Plasma Polymerization of Trimethylsilane in Cascade Arc Discharge

Y.-S. LIN, H. K. YASUDA

Department of Chemical Engineering, and Center for Surface Science and Plasma Technology, University of Missouri–Columbia, Missouri 65211

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ABSTRACT: Plasma polymerization of trimethylsilane (TMS) in cascade arc discharge was experimentally investigated. It was found that the deposition rates of methane and TMS plasma polymer were dependent on plasma parameters, and the surface characteristics of plasma polymer were also dependent on plasma variables. The following plasma variables were studied: arc current, argon flow rate, TMS flow rate, chamber pressure, substrate axial, and radial positions. Carbon, silicon, and oxygen were the main elements observed in TMS polymer films obtained by x-ray photoelectron spectroscopy (XPS). Powder-like TMS polymer films were observed by scanning electron microscopy (SEM). The size distribution of the powder-like particles was strongly dependent on deposition parameters. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1653–1665, 1997

Key words: plasma polymerization; cascade arc discharge, thin film deposition, vacuum deposition

INTRODUCTION

The cascade arc was first studied in 1956 by Maecker.[1] Until now, it has been applied almost exclusively for investigations of scientific interest. Kroesen[2] and Beulens et al.[3] achieved deposition rates in excess of 100 nm s^{-1} for hard carbon film on Si substrate. These deposition rates exceed by a factor of 30 of the highest values (for amorphous carbon coating) reported in the literature through 1988.[2] The cascade arc discharge produces much higher deposition rates, with the quality of deposited films at least as good as those obtained by conventional processes. The cascade arc as a plasma source for plasma polymerization was first investigated by Prof. D. C. Schram's group at Eindhoven University of Technology in the Netherlands,[2] followed by studies in Prof. H. K. Yasuda's research group, both at the University of Missouri–Rolla[4] and later at the University of Missouri–Columbia.[5]

The surface properties of plasma polymers are highly dependent on the chemical nature of the monomers and the conditions for plasma treatment and plasma polymerization.[6,7] As far as plasma polymerization and plasma treatment of materials are concerned, plasma can be divided into three major groups: (1) chemically nonreactive plasma, e.g. argon plasma; (2) chemically reactive plasma, e.g. O_2, N_2, and CF_4; and (3) polymer-forming plasma, e.g., CH_4 and TMS. In this study, the influence of operated parameters on the deposition rates of methane and TMS plasma polymers were investigated. Chemical composition and surface morphology of TMS polymer films were analyzed by x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

DESCRIPTION OF EXPERIMENTAL WORK

The Cascade Arc

The cascade arc consists of a cathode, a stack of electrically isolated copper plates, and an anode.

Correspondence to: H. K. Yasuda

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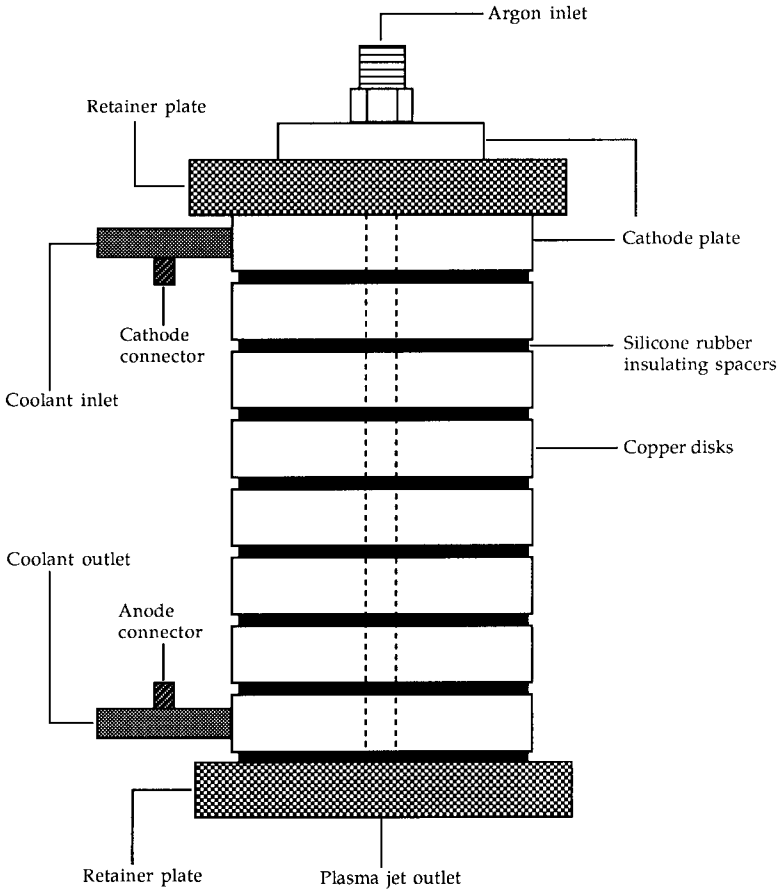

Figure 1 Assembled cascade arc.

Figure 1 shows the general schematic of the assembled cascade arc. The cathode was made of a tungsten tip. The copper disks were machined from a 99% copper–1% tellurium alloy. All copper disks were fabricated to allow for coolant flow through the interior. A 4% ethylene glycol aqueous solution was circulated through the components by way of $\frac{1}{4}$ in. (6.4 mm) o.d. copper tubes inserted through the outer wall of the disks. Coolant temperature was controlled around 55°F for all experiments. The anode was connected on the $\frac{1}{4}$ in. (6.4 mm) o.d. copper coolant outlet tube of the copper disk. The anode was connected to ground.

Deposition Rate Study

Axial Deposition Rate

The plasma chamber (see Fig. 2) consists of a 6 in. (152.4 mm) i.d Pyrex glass cross, a 6″ to 4″ i.d reducer, and a 4 in. (101.6 mm) i.d Y-section. The movable thickness monitor, a Leybold–Inficon XTC model, was mounted on the Y-section. The coaxial cable of thickness monitor connects the gold-coated sensor crystal for determining axial deposition rate. The sensor crystal was used as the substrate, centered perpendicular to the flowing plasma jet. Film thickness were recorded ev-

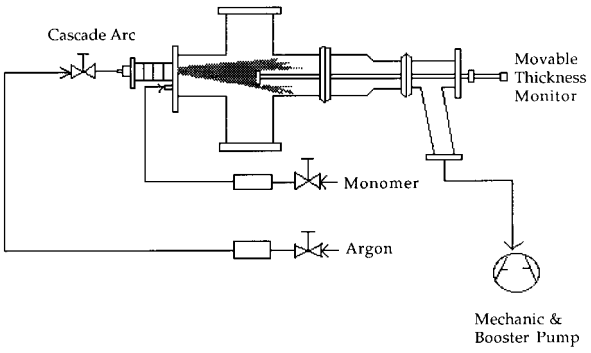

Figure 2 The cascade arc plasma chamber.

ery 15–30 s during the five minutes of deposition, then at one minute intervals until a constant (steady-state) deposition rate was obtained. The deposition rates were calculated as per unit area mass flow rate (Å $s^{-1}*g^{-1}$ cm^{-3}), where 1 Å $s^{-1}*g^{-1}$ cm^{-3} = 0.01 μg $s^{-1}*cm^{-2}$.

