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Soft Plasma Polymerization of Gas State Precursors from an Atmospheric Pressure Corona Plasma Discharge

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An atmospheric pressure nonthermal equilibrium corona plasma jet is described for depositing polymeric coatings with a high degree of functional chemistry retention. A long chain perfluorocarbon molecule was introduced as a vapor into a helium plasma at atmospheric pressure and coatings were deposited onto Si wafers at rates of 60−100 nm/min. XPS, FTIR and contact angle measurements indicate that a controlled polymerization reaction took place through the vinyl group of the monomer, with minimal fragmentation of the functional perfluoro chain. Electrical characterization of the corona plasma indicates that the power coupled into the jet was 6.8 W. It is proposed that low specific energy (J/cm^3) coupled into the plasma region is inherent to this plasma type and enables deposition of coatings with minimal fragmentation of the precursor monomer molecule. The system is inherently suitable for small-to-moderate area, high-added-value functional coating.

Introduction

Plasma polymerization is a well-established route to surface functionalization[1] and has found applications in diverse areas such as biotechnology,[2] adhesion,[3] electronics[4] and textiles.[5] Plasma polymerization was initially developed under vacuum conditions and used standard low pressure plasma technology to polymerize gas vapors and produce polymeric coatings in a technique referred to as plasma enhanced chemical vapor deposition (PECVD). In these early systems the vapor phase precursors were bombarded with aggressive plasma species, which produced fragmentation and rearrangement of the precursor monomers. As a result, a wide variety of random fragments were created that could deposit on to a substrate to produce a thin film layer which contained many of the atoms present in the starting monomer. Various models have been created to explain the reaction mechanisms in such systems.[6,7] Although PECVD became well-established, the coating functionality remained limited to simple materials such as SiO_x, SiN, or TiO_2 and complex chemistry could not be deposited using such systems.

From as early as 1983, Suhr[8] pointed out that the main efforts in organic plasma chemistry have always been directed toward highly selective reactions. Forch et al.[9] described "soft plasma assisted modification" as where the molecules to be polymerized do not dissociate completely, but are activated predominantly at particular reaction sites so that the process is very different from traditional plasma polymerization based on a high degree of, even total, monomer fragmentation, and where the product shows little resemblance to the original precursor molecule and deposited films show little or no repeating structure and no definable molecular weight distribution. This description follows Yoshimura and Hozumi,[10] who distinguished "polymerization sites" in the monomer molecule from "functional sites" containing the key molecular properties to be replicated in the polymer. They characterized "soft plasma conditions" as where the former sites carry out polymerization with the least damage to the latter. Ideally, the latter should be independent from the former.

Thus, the ideal "soft plasma polymerization" (SPP) is the ability to plasma deposit a solid film with a very high degree of structural retention of the starting precursor so that the deposited coating retains the molecular complexity, functionality and value of the monomer. The benefits of SPP processes are prospectively highly significant and

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well canvassed in the literature, opening the door to single-step industrial coating of substrates with, for example, complex and valuable, but sensitive, bioactive macromolecules such as enzymes and nucleic acids for applications such as biosensors, lab-on-a-chip, and biomedical devices and many other processes.

A range of plasma types and process control parameters have been identified delivering SPP in varying degrees. Thus, control of substrate temperature,[11] reactant pressure and flow rate, absorbed continuous wave power[12] and location of substrates at varying distance from the plasma region[6] have all been used to bring greater levels of control to the polymerization process.

Additionally, in the mid 1990s, a significant step forward occurred through the development of pulsed vacuum PECVD systems. These allowed the power coupled to the plasma to be pulsed in a manner that still created the active species in the plasma, but did not contain enough energy to fragment all of the bonds within a monomer. The resulting active species interacted with gas phase monomers and produced a soft polymerization reaction that deposited coatings with complex functional chemistry.[13,14] Various mechanisms have been reported to explain the polymerization mechanism within such systems, which can be driven by free radical[15,16] or ionic polymerization.[17,18] Despite the excellent film control offered by this process, these systems were still limited to vacuum processing and this has hindered commercial exploitation of the technology.

