ABSTRACT

WAGNER, DAVID HOLLIS, IV. Plasma Decomposition of a Palladium Salt for use in a Radioactive Implant. (Under the direction of Dr. Robert Black.)

The plasma induced decomposition of a tetraminopalladium chloride compound, Pd salt, has been investigated as a means of converting a soluble Pd salt into an insoluble metal for use in a polymer based implantable cancer treatment device. Pd salt insolubility ensures sealed source integrity is maintained when the polymer device is exposed to bodily fluids following implantation. The physical materials in the plasma as well as the processing parameters of the plasma system were modulated to determine the optimum set of parameters to maximize conversion efficiency of the Pd salt. Pd salt samples were prepared by depositing a non-radioactive tetraminopalladium chloride solution on a polymer substrate. Samples were oven dried and exposed to non-isothermal plasma. Visual inspection of the processed salt was conducted with an optical microscope to ensure that the residue remained confined within the physical structure of the polymer substrate. The chemical composition was analyzed by electron dispersive x-ray spectroscopy (EDS) to determine the ratio of chlorine ion (Cl^-) to palladium (Pd) as an indicator of the level of conversion.

Optimal Pd salt conversion was achieved with a 2-step process consisting of oxygen plasma substrate pre-treatment prior to the oxygen plasma process to decompose the Pd salt. Surface activation of the nylon 6,6 substrates prior to solution deposition enhanced Pd salt conversion by producing favorable substrate/analyte binding and increasing surface hydrophillicity, generating more disperse salt deposits.

Three minutes of oxygen plasma exposure at 230W at a pressure of 100mtorr was sufficient to achieve the desired surface properties. The ensuing plasma conversion process was performed for 15 minutes at 230W, in the presence of oxygen plasma at a vacuum pressure of 55-60mtorr. The pressure and power specification of 55mtorr and 230W represent the lowest operable pressure and the highest operable power of the system, improving the rate of conversion by enhancing the generation and the kinetics of the active species. Pd-to-Cl^- ratios of 95% proved that sufficient levels of conversion were attained (at a satisfactory rate). The processes investigated achieved the goal of producing a suitably insoluble form of the base Pd material to allow sealed source integrity to be maintained in the proposed cancer treatment device.

Plasma Decomposition of a Palladium Salt Compound for Use in a Radioactive Implant

by
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DEDICATION

To all those that have motivated me throughout this process and those that have been instrumental in pushing me through; primarily my mother and my fiancée Nailah.

BIOGRAPHY

David was born in High Point, N.C where he and his younger brother, Craig, were raised by his parents, Drs. David and Miriam Wagner. He received his Bachelors in Science from North Carolina State University in Biomedical Engineering. His career interests lie in working with small businesses to bring innovative technologies to market. David is currently engaged to be married to the lovely, Nailah Brown.

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1. Introduction

The American Cancer Society estimates that more than 560,000 Americans will die from cancer in 2009 with approximately 40% of those cases being from prostate, lung, or breast cancer [1]. Implantable low dose radiation sources are one treatment option for some of the less aggressive, clinically organ-confined forms of these cancers. This treatment, known as brachytherapy, traditionally involves direct implantation of radioactive sources into cancerous tissue [2]. Brachytherapy devices currently come as metallic radioactive seeds or point sources (traditionally I-125 or Pd-103) that are implanted as either a collection of free seeds or stranded together to form a linear source.

Recently, a novel linear brachytherapy source in the form of a radioactive source encapsulated in an epoxy-polymer matrix has become available for use in interstitial implants of various treatment sites. This source type employs a design that possesses mitigates many of the common clinical issues associated with seed sources currently on the market. CivaString (Civatech Oncology, 104 TW Alexander Dr. RTP, NC) is a Pd-103 source comprised of a polymer string backbone, providing intrinsic linear properties. Radioactivity is accurately distributed along the length of the device in injection molded micro-wells. The string, possessing gold fiducial markers for radiographic imaging, is encapsulated in a polymer tube and sealed with a medical grade epoxy. Compared to seeds, the polymer composition of the injection molded string reduces inter-source attenuation and provides an ideal format for precise radiation dosing per unit length [3]. The linearity of the device also allows an equivalent dose volume histogram of a collection of seeds to be achieved with ~20% less apparent activity, minimizing the quantity and thus the cost of the most expensive material in the device, Pd-103. The device format is also resistant to *in vivo* migration.

While CivaString possesses a number of intrinsic advantages, the polymeric composition of the device requires that the source material, tetraaminopalladium chloride ($Pd(NH_3)_4Cl_2$), henceforth referred to as Pd salt, be processed in a very specific manner. In their current form, there is no need for the radioactive source material in brachytherapy devices to be in an insoluble form. Hermetically sealed titanium encapsulated seeds do not allow for diffusion of the source material out of the seeds. The polymeric nature of CivaString requires an insoluble form of the source material to ensure source containment *in vivo*. To maintain a so-called "sealed source" requires that the Pd salt be reduced, precipitated, or decomposed to palladium metal. Salt deposits must also remain confined in the wells to ensure that the radioactivity is properly encapsulated. The culmination of these requirements is a unique set of processing constraints required to achieve insolubility, control the palladium distribution, and preserve the thermally sensitive polymer substrate. Plasma is widely used in the semiconductor industry and has some history as a mechanism for decomposing Pd salts into their corresponding metal[a] [4]. Plasma is also clean, highly controllable, and operates at moderate thermal temperatures making it an ideal processing solution. This study investigates the use of plasma to efficiently achieve conversion of a Pd salt to the required specification.

2. Background

2.1. Brachytherapy

Brachytherapy is a procedure involving direct implantation of radioactive sources into the target tissue, thus its application is limited to surgically accessible tumor sites. It has been employed in various anatomical sites; predominantly in the treatment of prostate cancer where transperineal ultrasound-guided permanent prostate brachytherapy has been utilized extensively for the treatment of early stage carcinoma of the prostate gland [2]. However, it is gaining adherence for other indications including lung and breast cancer [5],[6],[7].

Brachytherapy devices generally employ I-125 or Pd-103 contained in encapsulated seeds of various source designs [2]. Pd-103 provides a shorter half-life alternative (17 days) to the more commonly used I-125 (60 days), the merits of which are highly debated. Cesium has gained moderate adoption more recently as an even shorter half-life alternative, with high energy photons (Thomadsen 2008). The low-

[a] Specifically, a Pd precursor was converted into a layer of metallic Pd using hydrogen plasma at 10W power and 0.15mbar pressure for 30 minutes

energy photon emissions (20-30keV) of these isotopes allows for localized radiation, minimizing dose to surrounding normal tissue.

In the prostate, brachytherapy is an attractive treatment option due to reduced patient hospital stay (the procedure is a one day out-patient procedure limiting cost), reduced side effects over radical prostatectomy, and the delivery of much higher biological equivalent doses than IMRT[b] [8],[5]. Further, the clinical (survival) results associated with this technique are on par with both external beam and prostatectomy [8]. However, in the uro-oncology community, the selection of any one of the potentially curative treatments including radical prostatectomy, external beam radiation therapy, and brachytherapy remains controversial [2].

One of primary clinical issues with current brachytherapy devices surrounds how this therapy is administered. The positional accuracy of seeds can be compromised by inexact implantation, migration of seeds, and post-implant edema leading to a number of issues. These errors can result in distortion of the radiation treatment profile, seeds embolising in the lungs, and patient overdosing. To account for variable amounts of patient edema following each procedure pre-plans are often designed to deliver a radiation dose as much as 20% higher than necessary to most of the prostate gland [2].

[b] Permanent seed brachytherapy supports delivery of very high physical doses due to repair of normal tissue sublethal damage

A series of linear source products have been developed that are designed to improve these conditions including Amersham Healthcare's (Nycomed Amersham, United Kingdom) RAPIDstrand™, Advanced Care Pharmacy's (115 Hurley Road, Building 3A, Oxford, CT) Vari-Strand™, and RadioMed Corporation's (RadioMed Corporation, One Industrial Way, Tyngsboro, MA) RadioCoil. The linear format of these devices addressed issues with migration while providing improved post implant dosimetry; however these devices possess a number of shortcomings that have limited their utility. RAPIDstrand™ is comprised of seeds connected in fixed intervals with a bioabsorbable mesh, allowing for improved post implant dosimetry versus standard seeds. The bioabsorbable suture, however, is hygroscopic and can expand when exposed to body fluids, causing the device to get lodged in the needle. Vari-Strand™ is more easily expelled from the needle, but fabrication requires costly and time-consuming post processing to embed seeds into a synthetic bio-absorbable material. RadioCoil, a Pd-103 linear source design consisting of a radioactive coiled wire solves issues with both source dislodgement and time consuming post processing; however, the device fabrication proved to be difficult and very costly.

CivaString offers an amalgamation of many of the positive attributes of these predecessors while maintaining dosimetry parameters comparable to conventional sources. Any variations from the norm are compensated for by the problems solved by its innovative design, including (but not limited to) uniform activity distribution, ease of implantation, no post-processing, and the elimination of seed clumping upon delivery.

2.2. Palladium salt reduction

There are a number of methods of decomposing a Pd salt including chemical, thermal, and, less commonly, plasma. Sodium borohydride ($NaBH_4$) is a known reducing agent for chemically precipitating Pd metal from a Pd salt. $NaBH_4$ is utilized in catalyst recapture mechanisms as a simple and reliable means of reducing thin layers of Pd salt [9]. However, chemical precipitation is an imprecise means of Pd salt decomposition, requiring direct contact between the salt and the reducing agent. Further, in the $NaBH_4$ reduction reaction outgassing causes bubbling and sputtering of the solution. Aluminum is another common reducing agent but the reduction reaction is both imprecise and slow developing. Common limitations of chemical precipitation mechanisms include cleanliness, precision, and the rate of the reaction.

Alternatively, thermal processing allows for controlled, clean batch processing. However thermal decomposition of a tetraaminopalladium chloride compound requires temperatures in excess of 325C. It is reported in the literature that following decomposition of tetraaminopalladium chloride to $Pd(NH_3)_2Cl_2$ during drying, thermal decomposition can occur at 290°C [10]. Nonetheless, many substrates (with the notable exception of silicone) do not possess the requisite thermal resistance to withstand temperatures of 290C, thus limiting the choice of substrate materials. Moreover, thermal decomposition often results in moderate sputtering potentially causing contamination issues.

Plasma is a fairly clean process even though moderate ion etching or sputtering occurs with normal operating conditions [11]. Plasma etching is also robust, offering a high degree of flexibility. The shape and form of the substrate is not limited to a particular conformation, allowing substrates of various styles and dimension to be treated [4]. Coupling the energy into free electrons rather than heavier ions, also limits the heat input even though the particles move very rapidly. The high levels of reactivity generated at low temperature allow for a number of heat sensitive substrates to be used; including polymers, such as nylon 66, and PTFE, as well as glass and aluminum. Plasma processing provides ease of operation and a highly controlled, clean method of Pd decomposition.

2.3. Plasma

To generate a plasma, energy is added to a gas causing ionization. The resulting distinct state of matter comprised of electrons, ions, and active species is a plasma. As the electrons break away from their atoms or molecules, active species are produced that are available to transfer energy to other moieties. The resultant atmosphere is both highly conductive and characterized by high inter-particle activity. Even a partially ionized gas in which as little as 1% of the particles are ionized can express the characteristic electrical conductivity of a plasma [12].

Energy transfer from free electrons to gas molecules can occur by both elastic and inelastic collisions. Inelastic collisions involve a much larger energy transfer and are accompanied by excitation of the gas molecules leading to the generation of a wide range of energetic, metastable species [11]. In excitation an electron jumps to a higher energy level within the atom generating electronically excited species. The ensuing plasma glow is due to optical emission in the ultraviolet or visible regions produced by the electronically excited species. The hue of the glow is characteristic of the composition of the glow discharge gas. Argon plasma produces a bright blue color while air or nitrogen produces a pink color due to excited nitrogen molecules [13]. Dissociation, commonly resulting in the enhancement of chemical reactivity, also occurs with sufficient energy. For example, atomic oxygen is more reactive than an oxygen molecule, oxidizing organic molecules much more readily and converting them to carbon oxides and water vapor. As seen in Fig. 2.1, monoatomic oxygen rapidly converts a cellulose material to carbon dioxide, carbon monoxide and/or water [13].

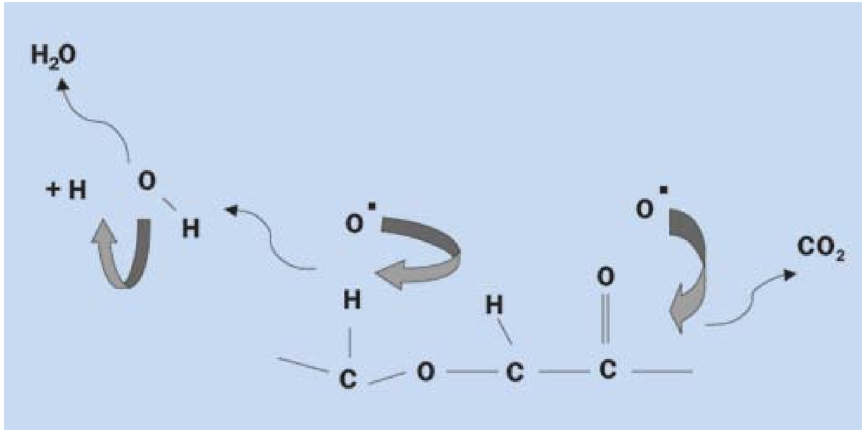

Fig. 2.1. A typical cellulose material can be converted to carbon dioxide, carbon monoxide and water at room temperature, rather than elevated temperatures (e.g. burning) and furthermore the oxidation is more controllable [14].

Ionization may or may not accompany dissociation [13]. With sufficient energy ionization will cascade resulting in an electron avalanche, drastically increasing the plasma density. The plasma ionization is quantified in terms of the number of free electrons per unit volume (plasma (or electron) density) and the proportion of atoms which have lost (or gained) electrons (degree of ionization).

2.4. Plasma etching

Plasma etching is a surface treatment capable of simultaneously producing surface cleaning, chemical functionalization, and surface roughening that affect the surface without altering the bulk material. Surface roughening serves to increase the total material surface area, producing a higher number of potential binding sites. Roughening can increase cell attachment as much as a 30% with surface cleaning and surface activation playing a secondary role [14]. Notably, oxygen plasma tends to produce mild chemical etching resulting in the nano-roughening of polymeric materials (see Fig. 2.2).

