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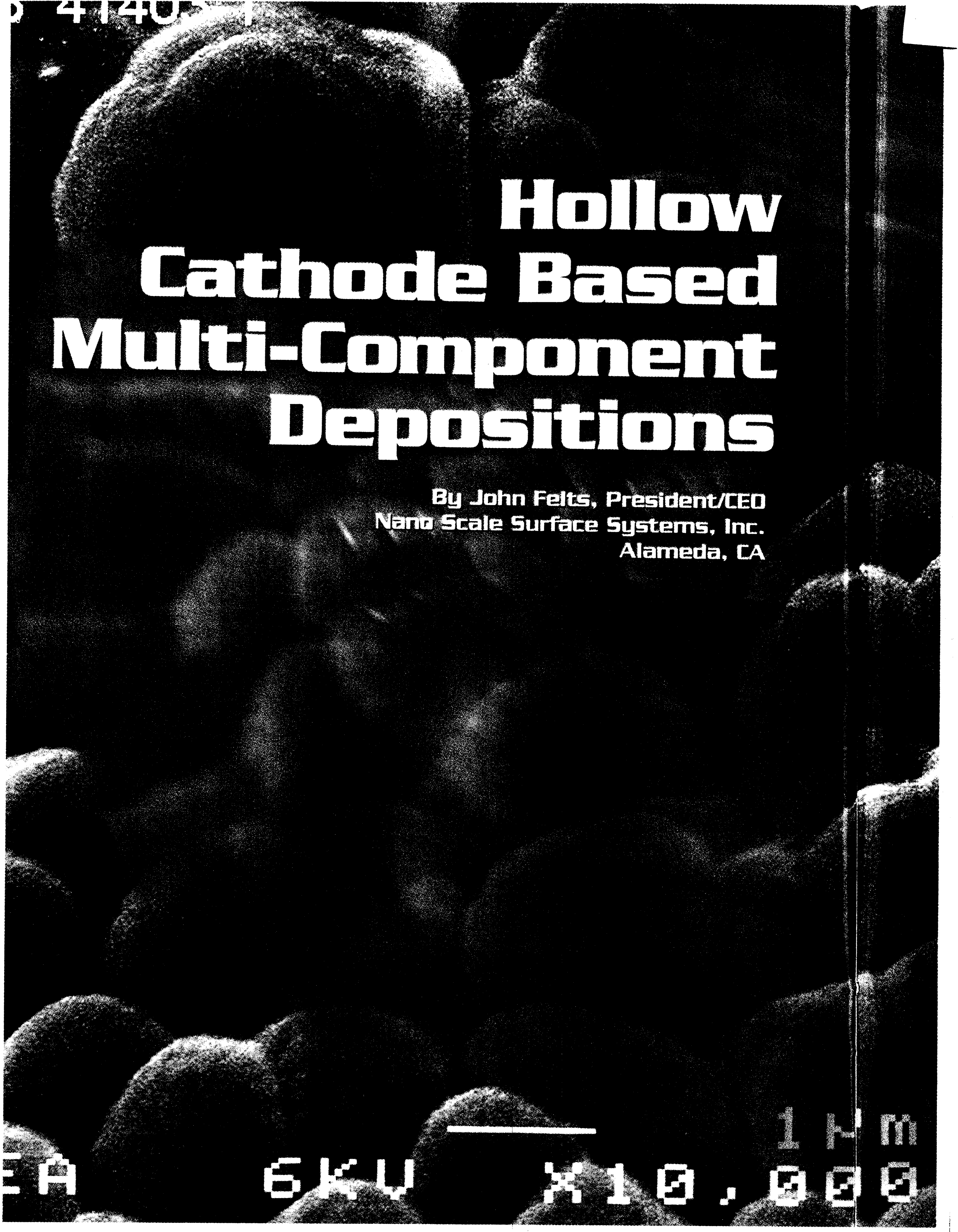