Radial Deposition Rate

To determine radial deposition rate profiles, aluminum foils (0.001 in. thickness) were used as the substrate to determine the per unit area mass deposition rate (mg s^{-1} cm^{-2}). Two aluminum plates (see Fig. 3) (3 in. diameter, 0.25 mm thickness) were used to support 13 0.7–0.85-mm-square aluminum foil chips: one was punched with 13 0.7-cm-diameter holes to allow plasma pass through and deposit on the aluminum foils; the other was employed as the support, mounted on the movable thickness monitor. The per unit area mass deposition rates were calculated by the weight gained on the area of a 0.7-cm-diameter circle over a given time interval. Figure 3 shows the radial positions of substrate, where X and Y are the horizontal and vertical radial positions of the aluminum chips. The X and Y are all from the center to 3 cm away from the center.

Samples for XPS and SEM Analysis

Silicon wafers ($N\langle 111\rangle$, polished) of 3 in. diameter were employed as the substrate for XPS and SEM analysis. They were adhered to the thickness monitor for plasma polymerization of TMS

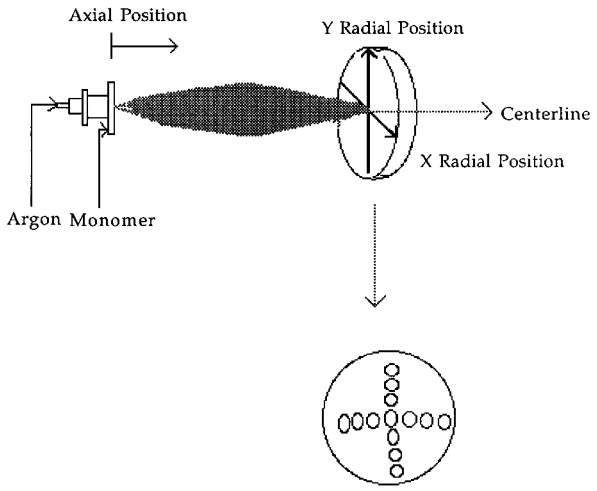

Figure 3 The axial and radial positions in cascade arc plasma chamber.

Table I Experimental Settings

Arc current	2–8 A
Ar flow rate	1000–2000 sccm
TMS flow rate	1.1–4.4 sccm (60–240 μg s)
Chamber pressure	550–8000 mtorr
Substrate axial position	2–17 inches
Radial position	0–3 cm

polymer. After 45 s treatment, concentric circles (interference fringes) appear on the silicon wafer surface. The 3 in. TMS deposited silicon wafers were cut for 0.7-cm-wide chips.

The samples for XPS were sent to Material Research Center, University of Missouri–Rolla, to evaluate the chemical compositions of TMS polymer films. The carbon, silicon, oxygen, and nitrogen spectra were fitted to curves using a computer program developed at the Materials Research Center, University of Missouri–Rolla. The areas under these curves were used to obtained estimates for atomic composition of the samples.

The samples for SEM were sent to Department of Geology, University of Missouri–Columbia, to evaluate the surface morphology of TMS polymer films. The magnifications of 5000–77,000 were sufficient to allow observation of powder-like particles in TMS polymer.

RESULTS AND DISCUSSION

The nature of the interaction of the plasma constituents with solid surfaces is determined by plasma reactor configuration and processing parameters.[6,8] In this study, the cascade arc discharge plasma parameters, such as arc current, argon flow rate, chamber pressure, TMS flow rate, substrate axial, and radial positions, were operated at the settings shown in Table I.

Deposition Rate Dependence on Operational Parameters

For the cascade arc discharge plasma process, argon was heated and ionized in the cascade arc, then expanded into the vacuum chamber as a plasma jet after emerging at the anode. Monomer was dissociated or ionized after reactions with excited or ionized argon in the expansion, creating reactive species. The reactive species were transported to the substrate where film deposition occurred.

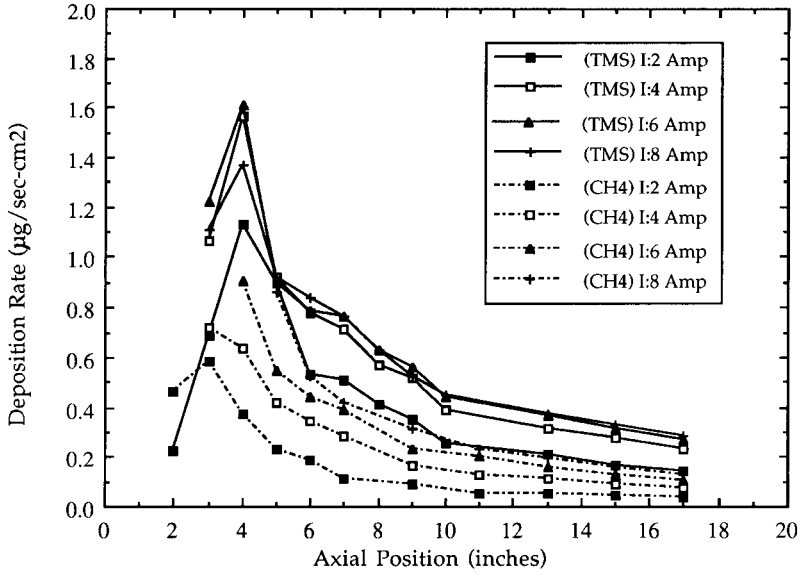

Figure 4 Axial position deposition rate profiles of TMS and methane plasma polymers were plotted as a function of arc currents under the conditions of 2000 sccm Ar flow rate, 550 mtorr chamber pressure, and TMS or methane flow rate of 120 $\mu g\ s^{-1}$.

As methane and TMS were introduced into argon plasma jet, the argon plasma was quenched. The axial deposition rate profiles of methane and TMS plasma polymer to substrate were determined for various plasma settings.

Figure 4 shows that the deposition rates of methane and TMS plasma polymers on sensor crystals increased with axial positions from 2 to 4 inches and decreased with axial positions increased from 3 or 4 to 17 inches for various arc currents. The axial deposition rates at axial positions less than 2 inches were not available since the sensor crystals were broken during deposition. The axial deposition rates of TMS plasma polymer were higher than methane plasma polymer in all current range. The higher electrical current had a higher axial deposition rate. At arc currents greater than 6 A, the deposition rate for TMS is only slightly dependent on arc current.