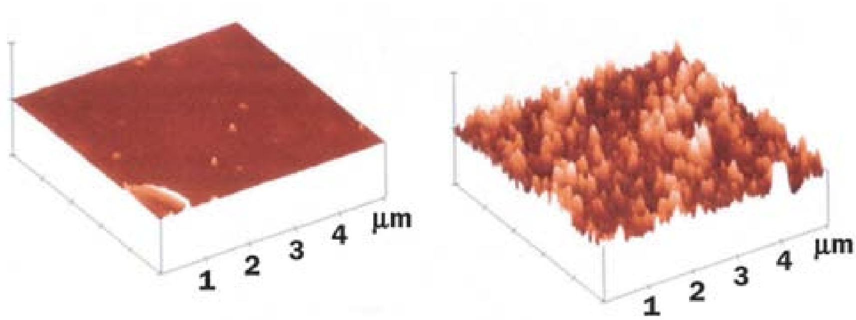

Fig 2.2. Oxygen plasma surface roughening on PET [14].

Surface functionalization involves the binding of functional groups to the exposed surfaces of a material thus altering the surface properties. When PTFE is exposed to reductive plasma, the overall fluorine concentration at the surface is reduced and replaced with functional groups such as hydroxyls that provide anchor points and a more hydrophobic surface [15] , [16]. Reductive plasmas commonly increase surface hydrophobicity, whereas oxidative plasmas produce more hydrophilic surfaces. Oxygen plasma increases surface wettability by removing surface contaminants and increasing the concentration of oxygen- and nitrogen-containing functional groups on the polymer surface [17]. The byproducts of these reactions are volatile compounds that are released as a gas or vapor. The chemical reactions produced in a plasma can be vast and complex. 29 different reactions have been identified in oxygen plasma alone [11]. Plasma can also be applied to indirectly influence a number of other reactions. The use of ions, radicals, and excited species at low temperatures in "plasma-enhanced" reactions lowers the activation energy of chemical reactions improving processing rates and efficiency [18].

Plasma etching is, however, load dependent. In reactive etching, loading effects dictate that etch rate decreases as the etchable surface area is increased [19]. The loading effect is ..

> *"…macroscopic in the sense that the presence of one wafer in a reactor influences the etch rate at a second wafer in another part of the reactor. This implies that transport processes in the plasma are rapid enough that no appreciable concentration gradients can exist for the etchant species within the bulk of the plasma [19]. Microscopic effects have also been observed, wherein the size and density of features being etched can influence the etch rate."*

An adjustment of the etching time must be made to compensate for each load and optimize processing [11]. Loading effects are exacerbated in reactions where the species has a long lifetime in the absence of etchable material but the active etch species reacts rapidly with the material being etched. Here, etching is the primary loss mechanism for the species, consuming large percentages of the etchant species. Thus, the generation of active species must be increased to prevent the average concentration of active species from decreasing as the excess etchable material rapidly consumes the plasma [19].

2.5. *Plasma systems*

In plasma systems the process gas is exposed to an RF potential, traditionally at a few hundred watts in a low pressure environment at 13.56MHz[c]. An oscillating electromagnetic field is generated, ionizing gas molecules by stripping them of electrons, thus initiating the plasma. The electrons in the gas are accelerated by the RF field ionizing the gas directly or indirectly producing secondary electrons [20]. Electric currents that oscillate at RF ionize air to create conductive pathways much more easily than DC signals [21]. In capacitively coupled systems, the RF is applied across two symmetric metal electrodes possessing nearly equivalent powered to grounded surface areas. The electrodes are only separated by a small distance and span nearly the entire dimension of the chamber, allowing for a high degree of plasma confinement, amplifying plasma potential[d]. These systems operate at either atmospheric or vacuum pressure and are commonly used for high resolution etching.

In each cycle of the RF field, the electrons are electrically accelerated up and down in the chamber, sometimes striking both the upper wall of the chamber and the substrate. Electrons absorbed into the chamber walls are fed out to ground and do not alter the electronic state of the system [22]. Ions, which move in the opposite direction of the negatively charged electrons, move relatively little in response to the RF electric

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[c] As mandated by the Federal Communication Commission
[d] The average potential that exists in the space between charged particles

field due to their larger mass. Electrons and positively charged ions collide with neutral gas molecules resulting in avalanche multiplication dramatically increasing the conductivity of the gas due to the enhanced plasma density [11] , [20].

Etching is relatively uniform since substrates are also located directly in the plasma field, and are normal to the gas flow. The energy of the ions incident on the substrate surface can surpass that of the plasma potential. In the presence of high plasma potentials, the energy of these ions can reach several hundred volts, producing high impact surface effects similar to what is achieved in reactive ion etching [19]. Unlike in reactive ion etching, there is a negligible charge imbalance across the substrates created by electron absorption [19]. The plasma, thus, develops only a slightly positive charge due to the higher concentration of positive ions compared to free electrons.

2.5.1. Applications of plasma treatment

In industry, plasma etching has been used predominantly for wafer patterning and processing. In wafer patterning plasma is applied to remove photoresists composed of organic compounds of carbon, hydrogen and oxygen; in a process commonly referred to as plasma ashing. In the absence of inorganic contaminants oxygen plasma removes all the photoresist as volatiles. Plasma has also been employed to create thin metallic films for catalytic reaction. Non-isothermal plasma is applied to convert a metallic precursor or salt into its corresponding metal [4]. Plasma has also been applied as a substrate surface treatment to enhance polymer wettability. In the development of ink pens, plasma treatment is utilized to improve the speed of ink filling and transfer [13].

3. Materials and Methods

3.1. Palladium solution preparation

A non-radioactive tetraaminopalladium chloride solution, generically referred to as Pd salt solution herein, was utilized for all testing. Precise volumes of Pd salt (and ultimately radioactivity when Pd-103 is used) were deposited because the Pd ion is molecularly dispersed in the Pd salt solution. The Pd salt solution was developed along with a modified form of the Pd salt solution with enhanced dispersive properties. The Pd salt solution was prepared from a palladium chloride solute (Fisher Scientific). A heated ammonium hydroxide (NH_4OH) solvent was used to bring the palladium chloride into solution [23]. The proper ratio of palladium chloride to NH_4OH was determined based on the desired Pd salt concentration. The solution was filtered to remove any particulate.

The solubility limit of the Pd salt is ~80-100 mg/ml and thus concentrations of 14, 28, and 56 mg/ml of Pd salt solution were developed. In the modified form of the Pd salt, the ratio of the water to the ammonia in the NH_4OH solvent was reduced to alter the evaporation properties of the solution. Ammonia keeps pH of the solution basic, preventing the Pd from precipitating out as one of a couple of compounds. The solution was filtered to remove any particulates.

3.2. Substrates

Nylon and silicone substrates in the form of planar sheets and injection molded strings were investigated as supports. Initial macroscopic tests were performed on flat sheets followed by experiments on injection molded strings of the same dimension as the final device.

In sheet testing, Pd salt solution was deposited and processed on nylon sheets (KNF Clean Room Products Corporation). Experiments were conducted with both nylon 6 and nylon 6,6 (which possesses medical grade qualities). The sheet dimensions were only constrained such that they allowed space for several deposits of the Pd salt solution. Both nylon and silicone were investigated in the string format depicted in Fig. 3.1. The nylon 6,6 utilized in this study was injection molded (Medical Murray) with 1.5mm x 0.3mm x 0.3mm microwells along its length. Twenty five of these wells were spaced approximately 1.675mm apart (center-to-center spacing).

Table 3.1. The substrates that were investigated and the form in which they were utilized.

Substrates Investigated	
Substrate	Conformation
Nylon	Sheet
Nylon 6	Sheet
Nylon 6,6	Sheet
Silicone	String
Nylon 6	String
Nylon 6,6	String

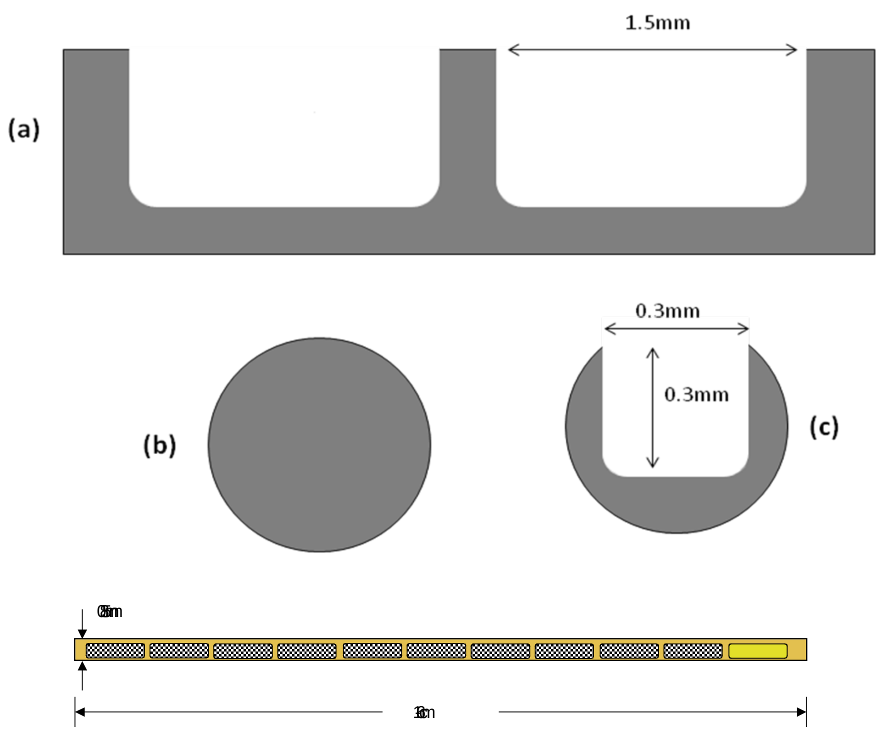

Fig. 3.1. Graphic detailing the structure/conformation of the nylon string. (a) provides a sectioned side view (longitudinal cut) of a couple of wells, (b) provides the general structure in the portion without wells, and (c) provides a sectioned view from a lateral cut.

3.3. Substrate modification

3.3.1. Substrate pre-treatment by RF plasma

RF plasma substrate pre-treatment was performed with a capacitively-coupled vacuum plasma system (PE-100 PlasmaEtch, at a resonant frequency of 13.56MHz[e]) utilizing one of two industrial grade feed gases (National Specialty Gases, 99.998% Ar or 99.998 O_2) . The RF power was independent of the plasma process and requires an active matching network to maintain power input. A schematic of the plasma system is shown in Fig. 3.2.

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[e] With the exception of initial proof of principle experiments conducted with an inductively coupled system at North Carolina State University

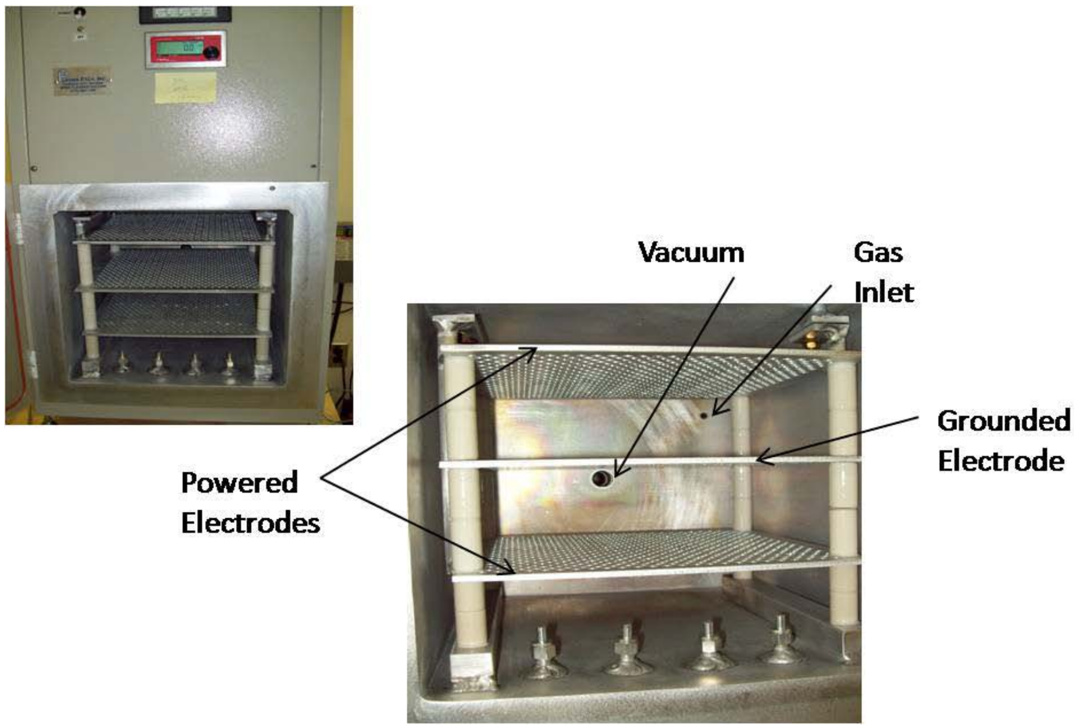

Fig 3.2. Schematic of an RF vacuum plasma treatment system. The parallel plate reactor consists of a grounded plate and a completely symmetric powered plate to which the RF is applied.

The substrates were plasma pre-treated (230 W and 100mtorr) for treatment times ranging from 1-60 min to enhance the dispersion of the Pd salt. The RF plasma in oxygen was used to oxidize the surface. The RF plasma in argon was applied to roughen the substrate surface. Before the substrate pre-treatments, the plasma chamber was evacuated to 60mtorr. Oxygen was then introduced in the chamber and circulated for 30s prior to plasma initiation. Samples were processed on the center of the electrode to avoid field distortions at the electrode boundaries.

3.4. Preparation of Pd salt for conversion

Pd salt deposition was performed with either a microsyringe or micropipette. For high volume deposits (200 - 500nl) a 0.2ul-2ul micropipette (Finnipipette II, Fisherbrand) was used to manually dispense the Pd salt solution on the substrate. The micropipette is accurate to roughly ±5% with decreasing accuracy at the lowest volumes. The microsyringe was applied for low volume deposits (60 - 200nl) (Fig. 3.3b). The microsyringe was guided by a computer controlled microsyringe pump (Micro 4, World Precision Instruments) operated by a custom LabView program (National Instruments) providing additional accuracy. Due to real or perceived benefits the solution on the substrate was dried in the Isotemp oven for at least 15 minutes at ≥100C, generating a yellowish looking dried Pd salt (Fig. 3.3c), possibly, the 2-ammonia form of the starting salt. The sample fabrication is captured in the schematic in Fig. 3.3.

