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Thin Solid Films 502 (2006) 40 – 43
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# A comparison of polyatomic ion deposited, RF magnetron sputtered and plasma polymer organosilicon films

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Available online 15 August 2005

**Abstract**

In this work organosilicon films are prepared by plasma polymerization and mass-selected polyatomic ion deposition (MS-PID) of divinyltetramethyldisilazane, and by rf magnetron sputtering of polydimethylsiloxane. The composition of coatings is determined by XPS and FTIR. A chemical derivatization method is applied to detect amines in silazane films. Plasma polymers and ion deposited films are found to be more organic; whereas magnetron sputtered coatings are dominated by $SiO_x$ species. Plasma polymers are deficient of nitrogen with silicon bound in various $Si_xC_yO_z$ species. Silicon in PID-films is bound mainly to nitrogen ($Si_xN$). The processes of aging in air or in water are also discussed.


*Keywords:* Plasma processing and plasma deposition; Ion bombardment; Organosilicon polymer

## 1. Introduction

Silicon containing plasma polymers have been extensively studied as possible candidates for various application fields. Siloxanes, silazanes, silanes or their mixtures with $O_2$, $N_2$, $N_2O$, $NH_3$ have been used as precursors.

Microelectronics require the films with good dielectric properties. Since polysiloxanes deposited by plasma polymerization possess excellent electrical and thermal properties, they are industrially used in electronic encapsulation applications or as passivation or insulation layers of integrated circuits and electronic devices [1].

Deposition of silicon containing thin films by plasma polymerization of organosilicon precursors is being increasingly used for the fabrication of transparent optical coatings. For example, $SiO_x$ coatings are known for their very low refractive index ($n$) and extinction coefficient ($k$). The addition of nitrogen in amount of several percent slightly increases $n$ and $k$. On the other hand, the increase of hydrogen or in particular NH groups content results in a considerable decrease of refractive index. Thus, depending on the plasma conditions and type of monomer the optical properties can be varied to produce the films with desired intermediate $n$ value or graded index optical films, in which the refractive index continuously varies as a function of depth [2,3].

As a result of their high chemical stability and low gas and water permeability, $SiO_x$ films are proposed as corrosion inhibitors [4,5]. SiCHN coatings have also a potential for use in high-power, high-frequency, and radiation-resistant applications [6].

## 2. Experimental

1,3-divinyltetramethyldisilazane, $CH_2{=}CH{-}Si(CH_3)_2{-}NH{-}Si(CH_3)_2{-}CH{=}CH_2$ ($M$ = 185 g/mol), referred to below as silazane, was used as the monomer in the plasma polymerization and polyatomic ion deposition experiments. The plasma polymerization experiments were performed in a glass tubular reactor with external ring electrodes and

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doi:10.1016/j.tsf.2005.07.231

Table 1
The elemental content of organosilicon films determined by XPS

| Deposition method | Elemental composition, atomic percent | | | | Experimental parameters |
|---|---|---|---|---|---|
| | C | Si | N | O | |
| Plasma polymerization | 61 | 14 | – | 25 | Silazane, 20 Pa, 25 W, 0.6 sccm; measured in 2 months after deposition |
| PID | 72 | 17 | 8 | 7 | Silazane, as-deposited, 15 eV, fluences are 1.4 to 6.8 × $10^{16}$ ions/cm$^2$ |
| PID | 65 | 15 | 5 | 17 | Silazane, 7-day aged, 15 eV, fluences are 1.4 to 6.8 × $10^{16}$ ions/cm$^2$ |
| rf magnetron sputtering | 33 | 19 | – | 48 | PDMS, 100 W, 5 Pa, 10 sccm; measured in 7 months after deposition |

standard excitation frequency of 13.56 MHz. The reactor was pumped by rotary and diffusion pumps, protected by a liquid nitrogen trap, to a base pressure of $1\times10^{-3}$ Pa. The tank with liquid monomer was connected with the reactor via a needle valve, which controlled the flow rate of monomer vapors. All depositions were performed with a flow rate of 0.6 sccm and a pressure of 20 Pa. The power of 5 and 25 W was applied.

