

Plasma Generation by Household Microwave Oven for Surface Modification and Other Emerging Applications

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Abstract

In this paper we describe a simple and inexpensive method to generate plasma using a kitchen microwave. The microwave generated plasma is characterized by spectroscopic analysis and compared with the absorption spectra of a gas discharge tube. A Paschen-like curve is observed leading to a hypothesis of the microwave plasma generation mechanism in air. We have also demonstrated that this microwave-generated air plasma can be used in a multitude of applications such as: a) surface modification of a substrate to change its wettability; b) surface modification to change electrical/optical properties of a substrate; and c) enhancement of adhesive forces for improved bonding of polymeric microfluidic molds, such as bonding polydimethylsiloxane (PDMS) chips to glass covers. These simple techniques of plasma generation and subsequent surface treatment and modification may lead to new opportunities to conduct research not only in advanced labs, but also in undergraduate and even high school research labs.

I. INTRODUCTION

Plasma is ubiquitous in nature and readily observed as lightning on a stormy night, or as a static electric spark the moment before touching a door knob on a dry winter day¹. It is also found naturally occurring in stars², solar winds³, upper atmospheric lighting⁴ and the awe generating lightning glow known as St. Elmo's fire⁵ that sailors wondered about for centuries. Practical applications of plasma span a vast domain including, but not limited to, fusion energy generation⁶⁻⁹, plasma TV displays¹⁰, plasma enhanced chemical vapor deposition (PECVD)¹¹, sputtering¹², semiconductor device fabrication^{13,14}, substrate cleaning¹⁵ and sterilization¹⁶. Plasma is also referred to as the fourth state of matter¹⁷. As the addition of energy to material in a solid or first state initiates a phase change to a liquid second state and then to a gaseous third state, adding a sufficient amount of energy to a gas may ionize the gas by ejecting electrons from the outer shells and/or through collisions of individual ions. Plasma, the fourth state of matter, is thus composed of a conducting soup of energised charged particles, electrons and ionized atoms/molecules that are generated by the application of strong electromagnetic or heat energy. Once this highly charged gas is brought in contact with a surface, some energy is transferred from the plasma to the substrate surface, changing the surface property of the substrate. Unfortunately, plasma instrumentation remains somewhat expensive, preventing its widespread use in teaching and research environments for institutions with small budgets. In this work, we show that a simple plasma treatment apparatus can be constructed from an inexpensive household microwave oven and a modified vacuum flask. Although some previous works have shown that plasma can be sparked when a gas held at low pressure is subjected to microwave radiation¹⁸⁻²², this technique has never received the attention it deserves when it comes to low cost laboratory technique for wide range of surface treatments. We demonstrate a number of cutting-edge applications of the plasma device that we have constructed which includes the surface modification of semiconductors, enhancement of bonding between certain polymers such as PDMS and glass and reduction of graphene oxide to graphene for electronics purposes.

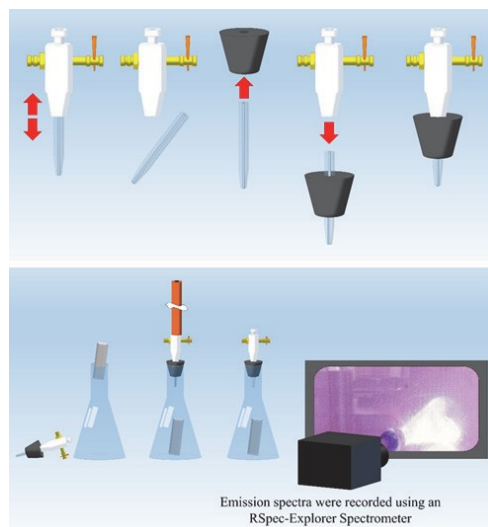


FIG. 1. A schematic of the construction of the sample holder for the microwave generated plasma is shown in this figure. One of the crucial parts needed is a simple air-tight valve. An inexpensive one can be fabricated from specialty parts as shown here, by modifying a PTFE and glass burette tip and rubber stopper. Bottom left to right: the sample is inserted into the Erlenmeyer flask; the vacuum valve is opened and the vacuum pump is used to evacuate the flask; the valve is closed and the vacuum hose removed; the flask is transferred to the microwave oven, and as the microwave is turned on, plasma is sparked to treat the surface for the desired length of time. To characterize the spectrum of the plasma, this process is repeated without a sample while placing a UV-Vis spectrometer in front of the microwave window.