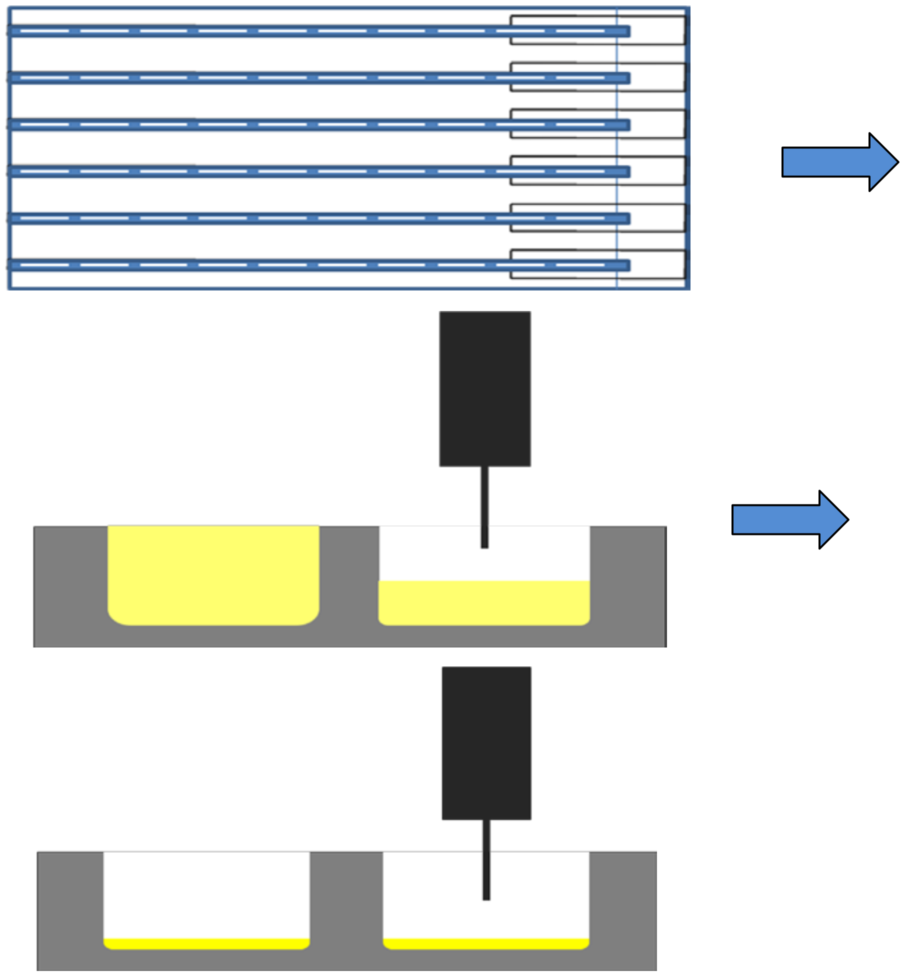

Fig. 3.3. Schematic of sample development. The strings are mounted in a cassette for Pd salt solution deposition (some pre-treated prior to deposition). The solution is deposited and oven dried, prior to plasma treatment.

3.4.1. Plasma conversion of Pd salt

Pd salt decomposition was carried out with RF plasma in oxygen, hydrogen or argon in order to eliminate ammonium or chlorine ions present in the Pd complex [16]. A single sample was processed to normalize chamber loading and ensure sufficient active species. The RF plasma was used as described in Section 3.3.1. The power was varied from 150 to 230 W, the samples were processed from 10-60 min, the gas pressure was adjusted between 55 and 300 mtorr, and the process temperature was varied from 40 to 60 C. All of the processing substrates were non-conducting. The sheets were placed directly on the electrode, while the strings were mounted in an acrylic cassette.

3.5. Processed Pd characterization

3.5.1. Energy-dispersive x-ray spectroscopy (EDS)

The chemical composition of the Pd residue was analyzed post-processing with EDS (Advanced Analysis Technology detector, 4Pi Universal Spectral Engine pulse processor/discriminator, and 4Pi physics model for standardless quantitative analysis) [22]. EDS was also conducted utilizing an instrument at MAGNi Research's instrumentation facility on a few occasions, allowing for the generation of a map of the location of each element by amalgamating a series of line scans. EDS was utilized to determine the surface chemistry composition; specifically the relative signal intensity from Pd and Cl. The presence of Cl^- ions served as evidence of unconverted salt. Organics from the substrate were also registered, but these were ignored. Element mapping was applied to analyze the entire sample and to identify the target areas (the slowest regions to convert) for standard EDS analysis. As a result, the thickest regions of Pd residue were targeted and analyzed. Line scans were also performed on several occasions to verify process uniformity. The line scans which were acquired over 100 points (at a rate of 3 sec/point), included a histogram tallying the cumulative number of counts of each element along the length of the scanned region. For the scans, background was defined as a ratio of ~20:1 Pd-to-Cl^- counts. It is also important to note that in all the analyzed samples, silicon or carbon peaks were present, verifying that analysis was conducted throughout the depth of the sample since the SEM electrons penetrated to the substrate surface.

3.5.1.1. Limitations of EDS

EDS provides, at best, an approximation of the quantity of an element. Thus, the relative concentrations of elements by atomic weight % and atomic % are estimations. To provide more accurate approximations, quantitative data was averaged over each sample. The accuracy limit of the EDS is approximately 2- sigma for standardless analysis[22]. Therefore, in the reported Pd-to-Cl ratios, 3-4% by weight of Cl^- is regarded as background. All error bars and the quoted accuracy of quantitative data is +/- one standard error. Statistical significance is determined using a t-distribution with a 95% confidence level.

Energy from the SEM electrons can also etch away lighter elements further limiting the detection of these elements. As a result, only Cl^- was examined to determine complete conversion. The presence of nitrogen could serve as an indicator of residual ammonia from an unconverted Pd salt compound; however it appears to fall out of the detection limit of the existing system. Nonetheless, the presence of residual Cl^- is a hallmark of incomplete Pd salt conversion and was easily detectable. Therefore the ratio of Pd to Cl signal is a guide to development. Further, there is evidence that EDS detects the substrate through the sample and thus detects sub-surface Cl signals. With these considerations, the quantitative EDS data should allow for general determinations to be made.

3.5.2. Optical microscope

The dispersion of the Pd salt samples was examined with an optical microscope (Omano OM4713) at a magnification of 10x and 30x. Images were captured with a simple web cam. A graticle was employed to measure the diameter of the dried residue. Micrographs were also used for empirical evaluation.

3.5.3. Scanning electron microscope (SEM)

A scanning electron microscope (Hitachi S-3200N, with a 4Pi Universal Spectral Engine digital imaging system) with a 20kV electron beam energy was utilized to take high magnification images of the surface topography of the processed Pd residue. Samples were not coated preventing the detection of an additional background signal from the coatant.

4. Results and Discussion

In previous testing, plasma treatment proved to be superior to both chemical and thermal methods of Pd salt decomposition. What follows is an assessment of plasma treatment for efficiently converting a Pd salt compound into an insoluble metal. This study is divided into those parameters that affect the processing environment and those that govern the operation of the plasma system.

4.1. Processing environment

The processing environment is defined here as the process gas, processing substrate, and the sample material, Pd salt. The conversion of the Pd salt was measured with EDS. The primary signals monitored in the spectra were Pd and Cl^-. Organics from the polymer were ignored, except to indicate that the electron beam penetrated through the depth of the sample to the substrate surface. Quantitative data was acquired across several regions and averaged over the entire sample surface.

4.1.1. Process gas

Experiments were conducted in the presence of hydrogen, oxygen, and argon plasma to determine the optimal process gas for Pd salt conversion. Argon is a chemically inert, heavier element that produces high impact physical interactions. Hydrogen and oxygen are examples of reactive gases with some history in the decomposition of platinum group metals[f] [4]. The Pd salt conversion results obtained in the presence of each gas are shown in Tables 4.1 and 4.2. Despite some suggestion in the literature that hydrogen plasma was favored for Pd salt decomposition results from

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[f] Both oxygen and hydrogen were used to reduce thin films of Pd salt into metal catalysts

two independent experiments show that a statistically significant increase in highest conversion rate was obtained with oxygen plasma.

Table 4.1. Pd-to-Cl ratio in initial H and O_2 experiments.

Process Gas	**Average Pd% by weight**	**Average Cl% by weight**
Oxygen	93.2 (+/- 3.27)	6.8
Hydrogen	67.68 (+/- 2.76)	32.32

Table 4.2. Pd-to-Cl ratio in initial Ar and O_2 experiments[g].

Process Gas	**Average Pd% by weight**	**Average Cl% by weight**
Oxygen Pre-treatment, Oxygen Process	98.25(+/- 0.13)	1.75
Argon Pre-treatment, Oxygen Process	93.90 (+/- 1.77)	6.10
Argon Pre-treatment, Argon Process	72.89(+/- 3.27)	27.11

Table 4.1 shows that the Pd salt was converted more effectively in the presence of oxygen plasma than hydrogen plasma. Further, the hydrogen plasma exposure time was 3x that of the oxygen plasma. Neither reaction was taken to completion, but the samples processed with hydrogen plasma were considerably less converted. Results indicate that the reactivity of the oxygen plasma is likely the differentiator in the two

[g] Each sample was exposed to 2 min of plasma pre-treatment and 20 min of plasma processing at 230W, 100mtorr

process gases. The hydrogen plasma experiments were operated with lower gas pressure (50 to 75mtorr), which favors greater plasma kinetics in these experiments. Thus the hydrogen plasma should have possessed higher energy species. The power input was 200W for both experiments. The enhanced kinetics of the hydrogen plasma however must be weighed against the fact that oxygen possesses heavier ions, and thus produces greater momentum effects with similar kinetics. Nonetheless, it is apparent that the combined physical and chemical effects of the oxygen plasma decompose the Pd salt more efficiently than the hydrogen plasma.

The effects of the reactive oxygen gas were also compared to argon plasma, a chemically inert gas with heavy ions that produce significant physical bombardment. The results from the experiments with argon plasma are reported in Table 4.2. Oxygen plasma converted the Pd salt more efficiently than argon plasma. The reactivity of the oxygen ion in conjunction with the physical etching seemingly outweighs the enhanced physical etching processes of argon plasma. The conversion mechanism therefore, is more complex than simple physical etching. The oxygen plasma seems to create a non-specific chemical reaction that bolsters the reduction of the Pd salt. The conversion rate trend can be further explained if one assumes that the physical etching of oxygen is sufficient to generate one of a number of physical effects known to catalyze chemical reactions. These processes include creation of surface defects that catalyze chemisorptions or reactions, dissociation of ion reactant molecules, or removal of involatile residues that can otherwise retard etching [19]. Thus oxygen ion bombardment enhances or enables chemical reactions via physical processes such as lattice damage, thermal spikes, and molecular dissociation [19].

Since the reactivity and energy transfer of the ions in a plasma process are dictated in large part by the etchant species, the choice of process gas is a critical determination in a plasma process. The oxygen gas seems to present the optimal balance of physical and chemical effects for the existing process.

4.1.2. Processing substrate

The optimal substrate provides a favorable interface for Pd salt conversion, while possessing the proper thermal resistance and mechanical properties for manufacturability. Silicone and nylon were investigated as potential plasma compatible substrates. Following plasma processing and as assessment of each material in the form of the 3-D strings, nylon clearly presented the desired processing efficiency and mechanical properties for device construction and performance. Nylon is easily injection molded into strands and is a harder material than silicone. Further, the surface properties of nylon are easily modified with plasma treatment whereas silicone is unaffected (or only slightly affected) by oxygen plasma (Ghandi 1983). Substrate modification allows the surface properties of the substrate to be chemically and physically tailored to increase the rate of Pd salt conversion – a critical factor since empirical evaluation revealed inhibited dispersion on unmodified substrates, slowing conversion. Dense accumulations of salt residue formed on virgin nylon, making it necessary to increase surface energy to create a more disperse salt residue that is more accessible to the plasma. Following surface modification (described in detail in subsequent sections) silicone and nylon showed comparable process efficiency results (Table 4.3).

Table 4.3. Pd-to-Cl ratio in substrate selection experiments with 20 minutes of plasma processing**.**

Substrate[h]	**Average Pd% by weight**	**Average Cl% by weight**
Silicone	98.32(+/- 1.29)	1.68
Nylon	98.25 (+/- 0.13)	1.75

As indicated in the literature, the shape and form of the substrate had little effect on the processing outcome. The results on the planar substrates (not shown here) proved reasonably consistent with what was realized in the 3-D injection molded strings where the wells were relatively shallow (approximately 0.3mm deep). This provided confidence that the results on the sheets translate to the final string devices.

4.1.3. Pd salt morphology

The effective density of the converted Pd metal residue is significantly lower than solid, sintered metal. Initially the dried crystals are highly dendritic and possess significant amounts of trapped water. When the salt is decomposed, the Pd grains

[h] Substrates underwent a surface modification regiment that is discussed in detail in section 4.1.3.1.

appear to be sub-micron in size and are loosely held in a spongy matrix. However, the effective density of the salt residue on virgin nylon is apparently high enough that the outermost grains shield some of the inner material from the plasma. Examination of the underside of the salt deposits revealed a central region of unconverted salt surrounded by a halo of converted Pd metal. The lack of conversion was clear under magnification based on the color and structure of the deposit (Fig. 4.1). The unconverted material was both highly crystalline and yellowish in color.

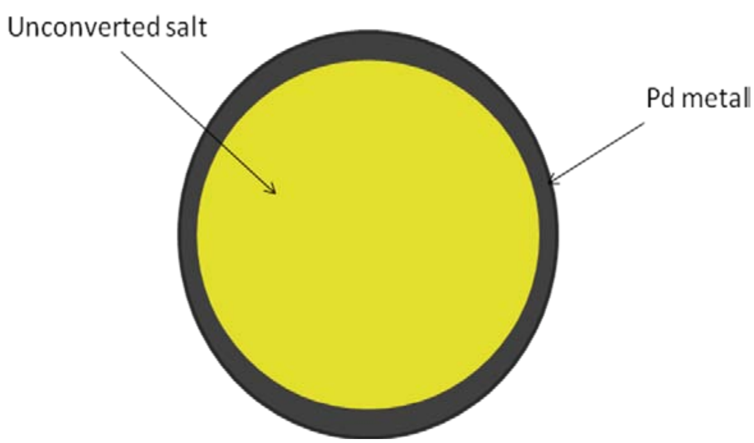


Fig 4.1. Schematic of the underside of a Pd salt deposit following processing on untreated nylon.