In the case of polyatomic ion deposition (PID), the most abundant silazane ion formed by electron impact with $m/z=170$ ($C_7Si_2NH_{16}^+$), corresponding to the molecular ion minus one methyl group or $[CH_2{=}{=}CH{-}Si(CH_3)_2{-}NH{-}Si(CH_3){-}CH{=}{=}CH_2]^+$was used. Films denoted as-deposited were analyzed by XPS immediately after deposition without exposure to air.

A parallel-plate electrode system with rf (13.56 MHz) planar magnetron was used for magnetron sputtering. The sputtering was performed in Ar at 5 Pa pressure and 10 sccm flow rate. The substrates were positioned 5 cm above the target and rf power ranged from 20 to 80 W. Polydimethylsiloxane $[-Si(CH_3)_2-O-]_n$ was used as the target.

The thickness of plasma polymerized and rf sputtered films was in a range of 100–300 nm, whereas only several nanometers films were deposited by polyatomic ion deposition.

Trifluoroacetic anhydride (TFAA) was used as derivatization agent to detect amines. TFAA is also sensitive to hydroxyl groups, a shortcoming which is discussed in the text where relevant.

## 3. Results and discussion

The elemental content of organosilicon films deposited by various methods is given in Table 1. All XPS peaks are referenced to aliphatic C 1s (C–C, C–H) at 284.5 eV, chosen to take into account a considerable amount (~15%) of silicon in the coatings, which shifts the carbon binding energy downwards slightly [7]. The peak positions vary with accuracy of 0.1 eV.

The films deposited by PID are very close in composition to the precursor ion, which contains 70% of carbon, 20% of silicon and 10% of nitrogen. Several percent of oxygen in as-deposited films arise from the substrate's $SiO_2$ layer, as the films were thin enough to allow observation of the substrate signal. Low energy ions form more organic polymer-like structures and higher energy ions deposit more inorganic SiCN coatings [8]. The PID-films are sensitive to aging in air, revealing a considerable increase of oxygen content within a 7-day period. The incorporation of oxygen proceeds via formation of surface hydroxyl groups, which is detected by the derivatization measurements [8].

Plasma polymers analyzed in 2 months after the deposition lack nitrogen and also exhibit an increased oxygen concentration. The deficiency of nitrogen in Si:C:N:O films due to high affinity of Si with O has been already reported [8,9]. No dependence of elemental composition of silazane plasma polymers on the discharge power is observed (Table 2). The plasma polymer samples were treated with TFAA immediately after the deposition without exposure to air, shipped to University of Illinois at Chicago and then analyzed by XPS. The fluorine concentration in amount of several percent proves the presence of secondary amines or hydroxyls in the as-deposited plasma polymers. However, their concentration is small. The lack of nitrogen in the aged samples can be explained either by the substitution with oxygen during plasma polymerization or by the hydrolysis reactions in air with elimination of volatile ammonia [8,10]. To solve this problem, the data on elemental content of as-deposited silazane plasma polymers are needed.

The elemental composition of PDMS is 57% of C, 29% of Si and 14% of O. The rf magnetron sputtered films have lower carbon and silicon, and considerably higher oxygen content (Table 1).

Table 2
The composition of silazane plasma polymers in dependence on discharge power

| Elemental composition, atomic percent | | | | | Experimental parameters |
|---|---|---|---|---|---|
| C | Si | N | O | F | |
| 61 | 15 | – | 24 | – | 5 W, 0.6 sccm, 2 months after deposition |
| 60 | 14 | – | 21 | 5 | As-deposited, after derivatization with TFAA |
| 61 | 14 | – | 25 | – | 25 W, 0.6 sccm, 2 months after deposition |
| 59 | 14 | – | 23 | 4 | As-deposited, after derivatization with TFAA |