Hollow Cathode Based Multi-Component Depositions

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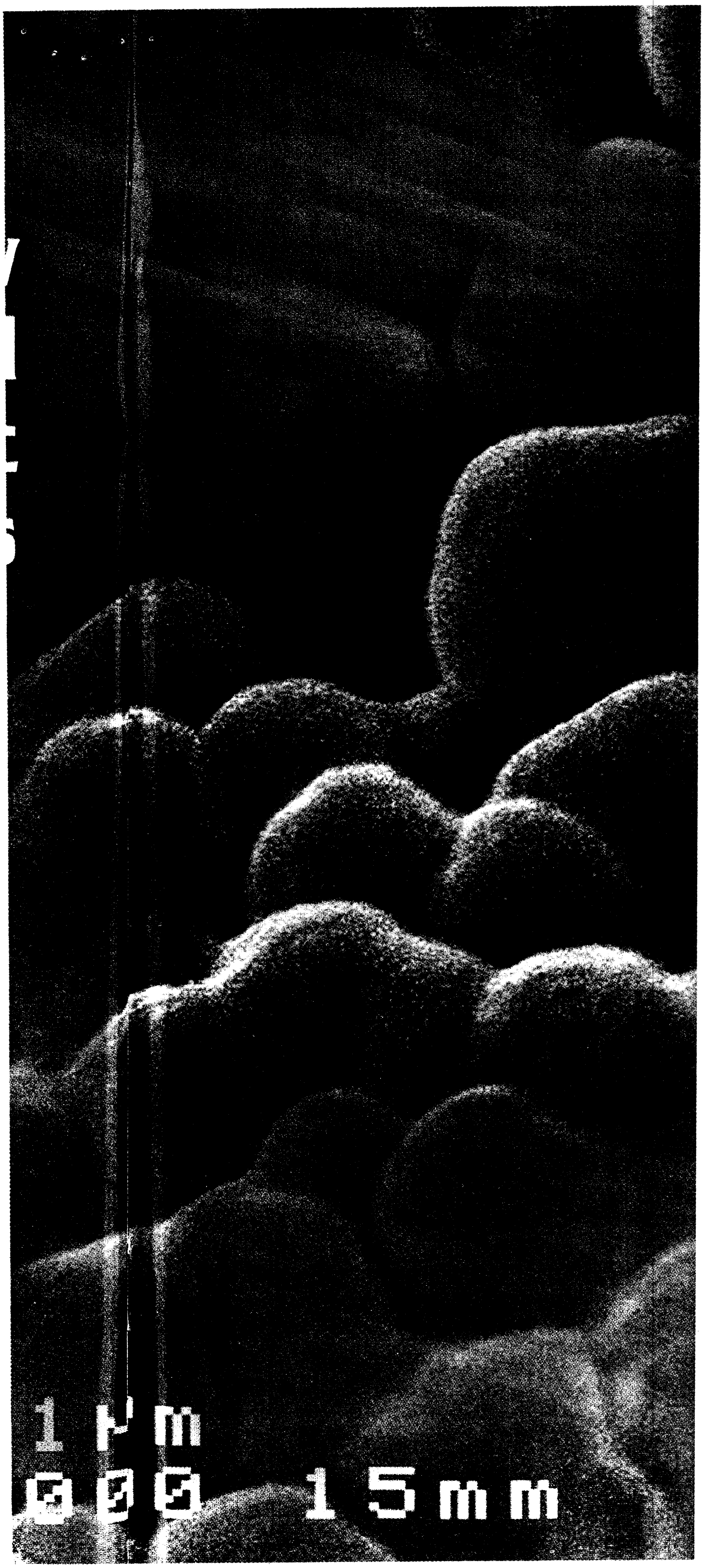

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Hollow cathode discharges have been reported as nove sources for generation of high density discharges Most of the work to date, however, has focused on hollow cathodes for cleaning[2], activation of reactive gases [3,4], a sources to deposit thin films via Plasma Enhanced Chemic Vapor Deposition (PECVD)1 and sputter deposition using th hollow cathode configuration [5,6]. Thin films are being deposite at higher and higher deposition pressures, with some claims o SiO_x depositions at atmospheric pressures (760 Torr).[7] Hollo cathodes can be used in a PECVD process to simultaneousl deposit thin film structures comprised of at least 2 components a matrix of an inorganic oxide of silicon, and a dopant of eithe a metal, polymer or ceramic material at pressures up to at leas 10 Torr. Composite structures that incorporate a metal, polyme or ceramic have potentially interesting applications for optical mechanical, energy storage and other chemical applications Furthermore, any depositions at or near atmospheric pressur offer the potential for significantly simplified deposition apparatus. The work herein describes several thin film structures tha were deposited using hollow cathodes at medium (0.5 Torr) t high (10 Torr) pressures. These structures included pure polymer films as well as silicon oxide doped polymer films.

Experimental

A generic configuration that takes advantage of the hollow cathode discharge is shown in **Figure 1**.[8,9] The hollow cathod effect is generated by a pair of conductive surfaces opposin each other with the same negative potential with respect to common anode. If the spacing is made (depending on the pressure and gas type) such that the space charge sheaths overlap electrons start to oscillate between the reflecting potentials o the opposite wall sheaths leading to multiple collisions as the electrons are accelerated by the potential gradient across the sheath region. The electrons are confined in the space charge

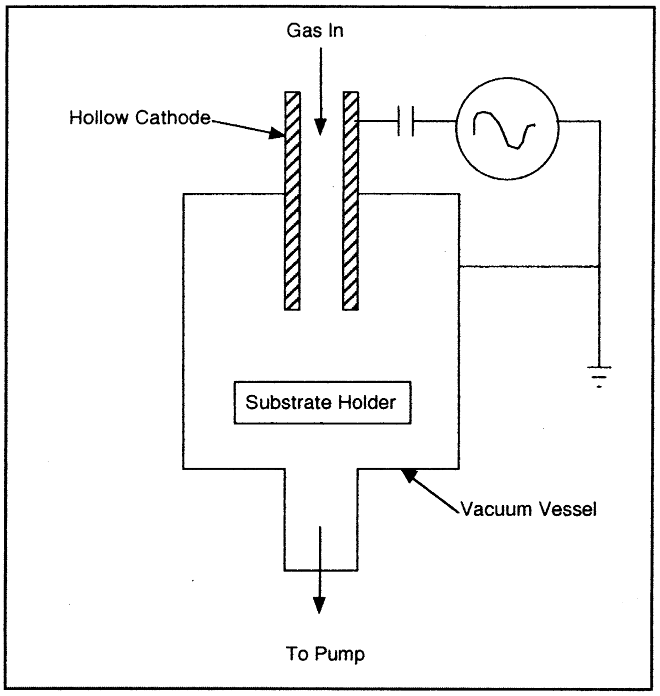

Figure 1. Generic Hollow Cathode Configuration.

