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10 ns pulsed atmospheric air plasma for uniform treatment of polymeric surfaces

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This letter reports an experimental study of a 10 ns pulsed dielectric barrier discharge in atmospheric air, excited with a train of 65 ns voltage pulses at a repetition frequency of 5 kHz. It is shown that these ultrashort pulses produce a homogenous discharge with very high electron density in excess of 10^{13} cm^{-3} and low gas temperature, which are particularly desirable for uniform treatment of thermally sensitive polymer films. Their treatment of polypropylene films is found to introduce microscale surface patterns as well as various carbon-oxygen bonds, both useful for improving the hydrophilic properties of polymeric materials. © 2007 American Institute of Physics. [DOI: 10.1063/1.2825576]

Polymeric materials are used extensively in food packaging, protective coatings, and sealing applications because of their excellent bulk properties such as transparency, high strength to weight ratio, and good thermal resistance.¹ Less desirable are some of their surface properties, for example low wettability, and weak adhesion to secondary phases that restrict considerably their application range.² Chemical activation of the polymer surface is the most utilized method to enhance surface characteristics; however, the use of aggressive solvents and caustic solutions on an industrial scale has detrimental ecological consequences. An environmentally benign surface treatment using gas plasmas is a desirable alternative,² made particularly attractive by the advent of the atmospheric-pressure glow discharges (APGDs) technology and the chamberless processing route they facilitate.³⁻⁵ For large-scale and uniform treatment of polymeric materials, it is important to produce homogenous and low-temperature APGD at temperatures well below 100 °C. While this can be achieved by using inert gases such as helium and argon,^{5,6} they are expensive and ineffective in promoting plasma reactivity.⁷ The ideal discharge gas is clearly the ambient air; however, molecular gases tend to produce hot and filamentary plasma resulting in a nonuniform surface treatment often with localized damages.⁶ Filamentary plasmas are common with either sinusoidal or dc excitations, whose applied voltage persists much longer than the timescale of the glow-to-arc transition (GAT).⁸ Recently, the use of submicrosecond voltage pulses has been shown to control effectively the GAT transition.⁹⁻¹² These submicrosecond pulsed atmospheric plasmas are glow discharges generated uniformly between two large parallel-plate electrodes and are different from pulsed corona discharges that are ineffective for large-scale surface treatment.¹³ In this study, we report a 10 ns pulsed atmospheric air plasma and its uniform treatment of polypropylene films.

The pulse generator was capable of delivering sub-100-ns voltage pulses up to 5 kV with rise time typically below 10 ns. Pulse repetition rates can be varied from 1 Hz to about 20 kHz, depending on the load conditions. Voltage pulses were applied between a rectangular metallic powered

electrode measuring 4 cm × 0.8 mm and a parallel dielectrically coated plate of 8 × 4 cm² as the ground electrode. The electrode gap was 0.5–2.5 mm, nominally at 1 mm. The electrode unit was of a dielectric-barrier discharge (DBD) configuration and it was opened to the stationary ambient air. Polymer films were placed on the ground electrode and exposed directly to the plasma. Current and voltage were measured with a Pearson 2877 current probe (2 ns useable rise time) and a Tektronix P5100 voltage probe (1.75 ns useable rise time). Signals were recorded on a Tektronix DPO 4104 oscilloscope. Optical emission spectra were obtained using an Andor Shamrock spectrometer with a grating of 2400 grooves/mm.

Figure 1 shows current and voltage traces of a 5 kHz pulsed DBD operating in atmospheric air. The voltage pulse has a full width half maximum (FWHM) of 65 ns and a rise time of 9 ns. Similar to previous studies,^{9,10} two current pulses are observed for each voltage pulse with their FWHM being 9 and 11 ns, respectively. These represent two pulsed atmospheric air plasmas, each with a pulsewidth of ~10 ns. The first current pulse is produced as the applied voltage exceeds the breakdown voltage of the gas. The second current pulse represents a secondary discharge occurring on the falling edge of the voltage pulse.¹⁴ The second discharge is a

