

Physicochemical properties of plasma-polymerized tetravinylsilane films controlled by the effective power

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Abstract: Plasma polymer films of tetravinylsilane were deposited on silicon wafers using an RF glow discharge operated at pulsed regime, where the effective power was ranging from 0.1 to 150 W. Spectroscopic and microscopic techniques revealed that physicochemical properties of plasma polymer are controlled by the effective power if the flow rate of monomer was constant. An organic/inorganic character (C/Si ratio), hydrogen concentration, and a content of vinyl groups in plasma polymer are governed by deposition conditions. We demonstrate changes of chemical and physical properties as a result of increased cross-linking of plasma polymer at higher powers; the Young's modulus increased from 13 to 122 GPa, hardness 1.9-15 GPa, refractive index (633 nm) 1.7-2.2, but the energy gap decreased from 2.5 to 1.0 eV with enhanced power.

Keywords: Thin films, plasma polymerization, pulsed plasma, tetravinylsilane

1. Introduction

Plasma-polymerized organosilicones constitute a class of materials with a rich and varied scientific background [1,2]. This class of materials possesses a special characteristic, which distinguishes it from other plasma polymers - the ability to vary and control the degree of its organic/inorganic character (i.e., the carbon content) and the polymer cross-linking by the appropriate choice of fabrication variables [3]. This allows one to control many physicochemical properties over wide ranges resulting in an extraordinary potential for useful applications, which are only now beginning to be tapped. Such films can find many applications as low-*k* dielectrics [4], gas barrier coatings [5], corrosion protection [6], or functional interlayers in polymer composites [7]. The current work is aimed at physicochemical properties of plasma-polymerized tetravinylsilane films that can be controlled by the effective power very effectively.

2. Experimental details

Tetravinylsilane, Si-(CH=CH₂)₄ (TVS, purity 97%, Sigma Aldrich), was used as the monomer for the thin film deposition on infrared-transparent silicon wafers ((100), 0.8×10×10 mm³, ON Semiconductor). Argon gas (99.999%) was employed for the cleaning procedure before plasma polymerization, Ar-plasma pretreatment of silicon wafers, and post-deposition treatment of samples.

The plasma-polymerized tetravinylsilane (pp-TVS) films were deposited on polished silicon wafers by plasma-enhanced chemical vapor deposition (PECVD) employing

an RF (13.56 MHz) capacitive coupling system with plan-parallel electrodes [8] operated at pulsed plasma. The effective power (W_{eff}) of the pulsed plasma can be controlled by changing the ratio of the time when the plasma was switched on (t_{on}) to the time when it was switched off (t_{off}), $W_{\text{eff}} = t_{\text{on}} / T \times W_{\text{total}}$, where the period was defined as $T = t_{\text{on}} + t_{\text{off}}$ and W_{total} is the total power.

The vacuum system was evacuated to a basic pressure of 1×10^{-5} Pa. The substrates were pretreated with argon plasma (10 sccm, 5.0 Pa, 5 W, continuous wave) for 10 min to improve film adhesion. The plasma polymer films were deposited at a flow rate of 3.8 sccm and a corresponding pressure of 2.7 Pa using TVS plasma under selected effective powers (0.10, 1.0, 10, 25, 50, 100, and 150 W). The t_{on} was set at 1 ms in all cases but t_{off} was varied in the range 1-99 ms to reach the required effective power for the total power set at 10, 50, 100, 200, 300, and 500 W as given in Table 1. Uniform plasma polymer films were deposited at a film thickness of about 1 μm determined by ellipsometry.

Mass spectroscopy (Process Gas Analyser, HPR-30, Hiden) was used to analyze neutral plasma products that were pumped from the plasma reactor. A batch of six samples was deposited simultaneously using a special bottom electrode enabling loading of up to six substrates under vacuum. When the deposition process was completed, the whole apparatus was flushed with argon gas (10 sccm, 5.0 Pa); after 60 min the chamber was evacuated to a basic pressure of 1×10^{-5} Pa, and after a further 12 h the prepared specimens were characterized by ellipsometry



and then removed to the load-lock chamber, which was flooded with air to atmospheric pressure. The specimens were conveyed from the chamber into a desiccator to avoid contamination before subsequent measurements. Six identical specimens were prepared in one deposition cycle.