sheath overlap which results in very high ionization and high ion density plasmas. This phenomena is described as the hollow cathode effect[7]. In the configuration used herein, the hollow cathode effect was generated in a metallic tube (typically 316 stainless steel or copper) with an inside diameter between 0.125-0.5" with an applied RF field at 13.56 MHz. A cylindrical electrode around the hollow cathode was used as the common cathode while the hollow cathode itself was held at or near ground potential. The reactive gases (including the silicon source gases in the case of depositing SiO_x) were injected into the hollow cathode discharge area. Where doping of the materials took place, the appropriate polymer was machined into an insert which was held in the primary hollow cathode inlet.[8,9]

The dopant materials were simultaneously deposited into a matrix of silicon dioxide which was generated under the following conditions:

Silicon Source Gas:	1,1,3,3-tetramethyldisiloxane (TMDSO)
Oxidizing Gas:	99.95% Oxygen
TMDSO Flow rate:	1-50 sccm
Oxygen Flow rate:	5-50 sccm
Power:	50-200 watts
Pressure:	50 mTorr - 10 Torr

The dopant material concentration was varied for each deposition using only the input power as a control. An SC Technology PCM-400 Optical Emission Spectrometer (OES) with an enhanced Hamamatsu CCD array detector was used to monitor and control the plasma depositions. Single emission lines specific to the deposition were selected for each experiment. The intensity of each line was monitored which was proportional to the amount of the dopant being incorporated into the thin film. In addition to the dopant, the OES system was used to monitor the dissociation of the organosilicon material.

Thin film doped materials were initially deposited onto 2 substrates cleaned glass microscope slides and silicon. In all cases the adhesion was excellent to both substrates based on a standard tape test. The glass microscope slides were cleaned with a conventional glass cleaner and blown dry with clean, dry air. In addition to the traditional samples, the high pressure SiO2 films were deposited the inside of polyethylene terepthalate (PET) bottles. The PET bottles were coated on the inside without any pretreatment or cleaning prior to the deposition.

In the cases of pure polymer films, silicon (high and low resistivity) and polyethylene substrates were employed. Neither the silicon nor the polyethylene were cleaned and were deposited in their as-received state. In all cases, adhesion was excellent.

After deposition, the thickness of the thin films were measured on masked samples of glass slides or silicon with a Dektak IIA profilometer outfitted with a microscope and video system. The steps were generated by placing strips of 3M Scotch Tape onto the glass prior to depositing the thin film. After the deposition, the Scotch Tape was removed revealing an uncoated stripe which served as the "step". The stylus of the profilometer was positioned to move across the uncoated area into the coated material giving a step and a means to determine the coating thickness.

In addition to thickness, the thin films were characterized by Fourier Transform Infrared (FTIR) Spectroscopy using a Bio-Rad FTS 175C. Thin films were deposited onto silicon chips which were transparent in the infrared. The coated silicon was then subjected to the infrared beam in the FTIR and spectra were generated. An on-line CDROM FTIR library from Sadtler Laboratories was used to analyze and make peak assignments on the FTIR generated spectra.[11]

Results/Discussion

Composite Film Structures

Several thin film nano composite structures were fabricated with the novel hollow cathode apparatus.[12] The films are referred to as nano composites, since they are a combination of SiO_x and the dopant material, and the dopant is uniformly dispersed through the structure. The resulting thin film exhibits the properties of both materials (the inorganic matrix and the dopant).

Fluorinated polymers have become an important class of engineering polymers for a wide range of applications. Several desirable properties of fluoropolymers include low coefficient of friction and high contact angle. Unfortunately, fluoropolymers also have poor adhesion to most materials and are soft. It would be desirable to retain the properties of polytetrafluoroethylene (PTFE), but to increase the durability of the material and to make it adhere to a wide range of materials. A thin film material was deposited which incorporated PTFE (from the

Table 1

Experiment #	TMDSO Flow (sccm)	PTFE	Power watts)	Contact Angle (degrees)
083198-2	1	None	150	57
083198-3	1.5	Yes	150	82
083198-4	1.5	Yes	200	106

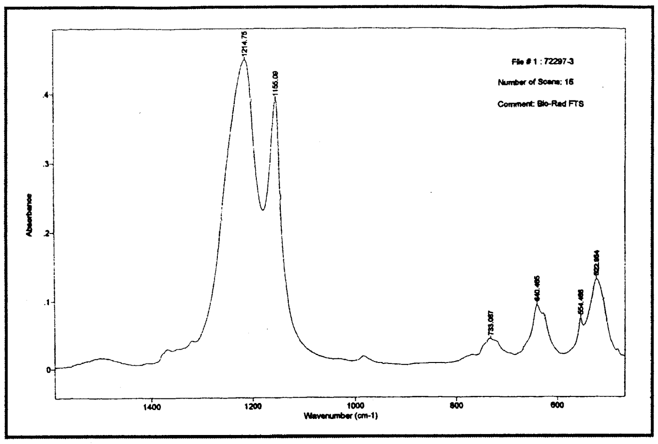

Figure 2. PTFE Thin Film FTIR.