II. PLASMA GENERATION BY A KITCHEN MICROWAVE

A. Materials and and methods

The main component of this low-cost plasma etching system is a regular kitchen microwave oven and a vacuum flask/sample holder. Any robust, vacuum-gauge glass container will work, but we have found the Erlenmeyer flask is the simplest and least expensive. The flat bottom of this glassware gives extra stability during sample preparation which may be useful in a teaching environment. A valve must be attached to the flask stopper which can be opened while evacuating the chamber and closed again to seal the vacuum. Speciality microwave-resistant valve parts can be purchased, but here we have sought a frugal alterna-

tive. The ideal substitute for this part was determined to be the detachable two-part tips found on many burettes (Fig.1). These parts consist of an all PTFE housing and stopcock into which a glass tip is loosely inserted. The glass tip of the burette can be easily removed by twisting it slightly. Next, a rubber stopper with a hole in the center, such as those for inserting thermometers into reaction vessels, is used. This part is selected to fit the mouth of the Erlenmeyer flask used above. The glass burette tip above is then inserted through the bottom of the stopper until it protrudes from the top by about 10mm. The PTFE stopcock housing is then placed back over the protruding burette tip. All of the edges of this system are then sealed with regular silicone. The seal is sufficient to hold a vacuum for many hours. A vacuum hose can be directly attached to the top of the valve allowing the system to be evacuated to various pressures with a small vacuum pump. Once the properly evacuated flask is put in the microwave and the oven is turned on, after a few seconds glowing plasma forms inside the flask. The time difference between the first observation of plasma and the time of turning on the microwave oven, i.e., the plasma initiation time, is recorded for different vacuum pressure. Furthermore, by flushing the evacuated system with various gases like argon, nitrogen, oxygen etc.this system can be used to determine the effect of different plasma chemistries. A schematic of the whole process is shown in Fig.1. In all of the following experiments, the substrate or sample is placed in an Erlenmeyer flask, the stopper is inserted, the vacuum hose is attached, and the pressure is lowered with a vacuum pump to the desired value. The valve is then sealed and the flask transferred to the microwave oven. Once the microwave oven is turned on after a short delay the plasma sparks, and then the plasma is allowed to glow for the desired amount of time.

B. Characterization of the microwave generated plasma

The plasma generated by this method is analyzed using two simple but revealing techniques: a) recording plasma initiation time as a function of the vacuum pressure and b) measurement of UV-visible emission spectra of the plasma glow. A Paschen-like graph^{23,24} is generated by plotting the plasma initiation time with the vacuum pressure of the flask to varying level (Fig.2). A trough-shaped curve resulted from this analysis, shows asymptotic tendencies and high and low vacuum pressure and a sweet-spot regime in between in which the plasma sparks within a matter of seconds.

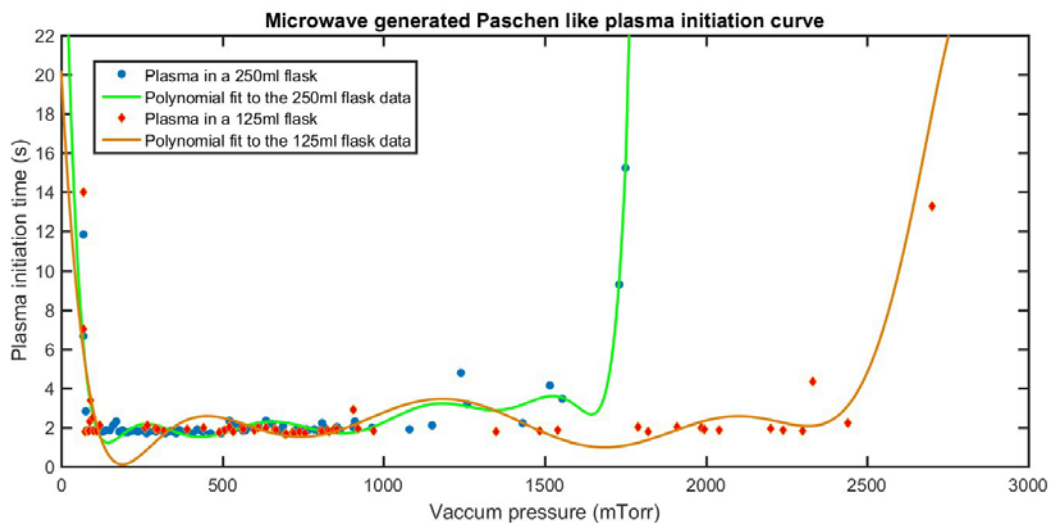


FIG. 2. A Paschen-like curve is observed when the pressure of the flasks are reduced and placed in the microwave oven to record plasma initiation time. At ambient pressures and high vacuum, the initiation time tends towards infinity, while in the intermediate regime, plasma sparks consistently within a few seconds. If the pressure in the flasks becomes too low, higher initiation time is observed pointing towards low number density of molecules in the flasks and corresponding lower collision cross section. Data for two flasks, one 125 ml and the other 250 ml show similar asymptotic behavior.