Figure 5 shows that higher argon flow rates give higher deposition rates for methane and TMS plasma polymer. The deposition rate was higher for TMS plasma polymer than for methane plasma polymer as argon flow rates were increased from 1000 to 2000 sccm. The deposition rates of methane and TMS plasma polymers increased, with axial positions decreased, except for the TMS plasma polymer which deposited to sensor crystal at argon flow rate 2000 sccm, which showed a decrease of deposition rates from 1.62 to 1.2 $\mu g\ s^{-1}\ cm^{-2}$ with a decrease of axial positions from 4 to 3 inches.

Figure 6 illustrates how deposition rates of methane and TMS plasma polymers to sensor crystal varies with chamber pressure. The deposition rates of TMS plasma polymer increased with chamber pressures increased from 1000 to 8000 mtorr. Deposition rate of TMS polymer to sensor crystal was obtained up to 2.1 $\mu g\ s^{-1}\ cm^{-2}$ at a chamber pressure of 4000 mtorr as the axial position was at 5 inches. The deposition rates of TMS plasma polymer varied only slightly with chamber pressures from 550 to 1000 mtorr. The deposition rates of methane plasma polymer to sensor crystal increased with chamber pressures increased from 550 to 2000 mtorr to 3000 to 4000 mtorr. The deposition rates of methane plasma polymer varied slightly with the chamber pressures increased from 550 to 2000 and 3000 to 4000 mtorr. The axial deposition rates of methane and TMS plasma polymers varied only slightly with axial positions from 7 to 9 inches.

Figure 7 shows that the deposition rates of TMS and methane plasma polymers to sensor crystal are highly increased with TMS flow rates increased, and the deposition rates of methane plasma polymer varied only slightly with the methane flow rates increased. The structure of TMS is $S_iH(CH_3)_3$; that is much more complex than methane of CH_4. The chemical bonds of

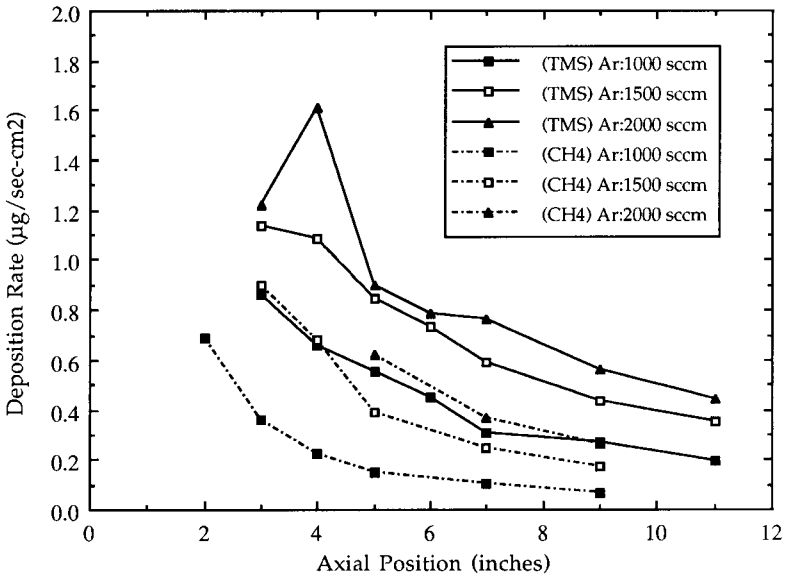

Figure 5 Axial position deposition rate profiles of TMS and methane plasma polymers were plotted as a function of Ar flow rates under the conditions of 6 A arc current, 550 mtorr chamber pressure, and TMS or methane flow rate of 120 μg s^{-1}.

Si—C, Si—H, and C—H involved the deposition of TMS plasma polymer to substrate. In a previous study, our group proved that the tightly cross-linked methane plasma polymer deposited to substrate was due to the addition of CH to substrate.[9] The much smaller atomic weight of carbon for 12 g mol than silicon of 28 g mol was believed to cause the smaller amount of mass deposition rates of methane plasma polymer than TMS plasma polymer to sensor crystal and to cause only a small variation of deposition rates of methane plasma polymer with methane flow rates.

Because plasma expansion occurred at the anode, the plasma expanded to the vacuum vessel.

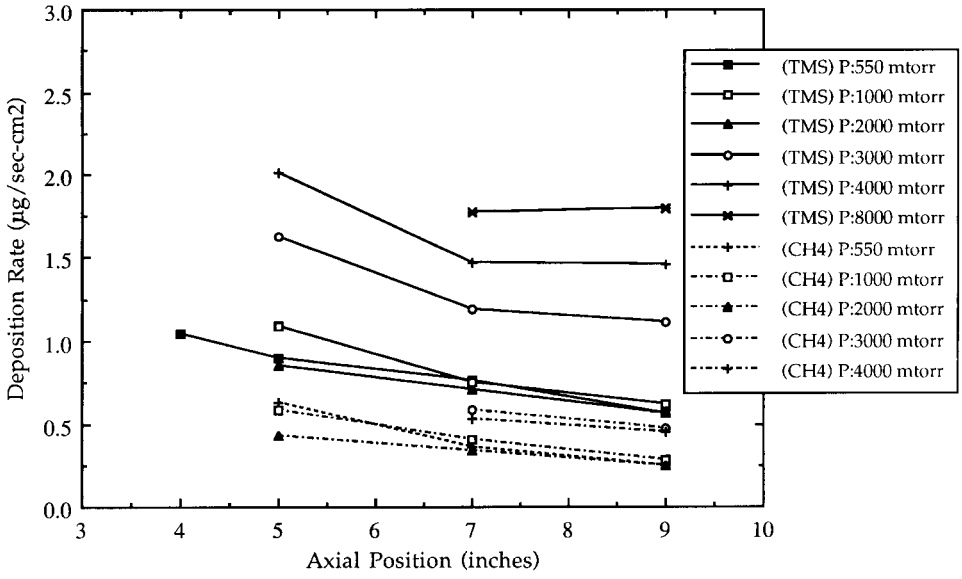

Figure 6 Axial position deposition rate profiles of TMS and methane plasma polymers were plotted as a function of chamber pressures under the conditions of 6 A arc current, 2000 sccm Ar flow rate, and TMS or methane flow rate of 120 μg s^{-1}.

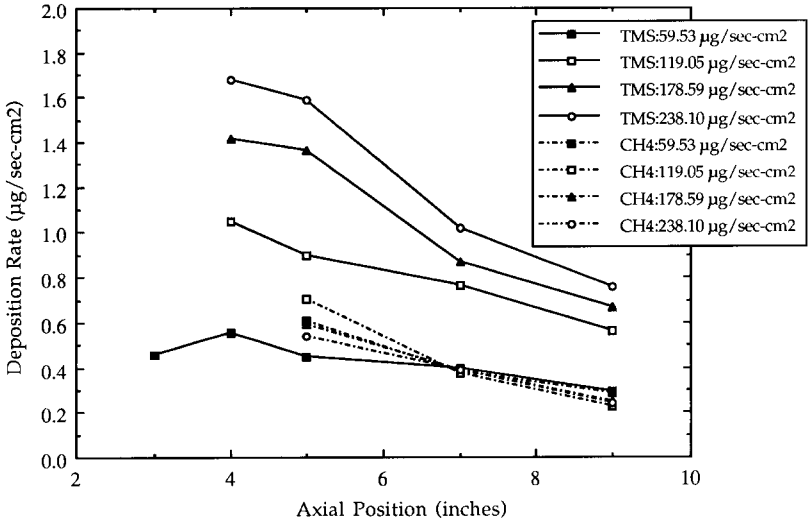

Figure 7 Axial position deposition rate profiles of TMS and methane plasma polymers were plotted as a function of TMS or methane flow rates under the conditions of 6 A arc current, 2000 sccm Ar flow rate, and 550 mtorr chamber pressure.