In recent years, Badyal et al. have developed a controlled polymerization process at atmospheric pressure. By combining a low-energy helium atmospheric pressure glow discharge plasma with a liquid aerosol precursor delivery system, it was possible to produce a series of thin films with soft polymerization and a high degree of retention of monomer functionality.[19,20] This technology was further developed by Dow Corning Corporation under the brand name "APPLD"[21,22] (atmospheric pressure plasma liquid deposition). Helium glow discharges were chosen as the preferred plasma option as they provide a nonthermal, homogeneous plasma that can be readily produced under ambient pressure.[23] The introduction of the liquid as an aerosol was preferred as this was thought to protect the bulk of the liquid precursor from the aggressive plasma species by encapsulating it within a droplet of several micrometers in diameter, thereby minimizing fragmentation of the precursor monomers. This technology has received considerable interest and a number of groups are now actively exploring this area,[24−27] as it offers a convenient route to deposit functional coatings under ambient conditions in a continuous online process.

It has long been thought that the soft polymerization from such systems has been due to a combination of the protection offered by the aerosol droplet and the low energy cold plasma.[19−22,25,26] In this paper, an attempt is made to decouple these two factors by introducing a precursor as a vapor rather than aerosol into a nonthermal plasma. The use of aerosol delivery systems produces a number of complexities related to the stability of the spray, control of droplet size, generation of an even precursor distribution over wide areas, the requirement to accurately dispense low volumes of liquid at a constant rate, and rapid build-up of unwanted deposits on reactor surfaces. The introduction of vapors rather than liquids allows for standard PECVD equipment (bubblers, mass flow controllers) to be used to generate an easily controlled, even flux of precursor onto a substrate. In this paper, a standard vapor generating bubbler system is combined with a helium plasma to produce coatings. 1H, 1H, 2H, 2H-Heptadecafluorodecyl acrylate (HDFDA) was chosen as a precursor monomer as it contains a polymerizable vinyl group and a long perfluoro chain that is easily characterized (Figure 1). This allows data to be readily compared to prior data published for vacuum polymerization[28] and for aerosol assisted[29] plasma deposition of HDFDA. Furthermore, fluorocarbon films have attracted significant attention, as they offer a convenient route to low surface energy coatings that can modify surface properties such as hydrophobicity, oil repellency,[5] cell attachment,[30] and chemical inertness.[31]

Experimental Section

A plasma jet was constructed based on the aerosol−plasma jet system described by O'Neill and O'Sullivan.[29] It consists of a dielectric head housing two tungsten needle pointed electrodes to which are applied in parallel an alternating current voltage as shown schematically in Figure 2.

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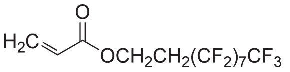

$H_2C{=}CHC(=O)OCH_2CH_2(CF_2)_7CF_3$

Figure 1. Chemical structure of HDFDA.

A space around each electrode allows a mixture of process gas and precursor vapor to enter the device. Very low frequency electrical power was delivered to both electrodes from a modified PTI 100W power supply at a frequency of ~19 kHz and a peak-to-peak voltage of ~23 kV. The resultant helium−vapor mixture exited the system through a 75 mm long × 15 mm diameter fluoropolymer tube in which the corona plasma was struck. Essentially, the configuration was a conventional point-to-plane type corona configuration in which a high voltage was applied to generate plasma from the tip of vertically positioned sharp tungsten needles. In the event, the system was run "open circuit", i.e., no physical counter-electrode in the form of a conductive plane needed to be placed to oppose the needles, as the high electric fields at the pin tips saw the surrounding ambient as the "ground plane" and discharged freely from the needle tips into the tube in the well-known corona discharge. Coatings were deposited onto substrates placed adjacent to the plasma outlet. Unless otherwise stated, all coatings were deposited onto 100 mm double polished p-type silicon wafer substrates.

Fourier transform infrared (FTIR) data were collected on a Perkin-Elmer Spectrum One FTIR. Coatings were deposited directly onto NaCl disks and spectra were collected using 32 scans at a 1 cm^{-1} resolution.