A schematic of these results can be seen in Fig.3. Since water is a polar molecule, we propose that the trace water vapor in the flask becomes ionized and accelerates due to the applied electrical field component of the microwave. At ambient pressure the number of constituent molecules in the flask is quite large and hence the mean free path is too short for the ions to gain momentum and cause an ionization chain reaction. Therefore plasma does not spark in this regime. As the pressure is decreased though, the mean free path becomes sufficiently large for the knocked out electrons and ions to gain enough momentum and kinetic energy to cause the nearby nitrogen atoms, the predominant molecule in air, to ionize upon collision. This creates a sky-blue plasma which is visible in the first 1-2 seconds after ignition. The chain reaction continues with oxygen molecules becoming ionized next due to collisions with nitrogen ions and ionized water. This regime is characterized by a deep purple and then pink plasma ball. When the vacuum pressure is decreased further to 68 mTorr or less for a 250 ml flask and 69 mTorr or less for a 125 ml flask, the collision cross

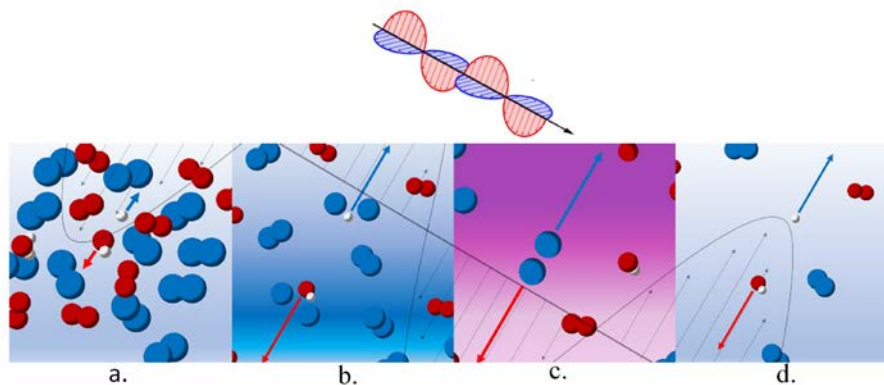


FIG. 3. The figure shows the mechanism of plasma generation. The electrical field component of the imposed electromagnetic microwave excites the polar molecules like water. Positive charge centers of the polar molecules would experience a force in the direction of the electric field while the negative charge centers would experience that in the opposite direction. Sufficiently strong applied electrical field component of the microwave would be able to tear the negative and positive charge centers apart, creating positive and negative ions in the flask. These ions would accelerate towards or opposite to the applied electric field depending on their charge and collide with other molecules present in the flask. If the ions gather enough momentum before the collisions they will be able to knock out electrons from the molecules/atoms they hit in turn ionizing them also. These secondary ions would also start to accelerate and may generate more and more ions along the way creating a chain reaction. This is the pathway of the Townsend-type avalanche²³ we normally observe in a gas discharge plasma. A comparison of the plasma generated in a gas discharge tube and that in a microwave shows similar absorption spectra and supports this mechanism of microwave plasma generation.

section of ions and electrons with molecules becomes too small for a plasma to spark, and hence the plasma ignition time tends towards infinity in this asymptotic limit. Thus two competing mechanisms are at interplay here: a) kinetic energy of the ions accelerating in an electric field to knock out electrons from atoms/molecules and b) collision cross section of the gas molecules in the flask. These two dominant regimes are visible in two asymptotic limits in Fig. 2 as explained above. In the sweet spot the collision cross section and the kinetic energy of the ions are just right to initiate plasma.