The decrease of deposition rates were anticipated with increasing axial position away from the nozzle and radial position away from the center, because the gas velocity and plasma density both decreased. Figures 8 and 9 show that the *X* and *Y* radial deposition rate distributions of TMS were plotted as a function of axial position. The maximum axial deposition rate was shown at 4 inches, and radial deposition rate distributions were spread out from the center. The wider radial deposition rate profiles were observed as the substrate moved downstream as the plasma expanded.

Surface Characteristics of TMS Plasma Polymer

Chemical Compositions of TMS Plasma Polymer

The XPS spectrum of TMS plasma polymer films indicated that the elements of carbon, silicon, and

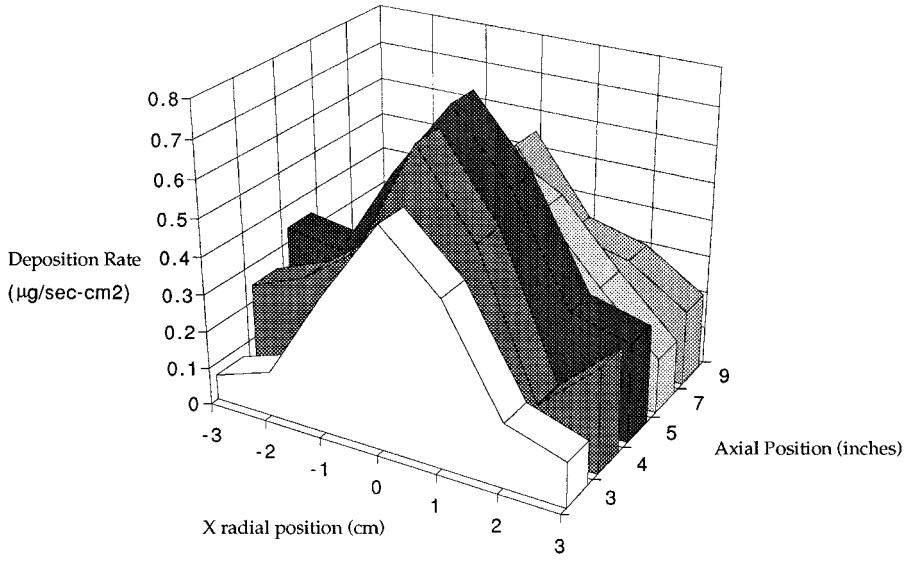

Figure 8 Deposition rates of TMS plasma polymer were plotted as a function of *X* radial and axial positions. Other plasma settings were as follows: arc current, 6 A; Ar, 2000 sccm; TMS, 2.2 sccm; and chamber pressure, 550 mtorr.

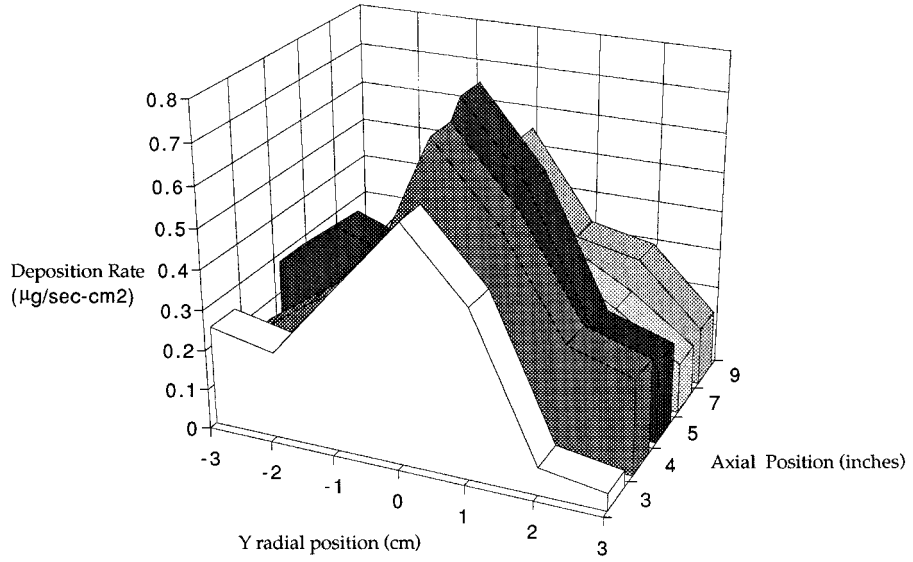

Figure 9 Deposition rates of TMS plasma polymer were plotted as a function of *Y* radial and axial positions. Other plasma settings were as follows: arc current, 6 A; Ar, 2000 sccm; TMS, 2.2 sccm; and chamber pressure, 550 mtorr.

oxygen were the main elements in TMS plasma polymer, as shown in Figure 10. As anticipated, carbon and silicon were observed in TMS plasma polymer. Oxygen was incorporated, mostly due to post-plasma reaction of trapped radicals in the deposit with atmospheric oxygen and humidity.

Figures 11 to 16 indicate that the atomic compositions of carbon, silicon, and oxygen are

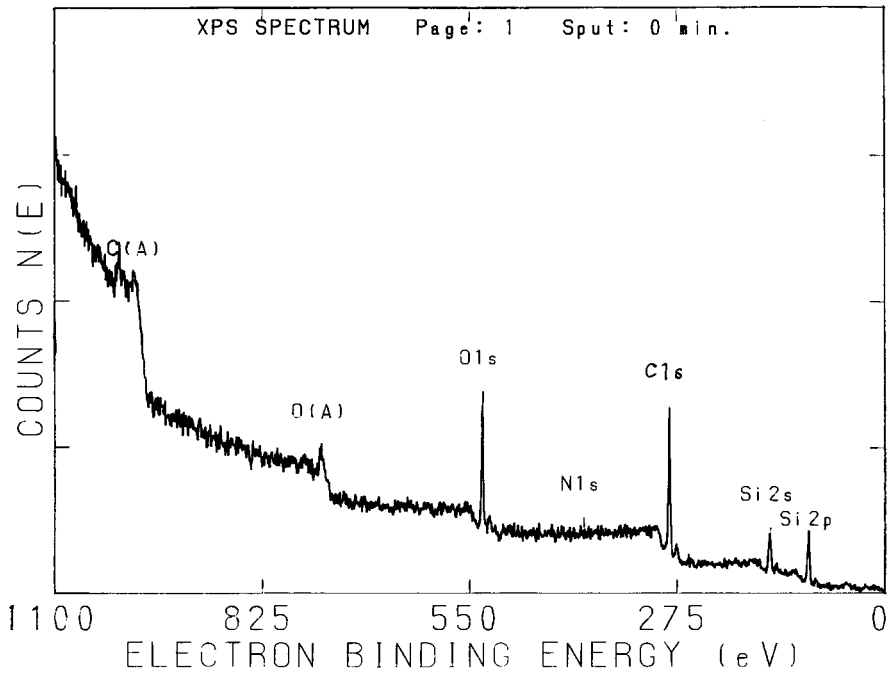

Figure 10 XPS spectrum of TMS polymer film for plasma settings at arc current, 6 A; Ar, 2000 sccm; chamber pressure, 550 mtorr; substrate axial position, 5 inches; radial position, 3 cm; and deposition time, 45 sec.