The exposed regions of the Pd salt deposits converted first, forming a crust of Pd metal on the outer surface of the residue that hindered conversion of the material underneath. Binding of the Pd salt to the substrate may have also contributed to the formation of the shell by preventing undercutting. The outermost region of the salt deposit is also the most dense region of salt further inhibiting isotropic processing. The salt accumulation is greatest in this region due to the creation of a ring deposit, commonly seen with the evaporation of solutions containing dispersed solids on a surface[24].

Since plasma is a surface treatment that is at least partially dependent on physical etching processes, the density and thickness of the material of interest influences the rate of processing. The thickest regions of salt residue consistently required longer duration plasmas to completely convert, whereas thin regions approach full conversion much more rapidly. As seen in Fig 4.2, on unconverted samples trace amounts of chlorine were visible on the thickest regions of the residue. The highest concentration of unconverted salt predictably appears in the thickest, most dense regions of the residue. Thus, the dispersion of the Pd salt samples is positively correlated with the rate of processing.

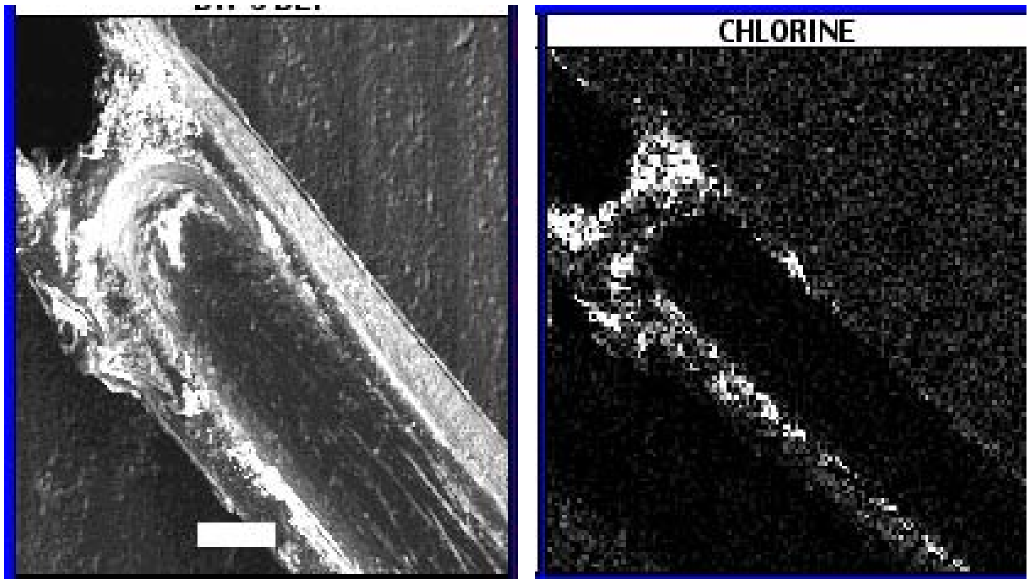


Fig. 4.2. The two images show the Pd residue (L) and the element map of the residual chlorine (characteristic of unconverted material). The white speckle in the chlorine image indicates the presence of Cl^- on the sample. Chlorine is visible along the rim of the well, consistent with the location of the thickest regions of the Pd salt.

To improve process efficiency it was necessary to create a more disperse salt morphology that was more accessible to the plasma. Increasing sample dispersion also minimized the volume dependency of the plasma Pd conversion to the extent that with representative volumes of Pd salt (≥ 9µg of dried Pd salt) conversion was not severely inhibited (see Fig. 4.3). With the appropriate pre-treatment the airiness or binding of the sample was altered combating the tendency for increased thickness to suppress processing efficiency. Substrate surface modification proved to be reasonably effective means of producing adequate dispersion.

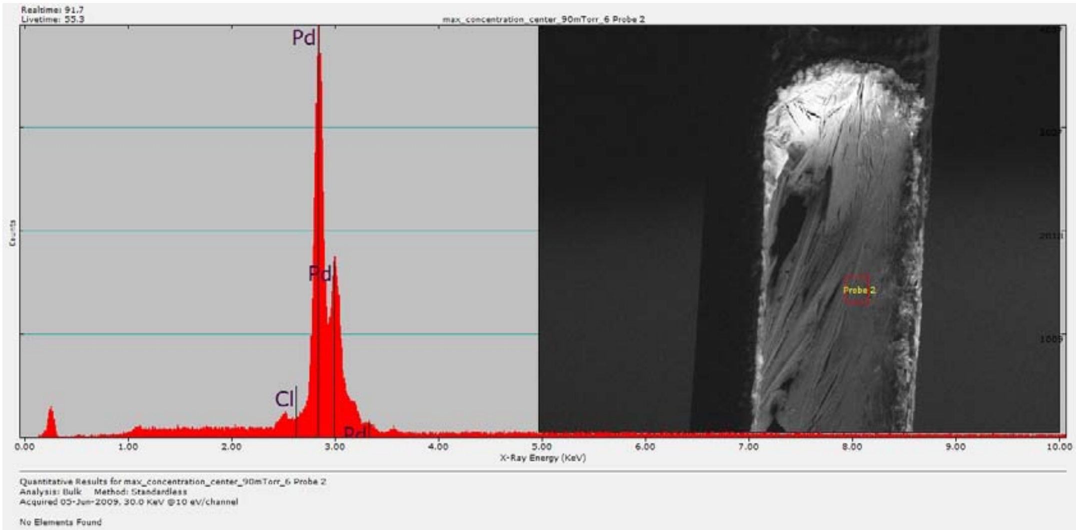


Fig. 4.3. Following pre-treatment Pd salt is completely converted after the nominal O_2 plasma treatment (even with 100nl of 54 mg/ml Pd salt concentration). The increased quantity of residual dried salt does not appear to inhibit the ability of the plasma to process it completely.

Table 4.4. Pd-to-Cl ratio in maximum Pd solution concentration experiments.

Solution Concentration	**Average Pd% by weight**	**Average Cl% by weight**
54mg/ml	94.86(+/- 0.37)	5.14

4.1.3.1. Substrate surface modification

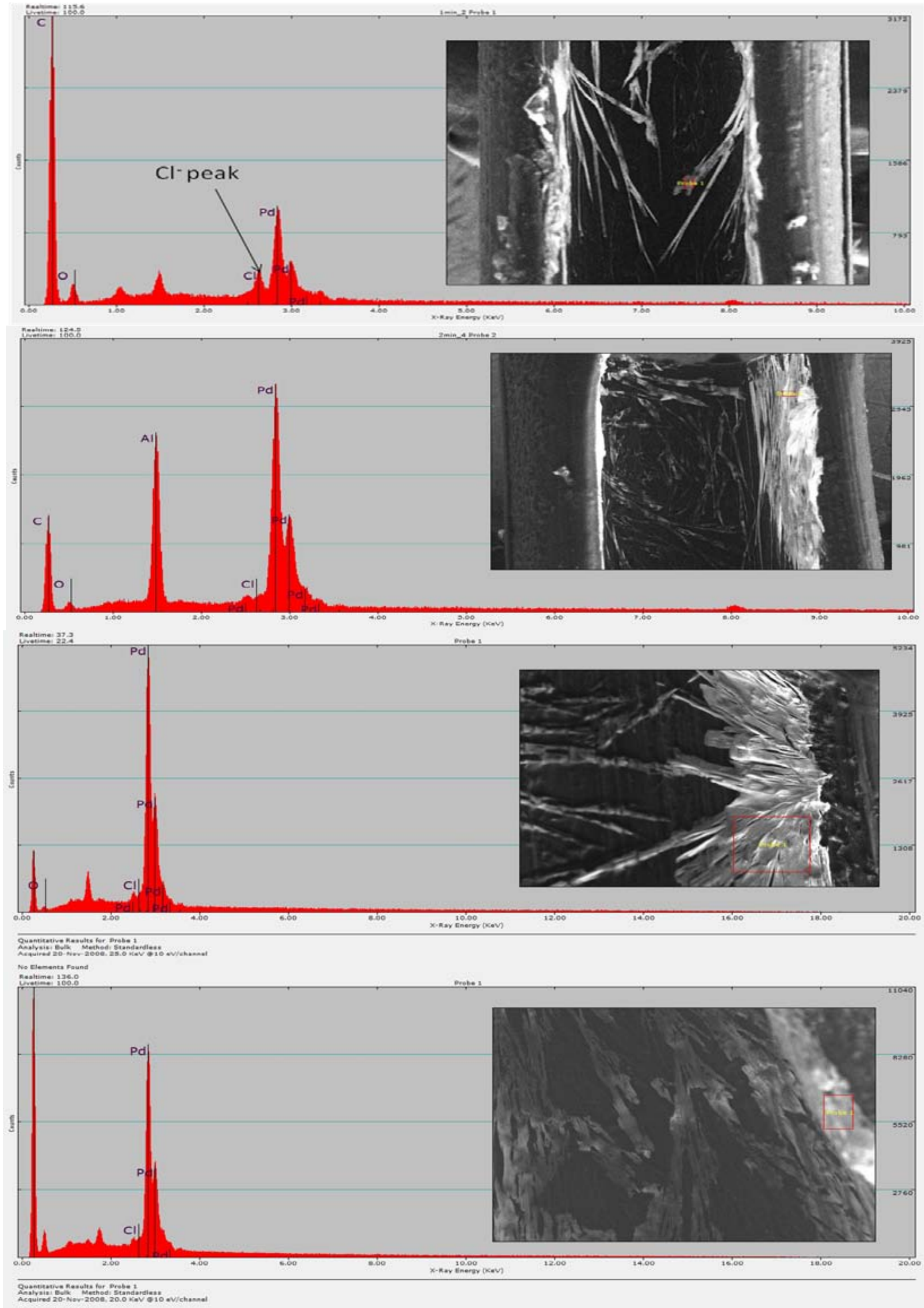
The surface properties of nylon 6,6 were modified to optimize it for catalytic support of Pd salt decomposition. Nylon has a moderate surface free energy (46.5 mN/m, Table 4.5) leading to a relatively dense salt residue and the formation of the aforementioned Pd shell when exposed to plasma. In the absence of substrate modification accumulations of Pd salt also tend to develop in corners and edges, allowing for denser accumulations of salt in these regions. Thus oxygen plasma pre-treatment of the substrate surface was employed to promote surface wetting and adjust the binding and distribution of the Pd salt to increase the etch rate.

Table 4.5. Approximations of surface free energy of several polymers [25], [26].

Polymer	**Solid Surface Free Energy (mN/m)**
PTFE	20
Silicone	20-25
Nylon 6,6	46.5

The process gas and the processing time were investigated for substrate pre-treatment. High power, short exposure plasma processes were more effective with oxygen plasma than argon. Oxygen plasma both cleans the carbon surface and creates oxygen containing functional groups. Though not reactive, argon plasma activates the carbon surface due to etching and removal of surface contaminants [16]. Historically, plasma surface modification of polymers requires short plasma exposure, 3-5 minutes, at low power, 50 watts [13]. However, to generate the desired surface hydrophillicity required additional power input. Nylon 6,6 substrates were plasma processed for 2-5 minutes at 230W. As shown in Fig. 4.4, 2+ minutes of pre-treatment time is necessary to generate complete conversion of the Pd salt with 20 minutes of processing. Only the difference between the untreated surface and the surface pre-treated 2+ minutes is statistically significant; however, it is imperative that conversion be complete and consistent throughout the Pd salt, thus 2+ minutes is required.

Fig. 4.4. The Pd salt on the nylon-6,6 wells pre-treated for 1 min (top) was not fully converted. Results verify that Pd samples reach full conversion with 2, 5, and 60 min (top to bottom) of pre-treatment. 60nl of the Pd was deposited in each well and plasma processed for 20minutes.


Realtime: 115.6
Livetime: 100.0
1min_2 Probe 1
C
O
Cl- peak
Cl
Pd
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X-Ray Energy (KeV)
Realtime: 124.0
Livetime: 100.0
2min_4 Probe 2
Pd
Al
C
O
Cl
Pd
Pd
Pd
Pd
X-Ray Energy (KeV)
Realtime: 37.3
Livetime: 22.4
Probe 1
Pd
Pd
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X-Ray Energy (KeV)
Quantitative Results for Probe 1
Analysis: Bulk Method: Standardless
Acquired 20-Nov-2008, 25.0 KeV @10 eV/channel
No Elements Found
Realtime: 136.0
Livetime: 100.0
Probe 1
Pd
Pd
Cl
Pd
X-Ray Energy (KeV)
Quantitative Results for Probe 1
Analysis: Bulk Method: Standardless
Acquired 20-Nov-2008, 20.0 KeV @10 eV/channel
No Elements Found

Table 4.6. Pd-to-Cl ratio in substrate plasma pre-treatment experiments.

Substrate Plasma Processing Time (min)	Average Pd% by weight	Average Cl% by weight
0	68.31(+/- 6.92)	31.69
1	91.5(+/- 5.69)	8.5
2	98.25(+/- 0.13)	1.75
5	98.8(+/- 0.14)	1.2
60	98.2(+/- 0.14)	1.8

3 minutes of plasma pre-treatment at 230W was prescribed to balance the competing issues of excessive salt dispersion and the need for sufficient plasma stabilization time. Plasma stabilization accounts for potential irregularities (due to the chamber content and variability in the amount of scrubbing necessary to remove residual contaminants evolved from previous treatments) occurring at the onset of the plasma cycle. As shown on the graph in Fig. 4.5, the majority of the surface effects leading to increased dispersion occur within the first few minutes of pre-treatment. If sufficient pre-treatment time is not allowed, chamber scrubbing could occasionally consume a significant portion of the surface activation time. Conversely, there is increased risk of excessive dispersion of the Pd salt when the pre-treatment time exceeds 5 minutes. With extended pre-treatment time, the majority of the salt residue adheres to the sidewalls of the wells leaving less material on the floor, eventually

resulting in the Pd salt cresting out of the wells. As seen in Fig. 4.6 pre-treatment of nylon sheets produces a similar effect. The Pd salt is much more disperse with considerably thinner accumulations distribute over a larger area. The same volume of Pd salt is deposited in both pictures. Pre-treating the entire 5 minutes likely provides a nominal improvement in conversion efficiency, but, without a considerable difference in processing outcome, there is little incentive to extend the overall processing time.