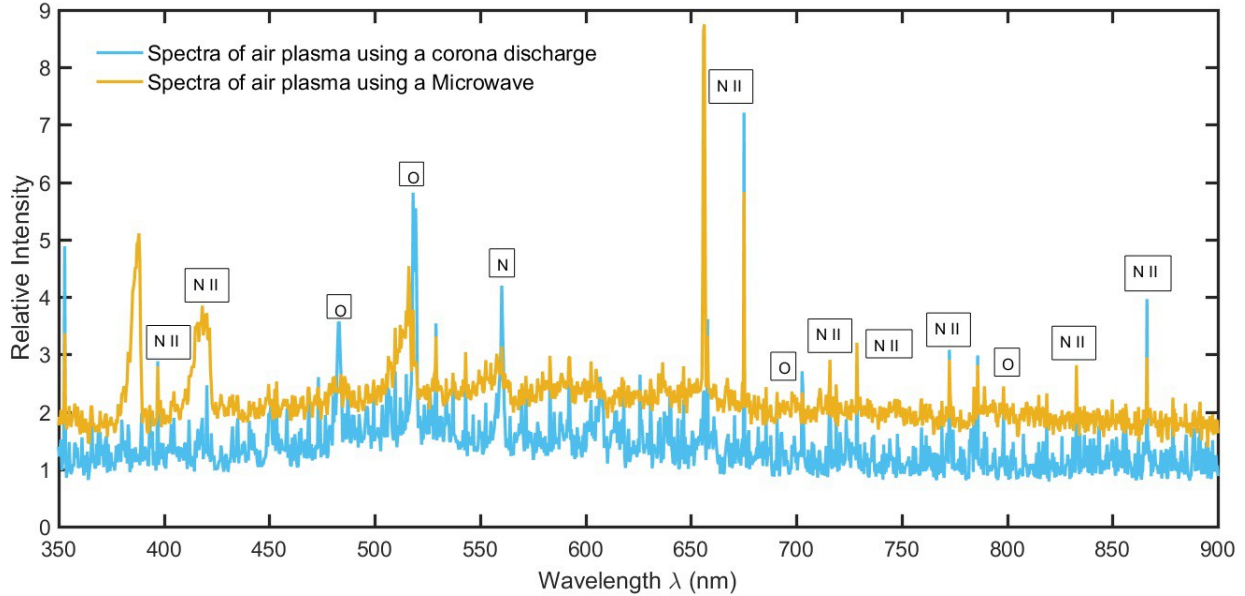


FIG. 4. The microwave generated plasma spectra is compared with the corona discharge (gas discharge) tube air plasma spectra. Nitrogen and oxygen lines are visibly identified in both the spectra.

UV-Visible absorption spectra of plasma are also recorded using a desktop CCD spectrometer (Exemplar, B&W Tek) Fig. 4. The spectra of the microwave plasma clearly show the dominant nitrogen and oxygen peaks indicating ionization of these molecules. To hypothesize the mechanism of the microwave plasma generation we have built a gas discharge tube with fixed electrodes, generated air plasma in it, and compared the spectra obtained from the gas discharge tube with that generated by the microwave. The reason behind this comparison is that gas discharge plasma is very well studied and the plasma generation mechanism of a gas under a constant strong electric field leading to Townsend avalanche is well known^{23,25}. The striking similarity of both the spectra lead us to hypothesize that although the source to energise gas is different in two cases: a) electric field in a gas discharge tube, while b) electromagnetic radiation in microwave generated plasma, the chain reaction is somewhat similar as described in Fig.3.

III. APPLICATIONS OF MICROWAVE PLASMA

Plasma treatment is a well-known technique to remove any contaminant, change surface energy, modify electrical and thermodynamic properties of a substrate for various purposes. A change in the surface energy of a substrate can easily be ascertained by measuring the contact angle of a liquid on the surface. The contact angle of a liquid drop, i.e., the angle measured where a three-component interface exists between a liquid drop, a solid surface, and the ambient air is measured by first taking cross sectional pictures of the drop using a camera and then analysing the contour of the drop using a software. Normally the designation of a hydrophobic material is reserved for surfaces with a liquid contact angle of greater than 90° s. Contact angles of less than 90° indicate a hydrophilic material with good wetting properties.

A. PDMS surface modification by plasma treatment

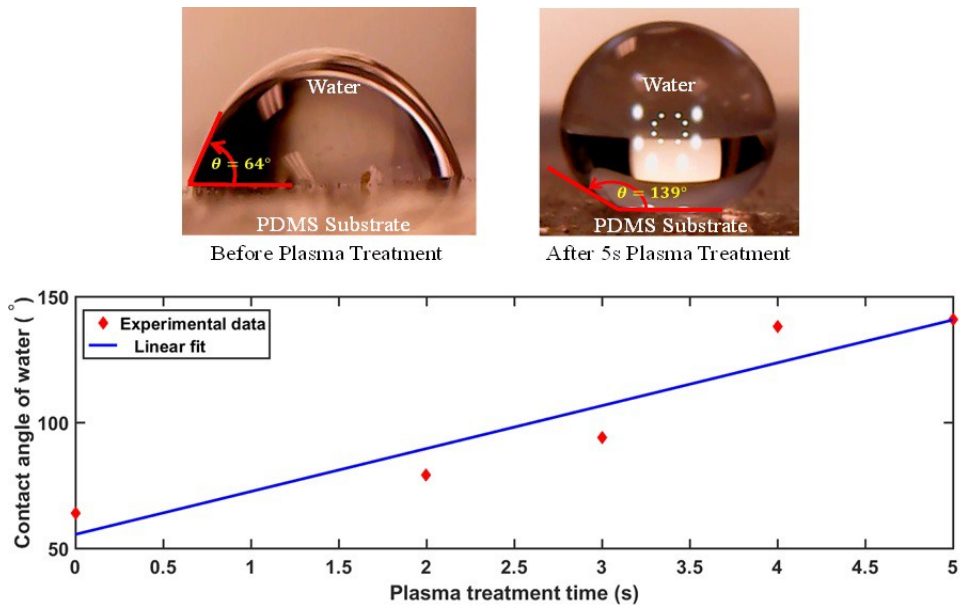


FIG. 5. Increasing contact angle with extended plasma treatment time shows a significant change in surface energy of the PDMS polymer substrate.