Contact angle measurements were obtained using the sessile drop technique using an OCA 20 video capture apparatus from Dataphysics Instruments. Drop volumes of 1.5 μL were used and images were collected 30 s after placing the droplet on the surface. Surface energy was then determined using the method of Owens and Wendt.[32]

X-ray photoelectron spectroscopy (XPS) survey spectra were recorded on a VSW spectrometer consisting of an hemispherical analyzer and a 3 channeltron detector. All spectra were recorded using an Al Kα X-ray source at 150 W, a pass energy of 100 eV, step size of 0.7 eV, dwell time of 0.1 s, with each spectrum representing an average of 30 scans. High-resolution C 1s spectra were collected on a Kratos Axis Ultra system using monochromated Al Kα X-rays with a pass energy of 40 eV.

Film thickness and thickness profile/mapping of the coatings were determined by a Woollam M2000 variable angle ellipsometer.

Electrical characterization of the device consisted of a Bergoz Instrumentation, France, CT-E5.0-B toroidal current transformer, which was used to measure the plasma current (I_d) and a North Star PVM-5 high-voltage probe, which was used to determine the applied voltage (V_{app}). The Bergoz current transformer toroid was positioned around the fluoropolymer tube of Figure 2 and 10 mm along the tube from the needle tips to capture the plasma discharge, whereas the high voltage probe was applied at the output of the power supply. The outputs of both probes were captured on a Tektronix TDS 2024 four-channel digital storage oscilloscope with a 200 MHz bandwidth.

Results

HDFDA was introduced into the plasma jet as a vapor from a standard bubbler set up. By controlling the flow of carrier gas and the bubbler temperature, the flow rate of the monomer could be altered. Initial experiments were carried out with a bubbler temperature of 80 °C and with various flow rates of helium of 1−15 standard liters per minute (slm). Coatings deposited under such conditions were found to produce a wet coating with minimal curing that can be attributed to insufficient activation and cross-linking. To enhance the curing of the precursor, we reduced the precursor flow to produce a higher plasma power per unit monomer, as described in vacuum polymerization systems by Yasuda.[6] The bubbler temperature was decreased to 56 °C and the helium flow was adjusted to 14 slm. This produced a series of cured dry coatings which were deposited for times of 10, 30, and 180 s. Gravimetric measurements indicate an average flow rate of 0.07674 g/min or 126 μL/min of monomer into the device at 56 °C. Standard tape adhesion tests were conducted according to ASTM D3359−02 and no evidence of coating delamination was detected on any of the dry, cured plasma samples. This indicates that the coatings exhibit reasonable levels of adhesion.

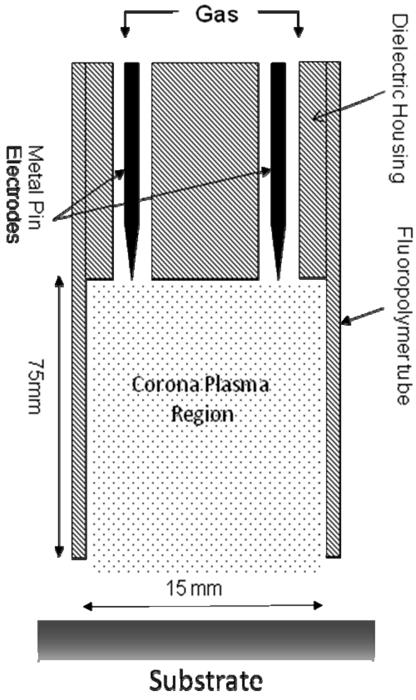

Figure 2. Schematic of 2-pin Electrode head of a pin corona discharge coating system.

FTIR analysis was carried out to probe the chemistry of the deposited films and a typical spectrum is shown in Figure 3. The presence of the dominant peaks centered at 1150 and 1200 cm^{-1} in the spectra of the coatings correspond to the CF_2 and CF_3 groups of the perfluoro chain. As both fluorocarbon peaks are still well resolved, it can be deduced that the fluorocarbon chain has not undergone significant levels of fragmentation and degradation. Further examination of the main peak at 1205 cm^{-1} clearly shows a systematic increase in peak intensity with time (Table 1), indicating that thicker coatings are deposited at longer times.