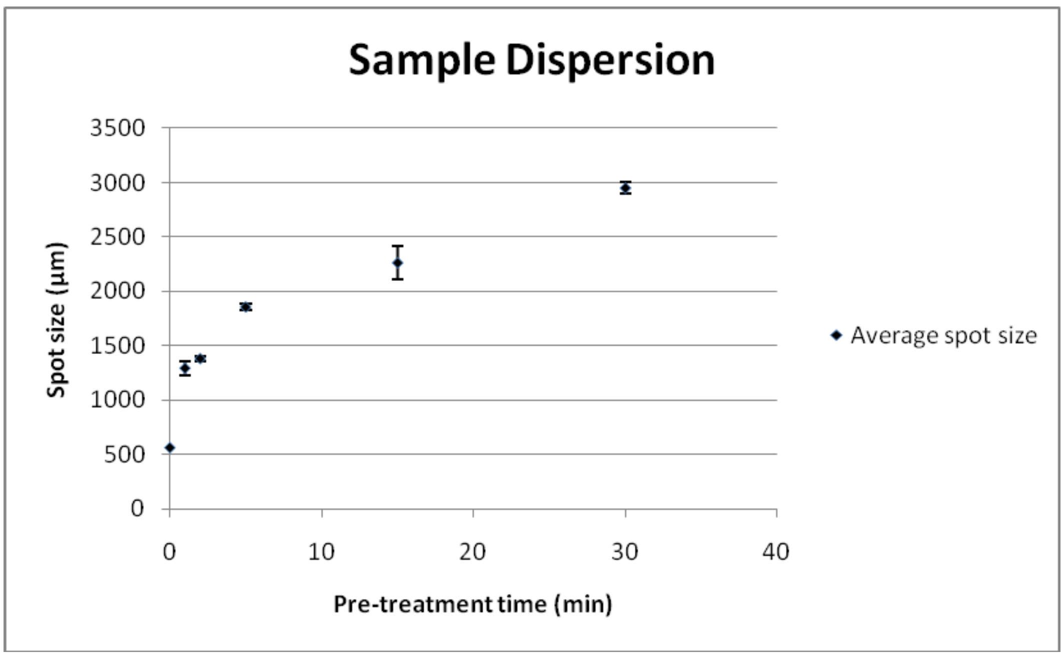

Fig 4.5. Graph of spot size of 100nl of Pd salt on a flat nylon substrate with varying amounts of pre-treatment exposure time.

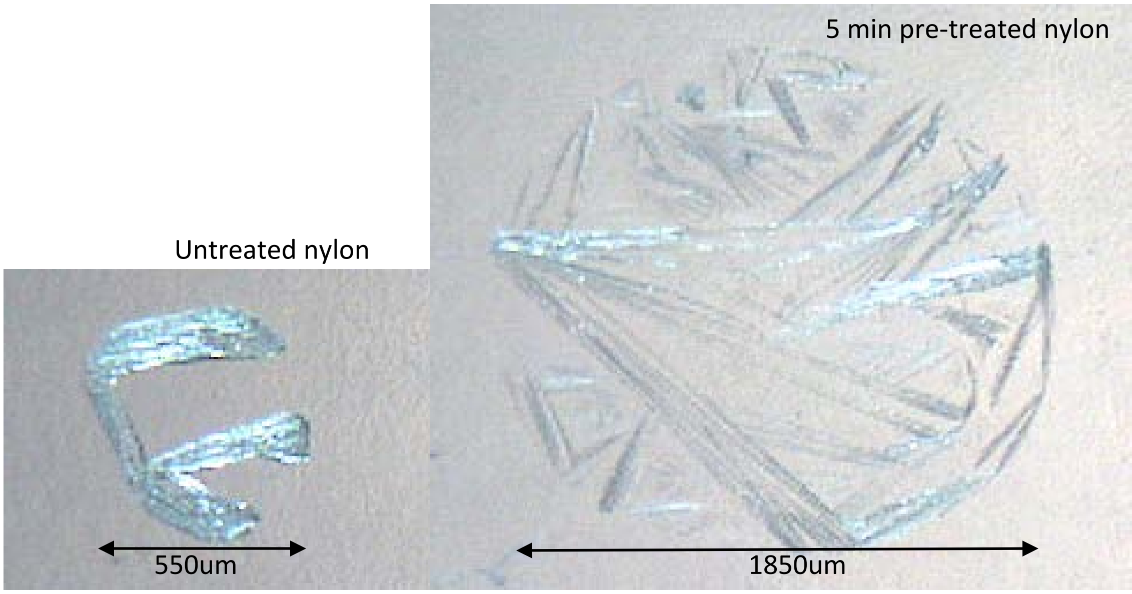

Fig 4.6. Pd salt dispersion on sheets**:** 100nl of 18mg/ml Pd salt solution was deposited on nylon sheets that had received no pretreatment (L) and 5 min (R) of oxygen plasma pre-treatment. Spot size diameter shown is the average diameter measured for each pre-treatment time. The pictures are scaled proportionally.

The nylon substrate surface properties appear to be enhanced by supplementing the kinetic effects of plasma with chemical surface alteration. Reactive plasmas break the C-C and C-H bonds in the polymer chain, creating sites on the substrate surface where active species can react, resulting in both chemical and physical changes to the polymer surface [27]. Oxygen plasma pre-treatment produces a combination of physical and chemical interactions on the nylon surface including substrate surface roughening, surface functionalization, and surface cleaning that improve the distribution of the Pd salt across the substrate. The relative contribution of each of these interactions on the properties of the substrate (and ultimately the conversion efficiency) is not well characterized. However, a brief analysis of each interaction is discussed below.

4.1.3.1.1. Surface roughening

Substrate surface roughening is generated in a plasma via ion bombardment. Fig. 4.7 illustrates the mild chemical etching produced by oxygen plasma on polymers. The difference in surface roughening on the nylon substrates pre-treated for 1 and 2 minutes with oxygen plasma, may partially account for the difference in the Pd conversion efficiency (91.5% vs 98.2% Pd concentration) noted in the previous experiments. The roughened surface both creates a more wettable surface (resulting in a thinner, more disperse salt layer) and potentially produces micro-channels in the substrate. These channels allow for undercutting, theoretically providing more isotropic processing of the Pd salt. Surface roughening also increases the density of nucleation sites. Discrepancies in argon and oxygen plasma processing results (in Table 4.2) could be at least partly attributable to argon pre-treatment augmenting the generation of these nucleation sites. Nucleation sites enhance salt binding, potentially impeding processing if undercutting is limited.

Delamination around the periphery of the converted Pd sponge (noted on some of the planar substrates) provided empirical evidence of undercutting. The degree of undercutting is inversely related to the ion energy. Even in relatively high power, low pressure plasmas (conditions known to increase anisotropy), the relatively low ion energy in plasma etching, compared to reactive ion etching for example, results in less-than-ideal anisotropic processing [19]. Thus the degree of undercutting is determined by the process gas, pressure, power density and frequency.

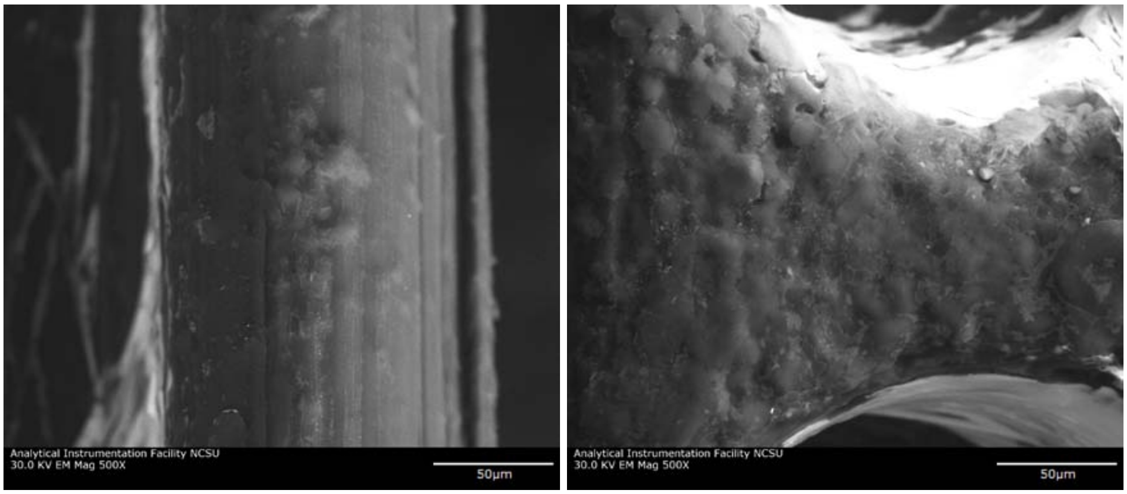

Fig. 4.7. There is a significant difference in the surface modification noted in the nylon substrates pre-treated for 1 (L) and 2 minutes (R).

4.1.3.1.2. Surface functionalization

Comparing argon and oxygen plasma substrate pre-treatments provides a clear indication of the benefits of surface functionalization. Functionalized oxygen pre-treated surfaces produced more complete conversion despite heavier argon ions, presumably producing more pronounced roughening. Fig. 4.8 shows that the dual chemical/physical effects of the oxygen plasma on the nylon substrate produced an improved surface morphology for Pd salt conversion compared to the chemically inert argon plasma. The surface wetting in these experiments appeared comparable; however, oxygen functionalization presumably influences the Pd salt binding or dispersion in a manner that makes it more accessible to the plasma.

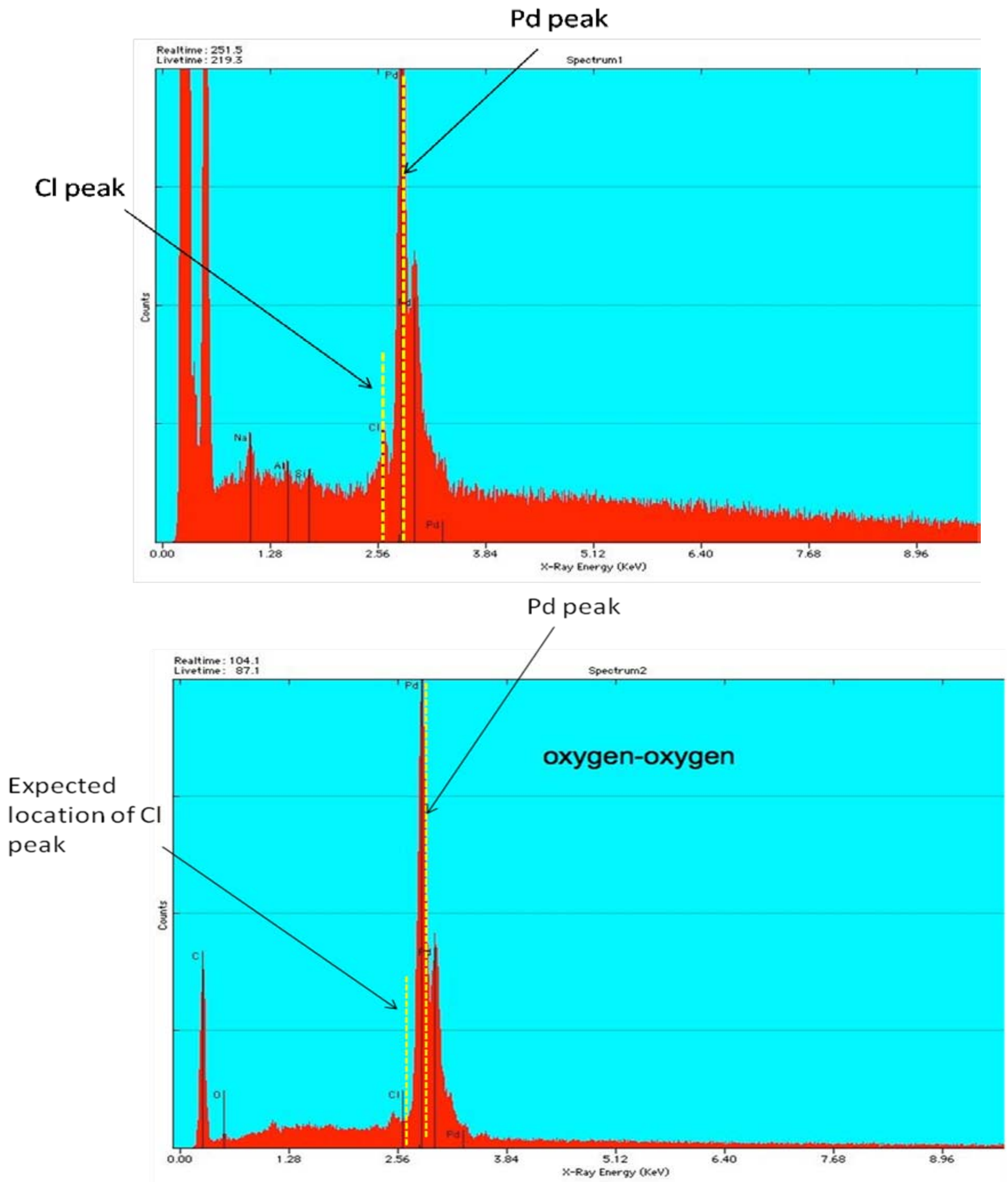

Fig. 4.8. The Pd samples that were O2 plasma processed on the O2 plasma treated nylon (bottom) were completely converted whereas the O2 plasma processed samples on the Ar plasma treated nylon (top) were not; suggesting that the Ar pretreatment was not as effective in altering the Pd salt morphology for conversion.

4.1.3.1.3. Surface cleaning

The substrate/Pd salt interface appears to be affected by more than surface functionalization and surface roughening. Results from both processing on silicone substrates and with argon plasma suggest that conversion efficiency is not solely dependent on sample dispersion. Nylon samples pre-treated with argon plasma remained unconverted despite exhibiting substantial Pd salt dispersion, whereas only marginally disperse samples processed on pre-treated silicone substrates were completely converted. Silicone has a relatively low surface energy (see Table 4.5) and is very resistant to plasma, severely limiting surface functionalization. In the absence of surface functionalization and with minimal expected roughening, the salt dispersion was inhibited on the silicone surface. As evident in Fig. 4.9, despite little, if any, enhancement in dispersion, pre-treatment of the silicone substrate produced surface properties that favored conversion. Samples were fully converted with 20 minutes of oxygen plasma processing. Conversely, the considerably more disperse samples on argon plasma pre-treated surfaces remained largely unconverted (Fig. 4.8). These outcomes run counter to the assumption that a disperse sample is necessary for efficient Pd salt decomposition. The complete conversion of a sample on an unfunctionalized, nano-roughened surface, while conversion on a well-roughened, unfunctionalized argon plasma treated surface was incomplete points to a third variable. Factors such as the surface cleaning of oxygen plasma evidently influence processing efficiency. The surface cleaning action of oxygen plasma, appears to have an appreciable effect on conversion efficiency; likely removing contaminants that negatively impact the binding and/or distribution of the Pd salt. Despite the low surface energy of silicone and the oxygen plasma generating little, if any, functionalization of the silicone surface, the binding of the sample, and possibly its effective density, were altered by the plasma, significantly enhancing conversion efficiency. Ultimately, there is some indication that surface roughening, surface cleaning, and surface functionalization all contribute to the generation of the favored format of the Pd salt residue.