A flat PDMS substrate is prepared by mixing the PDMS liquid elastomer and the curing agent (Sylgard 184) in 10:1 ratio followed by degassing and incubating for a couple of hours

resulting in a consistent, bubble-free soft solid block. Cured PDMS blocks are then cut to shape and placed in the vacuum flask. The flask is evacuated to (500 mTorr) and placed in the microwave for plasma treatment. Once the plasma sparks, the PDMS blocks are treated for 2, 3, 4, and 5 seconds respectively. The relative change in surface energy is evaluated by measuring the contact angle of a water micro-droplet placed first on an untreated and then on the treated surfaces using a micropipette. We have used the open source image processing software ImageJ with DropSnake plugin to measure the contact angle of the sessile micro-droplet²⁶. Fig. 5 clearly shows that the contact angle of water on the PDMS sample increases nearly linearly with time indicating a direct relationship between the change in surface energy and plasma etching. This technique is thus useful for making hydrophobic surfaces for water-resistant coatings and other applications, as well as for bonding PDMS to glass substrates, as investigated in detail in a later section.

B. Surface modification of ZnO thin films to change its opto-electrical property.

Plasma treatment of a metal oxide thin film can also change its opto-electrical property. A film of ZnO particles was prepared as previously described²⁷. Briefly, a suspension of ZnO particles were deposited on a glass microscope slide from a 60% (v/v) solution of ethanol. The film was air dried for several minutes and then annealed on a hot plate by ramping the temperature from ambient to 500 °C in 7 minutes. Previous work has shown that as the ZnO film cooled a layer of ambient moisture and gases, as well as ethanol which is trapped in the bulk microstructure of the ZnO, deposits onto the ZnO surface²⁸. This is verified by a strong OH band centered at 3400 cm⁻¹ in the FTIR spectrum of the film. The sample and substrate were transferred to the vacuum flask. The flask was then evacuated and the whole assembly was placed in the microwave oven as before. The plasma was sparked and allowed to interact with the ZnO surface for 4, 8, and 15 seconds. FTIR analysis of the treated surfaces show a decrease in the intensity of the OH band (centered at 3400 cm⁻¹). Our previous work²⁷ has shown that such modification of polycrystal and nanocrystal semiconducting films plays an important role in the electronic properties of the material.

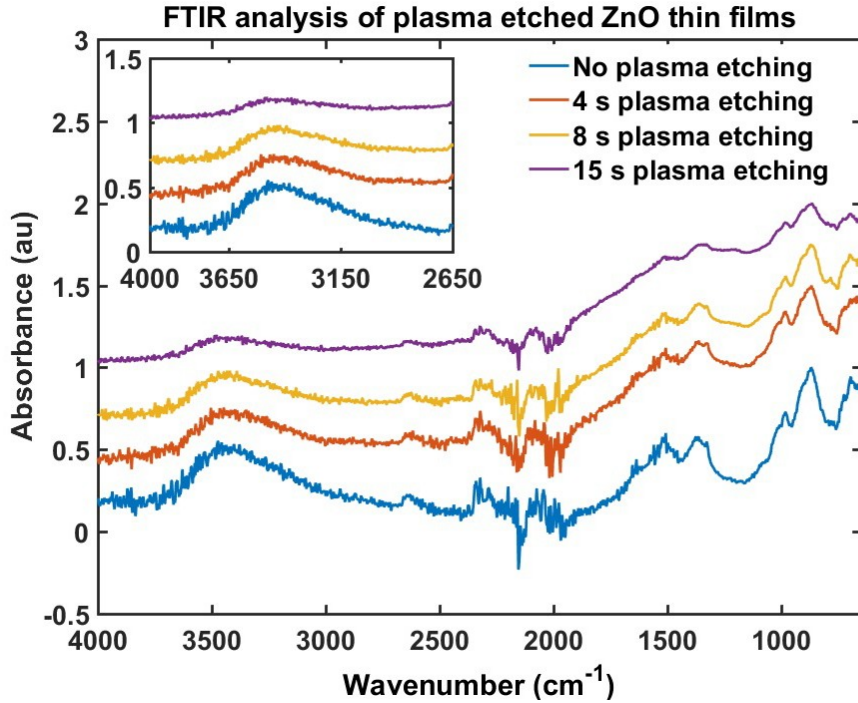


FIG. 6. The figure shows the result of plasma etching a ZnO thin film. The film was fabricated as for all devices (deposition from ethanol suspension) followed by sintering. The etching was conducted for 4, 8 and 15 seconds. The inset showing the band at 3400 cm^{-1} due to the -OH bond in alcohols. The intensity of this signal clearly diminishes as the film is etched indicating a loss of electron-withdrawing groups from the surface of the material. The large signal at around 2100 cm^{-1} is from CO_2 and the band at around 900 cm^{-1} is due to a small amount of glass particles that were scraped off of the device substrate. The graphs shown above are the FTIR analysis of ZnO nanowire thin films, however other ZnO thin films made of ZnO particles or nanoparticles also show similar behaviour under plasma etching.