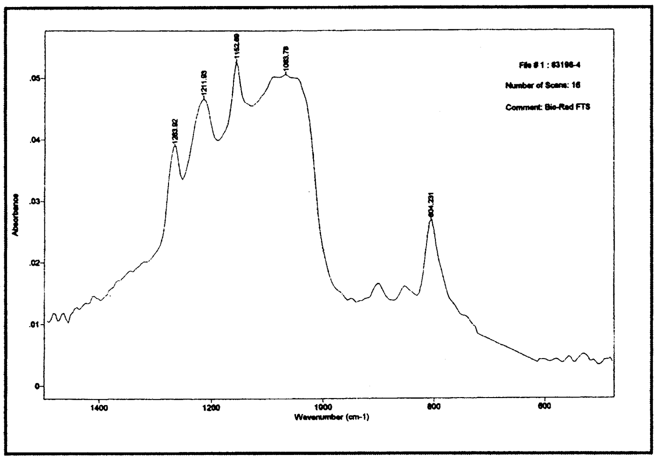

Figure 3. SiO_X/PTFE Thin Film FTIR.

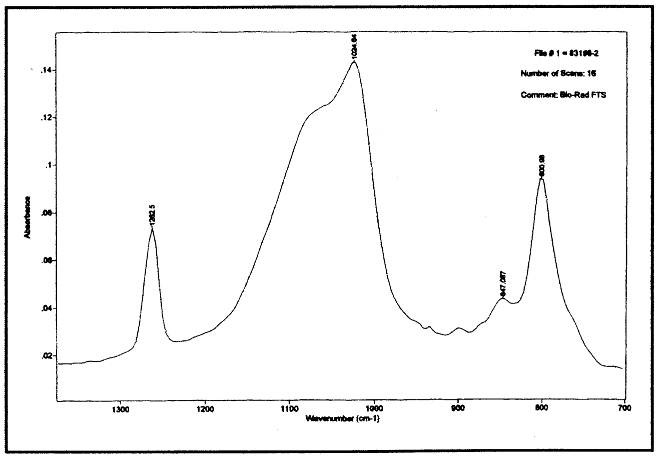

Figure 4. SiOCH Thin Film FTIR.

solid phase) into a matrix of SiOCH. The resulting film exhibited interesting surface properties (See **Table 1**). The PTFE incorporation was indicated by the FTIR peaks located at 1210-1211 cm^{-1} and 1151-1152 cm^{-1} (**Figure 2** - PTFE thin film and **Figure 3** -SiOCH film with PTFE doping). As reference **Figure 4** shows the FTIR spectra of a PECVD SiOCH thin film based on TMDSO and oxygen in a RF Plasma using the hollow cathode described above with no PTFE incorporation.

The average thickness for the above samples is shown in **Table 2**.

The PTFE depositions demonstrate that it is possible to incorporate the polymer into the silicon matrix.

In addition to polymers, the novel hollow cathode apparatus can dope SiOCH matrices with metallic ions and clusters.[12] Two metals were investigated, lithium and zinc. Lithium has potential application in the next generation of lithium ion and lithium polymer batteries as companies search for new electrolyte materials and novel means of manufacturing electrodes. Zinc has been used extensively in the architectural glass coating industry in the form of zinc oxide to protect silver in low emissivity stacks. Incorporation of zinc into a silica matrix has the potential to provide a variable index thin film material for thin film optical design as well as potentially offering conductivity. The depositions completed here focused on demonstrating the capability of ion and metallic incorporation in the silica matrix. **Table 4** gives the specific data for each deposition. Note that the lithium ESCA data was based on average data from a sputter etch profile through the thin film, while the ESCA analysis on the zinc samples was based on a surface survey, thus the very high carbon signal and the lower silicon signal.

Previous depositions that incorporated metals into silica matrices focused on the use of toxic metalorganic precursers[13], injecting fluorine and silicon containing gases into a sputtering plasma[14,15], and simultaneous evaporation and plasma polymerization[16]. In all cases, the deposition rates were relatively low 2-17 Å/sec. The rates in the work herein ranged from 21-82 Å/sec (**Table 5**) and higher flow rates should lead to higher deposition rates in a pilot/production implementation.

High Pressure SiO_2 Depositions

The same apparatus above was used to deposit thin film structures (with no insert) of SiO_x. Pressures were varied from 50 mTorr up to 10 Torr to determine if good quality films (which

Table 2

Experiment #	TMDSO Flow (sccm)	PTFE	Power (watts)	Thickness (Å)
083198-2	1	None	150	1000
083198-3	1.5	Yes	150	1222
083198-4	1.5	Yes	200	1225

Table 4

Experiment #	TMDSO Flow (sccm)	Metal	Power (watts)	ESCA (atomic %)				
				Si	O	C	Li	Zn
91097-3	3.8	Li	150	15	30	45	10	
102297-2	1.0	Li	150	24	58	0	18	
083198-5	1.5	Zn	100	15.3	34.2	37.1		9.6
083198-7	1.5	Zn	150	9.4	37.1	40.1		17.9
083198-6	1.5	Zn	200	2.2	36.1	34.1		15.2