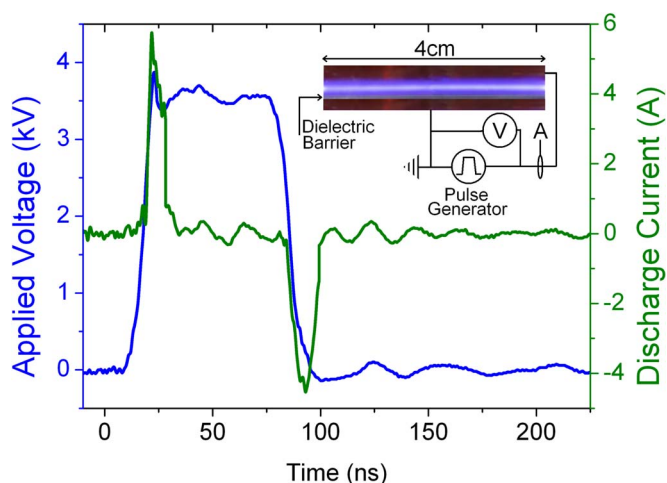


FIG. 1. (Color online) Traces of the applied voltage and discharge current. The inset shows the uniform large-area pulsed atmospheric air plasma.

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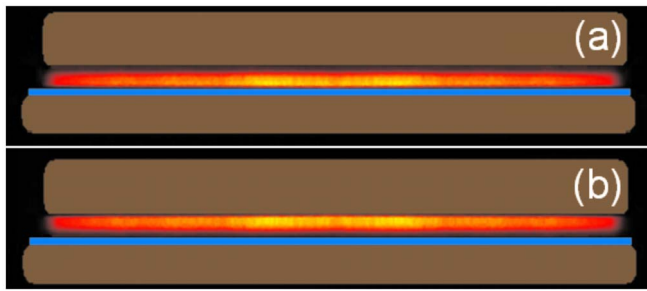


FIG. 2. (Color online) Single shot images taken with a 10 ns exposure time, with (a) taken during a positive current pulse and (b) taken during a negative current pulse. The blue line indicates the dielectric barrier.

direct consequence of surface charges stored on the dielectric barrier reigniting the discharge during the voltage falling phase.¹⁴ The smooth curve of the current pulses indicates a diffuse discharge, since the current trace of a filamentary discharge consists of many narrow spikes.³ Further evidence of the diffuse nature of the plasma is provided in Fig. 2, which shows its single-shot images with an exposure time of 10 ns. Clearly, the discharge is completely homogenous and streamer-free across the entire width of the electrodes. It is interesting that, during the positive current pulse, the peak intensity is positioned above the lower electrode and, in the negative current pulse, the peak intensity is closer to the upper electrode. This is due to the formation of the negative glow above the instantaneous cathode. As the gas voltage changes its polarity, the discharge's negative glow alternates its appearance between the two electrodes.

The electrical efficiency of pulsed atmospheric DBD is significantly higher than their conventional sinusoidal counterparts, partly due to the long plasma-off period that reduces power consumption^{8,10,11} and partly due to larger electron temperature (discussed below). The averaged power is about 0.27 W, lower than that in sinusoidally excited DBD in atmospheric air.³ However, the peak dissipated power is found to be 5.63 kW, more than four orders of magnitude above the averaged power. The current density in Fig. 1 is $J = 18.4 \text{ A/cm}^2$, unusually high for atmospheric DBD where typical current densities are in the 10–100 mA/cm² range.^{3,6,8} Given the electron mobility of $\mu_e = 592 \text{ cm}^2/\text{Vs}$ for atmospheric air,¹⁵ the space-averaged electron density is estimated to be $\sim 1.4 \times 10^{13} \text{ cm}^{-3}$ from $n_e = (J/E_g)/(e\mu_e)$, with E_g being the electric field averaged across the gas gap. The peak electron density is likely to be larger, as E_g is larger than the electric field in the plasma bulk where n_e reaches its peak.¹⁶ Therefore, the electron density in the pulsed atmospheric air plasma is a few orders of magnitude above that in a comparable sinusoidally excited atmospheric DBD.⁶

It is likely that the 65 ns pulsed excitation has shifted the electron energy distribution function (EEDF) toward its high energy tail. For nonequilibrium atmospheric air plasmas sustained by sinusoidal excitation, their electron temperature is determined by the slope of the EEDF at low energy and usually in the 1–3 eV range.¹⁷ Only a very small number of electrons have sufficiently high energies, in the 10–15 eV range, to be capable of ionization. While electrons with energies in the 1–3 eV range are highly effective in exciting the vibrational states of gas molecules, they have insufficient energy to cause ionization. By using fast-rising voltage pulses that are greater in magnitude than the minimum breakdown voltage of the gas, it is possible to shift the EEDF