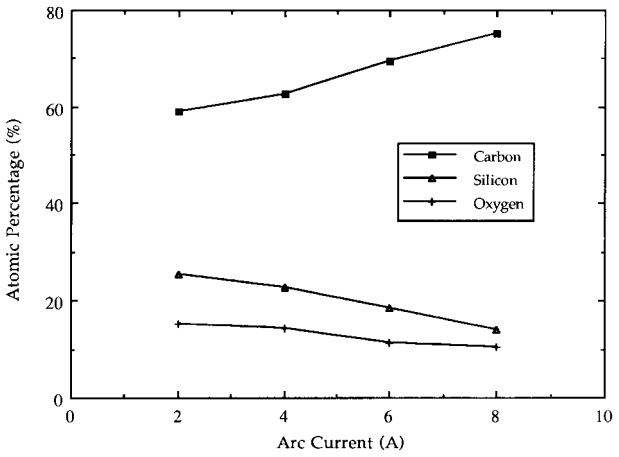

Figure 11 Atomic percentages of TMS thin film were plotted as a function of arc currents under the conditions of 2000 sccm Ar flow rate, 2.2 sccm TMS flow rate, 550 mtorr chamber pressure, 45 sec deposition time, and 9 inch axial position.

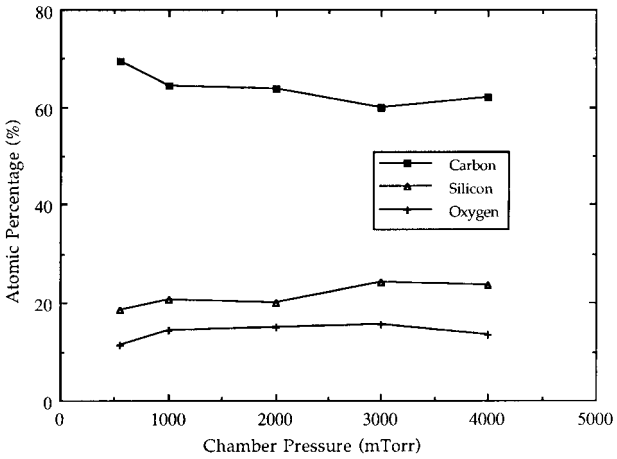

Figure 13 Atomic percentages of TMS thin film were plotted as a function of chamber pressures under the conditions of 6 A arc current, 2000 sccm Ar flow rate, 2.2 sccm TMS flow rate, 45 sec deposition time, and 9 inch axial position.

strongly dependent on arc current, argon flow rate, and TMS flow rate and are independent of chamber pressure, axial position, and radial positions.

Figure 11 shows that the atomic compositions of TMS polymer were increased (2.5% of carbon/A) and decreased (1.7% of silicon/A), with arc current from 2 to 8 A, and oxygen was 15% for all range arc currents. Figure 12 shows that the atomic compositions of TMS plasma polymer were increased as (1.8% of carbon/100 sccm Ar) and decreased as (0.5% of silicon/100 sccm Ar). According to Figure 14, carbon atomic compositions were decreased from 71 to 60%, and silicon atomic composition were increased from 17 to 25% when TMS flow rate was increased from 1.1 to 4.4 sccm, carbon was decreased (as 3.3% C/sccm TMS) and silicon was increased (as 2.4% Si/sccm TMS).

Surface Morphology of TMS Plasma Polymer

SEM examinations of TMS plasma polymer films revealed the appearance of spherical or spheroidal

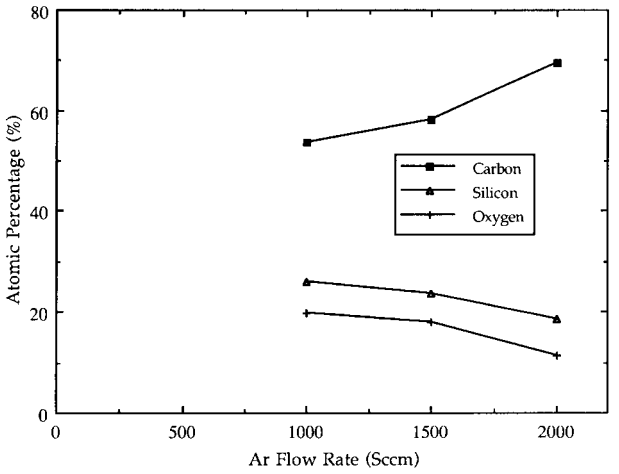

Figure 12 Atomic percentages of TMS thin film were plotted as a function of Ar flow rates under the conditions of 6 A arc current, 2.2 sccm TMS flow rate, 550 mtorr chamber pressure, 45 sec deposition time, and 9 inch axial position.

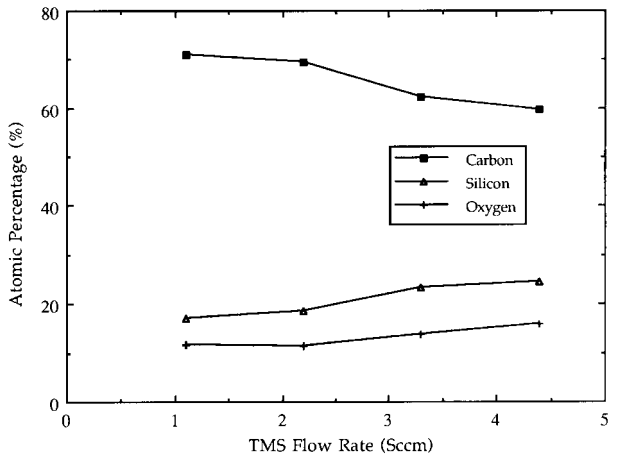

Figure 14 Atomic percentages of TMS thin film were plotted as a function of TMS flow rates under the conditions of 6 A arc current, 2000 sccm Ar flow rate, 550 mtorr chamber pressure, 45 sec deposition time, and 9 inch axial position.

particles embedded in a continuous matrix, as shown in Figure 17. The presence of particles usually had a marked effect on a film's quality. Powder formation should therefore be avoided by a suitable selection of the process variables. Effects of operational parameters on film morphology were investigated.

