Plasma–Polymer Interactions in a Dielectric Barrier Discharge

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***Abstract*—Atmospheric pressure plasma treatment of polymers is routinely used to improve surface properties such as adhesion and wettability. These changes in properties occur by functionalization of the surface by radicals and ions generated in the plasma, typically oxidizing the surface and increasing surface energy. One such device used, a dielectric barrier discharge, is modeled in this study. Images show the progress of the electron avalanche across the gap and the enveloping of surface features on the polymer by the plasma.**

***Index Terms*—Avalanche, dielectric barrier discharge, modeling, plasma, polymer.**

ATMOSPHERIC pressure plasmas are commonly used to treat large surface areas of polymer films, such as polypropylene, to impart enhanced surface properties such as adhesion and wettability [1]. The change in surface properties is produced by functionalization of the polymer by plasma generated radicals and ions. The gas chemistry used depends on the desired surface properties to be imparted. For example, O_2 containing plasmas increase surface energy by bonding of O atoms onto the polymer surface, thereby increasing its wettability. The polymer surface often consists of a mat of strands or tubules having diameters of 100s nm to a few microns [1]. The interaction of the plasma into crevices formed by the strands is an issue with respect to uniformity of functionalization. Dielectric barrier discharges (DBDs) are one class of devices used for generating atmospheric pressure plasmas for this purpose [2]. In the DBD shown in Fig. 1, a linear electrode tip is the biased cathode and the polymer sheet rolls on a grounded metal substrate.

A two-dimensional plasma hydrodynamics model addressing gas and surface chemistry was used to model the interaction of an electron avalanche in a DBD with the polymer surface. The model consists of a simultaneous solution of Poisson's equation for the electric potential with multifluid charged particle conservation equations followed by an update of neutral densities in a time-splicing manner. Gain and loss terms include electron impact ionization and excitation, heavy particle reactions and secondary electron sources from surfaces. The gas is humid air at 1 atm. Gas species include N_2, $N_2(A)$, N_2^+, N, N^+, N_4^+, N, $N(^2D)$, O_2, $O_2(^1\Delta)$ O_2^+, O_2^-, O, $O(^1D)$, O^+, O, O_3, H_2O, H_2O^+, H_2, H, OH, and HO_2. Radicals and ions from the plasma impinge onto the polymer, react with surface species and functional groups, thereby modifying their properties, and return gas phase products. Surface species are alkyl radicals, alkoxy radicals, alcohol groups, hydroperoxide groups, aldehyde, and acid groups.

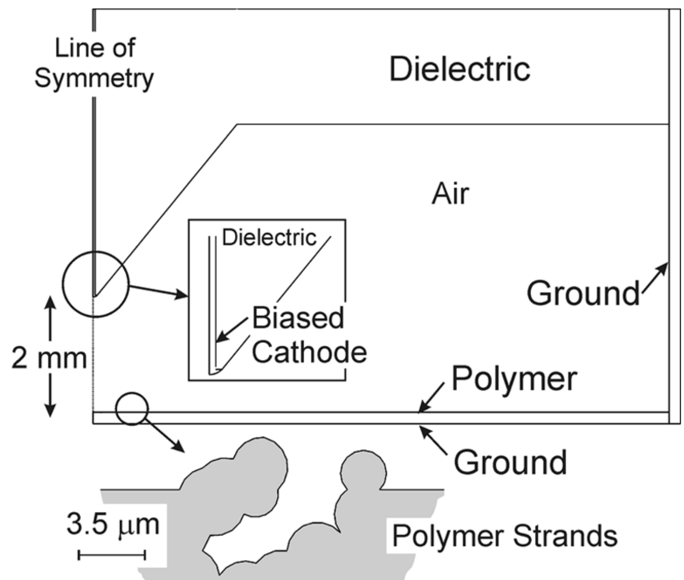

Fig. 1. Schematic of the DBD and surface resident strands.

The DBD was modeled as having a linear electrode, symmetric across the centerline shown in Fig. 1. The cathode is biased to -15 kV with a tip 2 mm above the polymer surface. Features resembling strands found on polypropylene are resolved at the submicron spatial scale on the surface of the polymer to enable investigation of plasma penetration. The unstructured mesh, created with SkyMesh2 [3], has 5937 nodes (3299 in the plasma). The resolution spans 0.5 mm–0.5 μm, a range obtained by having a series of sequentially finer refinement zones. Images were created with Tecplot v8 [4], Corel Draw v12 [5], and Adode Photoshop v7 [6].

Dynamics of the avalanche are imaged in Fig. 2 where the electron density is shown. Plasma, initially generated at the cathode tip, avalanches toward the polymer in the large normalized electric fields ($E/N \approx 1000\ Td$) produced by geometric enhancement and space charge beginning at 0.25 ns. The avalanche bridges the gap, impinging on the polymer, by 1.5 ns. Upon intersecting with the polymer, a secondary

Manuscript received September 15, 2004; revised November 8, 2004. This work was supported in part by the National Science Foundation under Grant CTS03-15353 and in part by 3M Inc.

