deposition process film growth is very fast and decelerates with increasing film thickness as a result of competition between the plasma polymerization and ablation processes [14]. A modulus descent with the film thickness could be a consequence of lower material compaction at the upper part of the film.

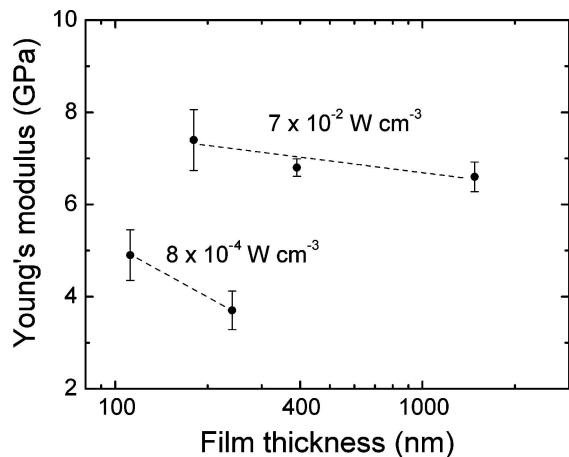


Figure 2 Thickness dependence of the Young's modulus for two sets of PP-VTES films deposited at different power densities.

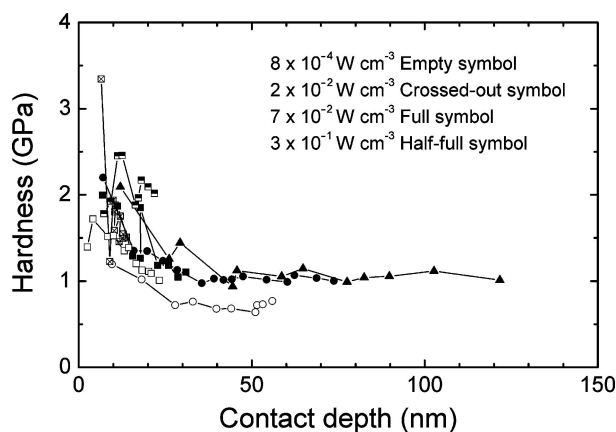


Figure 3 Depth profile of the hardness for PP-VTES films deposited at different power densities.

Fig. 3 shows a development of the hardness along the contact depth [8], which is the distance (from the film surface) along which contact between the indenter and the film is made. In simple terms, the depth profile of the hardness is shown in Fig. 3. One can see that the hardness ( $H_{\max}$ ) decreases from the film surface, within the range up to 20–30 nm, to the bulk value ( $H_{\text{bulk}}$ ) for most of the samples. This phenomenon could be a consequence of post-deposition oxidation at the film surface. The surface layer of films stored in the open air can react with atmospheric humidity resulting in oxygen incorporation into the polymer network. The oxygen is able to diffuse into the film material, increasing the cross-linking of plasma polymer [15]. There is no enhancement of the Young's modulus at the surface layer.

The proportionality between the hardness and the Young's modulus of thin films prepared by plasma techniques was referred to a-Si:H [5] and a-C:H films [5, 7]. The hardness was remarkably proportional to the Young's modulus for all films of a particular material group even though the deposition conditions were different. Fig. 4 presents the hardness versus Young's modulus of PP-VTES films with respect to the bulk and maximum hardness. The ratios of  $H/E$  for the bulk and maximum data are 0.185 and 0.302, respectively. To compare data, the  $H/E$  ratios were added to Table I for each group of amorphous material. For crystalline

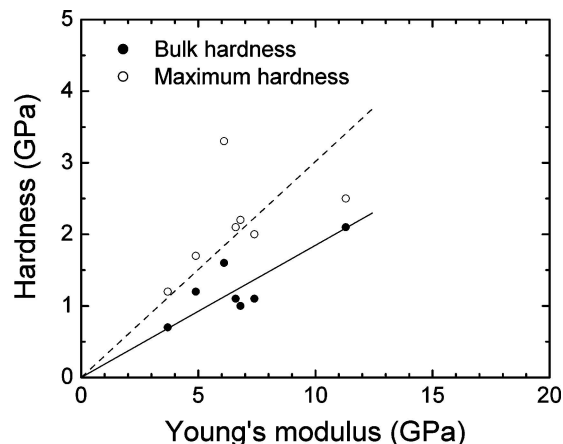


Figure 4 Hardness versus Young's modulus for pp-VTES films with respect to the bulk and maximum values of the hardness.

materials  $H/E$  depends strongly on the microstructure, but in amorphous materials the reason for the proportionality between  $H$  and  $E$  is not quite clear. According to Ref. [7], the proportionality between  $H$  and  $E$  in each group of amorphous materials can be related to the mean compressive elastic strain  $\varepsilon_y = H/2E$  around the indenter. Thus, the high values for PP-VTES films signify higher mean compressive elastic strain with respect to other amorphous materials. This interpretation corresponds with the elastic behavior of our material under a loading–unloading cycle.

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