In Figure 18, the particle size distributions of TMS films are plotted for various arc currents at 5 in. axial position under the condition of 2000 sccm argon flow rate, 2.2 sccm TMS flow rate, 550 mtorr chamber pressure, and 45 s deposition time. The spheroidal particles were mostly in the particle size range of 201–400 and $<$ 200 nm. Among arc currents of 2, 4, 6, and 8 A, the rougher film was obtained at 4 A. Arc currents of 6 and 2 A also showed particles on the surface of TMS films. Arc current of 8 A showed the larger particles produced in TMS polymer films. Figure 19 shows that there were much fewer particles on the surface of TMS films as substrate was moved from 5 inches (see Fig. 18) to 9 inches. In Figure 19, the rougher film was observed at 6 A. An arc current of 8 A also showed the larger particles produced in TMS polymer films.

In Figure 20, the particle size distributions of TMS films were plotted for various axial positions under the conditions of arc current at 6 A, Ar flow rate of 2000 sccm, TMS of 2.2 sccm, chamber pressure of 550 mtorr, and a deposition time of 45 s. As the substrate was moved to 7 and 9 in. axial positions, the larger particles in the range

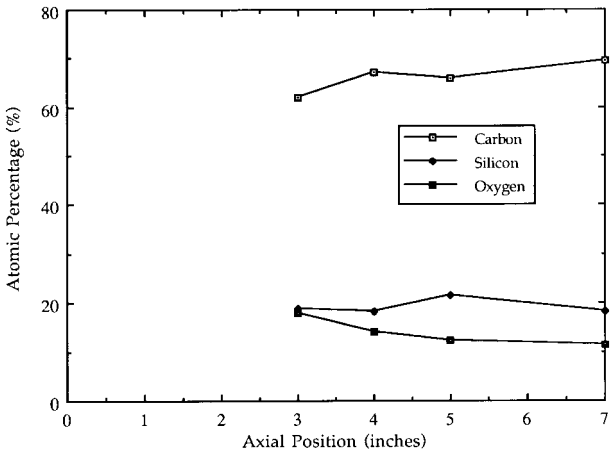

Figure 15 Atomic percentages of TMS thin film were plotted as a function of axial positions under the conditions of 6 A arc current, 2000 sccm Ar flow rate, 2.2 sccm TMS flow rate, 550 mtorr chamber pressure, and 45 sec deposition time.

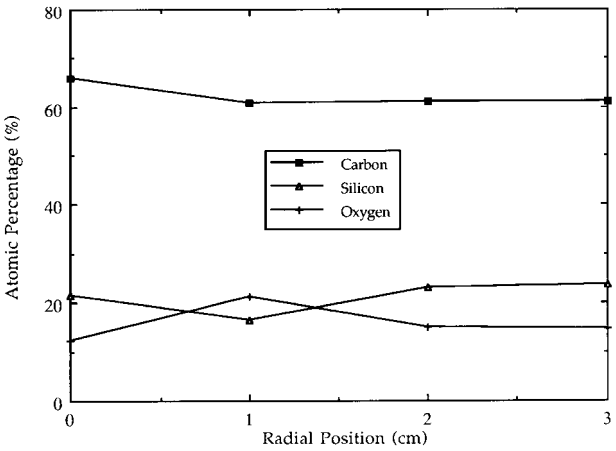

Figure 16 Atomic percentages of TMS thin film were plotted as a function of radial positions under the conditions of 6 A arc current, 2000 sccm Ar flow rate, 2.2 sccm TMS flow rate, 550 mtorr chamber pressure, 45 sec deposition time, and 5 inch axial position.

of 601–800 nm, 801–1 μm, and $>$1 μm became much less. The roughest film was shown as the substrate at 4 in. axial position.

Figure 21 shows the particle size distributions of TMS films for various axial position under the condition in Figure 20, except that Argon flow rate was decreased from 2000 to 1000 sccm. The roughest film may be shown as the substrate at the axial position between 4 and 5 inches.

In Figure 22, the particle size distributions of TMS films were plotted for various axial positions under the condition in Figure 20, except that the chamber pressure was increased from 550 to 3000 mtorr. The roughest film may be shown as the substrate at the axial position between 5 and 7 inches. As the chamber pressure was increased to more than 3000 mtorr, the larger particles at the range of 601–800 nm, 801–1 mm, and $>$1 μm can be formed at the 7 and 9 inch axial positions.

In Figure 23, the particle size distributions of TMS films were plotted for various axial positions under the condition in Figure 20, except that the TMS flow rate was increased from 2.2 to 3.3 sccm. The roughest film may be shown as the substrate at axial position between 4 and 5 inches. As the TMS flow rate was increased to more than 3.3 sccm, the larger particles can be formed at 7 and 9 inch axial position.

Figure 24 shows the particle size distributions of TMS films for various radial positions at a 5 inch axial position at a deposition time of 180 s. The rougher TMS films and larger particles of