Close inspection of the spectra clearly shows loss of the monomer peaks at 1625, 1635, 1412, 1074, and 984 cm^{-1}

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corresponding to loss of the C=C bonds of the acrylate group. However, the peak at 1738 cm^{-1} due to the carbonyl group of the acrylate is still retained in the coating. This indicates that a controlled polymerization of the precursor has occurred through the vinyl group of the monomer with retention of the functional chemistry of the larger fluorocarbon chain, as seen in pulsed vacuum[28] and aerosol assisted atmospheric pressure plasma[29] processes.

Examination of the coating in the region between 2800 and 3200 cm^{-1} shows an absence of peaks above 3000 cm^{-1} that could be associated with the symmetrical and asymmetrical bending and stretching of the C−H bonds of the vinyl group. Two distinct features are detected at 2851 and 2921 cm^{-1} that are characteristic of the asymmetric and symmetric stretches of saturated CH_2 groups. There is evidence of a weak peak at 2874 cm^{-1} and a broad peak from 2940 to 2990 cm^{-1} that may be due to the symmetric and asymmetric stretch of a terminal methyl group. However, the low signal-to-noise ratio prevents unambiguous assignment of these features. This loss of vinyl derived peaks, coupled to the presence of saturated alkane, fluorocarbon, and carbonyl signals, further indicates that the plasma reaction is driven through a controlled polymerization of the vinyl group with conversion to the alkane.

An additional peak can be detected at 1125 cm^{-1} in the spectra of both these samples and in the spectra of previously published plasma polymerized HDFDA coatings. As of yet, this peak has not been unambiguously assigned, though the authors postulate that this could be a secondary C−O species produced because of oxidation of polymer by plasma.

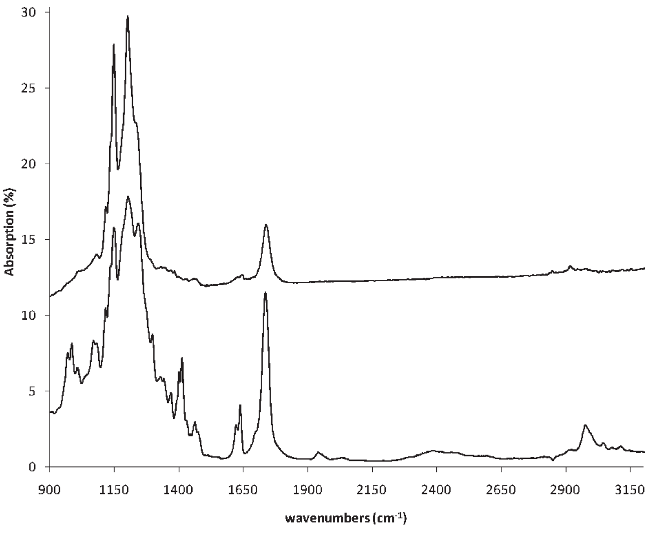

Figure 3. FTIR spectrum of HDFDA liquid precursor (bottom) and HDFDA coating deposited for 180 s on NaCl disk (top).

Contact angle analysis was carried out to probe the surface energy of the coated substrates. As shown in Table 1, the hexadecane contact angle values were largely independent of deposition time. All samples were found to produce significantly higher hexadecane contact angle values than the uncoated wafer (15°). All coated samples were found to be hydrophobic, with water contact angle values in excess of 90°. The water contact values were found to increase with increased deposition time. This may be explained in terms of increasing surface coverage of the substrate with increased processing time.

XPS analysis was also undertaken to determine the elemental content of the coatings. The XPS analysis of the 10 s sample revealed significant levels of silicon. This suggests that the coating is either patchy or else the coating thickness may be below 10 nm, which would result in concurrent analysis of the substrate and coating occurring during the analysis. High levels of oxygen were also detected. These may be derived from oxidation of the coating or from the native silicon oxide present on the wafer surface. The presence of a patchy coating coupled to significant oxidation of the deposit may help to explain the relatively low water contact angle value produced by the 10 s coating.