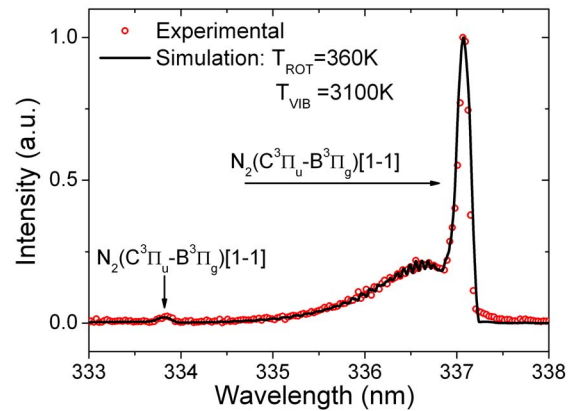


FIG. 3. (Color online) Measured and simulated optical emission spectra of the second positive nitrogen system.

and produce a far higher proportion of high energy electrons for inducing ionization.¹⁷ Also narrow pulsewidth restricts the duration over which plasma instabilities can be sufficiently developed and allows for larger applied voltage and high gas ionization. Therefore, the use of narrow pulsewidth helps indirectly enhance the gas ionization rate.

Despite very high peak power and current density, the low averaged power of the pulsed air APGD suggests that its rotational temperature should be relatively low. To attest this, experimental and simulated spectral data are shown in Fig. 3 for the pulsed air discharge of Fig. 1 at a peak voltage of 3.5 kV. Optical emission was directed into the spectrometer via a fiber optic cable and measurements were obtained using a 1 ms exposure time. By comparing the measured spectrum to the simulated spectrum of the nitrogen second positive system, it is possible to estimate the rotational and vibrational temperatures. Due to the highly collisional nature of atmospheric pressure discharges, it can be assumed that the rotational temperature is very close to the actual gas temperature with errors reported as low as 2.4%.¹⁸ SPECAIR, a program specifically designed for modeling of air discharges, was used to model the emission data. The best fit between experimental and simulated data was obtained at $T_{\text{rot}} = 360 \text{ K}$ and $T_{\text{vib}} = 3100 \text{ K}$. For air plasmas generated at atmospheric pressure, these temperatures are uncharacteristically low, for example, dc driven air discharges operated at low currents (tens of milliamperes) typically have gas temperatures above 1000 K.¹⁹ The emission line at 334 nm is a vibrational transition and appears very weak. This fits well with the suggestion that pulsed discharges produce high energy electrons that ionize gas molecules rather than exciting their vibrational states.¹⁷ Gas temperatures are further reduced by the long plasma-off period between each voltage pulse. Polymer samples treated continuously for 5 min in the pulsed APGD showed only a 10 °C rise in surface temperature.

It is of interest to see whether the desirable properties of the pulsed air plasma, may translate into clear benefits for their potential applications. To this end, the pulsed air plasma was used to treat polypropylene films. Following plasma treatment, each sample was sputter coated with a nanometer layer of gold to prevent surface charging and observed using a scanning electron microscope (SEM) operating at an accelerating voltage of 10 kV. Figure 4 shows a series of SEM images of a polypropylene film treated with the pulsed air discharge of Fig. 1, from which it is clear that very few

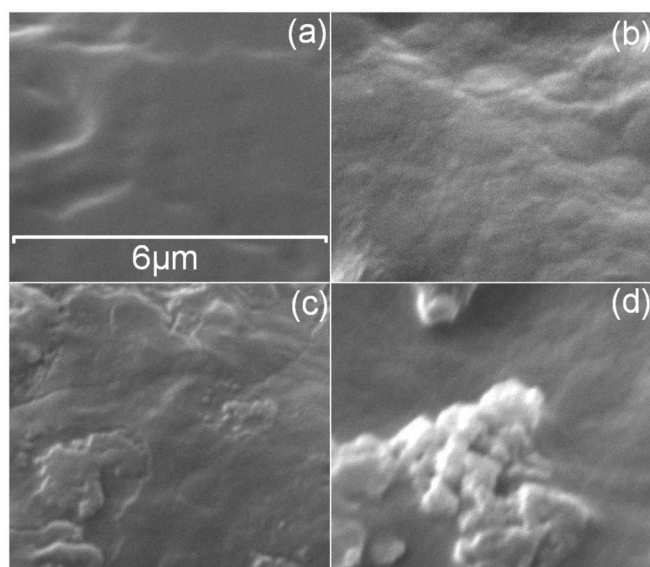


FIG. 4. SEM images of a polypropylene film after the pulsed air plasma treatment for (a) 0 s, (b) 10 s, (c) 60 s, and (d) 300 s.