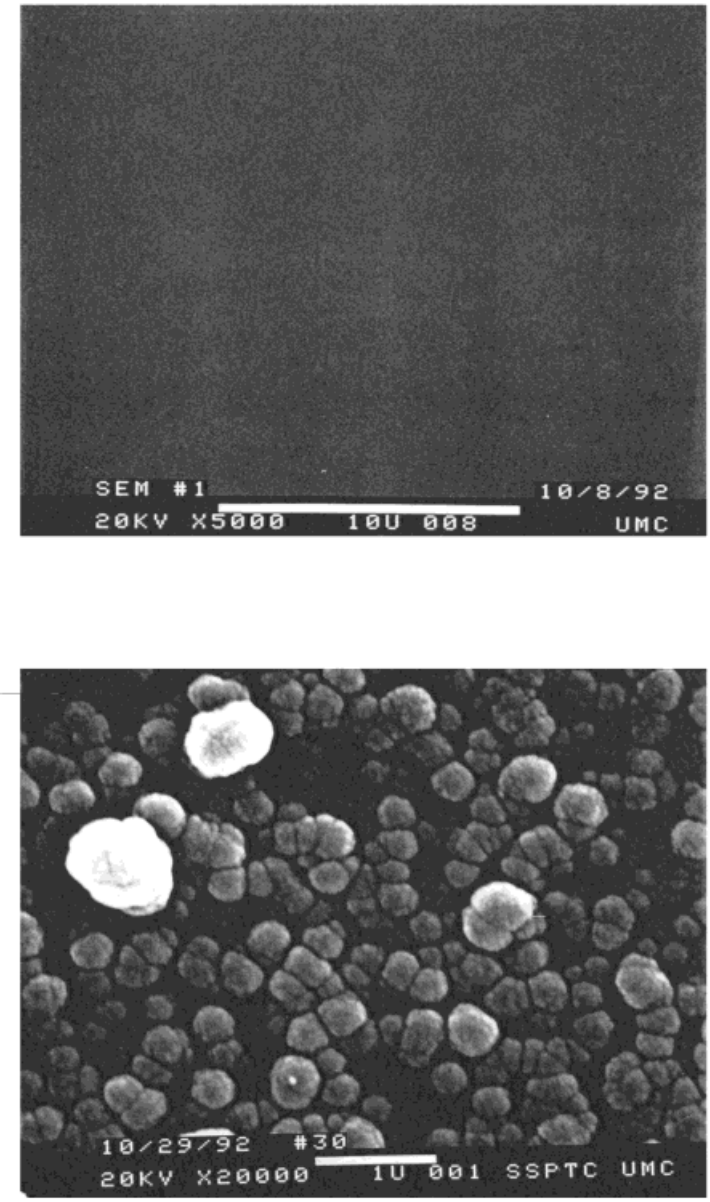

Figure 17 SEM pictures of (a) untreated and (b) TMS plasma-treated silicon wafer at plasma settings of arc current, 6 A; Ar, 1500 sccm; TMS, 2.2 sccm; chamber pressure, 550 mtorr; substrate axial position, 5 inches; radial position at the center, and deposition time, 45 sec.

601–800 nm and > 1 μm were formed at the substrate.

Because plasma expansion occurs in the anode nozzle and is expanded to vacuum vessel, the roughness of TMS films may vary with axial position and radial position under a certain condition. As the substrate is moved downstream, smaller and fewer spheroidal particles can be formed in TMS film. As the substrate is moved upstream, larger and more spheroidal particles can be formed in TMS film. The operational parameters may affect the roughness of TMS films. In Figure 20, the rougher film were shown as substrate at 3, 4, and 5 inches; this seems to match the higher axial deposition rate shown in Figure 4 as substrate at a 4 inch axial position. As the substrate was moved upstream, the deposition rate may be decreased because the gas velocity is too high to

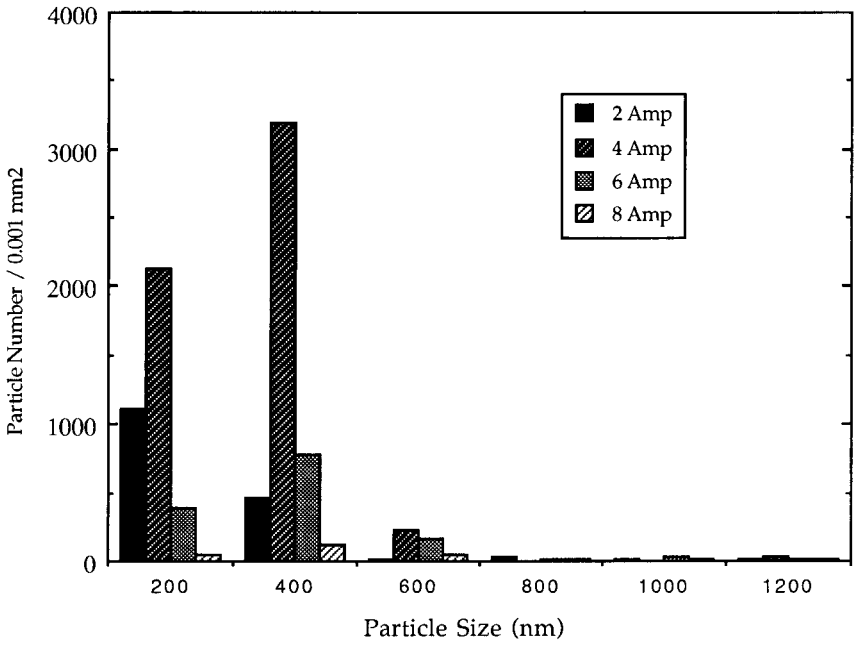

Figure 18 The particle size distributions of TMS films were plotted as a function of arc currents under the conditions of 2000 Ar flow rate, 550 mtorr chamber pressure, 2.2 sccm TMS flow rate, 45 sec deposition time, and 5 inch axial position.

accumulate efficiently on the substrate. Figure 21 shows that less particles formed on the substrate as the argon flow rate decreased from 2000 (Fig. 20) to 1000 sccm because the deposition rate decreased with a decrease in the argon flow rate. Figure 22 shows that fewer and larger particles

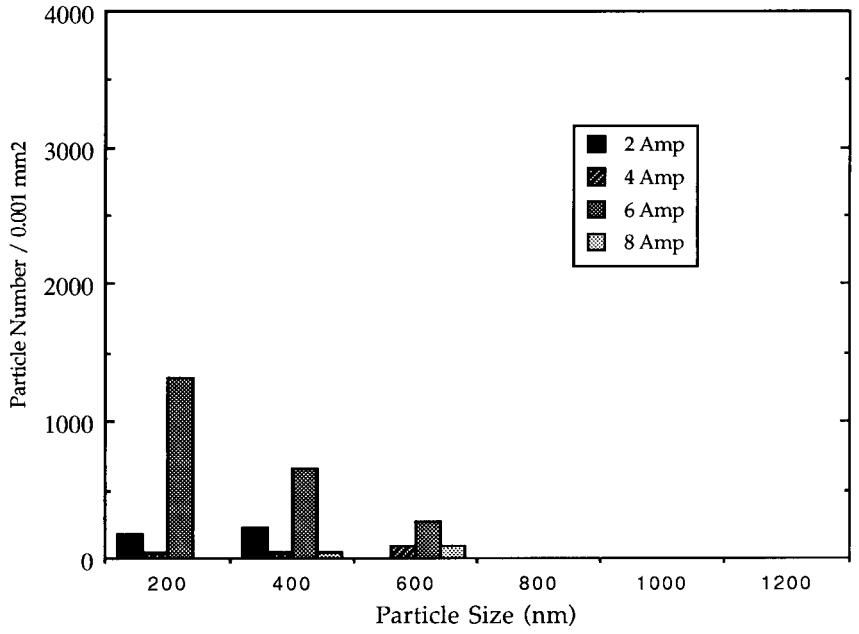

Figure 19 The particle size distributions of TMS films were plotted as a function of arc currents under the conditions of 2000 Ar flow rate, 550 mtorr chamber pressure, 2.2 sccm TMS flow rate, 45 sec deposition time, and 9 inch axial position.

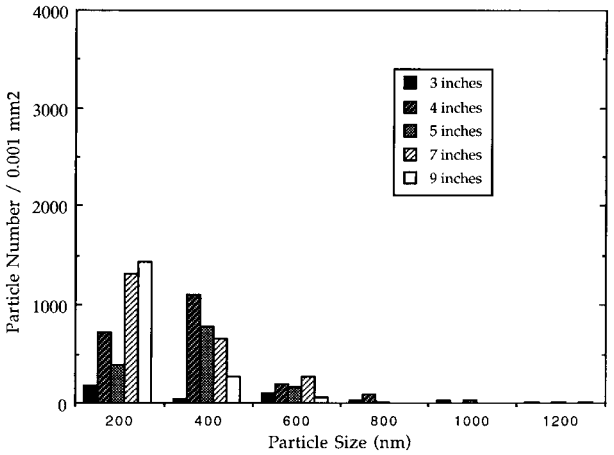

Figure 20 The particle size distributions of TMS films were plotted as a function of axial positions under the conditions of 6 A arc current, 2000 Ar flow rate, 550 mtorr chamber pressure, 2.2 sccm TMS flow rate, and 45 sec deposition time.