For the coatings deposited at longer times of 30 and 180 s, the elemental composition of the coating is very similar to that of the unreacted monomer (41% C, 53% F, and 6% O). The spectra from these samples are almost completely devoid of Si, indicating complete coverage of the substrate with a thick polymer layer. A slight increase in oxygen content was detected in the coatings, which can be attributed to some minor oxidation of the deposited material by the plasma. However, the results for these two samples are largely similar to results previously seen in soft plasma polymerization reactions and agree with the FTIR data in suggesting that the functionality of the monomer has been largely retained in the coating.

To further probe this point, curve fitting of the high-resolution C 1s XPS spectra was undertaken for the 30 s sample and the results are shown in Figure 4. The spectra clearly reveal two peaks at 292.4 and 294.6 eV that can be attributed to the CF_2 and CF_3 species, respectively. A peak at 290 eV can be assigned to the ester functionality, though it is likely that some monosubstituted fluoro species also contribute to this feature. Finally, there is a broad feature from 284 to 289 eV, which can be assigned to at least two different hydrocarbon features, possibly modified by the presence of electronegative F and O

Table 1. XPS, Contact Angle, and Thickness Data for HDFDA on Silicon

	XPS elemental composition (%)				contact angle analysis				
deposition time (s)	Si	C	O	F	water (deg)	hexadecane (deg)	surface energy (mJ/m^2)	FTIR peak height (a.u.)	ellipsometry thickness (nm)
180	0	41	8	51	114	76	11	17.52	
30	2	40	8	50	112	77	11	6.28	50
10	39	20	17	24	97	76	16	1.53	10

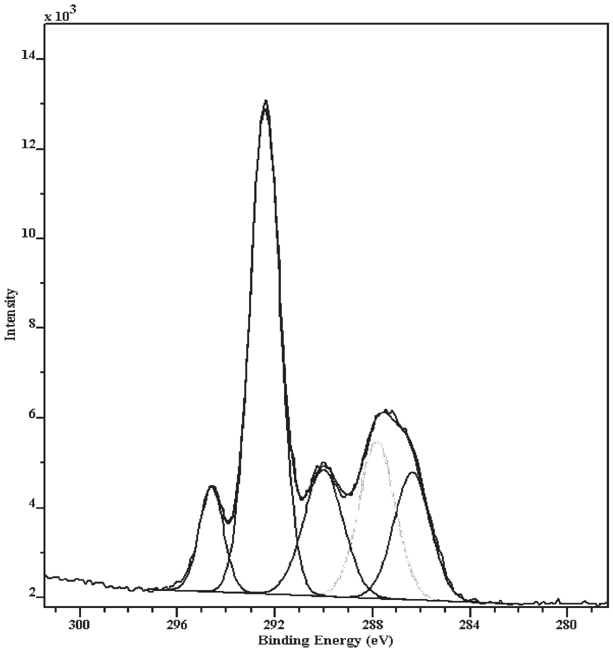

Figure 4. Curve fitting of the C 1s XPS spectrum of HDFDA deposited on Si wafer for 30 s.

species in close proximity. The intensity of the peak at 290 eV suggests that some oxidation of the fluorocarbon has occurred as a result of the process, though the degree of oxidation cannot be determined accurately because of the presence of overlapping features at this energy. The fluorocarbon peaks were well-resolved and the ratio of CF_2 to CF_3 was determined to be 5.8:1. This is lower than the 7:1 expected from the starting monomer, which indicates some degradation of the monomer has occurred, though the peak ratios would suggest that greater than 80% retention of the perfluoro chain has been achieved; this compares favorably with previously reported soft plasma polymerization processes.[28]