C. Reduction of graphene oxide to graphene

Graphene is a 2D wonder material²⁹⁻³¹ with many potential applications ranging from flexible electronics, energy storage, sensors to molecular sieving³²⁻³⁵. One hurdle in further developing graphene applications commercially however is the difficulty in preparation of bulk graphene in mass scale. Apart from chemical vapor deposited Graphene is most easily produced in bulk by the reduction of graphite oxide solutions, but this can be time-consuming and is not an environmentally friendly process. Some recent works have shown alternative

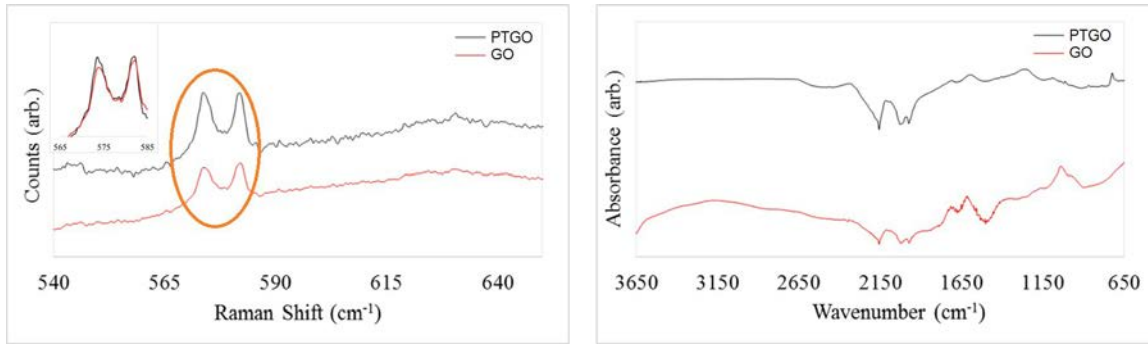


FIG. 7. Raman spectra and absorption studies for graphene oxide (GO) and plasma treated graphene oxide (PTGO) films.

optical and thermal processes for obtaining reduced graphene oxide using laser^{36,37}. We show that plasma generated by our simple system is capable of providing the local energy needed to reduce dielectric graphene oxide films to conductive graphene.

First, graphene oxide (Graphenea Inc.) is drop casted onto polyethylene terephthalate (PET) film. After drying for 24 hours at 50 ° C, the GO-coated foil is cut into squares. The sheet resistance of each square is measured using a Keithley Source Meter with a four-point Kelvin probe. The resistance prior to plasma etching show a large value on the order of 10 MΩcm⁻².

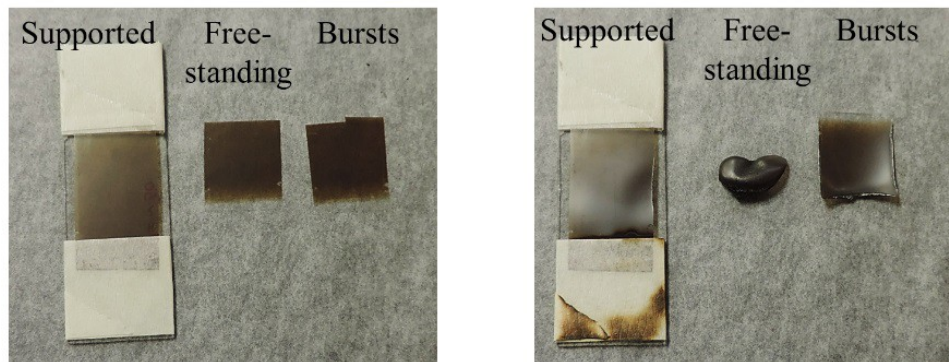


FIG. 8. Graphene oxide films before (L) and after (R) treatment in 4 seconds of air plasma. Clearly the free-standing sample is not very useful for applications despite is large change in resistance. A similar change in resistance was attained by treating the bursts-sample with four separate 1-second pulses of plasma, which prevented the plastic substrate from warping significantly.

One graphene oxide square is taped on either end to a glass substrate and then placed in the plasma etching flask. It is then evacuated for 1 minute (to a pressure of 300 mTorr).