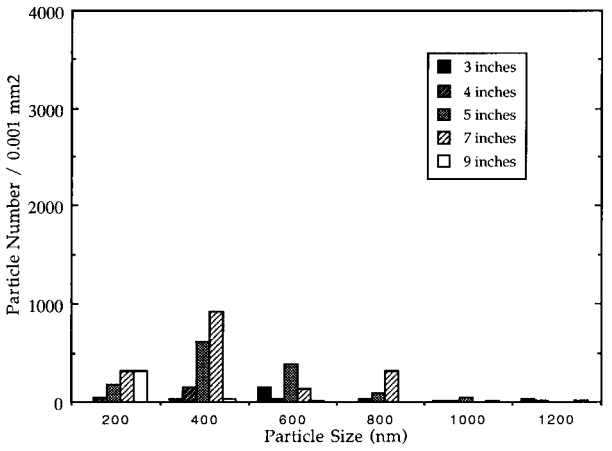

Figure 22 The particle size distributions of TMS films were plotted as a function of axial positions under the conditions of 6 A arc current, 2000 Ar flow rate, 3000 mtorr chamber pressure, 2.2 sccm TMS flow rate, and 45 sec deposition time.

formed in TMS films as the chamber pressure increased from 550 (Fig. 20) to 3000 mtorr. Figure 23 shows that more particles formed on the substrate as TMS flow rate increased from 2.2 (Fig. 20) to 3.3 sccm.

CONCLUSIONS

A deposition rate up to 2.1 μg sec^{-1} cm^{-2} is obtained for plasma polymerization of TMS in a cascade arc plasma jet, with powder particles observed in the deposited films. The deposition rates of TMS plasma polymer to sensor crystal and aluminum chips were all higher than methane plasma polymer deposited to these substrates. The number and size of powder particles vary with plasma parameters. XPS results show that carbon (50–70%) and silicon (18–35%) are the main elements in the film, with oxygen incorporated into the films subsequent to exposure to air. Atomic percentages of carbon and silicon vary

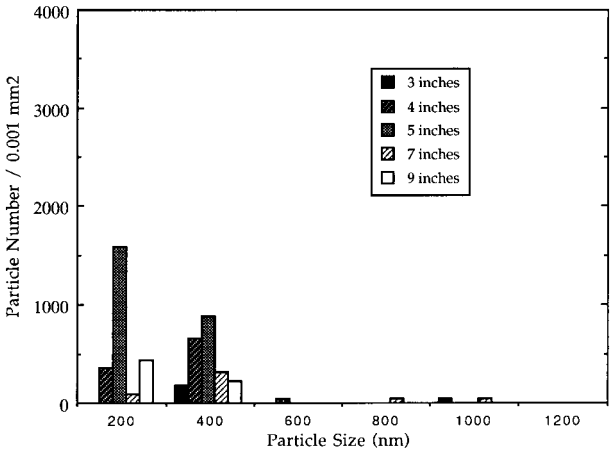

Figure 21 The particle size distributions of TMS films were plotted as a function of axial positions under the conditions of 6 A arc current, 1000 Ar flow rate, 550 mtorr chamber pressure, 2.2 sccm TMS flow rate, and 45 sec deposition time.

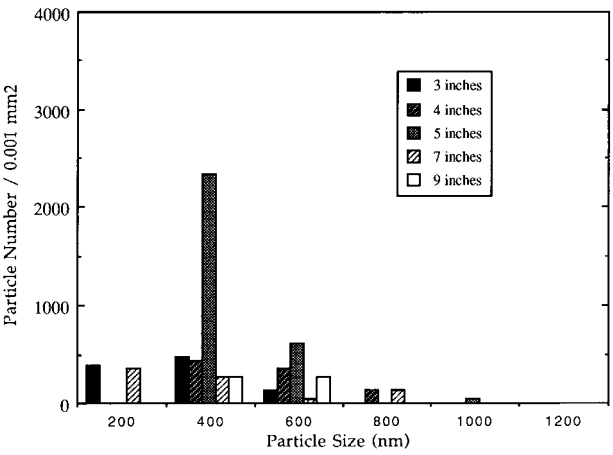

Figure 23 The particle size distributions of TMS films were plotted as a function of axial positions under the conditions of 6 A arc current, 2000 Ar flow rate, 550 mtorr chamber pressure, 3.3 sccm TMS flow rate, and 45 sec deposition time.

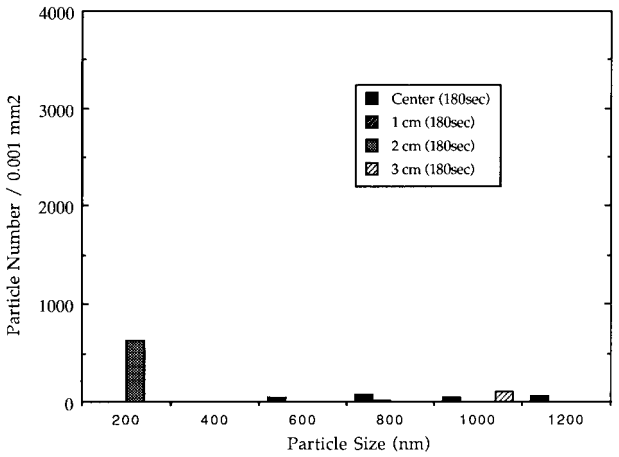

Figure 24 The particle size distributions of TMS films were plotted as a function of radial positions under the conditions of 6 A arc current, 2000 Ar flow rate, 550 mtorr chamber pressure, 2.2 sccm TMS flow rate, 45 sec deposition time, and 5 inch axial position.

with arc current, argon flow rate, and TMS flow rate and are independent of axial position, radial position, and chamber pressure.

Increasing arc currents in the range of 2–8 A results in a higher deposition rate, a higher carbon content, and a lower silicon content. Increasing argon flow rates in the range of 1000–2000 sccm results in higher deposition rates, higher carbon content, and lower silicon content for films deposited from TMS. Deposition rate and film particle content of TMS plasma polymer were dependent on chamber pressure. Increasing TMS flow rates in the range of 1.1–4.4 sccm results in higher deposition rates, lower carbon content, and higher silicon content.

A maximum is observed in the dependence of deposition rate and the degree of surface roughness on axial position for given set of experimental parameters.

Deposition rate decreases with an increase in the radial distance from the jet centerline. Numerous particles are observed at the center, but away from the center (at radial positions from 1–3 cm).

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