$t_{\text{on}} : t_{\text{off}}$	W_{Total}	W_{eff}
[ms] [ms]	[W]	[W]
1 : 99	10	0,1
1 : 9		1
1 : 49	50	1
1 : 1		25
1 : 9	100	10
1 : 3		25
1 : 1		50
1 : 19	200	10
1 : 7		25
1 : 3		50
1 : 1		100
1 : 11	300	25
1 : 1		150
1 : 49	500	10
1 : 19		25
1 : 9		50
1 : 4		100
1 : 1		250

Table 1. Selected deposition conditions using pulsed plasma.

The bulk elemental composition (Si, C, O, and H) of the thin films was studied by conventional and resonant Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection Analysis (ERDA) methods using a Van de Graaf generator with a linear electrostatic accelerator.

Infrared measurements in the wavenumber range of 500 to 4000 cm^{-1} were made using a VERTEX 80 vacuum Fourier transform infrared (FTIR) spectrometer (Bruker Optics). Transmission spectra were obtained on films deposited on infrared-transparent silicon wafers. An absorption subtraction technique was used to remove the spectral features of silicon wafer, and background correction was carried out before each measurement. The spectral resolution was 4 cm^{-1} . Approximately 256 scans were recorded to achieve a reasonable signal-to-noise ratio.

An in situ phase-modulated spectroscopic ellipsometer UVISEL (Jobin-Yvon) was employed to determine the film thickness and optical properties of the pp-TVS films. The measurement range was 250 – 830 nm with a step of 2 nm; the angle of incidence was 70° and the spot size (100×300) μm^2 ; the integration time was set at 200 ms. The dispersion dependence of the dielectric function was fitted using the five-parametric Tauc-Lorentz formula,

which has been derived for the parameterization of the optoelectronic response of amorphous dielectrics [9].

The near-surface mechanical properties of the pp-TVS films were investigated using a 2D TriboScope (Hysitron) attached to an NTegra Prima Scanning Probe Microscope (NT-MDT) enabling in situ topography analysis. A Berkovich tip with a radius of curvature of about 50 nm was used. The Young's modulus and hardness of film were determined from unload-displacement curves measured under cyclic nanoindentation [10,11] using the Oliver-Pharr method [12].

3. Results and discussion

Mass spectroscopy enabled us to monitor plasma species during deposition process. We found out that the mass spectra corresponding to the same effective power are similar each other. Typical spectra recorded at effective powers ranging from 0.1 W to 150 W are shown in semilogarithmic graph (Fig. 1). The mass spectra obtained at higher powers showed reduction mainly in heavier but also in medium species. A production of hydrogen that is eliminated from monomer fragments increased with enhanced power. The ion composition was assigned as proposed in Table 2. An increasing number (1-4) of vinyl groups bonded to the silicon atom were eliminated from TVS molecules at enhanced effective powers.

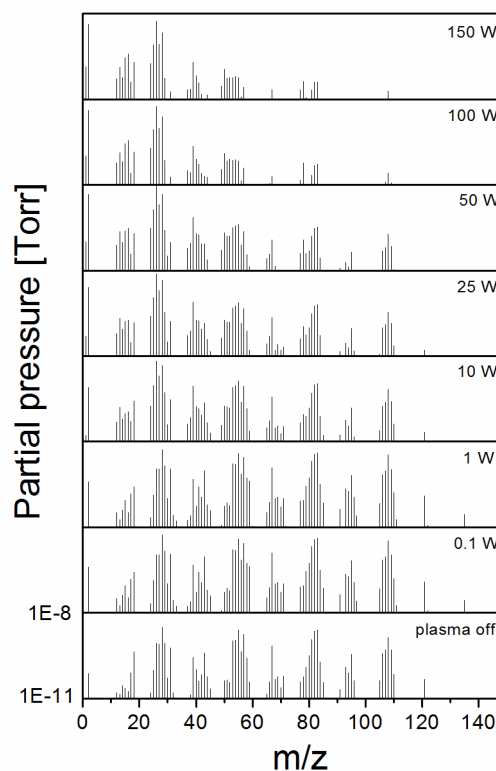


Fig. 1. Typical mass spectra corresponding to the effective power.