Ellipsometry data were collected from the 10 and 30 s samples. These coatings were found to have thickness values of 10 and 50 nm, respectively, indicating that the deposition rate was in the region of 60−100 nm/min. This is significantly higher than the deposition rates quoted for vacuum plasma coatings produced from HDFDA[28] and is similar to the deposition rates seen in aerosol assisted atmospheric pressure plasma deposition of a range of precursors.[19,25,29] Thickness mapping of the coated wafers indicates that the coating occupies a circular region of approximately 3−4 cm in diameter on the wafer surface. Attempts to extract thickness data from the 180 s sample were unsuccessful because of the rough nature of the deposited coating. Examination of the surface using optical and electron microscopy revealed the presence of numerous discrete particles within the coating and the resultant roughness distorted the ellipsometry measurements. Particle formation due to gas phase nucleation is a well-documented issue within such plasma devices. However, extrapolating coating thickness from the peak heights in the FTIR spectrum would suggest that the 180 s coating is approximately 3 times thicker than the 30 s coating.

As the vapor deposited coatings have been shown to have the same functional chemistry retention and deposition rate as seen in aerosol assisted atmospheric pressure plasma coatings, it can be deduced that the key to controlling the reaction mechanism cannot be predominantly dependent upon the presence of the monomer as an aerosol droplet. It seemed likely that the key control parameter is the low power coupled per unit of monomer, resulting in coatings being deposited in the power deficient regime described by Yasuda in vacuum polymerization systems.[6] It is therefore logical to conclude that the plasma properties must be a highly significant factor which controls the mechanism of polymerization. Therefore, diagnostics were applied to the plasma to determine the properties of the device.

Temperature within the plasma was monitored using an FLIR SC600 infrared camera. Throughout the experimental range investigated the temperature within the device was maintained below 100 °C, as shown in Figure 5.

The temperature within the plasma was also monitored by the simple expedient of placing a graduated glass alcohol thermometer so that the thermometer bulb was 15 mm below the electrodes inside the fluoropolymer tube and fully immersed within the helium gas flow and any corona discharge. A gas baseline temperature of 8 °C was recorded after 5 min of helium gas flow at 14 L/minute in the absence of plasma. A plasma was then struck and after 10 min of discharge the temperature recorded by the thermometer was found to stabilize at 18 °C, clearly indicating the nonthermal equilibrium and low power nature of the discharge.

Electrical characterization of the plasma using North Star high voltage and Bergoz Instrumentation current probes connected to the digital oscilloscope showed the following data. Under the conditions selected, the plasma was found to operate at a frequency of ~19 kHz and voltage of ~23 kV (peak−peak). Figure 6 shows the V_{app} vs time and I_d vs time characteristics of the discharge.

It is seen that the peak-to-peak voltage was about 23 kV and the peak current about 8 mA. The curves show that most of the current is displacement with current about 90° out of phase with voltage. The actual discharge power was calculated as the average over 10 periods of the current−voltage product and was found to be 6.8 W with a ±6% variation over 5 runs.

Discussion

A low power, nonisothermal equilibrium, atmospheric pressure corona plasma has been generated from a single electrode with pin geometry and used to deposit plasma polymerized coatings from HDFDA monomer precursor in the purely gas state.

By introducing the fluorocarbon monomer vapor into such a helium corona, it was possible to deposit a cured polymeric coating that retained the chemical structure of the precursor monomer so that the process can be characterized as soft plasma polymerization (SPP). The coating was hydrophobic and was put down at reasonable