Table 5

Experiment #	TMDSO Flow (sccm)	Metal	Power (watts)	Thickness (Å)	Rate (Å/sec)
91097-3	3.8	Li	150	3784	28
102297-2	1.0	Li	150	2984	24.9
083198-5	1.5	Zn	100	1195	27
083198-7	1.5	Zn	150	630	21
083198-6	1.5	Zn	200	2461	82

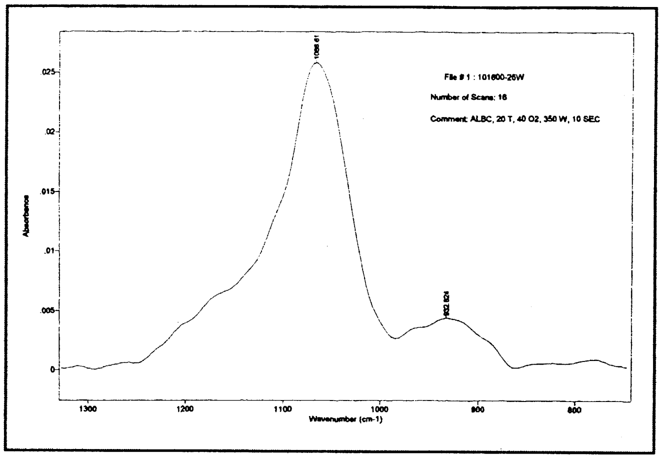

Figure 5.. SiO_2 Thin Film FTIR.

were characterized with good adhesion and FTIR characteristics as shown in **Figure 5**) could be deposited at pressures typically considered high. The following design of experiment matrix was completed:

Parameter	Low Condition	Mid-Point	High Condition
TMDSO Flow	15	32.5	50 sccm
Oxygen Flow	20	35	50 sccm
Power	50	75	100 watts

The above was completed at both 5 and 10 Torr total deposition pressure (see **Table 6 and 7**). Thin film thickness and FTIR characteristics were measured for each deposition condition and compared to depositions @ 50 mTorr that provided good adhesion and gas barrier properties. Of most interest from the FTIR spectra was the location of the Si-O-Si stretch peak position (typically 1060-1100 cm^{-1} for SiO_2) which was a good indicator of the inorganic nature of the thin film, higher wavenumbers indicating a more inorganic SiO_2 structure, and lower wavenumbers indicating a more organic (incorporation of $Si\text{-}CH_3$) less SiO_2 structure.[17] In addition to thickness and FTIR, the occurrence of powder was also tracked for the 10 Torr depositions. The following are the experimental results:

(NOTE: Deposition time for all conditions was 5 minutes)

Table 6. 5 Torr Deposition Conditions

TMDSO Flow (sccm)	02 Flow (sccm)	Power (watts)	Thick (Å)	Si-O-Si Pk (cm^{-1})	Powder
15	20	50	1557	1051	no
15	50	50	1487	1063	no
50	20	100	5258	1040	no
32.5	35	75	1487	1050	no
32.5	35	75	1500	1052	no
50	20	50	5173	1040	no
15	50	100	2062	1062	no
50	50	50	5950	1047	no
15	20	100	530	1057	no
50	50	100	5554	1054	no

Table 7. 10 Torr Deposition Conditions

TMDSO Flow (sccm)	02 Flow (sccm)	Power (watts)	Thick (Å)	Si-O-Si Pk (cm^{-1})	Powder
15	20	50	1394	1039	yes
15	50	50	1566	1082	no
50	20	100	9499	1040	no
32.5	35	75	8566	1082	no
32.5	35	75	8924	1086	no
50	20	50	5780	1069	no
15	50	100	1020	1054	yes
50	50	50	10,910	1087	no
15	20	100	1093	1048	yes
50	50	100	19,457	1090	no

The above results were analyzed using SateEase™ Design of Experiments Software (the matrices were designed using the same software program). The following models were found for thickness and Si-O-Si peak positions:

Thickness:

5 Torr	Thickness = -337 + 116 *TMDSO Flow	$R^2=0.95$
10 Torr	Thickness = -3078 + 289 *TMDSO Flow	$R^2=0.62$

Si-O-Si Peak Position:

5Torr

Si-O-Si Pk = 1052 - (0.37*TMDSO Flow) + (0.32 * O2 Flow) $R^2=0.89$

10 Torr

Si-O-Si Pk = 1014 + (0.45*TMDSO Flow) + (0.98 * O2 Flow) $R^2=0.61$

Note that the 10 Torr models had poor statistical fits. It is also interesting to note that only the TMDSO flow rate was significant (at both pressures) in terms of deposition rate, suggesting higher flows should be investigated. Additionally, at 5 Torr the flow rate was inversely proportional to the location of the Si-O-Si peak position, so that the most SiO_2 like materials were produced at the lowest flow rate and therefore the lowest deposition rates. The 10 Torr process conditions, however, had the opposite effect showing that the most SiO_2 like were deposited at high flows. Typical spectra are shown in **Figures 6** and **7**.