The mean deposition rate was calculated from the film thickness determined by ellipsometry and deposition time. The deposition rate depends on the effective power for different total powers as given in Fig. 2. The magnitude was only 3 nm min⁻¹ at 0.1 W but steeply increased to the maximum 233 nm min⁻¹ at 25 W and then decreased with enhanced power as it is typical for the monomer deficient region [13].

m/z	Ion composition
2	H ₂ ⁺
15	CH ₃ ⁺
24	C≡C ⁺
25	HC≡C ⁺
26	HC=CH ⁺
27	H ₂ C=CH ⁺
28	H ₂ C ⁺ -CH ₂
29	H ₃ C-CH ₂ ⁺
31	SiH ₃ ⁺
39	H ₂ C=C=CH ⁺
43	H ₃ C-CH ₂ -CH ₂ ⁺
55	C ₂ H ₃ Si ⁺
57	C ₂ H ₅ Si ⁺
67	C ₃ H ₃ Si ⁺
83	C ₄ H ₇ Si ⁺
95	C ₅ H ₇ Si ⁺
109	C ₆ H ₉ Si ⁺

Table 2. Ion composition assigned to mass spectra.

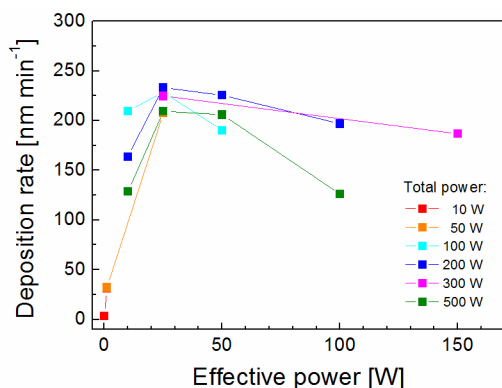


Fig. 2. Deposition rate as a function of the effective power for different total powers.

The deposited films were analyzed by various spectroscopic techniques (RBS, ERDA, and FTIR) in order to compare their elemental composition and chemical structure. The silicon concentration was about 10 at.% independent of effective power. However, the carbon

concentration increased at the expense of hydrogen atoms with enhanced power. At a low power of 0.1 W, the carbon concentration was 39 at.% and only slightly increased to 46 at.% at 25 W, but then increased up to 62 at.% at 150 W. The hydrogen concentration decreased from 52 at.% to 27 at.% with enhanced power. Infrared spectroscopy revealed that the concentration of CH_x and SiH groups decreased with enhanced power as a result of eliminated hydrogen atoms confirmed by mass spectrometry and RBS/ERDA measurements. Important information is that the concentration of vinyl groups decreased with enhanced power, and this trend corresponds to a reduction in vinyl groups monitored by mass spectrometry.

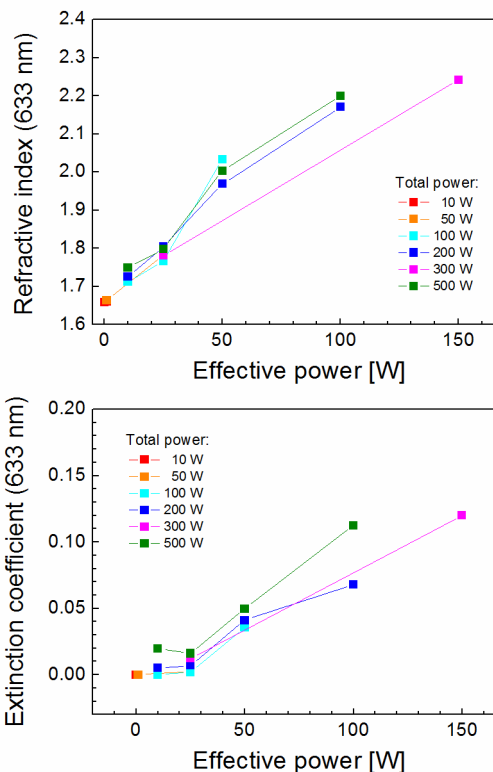


Fig. 3. Refractive index and extinction coefficient at 633 nm for pp-TVS films deposited at different effective powers.