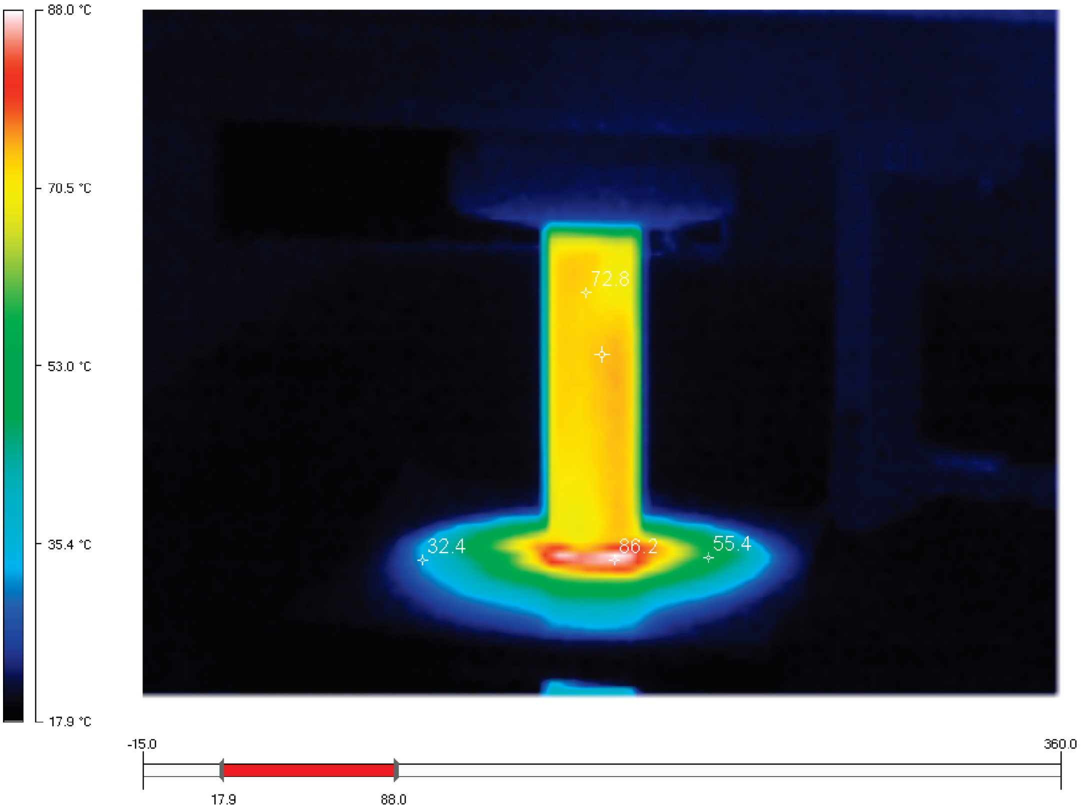

Figure 5. Color-mapped temperature scan of corona discharge inside tube.

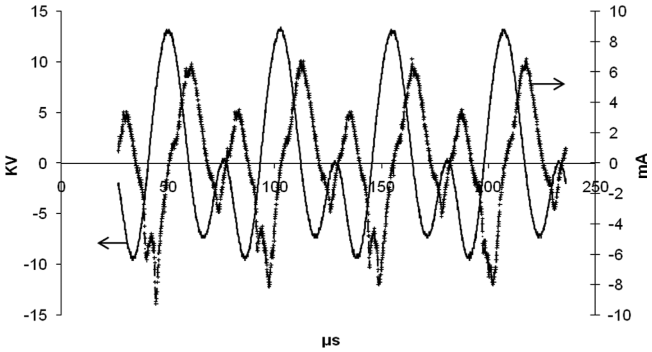

Figure 6. V_{app} vs t (light trace) and I_d vs t (dark trace) corona discharge characteristics.

deposition rates. Analysis of the coatings clearly shows that the precursor has undergone a controlled polymerization through the vinyl component of the acrylate group with minimal fragmentation of the functional chemistry of the monomer. The resultant coatings produced XPS and FTIR spectra that could previously only be produced by pulsed vacuum plasma or by aerosol assisted plasma processing.

Although there have been reports of plasma polymerization of siloxanes, fluorocarbons[33] and hydrocarbons[34] from corona discharge sources, there have been no reports that soft polymerization could be achieved using gas precursors. It is proposed that the ability of the corona discharge to achieve SPP in this work is due to the low specific energy of the discharge. The empirical work of Warburg[35] and his school around 1909 and Becker in 1920[36] connected key plasma discharge parameters with the efficiency of chemical reactions in the discharge. Becker showed that the governing reaction parameter, R, is proportional to the power input per flow of gas, i.e., to the specific energy in J/cm^3. Further studies by Rutscher and Wagner[37] in 1993 and by Hegemann et al. in 2007[38] showed that in nonisothermal plasma chemistry, including, of course, plasma polymerization, the specific energy (J/cm^3) is indeed the decisive parameter.