A surprising result was found at the end of the chamber on the viewport where there was significant deposition after each run. The coating was so thick that it could be removed as a solid piece of SiO_x which was then analyzed with FTIR (see **Figure 8**). This suggests that the sample locations used during the experiment (below the hollow cathode) were not the areas of

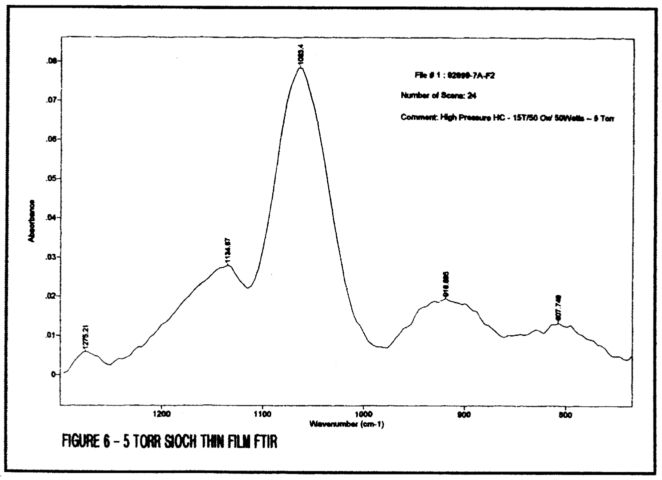

Figure 6. 5 Torr SiOCH Thin Film FTIR.

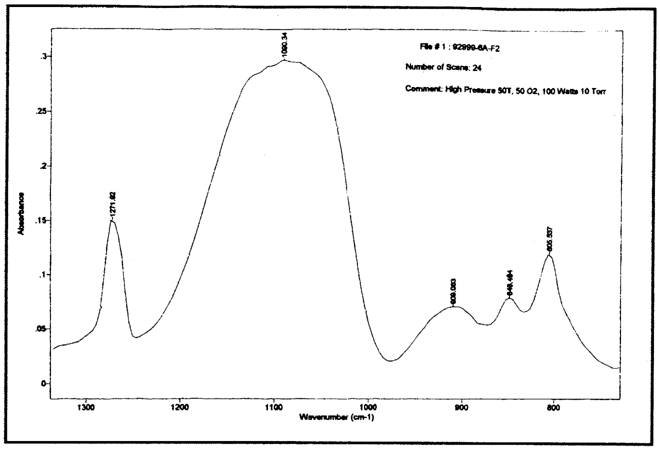

Figure 7. 10 Torr SiOCH Thin Film FTIR.

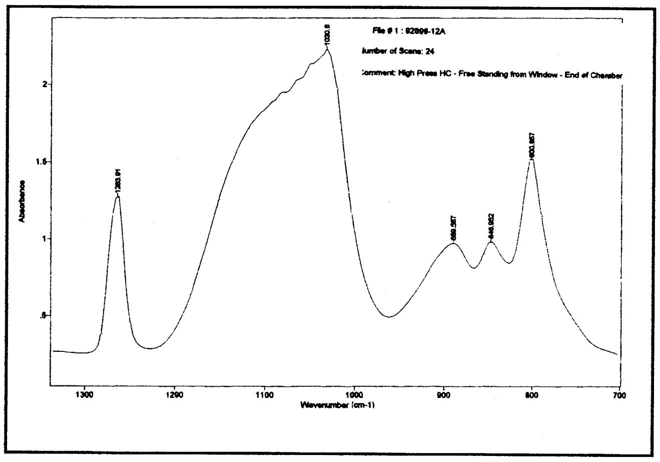

Figure 8. 10 Torr Free-Standing SiOCH Thin Film FTIR.

highest deposition. In fact, the coatings taken from the viewport were approximately 30-40,000Å (3-4 microns) thick which equates to a deposition rate of 133Å/second. The coatings did, however, have high organic content (as indicated by the intensity of the peaks at 1263 cm^{-1} due to Si-CH$_3$ and at 800 cm^{-1} due to Si-(CH$_3$)$_2$.

The occurrence of thick deposits on the end of the chamber (opposite the opening of the hollow cathode) showed that the electrode configuration could be used as a high rate deposition source. Based on this result, apparatus was fabricated to deposit semiconductor grade SiO$_2$ based thin film materials onto 8" wafers.18 The source was configured similarly to the apparatus above and gave depositions that were uniform with 5% across the 8" wafers.

As noted above, several depositions were completed onto the inside of PET bottles. The work was intended to look at increasing the pressure of the current process utilized for coating bottles (50 mTorr). The end application is to increase the shelf-life of carbonated soft drinks by reducing the carbon dioxide loss rate through the PET wall. The developed 50 mTorr process offers shelf-life improvements of 3x, unfortunately, none of the high pressure coated bottles offered any improvement on shelf-life. The lack of barrier properties was not surprising due to the significant organic content of the films and the implied lack of density.

Polymeric Film Depositions

Based on the experiments completed above and the observation of the very thick depositions at high pressures, a series of experiments was completed to investigate the deposition of pure polymer films. Polyethylene and PTFE materials were successfully deposited using the apparatus described earlier. In these depositions, the organosilicon gas was eliminated from the process, only Argon and Oxygen gases were used.

The basis of these depositions was to look at making both continuous as well as microporous structures for several applications including very low dielectrics as well as adsorbing layers for microliters of fluids.