Substrate	Initial resistance R_i ($M\Omega\text{cm}^{-2}$)	Final resistance R_f ($M\Omega\text{cm}^{-2}$)	ΔR (%)
Supported	5.4	0.2	96.3
Free-standing	10.5	0.1	99.0
Bursts	7.9	0.1	98.7

The flask is placed in the microwave for 4 seconds. The other two squares are also treated for 4 seconds, but neither affixed to substrates and one treated for 4 and 1 second intervals instead of continuous exposure. The third is exposed to plasma for 4 seconds continuously. The three types are referred to as supported, bursts, and free-standing, respectively.

The resistance following plasma etching is measured and showed a reduction of resistance of about two orders of magnitude. The lowest final resistance is obtained for the free-standing sample, but the heat from the plasma caused the plastic foil to warp, making this process less useful for flexible electronic applications.

D. Bonding of Microfluidic Channels to Substrates

Many materials like polypropylene (PP), polyether ether ketone (PEEK), PDMS or polyoxymethylene (POM) are extremely hard to bond with other materials. Requirement of high bonding strength, durable and irreversible bonding of metal, glass and plastics present special challenges for the manufacturing industry. Plasma treatment of a surface with other applied cleaning procedures produce better adhesion capability and bonding strength on the surfaces to be joined.

Microfluidics is an emerging technology with fluid flow in micrometer or less size channels and has tremendous applicability³⁸. Applications for microfluidics include mobile chemical analysis³⁹, medical diagnostics⁴⁰, drug delivery⁴¹, soft robotics⁴², RNA encapsulation⁴³, and nanomaterials synthesis⁴⁴ to name a few. In order to fabricate robust microfluidic devices, it is necessary to have a strong bond between the microfluidic polymer mold (typically PDMS) and the substrate. A strong bond prevents the device from leaking, becoming damaged, or the development of passages by which the confined solutions could escape the network of channels. Plasma has been used in this application extensively, as it converts the exposed surface of the PDMS into dangling silane groups, allowing a very strong bond to glass to be formed. We demonstrate that the plasma generated in our simple microwave system can be

used for this purpose.

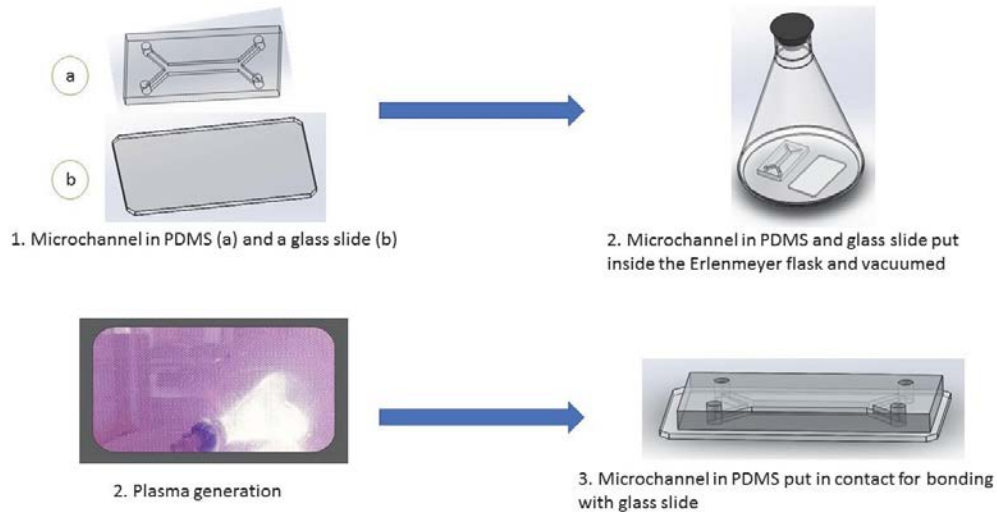


FIG. 9. A schematic to bond PDMS mold to glass to make microchannels.

The following steps are taken to create PDMS microfluidic channels bonded on glass: (1) A microchannel mold is created (typically using photolithography or other methods). (2) A mixture of liquid PDMS and cross-linking agent is then mixed in the 10:1 ratio and poured into the mold in a petri dish. The petri dish is kept in an incubator at 65°C for a couple of hours. (3) The hardened PDMS is taken off the mold. A replica of the microchannels is obtained on the PDMS block. (4) To complete the microfluidic chip and to allow the injection of fluids for future experiments, the inlets and outlets of the microfluidic device are punched with a biopsy puncher whose diameter is slightly less than the size of the tubes to be connected. This will ensure tight fitting of the inlet/outlet tubes to the channels. (5) Finally, the side of the PDMS with open microchannels and the glass slide are treated with plasma to obtain closed channels with one flat inner wall of glass and all other walls of PDMS. (6) The plasma treatment irreversibly bonds PDMS with glass and makes the microfluidic chip.