Optical characterization of the films requires not only an appropriate parameterization of the material optical constants but also a realistic model of the sample structure. Our model consisted of a semi-infinite substrate (crystalline silicon together with a silicon dioxide layer), a plasma polymer layer, and a surface overlayer corresponding to the surface roughness of the film. The overlayer was modeled as the effective medium [14] with a fixed ratio (50%) of the plasma polymer and air. The refractive index and the extinction coefficient at a wavelength of 633 nm for all the samples are shown in Fig.

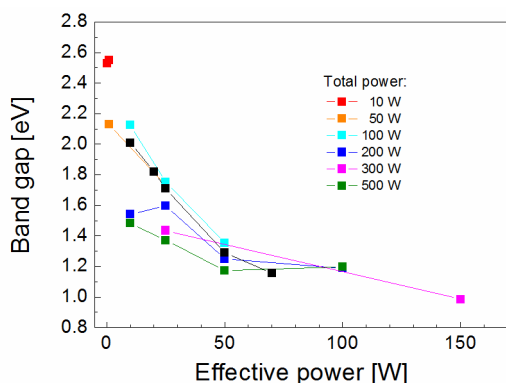


Fig. 4. Band gap for pp-TVS films as a function of effective power.

3. The refractive index (extinction coefficient) significantly increased from 1.66 (0.000) corresponding to a power of 0.1 W to 2.24 (0.120) corresponding to a power of 150 W. The band gap can be controlled by effective power in range 2.53 eV (0.1 W) - 0.99 eV (150 W) (Fig. 4).

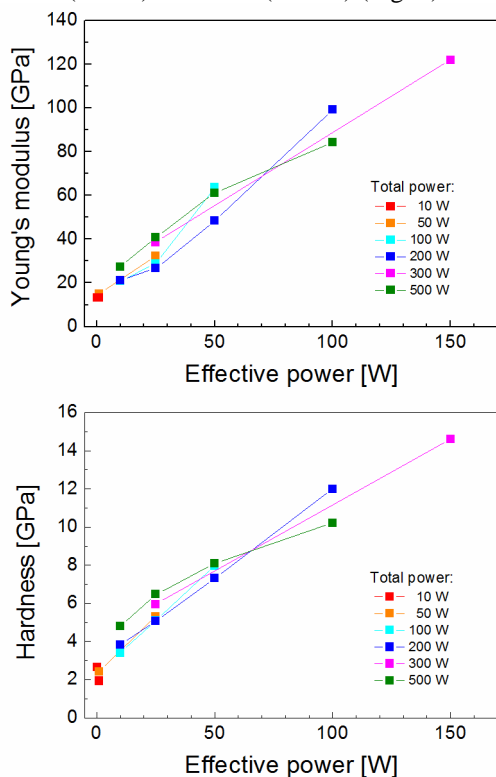


Fig. 5. Young's modulus and hardness for pp-TVS films deposited at different effective powers.

Nanoindentation measurements were used to investigate selected mechanical properties (Young's modulus and hardness) of pp-TVS films. The Young's modulus and hardness of plasma polymer could be varied from 13.3 GPa (0.1 W) to 122 GPa (150 W) and from 1.93

to 14.6 GPa, respectively, as was determined from nanoindentation measurements (Fig. 5). Both the mechanical parameters increased with enhanced power due to a higher crosslinking of the plasma polymer network. If the plasma energy (power) increases, monomer molecules are more activated and fragmented, forming a higher density of free radicals; the reactive species result in a highly crosslinked polymer.

4. Conclusion

An increased effective power (0.1–150 W) influenced the elemental composition and chemical structure of pp-TVS films, where C/Si ratio rose (4.3–5.9), and a content of hydrogen atoms and vinyl groups decreased. A higher cross-linking of plasma-polymer network with enhanced power influenced optical and mechanical properties of pp-TVS films. We conclude that the chemical and physical properties of plasma polymer films can be controlled by the effective power without regard to the total power used. An 8-fold increase of the Young's modulus and hardness, an increase of the refractive index (633 nm) by 35% and the extinction coefficient (633 nm) from zero to 0.12, and a decrease of band gap by 61% with enhanced power was found out in our study. The plasma polymer of wide-range properties has a high application potential for electronic, optical, and mechanical devices.

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