6-30-2013

Nanodielectric Properties of High Conductivity Carbon-Loaded Polyimide Under Electron-Beam Irradiation

Amberly Evans Jensen
*Utah State University*

JR Dennison
*Utah State University*

Justin Dekany
*Utah State University*

Gregory Wilson
*Utah State University*

Follow this and additional works at: [https://digitalcommons.usu.edu/mp_conf](https://digitalcommons.usu.edu/mp_conf)

**Recommended Citation**
Nanodielectric Properties of High Conductivity Carbon-Loaded Polyimide Under Electron-Beam Irradiation

Amberly E Jensen, JR Dennison, Justin Dekany, and Gregory Wilson
Materials Physics Group, Physics Department, Utah State University
Logan, UT, USA
Amb.Eva@aggiemail.usu.edu, JR.Dennison@usu.edu

Abstract— Electron irradiation experiments were conducted to investigate the electron transport, charging, discharging, cathodoluminescence and emission properties of high-conductivity carbon-loaded polyimide (Black Kapton™). We discuss how these results are related to the nanoscale structure of the composite material. Measurements were conducted in an ultrahigh vacuum electron emission test chamber from <40 K to 290 K, using a monoenergetic beam with energies ranging from 3 keV to 25 keV and flux densities from 0.1 nA/cm² to 100 nA/cm² to deposit electrons in the material surface layer. Various experiments measured transport and displacement currents to a rear grounded electrode, absolute electron emission yields, electron-induced absolute photon emission yields and photon emission spectra (~250 nm to 1700 nm), and arcing rates and location. Numerous arcing events from the material edge to an electrically isolated grounded sample holder (particularly at lower temperatures) were observed, which are indicative of charge accumulation within the insulating regions of the material. Three types of light emission were also observed: (i) short duration (<1 s) arcing resulting from electrostatic discharge, (ii) long duration cathodoluminescence that turned on and off with the electron beam and (iii) intermediate duration (~100 s) glow that dissipated exponentially with time after infrequent and rapid onset. We discuss how the electron currents and arcing, as well as light emission absolute intensity and frequency, depend on electron beam energy, power, flux and temperature.

Keywords— arcing, luminescence, conductivity, electron flux, low temperature, space environment interactions, materials testing, carbon composites

I. INTRODUCTION

High conductivity Black Kapton™ (HCBK) is a common nanodielectric composite material, with an insulating polyimide matrix that has been loaded with nanoscale turbostratic carbon particles to increase its electrical and thermal conductivity. On a macroscopic scale, HCBK acts as a good conductor, with conductivities ranging from 10¹ to 10³ (Ω-cm)⁻¹ depending on the fraction of carbon-loading [1]. However, on the nanoscale the material exhibits both conducting and dielectric properties. The length scale is set by the size of the turbostratic carbon soot particles (~100-500 nm) and the carbon-depleted surface regions (~100-5000 nm depth) with separation of carbon-depleted regions (~3000-5000 nm) as shown in Fig. 1. This range of separation distances is comparable to the penetration depths of ~0.5-25 keV electrons into the composite of 800 to 11,000 nm [2].

Charging studies on polymers and carbon composites have revealed that sample arcing and luminescence occur as a result of electron beam bombardment [3-5]. Both insulating regions and electrically isolated carbon particles (floating conductors)

Research was funded by the NASA Goddard Space Flight Center.

Jensen, et al.,

Fig. 1. Scanning electron micrograph of high conductivity carbon-loaded polyimide (Kapton™ 275XC230) showing ~0.1 um to 0.5 um diameter graphic carbon black particles (darker areas) in a polyimide matrix with 1 um to 5 um diameter regions with no carbon particles near the surface (lighter areas). Image acquired at NASA Goddard Space Flight Center with an environmental SEM using a 5 kV beam.

Proc.2013 IEEE International Conference on Solid Dielectrics (ICSD)
provided incident electron energies of 5 keV to 25 keV with stable, uniform, well-characterized beam fluxes of 0.1 nA-cm⁻² to 400 nA-cm⁻² at typical beam spot diameters of ~3 cm [12]. The results discussed here are from tests at room temperature and 40 K, beam energies of 5, 7, 10, 15, 22 and 25 keV and beam current densities of 1, 10, 38 and 40 nA/cm². Absolute current densities were measured before and after each experiment with a conventional Faraday cup and relative fluxes were monitored in real time with a pseudo Faraday cup (B in Fig. 3a). Currents were measured from the back of the sample to ground, using fast sensitive picoammeters with <0.2 pA resolution [3]. A digital storage oscilloscope (Tektronix TDS 2040 1 GHz) acted as a shunt ammeter measuring the voltage drop across a 47 Ω metal-film resistor, typically with a 10⁻³ A threshold, 4 ns resolution, and 10 µA sensitivity [9].