Polytetrafluoroethylene (PTFE)

Additional PTFE depositions were carried out in the apparatus built to coat semiconductor wafers. Due to contamination issues, only 2 depositions were completed as summarized in **Table 8**:

Both depositions demonstrated the surface properties of PTFE, that is, they were hydroscopic with high contact angles to water. In addition, on the silicon that was coated, the adhesion was excellent.

After completing these depositions, additional work was completed to coat wire in a simplified roll-to-roll modification (see **Figure 9**). Steel wire (approx. 10 feet) was rolled through the deposition zone utilizing the conditions above from 20603-6L. The resulting wire was then dipped in water to check that the water did not wet the surface. Adhesion was excellent. Additional work is underway to optimize the coating apparatus as well as the coating process.

Table 8. PTFE Film Depositions

Experiment #	Argon Flow (sccm)	Power (watts)	Thickness (Å)	Rate (Å/sec)
20603-6L	190	5	10723	44.6
20603-7L	190	4	6094	25

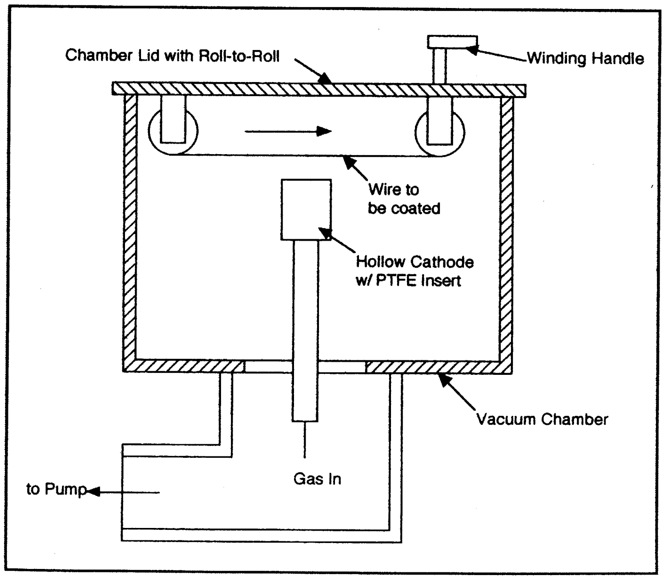

Figure 9. Roll-to-Roll Configuration.

One additional note, the PTFE films all resulted in "smooth" surfaces (as determined by Scanning Electron Microscopy – SEM).

Polyethylene

Several polyethylene insert materials were investigated including high density (HDPE), Ultra high molecular weight (UHMWPE) and low density (LDPE). Based on the deposition rates, adhesion and overall properties, only LDPE results will be reported here. Several screening experiments (to identify variables and ranges) were completed prior running a full factorial designed experiment (See **Table 9**).

The FTIR data was taken from the spectra obtained when coated silicon was analyzed (See **Figure 10**). The peak intensity was measured and then normalized to the thickness of the deposited film (as determined by profilometer measurements). Since the goal was to deposit porous materials, the lower the resulting normalized value for the intensity of the indicated peaks, the higher the void fraction and therefore the more porous the material. Based on the above experiment, the following were determined with the statistical analysis software:

Thickness = 44790 + 26400 power* (R^2 *Adj = 0.6539)*

*2800/thickness = 2.48 – 0.77*Argon Flow – 0.46*Power + 0.95*Ar*Power* (R^2*Adj = 0.79)*

*2900/thickness = 3.95 – 1.175*Argon Flow – 0.77*Power + 1.53*Ar*Power* (R^2*Adj = 0.77)*

Table 9.

Run # (sccm)	Argon (sccm)	Oxygen (watts)	Power (Å)	FTIR Data		
				Thick	2800cm-1	2900cm-1
	10	10	5	102955	0.82	1.32
	100	40	4	14603	0.904	1.43
	10	10	4	14389	5.4	8.6
	100	10	4	30191	1.43	2.41
	55	25	4.5	21158	2.9	4.73
	100	40	5	93286	1.89	2.74
	10	40	5	46819	2.75	4.15
	100	10	5	53518	2.42	4.15
	10	40	4	26192	3.8	6.06

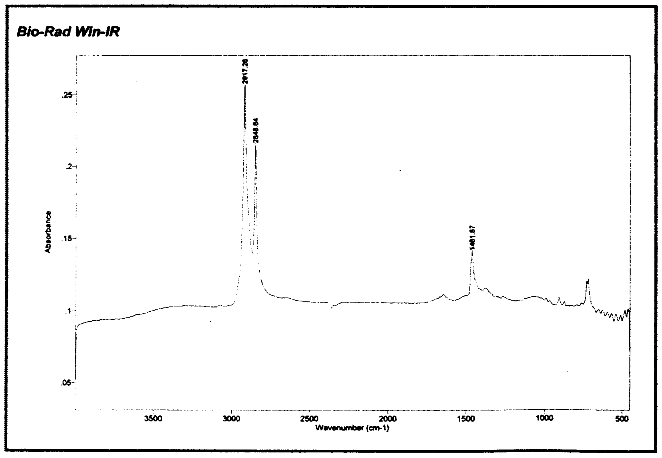

Figure 10. Pure LDPE Thin Film.