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Digital Object Identifier 10.1109/TPS.2005.845899

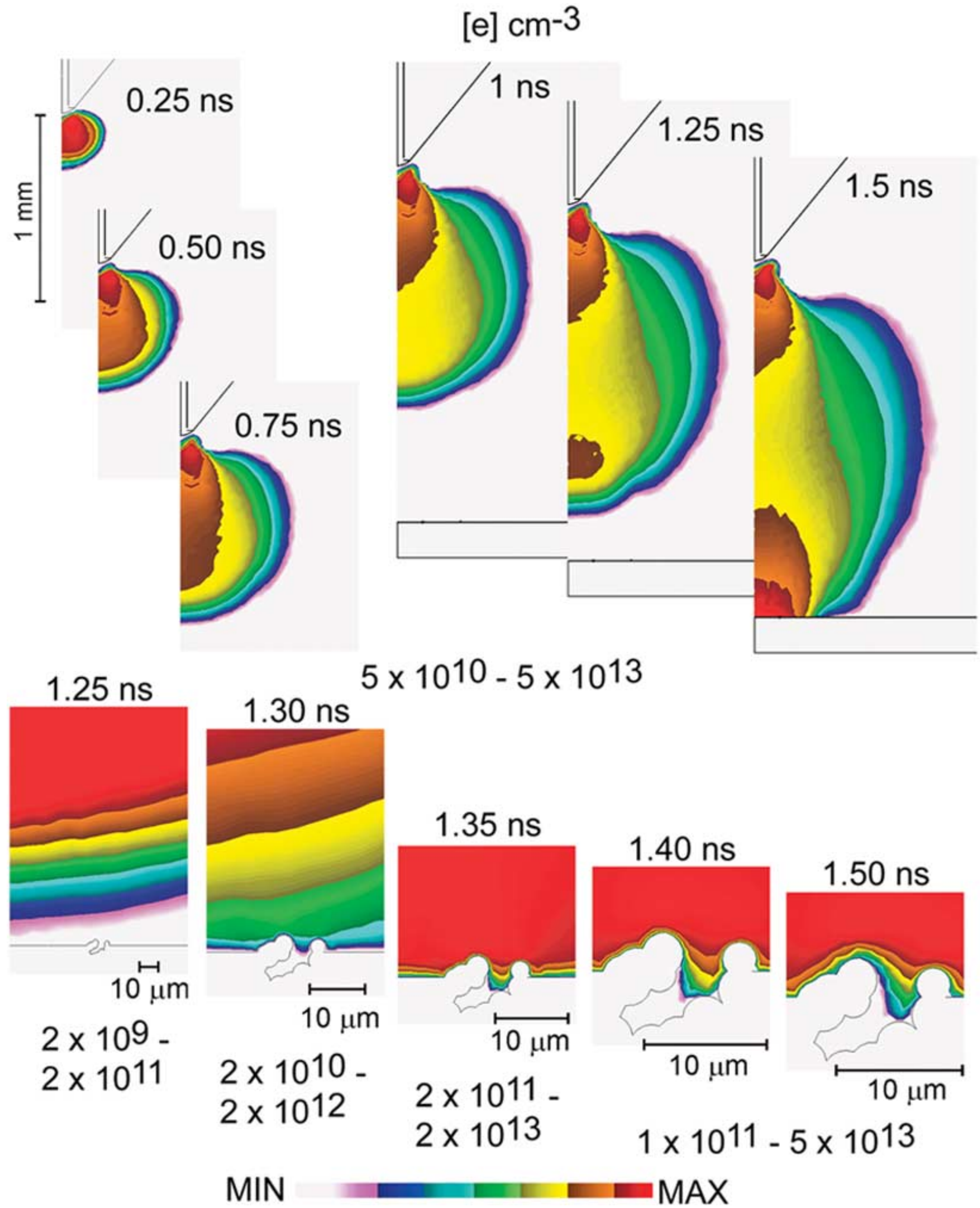

Fig. 2. Electron avalanche during a single pulse in an atmospheric pressure DBD (log scale, cm^{-3}): the avalanche is initiated at the tip of the cathode and progresses toward the polymer surface. Plasma penetrates into the surface features to a limited extent.

cathode directed avalanche develops. When the avalanche intersects with the polymer, the plasma envelopes the surface features and enters into the depressions to a limited extent. The electron density in the features decreases over several orders of magnitudes from the protruding tops of the strands to the internal surfaces. The electron flux at the head of the avalanche negatively charges the surfaces of the features in advance of the main body. The penetration of the plasma into these features is retarded by the negative surface potential. Deeper penetration of ions into the features enables radical and ion dependent surface reactions to occur on at sites not directly exposed to the avalanche.

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