In this work, two very simple models were used to estimate specific energies. Model 1 was based on the following assumptions:

All discharge energy is coupled uniformly into the gas volume enclosed by the tube;

The discharge energy is partitioned evenly over all elementary entities (atoms/molecules);

The gas mix of helium plus HDFDA precursor is modeled as an ideal gas at SLC (standard laboratory conditions).

Specific energy was found to be 0.029 J/cm^3 or 0.72 kJ/mol or 0.02 eV/entity. These appear to be tiny values from

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the perspective of molecular bond breaking, viz. the dissociation energies of C−C 348 kJ/mol, C−O 360 kJ/mol, C−H 413 kJ/mol, C−F 488 kJ/mol, O═O 498 kJ/mol, and the pi-bond of the C═C bond approximately 264 kJ/mol.

However, if we calculate specific energy on another set of assumptions (model 2):

The helium is only an inert background gas and the plasma directly or indirectly, e.g., via helium metastables, eventually imparts all energy to the HDFDA;

Such energy is partitioned evenly over all HDFDA molecules;

The HDFDA gas is, again, modeled as an ideal gas at SLC;

We obtain a very different set of values, namely, specific energy of 54 J/cm^3 or 1327 kJ/mol or 35 eV/entity.

Clearly, both sets of assumptions are wrong and represent two extreme models of plasma energy coupling into the HDFDA monomer molecules. However, it is clear that model 2, where all of the total discharge energy finds its way into the HDFDA molecules, is far closer to reality than the energy equivalence model 1, in which every atom and molecule receives about the same energy.

Substantial discharge energy is likely to be both absorbed by the surfaces contacting the plasma (e.g., through quenching of helium metastables) and lost by radiation before reaching a HDFDA molecule. Furthermore, some proportion of the helium atoms is likely to retain absorbed energy throughout their residence time in the plasma and until and including relaxation back to the ground state without transferring it to HDFDA molecules. Thus, it is clear that some unknown part of the specific energy coupled into the process will never reach the HDFDA and will not be available to drive its polymerization. Such deductions from the specific energy value of model 2 (1327 kJ/mol) could result in a value not inconsistent with the energy needed to dissociate the C═C pi-bond (~264 kJ/mol).

What the film analysis data show is that although the C═C pi-bond is dissociated, the next highest bond dissociation energy, the C−C bond at 348 kJ/mol, is not disrupted by the process, indicating that the upper limit of specific energy available for HDFDA fragmentation from this process must be < 348 kJ/mol. Thus, the particular plasma generated within this process appears to deliver sufficient energy to the plasma region to break the weakest monomer bond, thereby enabling the molecule to react and polymerize, but without providing the energy required to break higher energy bonds, in particular those of functional sites. In short, the monomer is not fragmented and the process delivers soft polymerization.

Conclusions

This paper details what appears to be the first reported soft plasma polymerization from gas state precursor using a cool, atmospheric pressure, highly nonisothermal equilibrium corona discharge.

Electrical characterization of the plasma suggests that the retention of chemical functionality is likely to be very strongly related to the low level of power, specifically the low energy density (J/cm^3), coupled into the plasma. It appears that with this type of corona discharge, essentially damage-free polymerization of monomer molecules to deposit a functional coating can be readily achieved by use of precursor in the conventional gas state, i.e., operating in standard PECVD mode, so that the use of precursor in the liquid state as nebulized droplets is not required to achieve SPP as has been suggested.[19−21,25−27] This would appear to reduce the need for costly and complex liquid delivery apparatus in many applications using low power corona plasma to achieve functional coatings.

It is proposed that this corona plasma type is inherently predisposed to deliver low specific energy into the reaction zone and, hence, to SPP, even using gas precursors. Although the discharge is not a large area coating source, it is perfectly applicable to substrates < 1 m^2 seeking a high level of sophisticated functionality via surface coating.

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