changes in the surface morphology occur from 10 to 60 s of treatment. After 5 min of plasma treatment, the surface changes significantly with the entire treated area covered predominantly in raised formations. Similar structures have been reported in studies with low-pressure plasmas.²⁰ Several explanations are proposed for the appearance of such structures including recrystallisation processes initiated by the plasma or the appearance of additives introduced during the production process, however, more research is needed before a conclusion can be reached.

The chemical composition of polypropylene film was investigated by an x-ray photoelectron spectroscopy system (XPS) employing aluminum x-rays with an anode voltage of 8 kV and current of 20 mA. From low resolution XPS data (not shown), the oxygen to carbon ratio was calculated. The O/C ratio was found to shift from a few percent, which is likely to be a result of surface oxidation after manufacture, up to 47.2% after 5 min of the plasma treatment. This is highly consistent with other studies where the O/C ratio has been raised up to a saturation point of 47.9%.²¹ A large shift in the O/C ratio is a clear indication that surface functionalization is being induced through the interlock of oxygen based polar species resulting from the interaction of the film surface with the species present in the gas discharge.²² Figure 5 gives a detailed XPS spectrum of the C 1s peak to allow analysis of the oxygen-containing functional groups formed through polymer-plasma interaction. It is clear that exposure to the pulsed air plasma significantly reduces the C 1s peak at 285 eV. Additionally, as the treatment time increases a peak appears at 289.3 eV, this corresponds to the O—C=O functional group. From these results, it can be concluded that the plasma attacks C—C bonds in the polypropylene chains to form various carbon oxygen bonds, such oxygen-containing groups are known to substantially improve the hydrophilic properties of polymeric materials.^{1,21,22} Results in Figs. 4 and 5 are, therefore, very desirable.

In conclusion, monopolar high-voltage 65 ns pulses at 5 KHz are capable of generating and sustaining diffuse atmospheric air plasma over a wide surface area. The air plasma

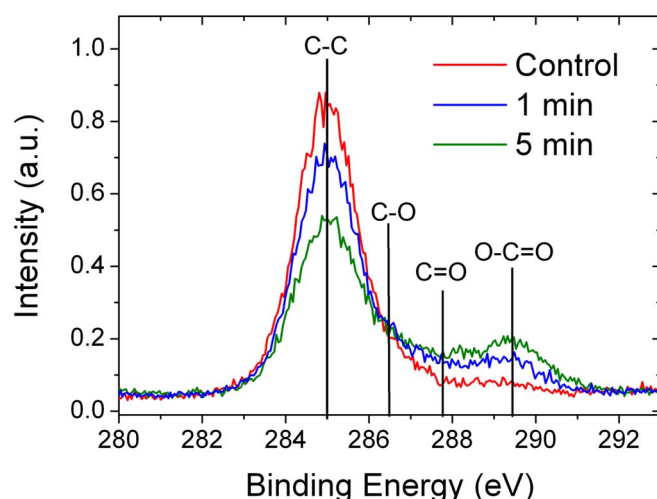


FIG. 5. (Color online) High resolution XPS data showing changes to carbon (C 1s) in a polypropylene sample exposed to the pulsed air plasma.

has a narrow pulsewidth of about 10 ns, resulting in a very low gas temperature and a very low averaged power. However, the fast-rising pulses allow for the use of high applied voltage that is greater in magnitude than the minimum breakdown voltage of the gas, thus, producing far higher proportion of high energy electrons capable of ionization and increasing the ionization efficiency. With a peak dissipated power of 5.63 kW, the electron density is found to be in excess of $1.4 \times 10^{13} \text{ cm}^{-3}$. Through SEM images and XPS analyses, it is shown that the pulsed air APGD offers an excellent route to enhancing surface characteristics of polymeric materials, in particular their hydrophilic properties.

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