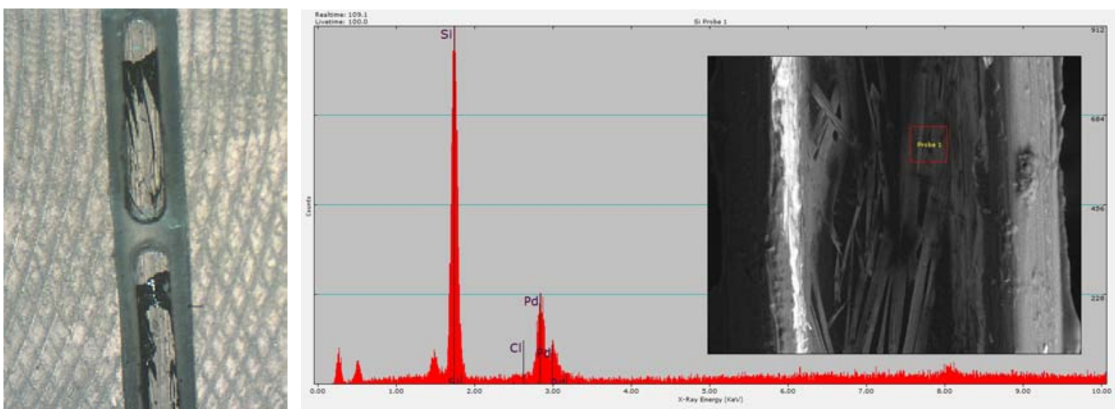

Fig. 4.9. Despite sub-optimal sample dispersion (L) the Pd salt samples were processed after 20 min of oxygen plasma @ 230W on silicone pre-treated for 2 minutes with oxygen plasma (R). These results are comparable to those achieved on pre-treated nylon 6,6.

4.2. Plasma processing parameters

Based on the studies of the Pd salt morphology, process gas, and processing substrate the following nominal processing parameters were established for achieving full conversion:

Table 4.7. Nominal processing parameters.

Substrate Pre-Treatment	
Power (watts)	230
Time (minutes)	2-5
Pressure (mtorr)	100
Temperature (C)	unmonitored
Pd Conversion	
Power (watts)	230
Time (minutes)	20
Pressure (mtorr)	100
Temperature (C)	unmonitored

To improve processing efficiency without altering the process gas and/or substrate material, the plasma processing parameters, including power, pressure, and temperature were modulated. It is somewhat difficult to decouple the individual roles of these parameters because each influences the generation and/or the kinetics of the active species [11], [16]. Nonetheless, these parameters have a pronounced effect on the conversion process. In a plasma, reactions are generally initiated and/or accelerated by energetic ions, thus the volume and kinetics of the active species is critical [19].

4.2.1. Power

The power input influences both the generation and the energy of the active species. Increasing power density bolsters the plasma environment by increasing the mean electron and ion energy as well as the plasma density. As a result, etch rates generally increase monotonically with power (however at a diminishing rate). Compared to the nominal process parameters (20 minutes of exposure at 230W) samples processed with lower power plasma did not convert without a disproportionate increase in the processing time (Fig. 4.10). While statistical significance was not established in the data sets, as seen in Table 4.8, the relationship between power and time was not inversely proportional. A ~25% reduction in power input required a 50% increase in plasma exposure to achieve full conversion.

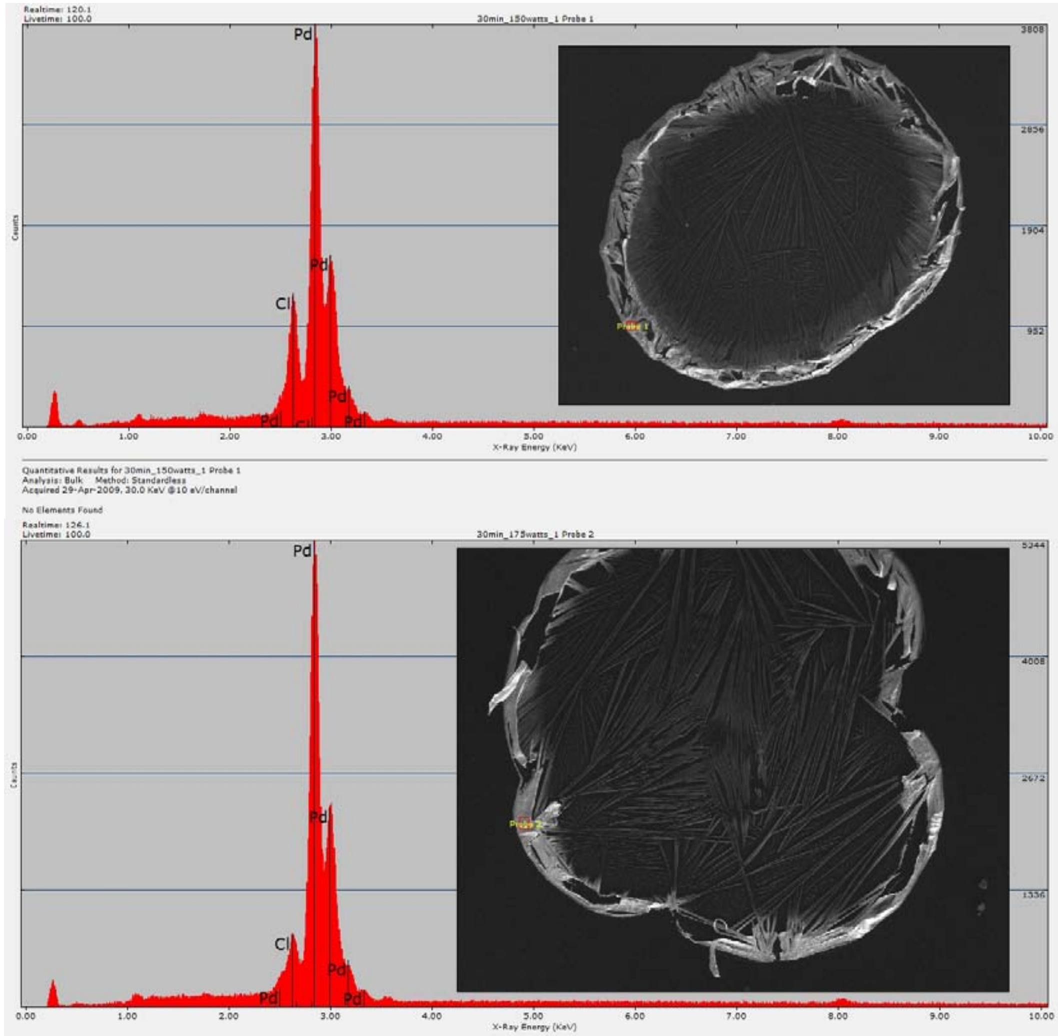

Fig. 4.10. The Pd salt on the nylon-6,6 wells sheets that was processed for 30 min at 150W (top) shows much less complete processing than the samples process at 175W (bottom). Both are less complete than samples processed at 230W.

Table 4.8. Pd-to-Cl ratio in power modulation experiments.

Power (30 min Process)	Average Pd% by weight	Average Cl% by weight
150	92.9(+/- 4.33)	7.1
175	95.5(+/- 1.98)	4.5
230	99.1(+/- 0.05)	0.9

Amplifying power input provides clear advantages, however to ensure a proper transmission of energy, the plasma field must be consistent. Experimentation showed that the electric field was sensitive to a number of factors.

4.2.1.1. Electric field uniformity

A controlled plasma process requires that the uniformity of the plasma field be consistent. The electric field dictates the path of ion/electron movement and thus processing anisotropy and regularity. Perturbations in the electric field affect both the plasma uniformity and directionality. Further, the electric field intensity dictates both the magnitude of ionization and the kinetics of the active specieses [11]. However, the sensitivity of the plasma to both large insulating and conductive elements was profound. Analysis from samples in the vicinity of these elements showed inefficient conversion due to apparent electric field perturbations.

4.2.1.1.1. Dielectric elements

The fixture used to orient the devices in the chamber was composed of acrylic. Acrylic is generally a passive element in the plasma; however, the geometry of the component can produce localized field effects that stifle processing efficiency. Regions of the acrylic that extended above the plane of the substrate, as in the case of the modified cassette design shown in Fig. 4.11, appeared to introduce field effects around the raised surface. Resultantly, plasma activity was weakened in the direct vicinity of the raised surface, in theory due to the field lines bending away from the substrate, toward the raised corners. Analysis from Table 4.9, Fig. 4.12 supports this conclusion; showing a gradient of decreasing conversion as data was sampled closer to the raised surfaces. Data sampled 0 - 1mm displayed a statistically significant difference in processing efficiency compared to data sampled 1 - 2.5mm from the raised edge. Similarly, the difference between data sets sampled 1 - 2.5mm and 2.5 – 4mm from the raised surface is statistically significant.

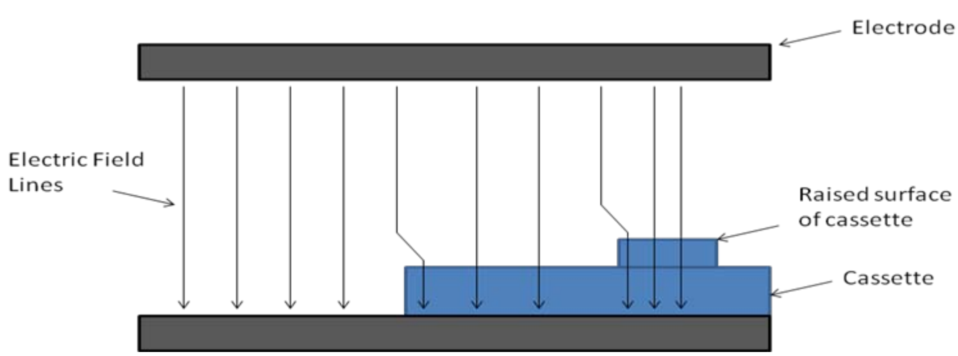

Fig. 4.11. Electric field effects seen around the raised surface of the dielectric cassette used for mounting the strings.

Table 4.9. Pd-to-Cl ratio in experiments testing field distortion near a raised surface[i].

Distance from raised surface	**Average Pd% by weight**	**Average Cl% by weight**
0 – 1mm	66.8 (+/- 1.59)	33.2
1 – 2.5mm	82.57 (+/- 2.06)	25.32
2.5 – 4.0mm	92.71(+/- 0.78)	7.29
4.0 –6.0mm	94.36(+/- 0.20)	5.83
15 – 20mm	94.86(+/- 0.31)	5.14

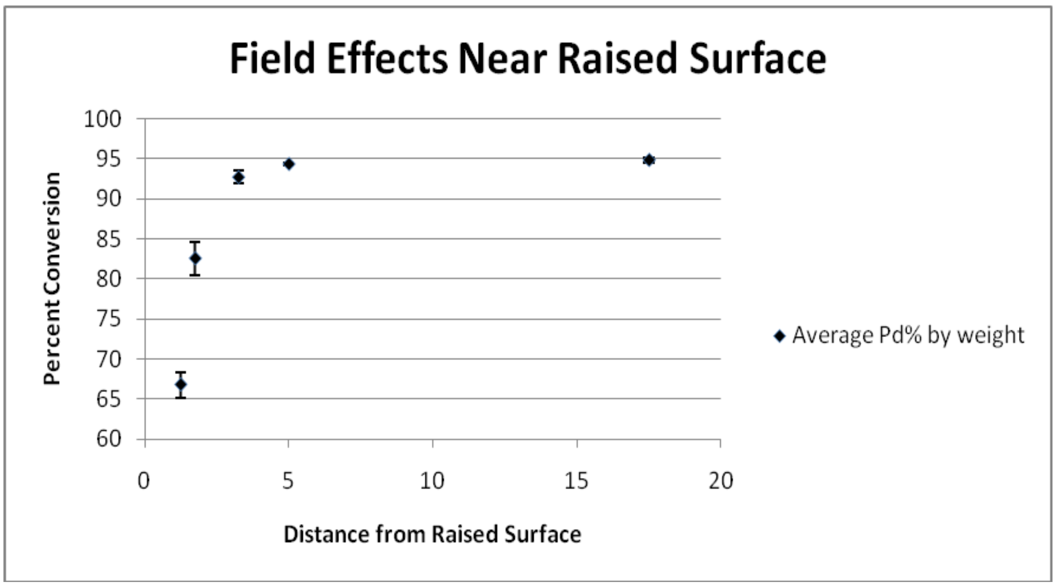

Fig. 4.12. Graph of electric field effects seen around the raised surface of the dielectric cassette used for mounting the strings. As the distance from the raised surface increases, the conversion efficiency improves since the field lines are no longer distorted. The averaged data from each interval is plotted at the center point of the given interval (i.e. the data acquired 0 - 1mm from the raised surface is plotted at 0.5mm).

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[i] 54 mg/ml Pd salt solution was utilized, resulting in slightly reduced conversion efficiency even at the central well

Samples processed in an open glass tray (seen in Fig. 4.13) where the substrate was positioned below the highest plane of the enclosure also showed markedly reduced conversion efficiency. Presumably, field distortion around the glass dielectric affected the samples processed in the tray. There is also evidence from the literature that placing a glass plate on top of the electrode decreased the maximum electric field [28]. The samples remained unconverted even as the processing time was increased 50% above nominal.