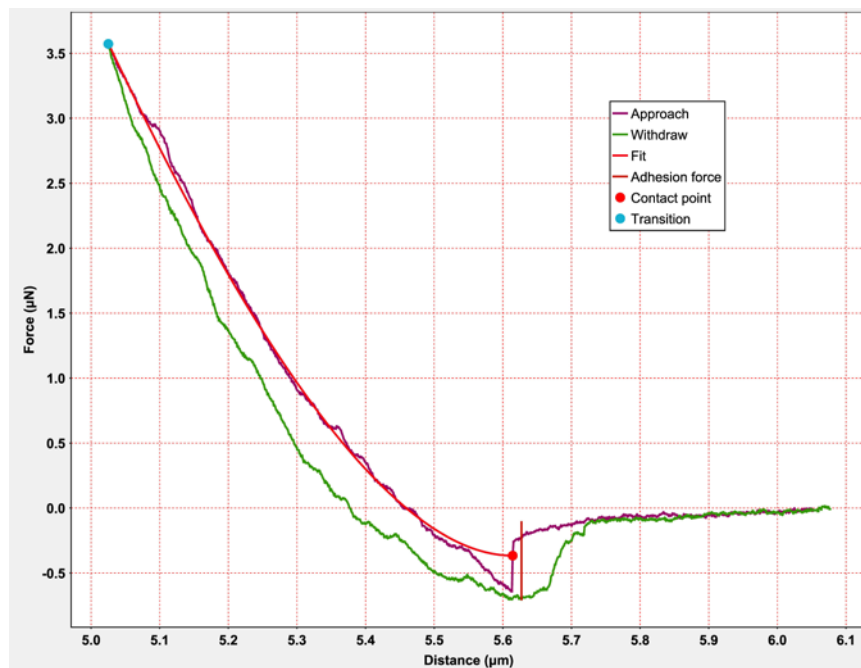


FIG. 10. Adhesive force of the untreated PDMS surface is measured using AFM force spectroscopy method.

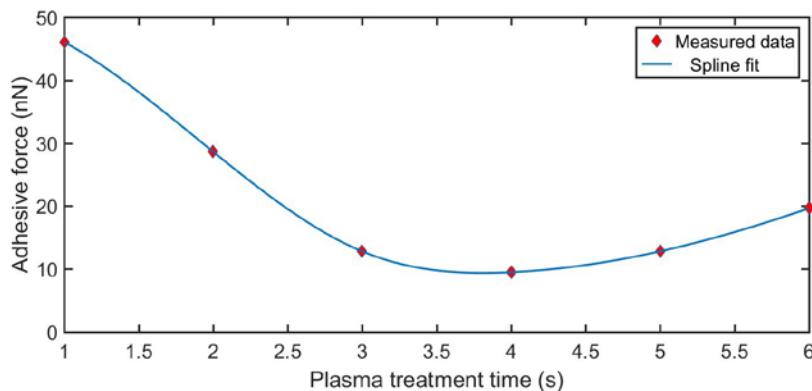


FIG. 11. Adhesive force of the PDMS surface is measured using AFM force spectroscopy method before and after various degrees of plasma treatment.

A freshly made PDMS replica and a glass microscope slide in two different vacuum flasks were used in this experiment. The flasks were evacuated to 500 mTorr (0.5 Torr) and three seconds of plasma exposure was used on both of them. After plasma treatment, the glass slide was removed and placed on a flat surface. The PDMS sample was then removed and the treated surface is placed in the desired location on the glass slide; the two components were then pressed together gently and allowed to sit for ten minutes. A schematic of the

whole process is shown in Fig.9.

We have also measured the adhesive force of a PDMS surface before and after treatment using force-distance microscopy mode of an atomic force microscope (Nanosurf C3000 Flex-AFM) and the representative graph is shown in Fig.10. The relative change in adhesive force due to surface plasma treatment is shown in Fig.11.

IV. CONCLUSION

In this work we have demonstrated that a simple plasma etching device can be constructed from a household microwave oven and a vacuum flask. We have showed that this apparatus can be used in surface treatment of a substrate for several cutting-edge research applications. Varying degree of plasma exposure to a PDMS substrate leads to change in surface energy and hence a change in contact angle of a water droplet on the substrate was observed before and after the surface treatment. Upon exposure to plasma a change in opto-electrical properties of a metal oxide semiconductor such as ZnO was demonstrated using FTIR spectra analysis. Significant change in electrical resistance of graphene oxide thin films was also observed as an effect of plasma exposure. Moreover, it was also shown that irreversible bonding between certain elastomers like PDMS and glass can be achieved to make microfluidic channels with this simple technique. Needless to say that the domain of these applications is enormous and our hope is that this paper, through this frugal alternative to conventional and expensive plasma treatment, would enable more researchers to delve into these cutting edge research areas leading to more innovation and discovery.

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VI. ACKNOWLEDGEMENT

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