Although the model fits were not good, the basic models make sense since thickness was clearly a function of the applied power. The FTIR results were more complicated given the interactive term (power and argon flow) but suggest that highly porous materials can be fabricated at lower power and pressure.

A second set of experiments were conducted using the above conditions as a basis. Low Density Polyethylene (LDPE) was selected as the starting material due to the relative transparency in the infra-red . Infra-red transparency was considered important since any possible liquid that would be absorbed into the structure could then be analyzed with an FTIR. As before, an insert was fabricated from the dopent material (in this case low density polyethylene (LDPE)). Since a pure film was desired, no organosilicon materials were used. Argon gas and oxygen (to activate the LDPE) were used. Several depositions were completed varying gas flow and power. The resulting films were analyzed with SEM to determine if a porous structure was deposited. Several variables were considered including the hole size (opening) of the insert (hollow cathode), power level, and height of the LDPE insert. In this case, substrates in each experimental run included FTIR silicon (transparent in the infra-red), 10 mil LDPE film and a 4" silicon wafer. In all cases the argon/oxygen flow was fixed at 10 sccm Argon and 40 sccm oxygen. Time was also fixed in each experiment. **Table 3** summarizes several of these experiments:

Based on the above, the deposited films were first evaluated with a drop of water which was put onto the surface. The resulting diffusion of the water on the surface (whether it wets or not) was used as a screening to SEM analysis. Based on the wettability, several samples were analyzed and while most of the thin film surfaces were smooth (**Figure 11**), one condition (41403-1) clearly showed the porous structure that was desired (**Figure 12**). Additional optimization of this coating condition is underway to determine if the size and spacing of the pores in the structure can be optimized for different liquids and or for controlled density.

Future Work

Work will continue of the application of composite as well as pure polymer thin films to two and three dimensional substrates. Work on coating wire and wire-based materials in the simplified roll-to-roll system developed for the work herein will continue to be optimized. In addition, work is continuing on the deposition of PTFE materials on silicon, metals as well as three dimensional polymeric materials.

Table 3. LDPE Porous Deposition

Experiment #	Insert Height	Hollow Cathode Hole Dia.	Power Level
40803-2L	1"	1/2"	4.75
41403-1L	1"	5/16"	3.5
41503-3L	0.83"	5/16"	3.5
41503-4L	1"	5/16"	3.0
41803-1L	1"	1/2"	4.5

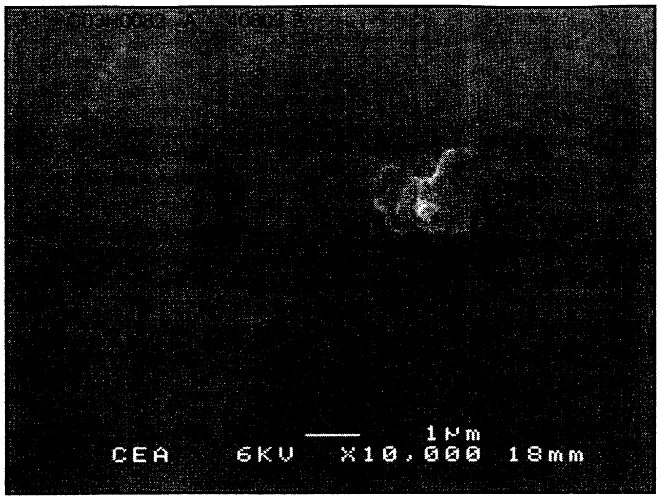

Figure 11.

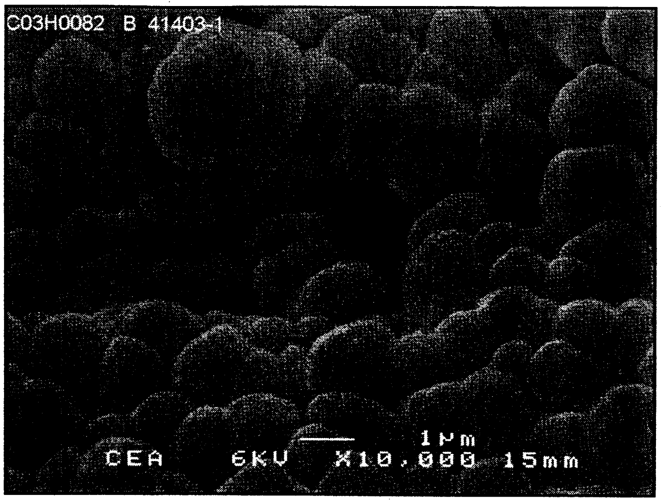

Figure 12.

Summary

A hollow cathode apparatus was developed that allows co-deposition of a PECVD thin film of a silicon based material such as SiO_x or SiOCH simultaneous with inclusion of a polymeric or metallic dopant material at pressures ranging from 50 mTorr to 10 Torr. The apparatus also allows high rate deposition of PTFE and polyethylene thin film materials with varying porosity. Thin films of silicon oxide which incorporated PTFE, lithium and zinc were presented. High rates of up to 82 Å/second make this apparatus an interesting possibility for roll coating applications. Additional work in the optimization and characterization of the deposited thin films in addition to investigations into other polymeric and metallic dopant materials will be completed in the coming months.

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