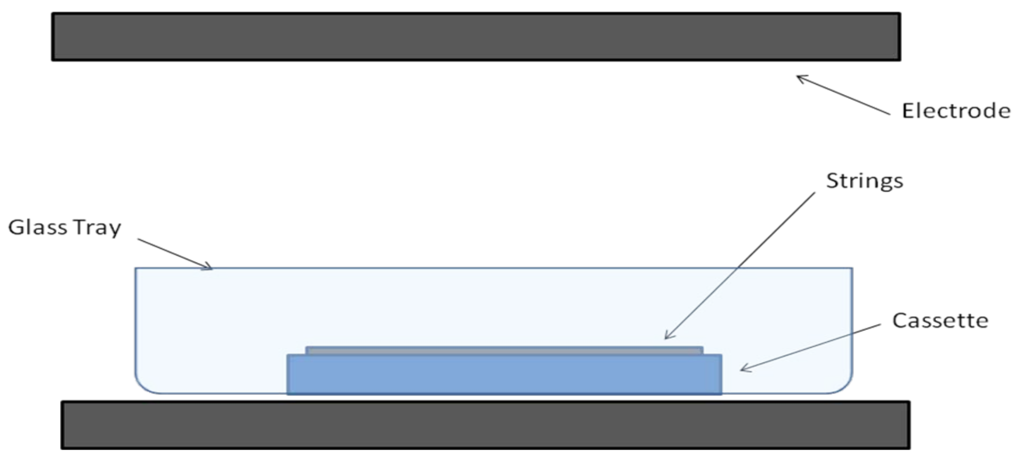


Fig. 4.13. Schematic of the cassette in the glass tray.

4.2.1.1.2. Conductive elements

The presence of large conductive elements in the plasma had similarly deleterious effects on the conversion efficiency of the plasma treatment. Employing an aluminum cassette produced inconsistent and incomplete conversion. The aluminum cassette was in direct contact with aluminum electrode, potentially causing the cassette to act as an extension of the aluminum electrode. Electrical coupling of these components would essentially alter the geometry and surface area of the grounded electrode. In a parallel plate system this results in a non-uniform distribution of the electric field across the composite cassette/electrode. The inconsistent processing results seen in Table 4.10 are in agreement with this theory. Subsections of the untreated nylon samples (generally expected to process slowly) expressed nearly complete conversion (Fig. 4.14). Conversely, efficiency was reduced in several samples where complete conversion was expected. Intra-well and well-to-well non-uniformity was an indication of electric field perturbation despite several regions of the samples converting fully.

Electric field non-uniformities at the edges and corners of the aluminum cassette likely produced a localized amplification in field intensity, while reducing intensity in neighboring regions; analogous to fringing effects that occur at electrode edges. Fringing effects often result in higher etch rates around the periphery of the electrode with a gradual decline towards the central region [29]. These fringing effects can produce non-uniform etching due to localized heating, as well as localized bombardment, by high velocity particles [11]. The etched channels in the aluminum cassette provide a number of sites where localized edge effects could be present. Presumably these localized effects were the source of the inconsistent results.

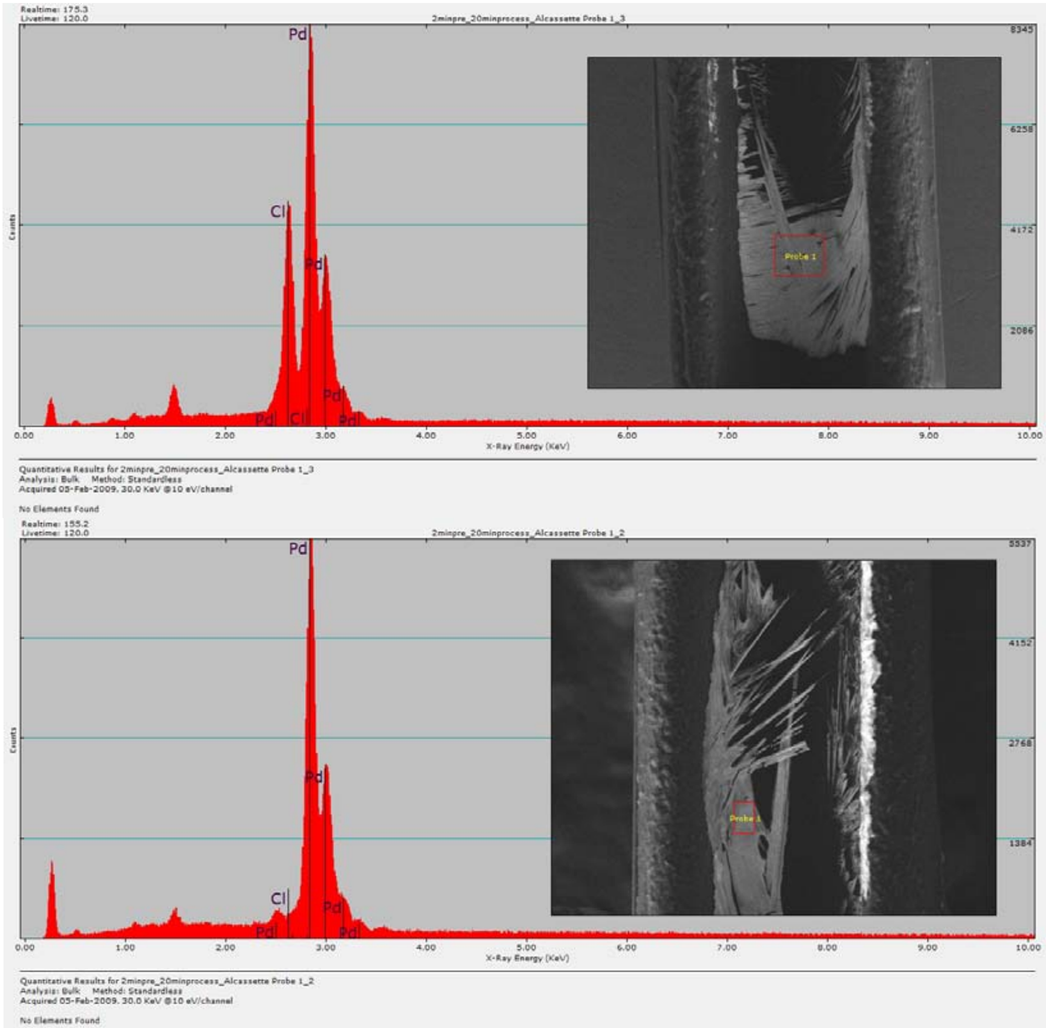


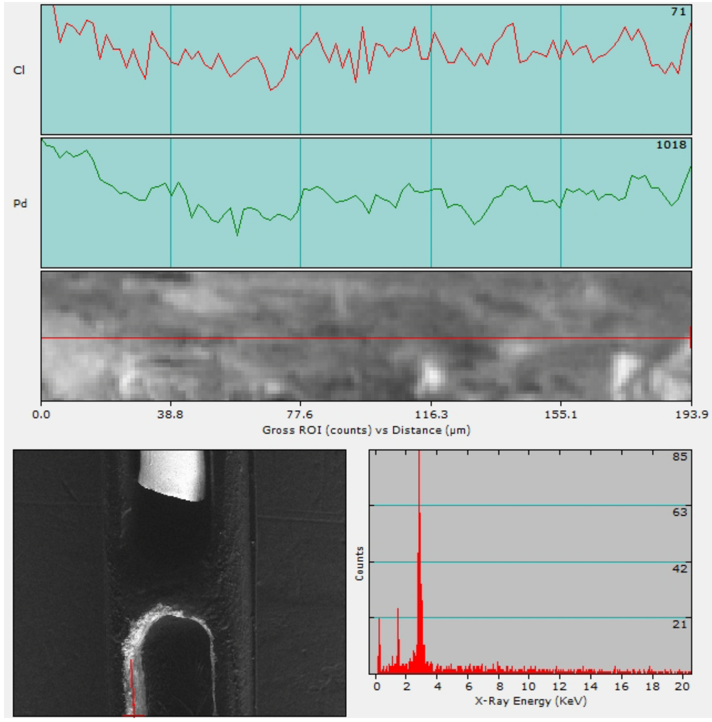
Fig. 4.14. The samples processed for 20min on untreated nylon (top) in the aluminum cassette were not fully converted, however some regions showed more conversion than anticipated. Several regions of the sample which was processed for 20min on nylon pre-treated for 2 min in the aluminum cassette (bottom) was not completely converted as well.

Table 4.10. Pd-to-Cl ratio in experiments testing field distortion due to the aluminum cassette.

Processing Parameters	**Average Pd% by weight**	**Average Cl% by weight**
No pre-treatment, 20 minute process	91.48(+/- 0.65)	8.52
2 min pre-treatment, 20 minute process	87.34(+/- 6.38)	12.66

Processing efficiency in the area surrounding the gold fiducial markers was also investigated; however efficiency did not appear to be inhibited in the neighboring wells. Aside from a single anomalous discovery of a trace amount of Cl^- there was no evidence of localized non-uniformities in the direct vicinity of the gold markers. This discovery was viewed as an anomaly for several reasons. Analysis was conducted in several regions, with several samples possessing gold markers, with no further sign of Cl^-. Additionally several line scans of the regions surrounding the anomalous results (Fig. 4.15) revealed only background levels of Cl^-. It follows that the small volume of gold had no perceptible effect on process efficiency in the wells adjacent to the marker.

Fig. 4.15. Samples processed in the wells adjacent to the gold markers were fully processed. The line scan confirms that throughout the sample the Pd is fully decomposed. The samples are processed for 20min on nylon pre-treated for 2 min.


Cl
71
Pd
1018
0.0
38.8
77.6
116.3
155.1
193.9
Gross ROI (counts) vs Distance (µm)
85
63
42
21
Counts
0 2 4 6 8 10 12 14 16 18 20
X-Ray Energy (KeV)

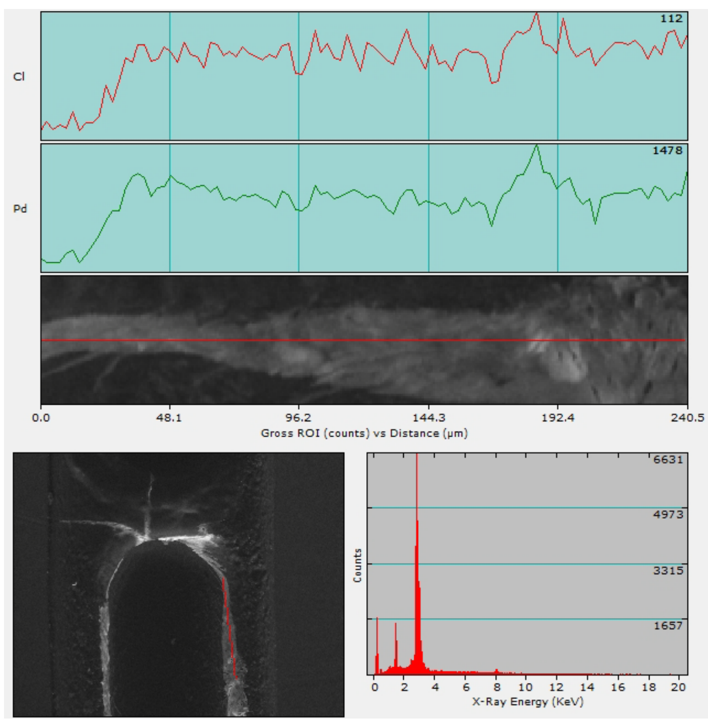

Cl
112
Pd
1478
0.0
48.1
96.2
144.3
192.4
240.5
Gross ROI (counts) vs Distance (µm)
6631
4973
3315
1657
Counts
0 2 4 6 8 10 12 14 16 18 20
X-Ray Energy (KeV)

Table 4.11. Pd-to-Cl ratio in experiments testing field distortion around the gold markers.

Processing Parameters	Average Pd% by weight	Average Cl% by weight
2 min pre-treatment, 20 minute process (well nearest the gold markers)	97.6(+/- 0.50)	2.4

To mitigate issues associated with field effects and maintain uniform processing the use of all ancillary material in the plasma was carefully analyzed. Samples were mounted on an acrylic cassette with the material to be processed offset at least 5mm from all raised surfaces.

4.2.2. Chamber pressure

Chamber pressure influences the kinetics of the reactive species and indirectly affects the supply of active species. Optimizing process pressure requires balancing the competing factors of mean free path and plasma density. Decreasing pressure extends the mean free path enhancing the kinetics of the active species. The energy of the active species is increased as a result of fewer collisions impeding particles accelerated along the field lines [19]. However, this is accompanied by a corresponding reduction in plasma density resulting in less oxygen, and the resultant active species, per unit volume in the plasma.

It was determined that the optimal process pressure was 55-60mTorr. The vacuum pump and the existing mass flow regulator limit the chamber pressure to between 55-300mTorr. As indicated in 4.12, high pressure experiments conducted at 200 and 300mTorr were significantly slower to convert, whereas conversion occurred more rapidly on samples processed at 55 and 70mTorr.

Table 4.12. Pd-to-Cl ratio in chamber pressure experiments.

Chamber Pressure (mtorr)[j]	**Average Pd% by weight**	**Average Cl% by weight**
55 (10min process)	91.4(+/- 2.71)	8.6
70 (11min process)	88.3(+/- 10.28)	11.7
70 (15 min process)	98.5(+/- 0.15)	1.5
70	98.8(+/- 0.19)	1.2
100	98.2(+/- 0.13)	1.8
200	81.8(+/- 15.39)	18.2
300	56.4(+/- 5.49)[k]	43.6

In plasma Pd conversion, increased particle velocity is critical. Samples processed for 10 minutes @ 55mtorr are mostly converted – even more so than those processed 10% longer at 70mtorr (Table 4.12) due to enhanced kinetics. At low pressure, energetic species angled normal to the target surface impact the bonds stabilizing the Pd salt with greater momentum producing greater sample penetration and enabling the active species to burrow through thicker accumulations of Pd salt. Experiments conducted at

[j] 20 min plasma processing time unless otherwise specified
[k] The reported error is calculated as three standard deviations there is a single 300mtorr measurement

300mtorr, while maximizing plasma density, lack these high energy particles and thus slow conversion. Processing at 200mtorr improved the rate of conversion compared to the samples processed 300mtorr, but remained less converted than samples processed at low pressure. The difference in mean conversion efficiency between the low pressure samples and the high pressure samples was not statistically significant. A broad range of conversion levels were produced across the samples. In high pressure environments reduced kinetics restrict plasma from etching through some of the densest regions of the sample. Thus at extremes there is a wide variance in the level of conversion. This increases standard deviation making statistical significance difficult to achieve.

These results indicate that the Pd conversion is likely a kinetically dominated reaction. Increasing plasma density causes further saturation of the Pd salt with low energy species. The resultant reduction in mean free path compromises the kinetic effects of the reactive species in the face of high levels of inter-particle collision. With sufficient plasma density to fully interact with the sample, reducing pressure provides a more favorable environment for Pd salt conversion. System limitations restrict this value to 55-60mtorr.

4.2.2.1. Gas flow

Pressure is affected by outgassing of the etchable material in the chamber. Thus monitoring the pressure in isolation can be misleading if the chamber load is altered. Sufficient gas flow is critical to ensuring a sufficient supply of reactive gas. However, flow rate typically has only a small influence on etch rate. Flow rate is most relevant at extremes where the flow rate either limits the available supply of reactant or flow is so high that convection becomes a major pathway for loss of active species [19]. As such, the volume of reactant in the chamber at any given time is dependent on the balance between generation and loss of active species in the plasma (i.e. by convective flow) [19]. The rate of loss in the chamber is inversely proportional to the residence time t_r, given by:

$$t_r = Vp/760F$$

p= pressure in torr and V and F are the plasma volume and flow rate. Residence time is a measure of mean time a molecule spends in the plasma. Taking the idealized example where the chamber pressure is low (.06Torr), the associated flow rate is 3cc/min. Inputting the chamber volume gives the following equation,

$$t_r = [(28317cc)(.06)]/[760(3cc/min)]$$

$$t_r = (1699cc)/(2280cc/min) = \sim 0.745min \text{ or } 45 \text{ seconds}$$

Therefore, for the optimized processing parameters, the dwell time (the mean time a molecule spends in the plasma) is approximately 45 seconds.

In a commercial operation where loads, and thus outgassing, vary, the gas flow is critical. If the load is altered the mean free path and plasma density must be rebalanced to find a new optimum. With relatively consistent (and minimal) loading, flow rate was not independently tracked for each experiment since minimal outgasing was produced and chamber pressure was dominated by the oxygen input. Thus the flow rate is relevant because it is the primary means of modulating the chamber pressure.

4.2.3. Temperature

Temperature is especially difficult to quantify in a plasma, complicating attempts to modulate the plasma temperature in a controlled fashion. As previously noted, plasmas are characterized by the absence of thermal equilibrium between gas molecules and electrons. A plasma essentially consists of a collection of highly reactive particles in a relatively temperate environment [11]. Due to the lack of heat transmission in a vacuum, thermal temperatures are generally between 50-100C, despite electron temperatures reaching 10,000K.

In reactive etching, temperature influences etch rate primarily through its effect on the rates of chemical reactions. Generally the relationship between temperature and etch rate is generally subject to Arrhenius dependence. The etch rate is thus defined by the following equation:

$$\text{Etch rate} \sim \exp(-Q/kT),$$

where Q is activation energy (material dependant), T is absolute temperature of substrate, and k is Boltzman constant [19]. Consequently, increasing temperature augments etch rate. As evidence, conversion efficiency was augmented in preliminary tests[I] where electrode temperatures were excess of 130C. Here the samples processed considerably faster (in less than 1/3 of the time) than those samples where the electrode temperature was ~60C. The effects of both thermal and plasma temperature are discussed here.

4.2.3.1. Plasma (electron) temperature

The plasma temperature has a direct bearing on the degree of ionization and thus the processing efficiency of the plasma. Increased temperature results in increased ionization, producing a plasma with a more dense concentration of reactive species. However, the most direct means of adjusting the plasma temperature in the current system is by adjusting the power input and/or chamber pressure. By increasing the power input and/or decreasing the chamber pressure the average kinetic energy of the particles (or temperature) can be increased. However, with electron temperatures in excess of 10,000K, it is difficult to measure and modulate the plasma temperature. The only reasonably measurable parameter is the thermal temperature of the electrode and the heat it conducts into the system.

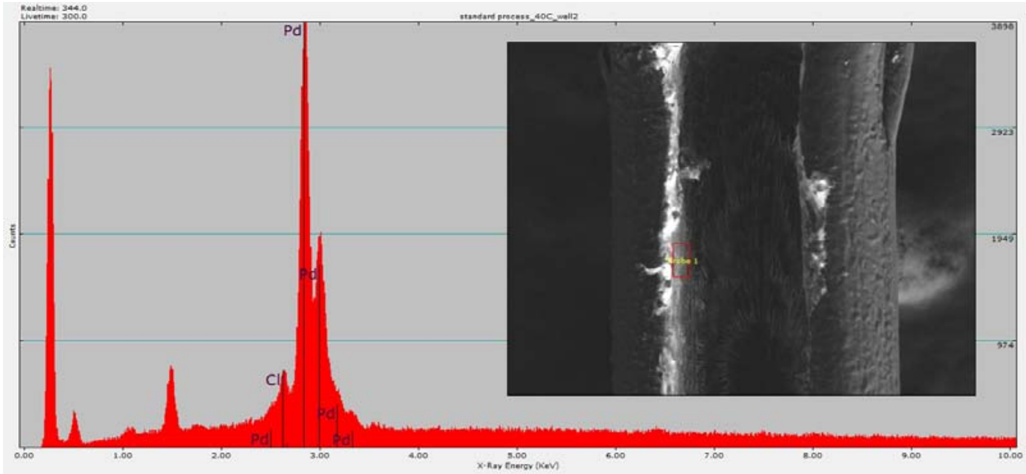
4.2.3.2. Chamber (thermal) temperature

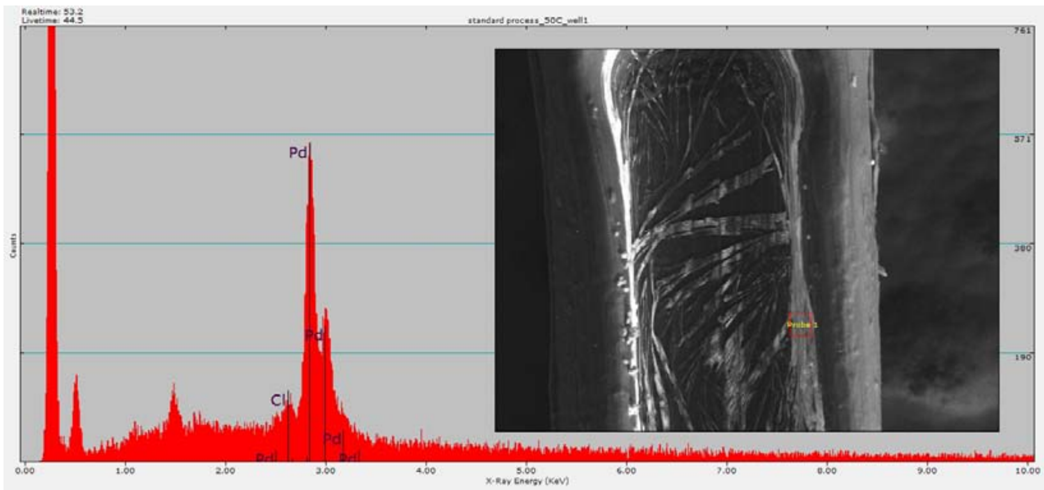
In the wafer industry, plasma-induced heating is a major source of temperature rise in thermally isolated wafers. Thus, controlling substrate temperature is usually

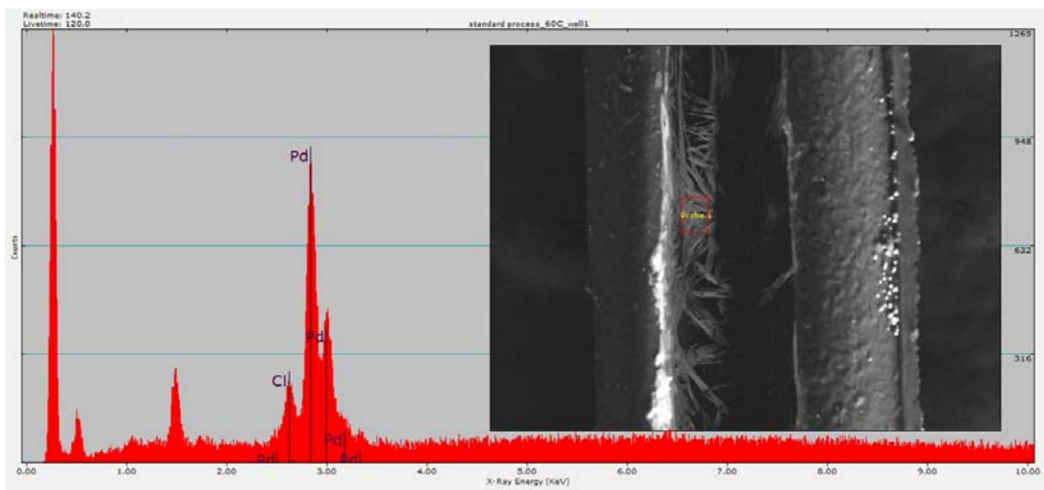
[I] Tests were conducted in an inductively coupled plasma system where there was a direct measure of electrode temperature desirable for obtaining uniform and reproducible etch rates [19]. To stabilize the heat input from the electrodes during a plasma, fluid was circulated around the electrodes at temperatures ranging from 40-60C [m]. The electrode temperature was brought into equilibrium with the circulating fluid, thus controlling thermal input into the chamber. Results suggested that stabilizing the electrode temperature reduced the conversion efficiency compared to the samples processed with uncontrolled temperature (Fig. 4.16). Presumably the circulating fluid served as a heat sink, reducing heat-induced catalysis. At 60C this is not surprising since essentially all the applied power is dissipated as heat [19]. There is often an appreciable amount of heat generated from the exothermic reactions that produce etching. As previously noted the thermal temperature in a plasma is also routinely between 50-100C. Thus, to avoid inhibiting conversion efficiency, the circulating fluid would likely have to be much warmer then what can be achieved in the experimental system.

[m] The temperature bath is limited to circulating fluid of up to 80C

Fig. 4.16. The Pd salt samples processed for 20 min on the nylon-6,6 pre-treated for 2min at 40C, 50C, and 60C (top-to-bottom) did not reach completion.


Realtime: 344.0
Livetime: 300.0
standard process_40C_well2
Pd
Pd
Cl
Pd
Pd
Pd
3898
2923
1949
974
Counts
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00
X-Ray Energy (KeV)


Realtime: 53.2
Livetime: 44.5
standard process_50C_well1
Pd
Pd
Cl
Pd
Pd
Pd
761
571
380
190
Counts
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00
X-Ray Energy (KeV)


Realtime: 140.2
Livetime: 120.0
standard process_60C_well1
Pd
Pd
Cl
Pd
Pd
Pd
1265
948
632
316
Counts
0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00
X-Ray Energy (KeV)

Changes in thermal (electrode) temperature are probably not a dominant factor in the degree of ionization within the chamber. Considering the power output in the chamber the average kinetic energy of the particles is probably great enough that the reductive effect of cooling the electrodes is negligible. The electrode temperature likely had a much more prominent effect on the Pd sample itself; disrupting the bonds of the Pd salt to allow for more efficient conversion. However, it is difficult to draw definitive conclusions from these results. A more extensive study is necessary to properly establish the relationship between temperature and the conversion rate of the Pd salt. However, the material properties of the polymeric substrate (i.e. the thermal tolerance of the nylon) limit the potential gains of increased temperature thus limiting the usefulness of continued investigation.

5. Conclusion

A robust, commercially acceptable manufacturing process has been developed to convert a Pd salt into an insoluble metal. This process involves the application of oxygen plasma to both the substrate and the Pd salt. Oxygen plasma produces a complex set of chemical and physical effects including surface cleaning, surface functionalization, and surface roughening on both the substrate surface (during pre-treatment) and the Pd salt (during plasma conversion).

The physical conformation of the Pd salt is critical to conversion efficiency. The boundary between the Pd salt and the processing substrate dictates salt dispersion, and thus the accessibility of the plasma to the salt. To optimize the physical conformation of the Pd salt, pre-treatment of the nylon was employed prior to plasma treatment. Plasma pre-treatment enhanced surface hydrophillicity such that the Pd solution wet the polymer surface generating a more disperse salt residue. The improved surface hydrophillicity is the byproduct of the both surface roughening, surface cleaning, and the addition of functional groups such as hydroxyls on the substrate surface. The nano-roughening of the oxygen plasma treatment also created microchannels on the substrate surface that theoretically allowed the plasma to undercut the Pd salt samples and simultaneously process the residue from both the top and underside. The cumulative result of the plasma treatment was a modification of the nylon substrate surface properties such that the morphology of the deposited Pd salt is enhanced for plasma treatment.

To further enhance processing efficiency the pressure, power, and temperature were modulated to bolster both the plasma kinetics and plasma density. Enhancing plasma kinetics augments both plasma generation and ion assisted etching. An optimum power input of 230W and an optimum chamber pressure of 55-60mtorr were established. These parameters represent the lowest operable chamber pressure and the highest operable power input, thus the conversion efficiency of the plasma was augmented by maximizing the kinetics of the active species. The physical bombardment produced by these energetic particles compliments the intrinsic chemical effects of the reactive oxygen by producing greater sample penetration and reducing the activation energy to initiate the decomposition reaction. However, complicating the transmission of this plasma energy was the sensitivity of the plasma process to electric field effects. Both dielectrics extending above the plane of the substrate and conductors with large surface areas negatively impacted conversion efficiency. Materials choices and the geometry of the fixtures that utilized in the plasma were thus limited to accommodate potential field effects. Temperature experiments yielded somewhat nebulous results – the circulation fluid appeared to serve as a heat sink reducing conversion efficiency. As such thermal input was left uncontrolled.

6. Future Recommendations

Although this work sufficiently optimized the plasma parameters for conversion of the Pd salt material, further investigation is necessary for utilization of this methodology in a commercial setting. Additional research is required to fully define the relationship between the relevant processing parameters and conversion efficiency. While the plasma temperature has likely been maximized, by operating at the highest operable power and lower pressure, an accurate measure of the thermal temperature and its effects on the Pd salt conversion would be instructive. There is also some question as to which bonds the oxygen plasma is breaking and what volatiles are being outgassed. To truly optimize the processing efficiency requires a more complete understanding of the Pd salt chemistry and the reactions initiated by the oxygen plasma.

An end-point detection mechanism could provide insight in to how the reactions progresses. The theory is that the vast majority of the activity occurs in the first minute, hence the darkening of the Pd salt almost immediately upon exposure to the plasma. Adapting a spectrometry system to this application could verify these assumptions. Further consideration should also be given to the loading effect. The prescribed plasma process parameters are defined based on a narrow range of loads. To develop a scalable process, plasma processing parameters need to be adjusted and rebalanced to account for the load. Nonetheless, the prescribed process methodology involving nylon pre-treatment for 3 minutes with oxygen plasma at 230W, 100mtorr followed by oxygen plasma conversion for 15 minutes at 230W, 55mtorr provides an efficient means of converting the soluble Pd salt into an insoluble metal.

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