Three cameras and two fiber optic spectrometers were used to collect optical data [4, 9, 13]. Low light intensity was monitored with an SLR CCD still camera (Canon, EOS Rebel XT DS126071; ~400 nm to 700 nm, 30 s/frame), a VIS/NIR image- intensified CCD video camera (Xybion, ISG-780-U-3; ~400 nm to 900 nm, 30 frames/s), and an InGaAs video camera (Goodrich Sensors Unlimited, SU320MS-1.7RT; ~800 nm to 1700 nm, 60 frames/s). UV/VIS (Stellarnet, 13LK-C-SR; ~200 nm to 1080 nm with ~1 nm resolution) and NIR (Stellarnet, RW-InGaAs-512; ~1000 nm to 1700 nm with ~3 nm resolution) spectrometers were also used. The spectral response and range were determined and the sensitivity of the instruments was calibrated with NIST traceable sources [8]. An additional InSb video camera, discreet detectors and filter combinations (~1000 nm to 5500 nm) were used to monitor IR emissions; no IR in the ~1100 nm to 2500 nm range was observed for any of the experiments reported here.

Two methods were used for sample cooling, a liquid N₂ cryogenic reservoir (~150 K to ~400 K with a stability of ±4 K maintained over typical 2 hr experiment durations [14]) and a two-stage, closed-cycle helium cryostat (<30 K to >450 K, with long-term controlled stability of <0) [2].

The samples (10 mm diameter) of several grades of commercially available high conductivity Black Kapton™ material of increasing conductivity: Dupont 100XClO2E5 [25 µm, 2·10⁻³ (Ω-cm)⁻¹]; Dupont 100XClO2E7 [25 µm, 2·10⁻³ (Ω-cm)⁻¹]; Dupont 275XC230 [66 µm, 1·10⁻³ (Ω-cm)⁻¹]; and a laminate composite with a Kevlar™ layer sandwiched between two layers of 275XC230 [254 µm, 5·10⁻⁹ (Ω-cm)⁻¹], Dunmore 1100 Dun-Lam⁰⁰ [thicknesses and room temperature conductivities across sample thickness measured at USU] [1]. At the low end of this temperature range, for Kapton™, the lower dark current conductivities [2·10⁻⁹ (rad-s⁻¹)-(Ω-cm)⁻¹] at room temperature and 5·10⁻¹⁰ (rad-s⁻¹)-(Ω-cm)⁻¹ at 125 K] and radiation induced conductivities [6·10⁻²⁰ (Ω-cm)⁻¹] at room temperature and 7·10⁻²⁵ (Ω-cm)⁻¹ at 125 K] led to reduced charge dissipation and enhanced charging and electrostatic discharges at low temperatures. The electrostatic breakdown field strength of Kapton™ at room temperature is 3·10³ V-m⁻¹ [15].

HCBK samples were optically cleaned and underwent a ~12 hr vacuum bakeout at ~390 K and <1·10⁻⁵ Pa to eliminate adsorbed water and volatile contaminants, and were placed in an ultrahigh vacuum chamber (base pressure <1·10⁻⁵ Pa) for >24 hrs to allow for outgassing before measurements were made. The samples were mounted on Cu pedestals flush with an ~0.6 mm gap between the sample and a grounded multi-sample carousel (see Fig. 3(a)) [4].

III. RESULTS

All types of Black Kapton™ samples studied exhibited readily observable electrical discharges and luminescence when subjected to electron beam bombardment, as illustrated in Fig. 4. Three types of light emission with simultaneous current signatures were observed: (i) short duration (<1 s) arcing resulting from electrostatic discharge, (ii) long-duration sustained glow (cathodoluminescence) that turned on and off with the electron beam, and (iii) intermediate duration (~10-100 s) glow that dissipated exponentially with time after infrequent and rapid onset. Arcs, sustained glow, and flares were all detected in the electrometer, oscilloscope, Vis SLR camera, Vis/NIR CCD video camera, and NIR InGaAs video camera; coincidence was almost always seen, except when the signals were below detection thresholds for specific instruments.

A. Arcs

HCBK exhibited numerous short duration (<1 s) electrostatic discharge or arcing events, as seen in Figs. 4 and

![Fig. 2. Block diagram of instrumentation for collecting the pulse charging surface voltage, electrode current and cathodoluminescence data induced by electron beam bombardment. Instrumentation includes electrometers and a storage oscilloscope for current measurements and UV/VIS and IR spectrometers, an SLR CCD still camera, and CCD visible and NIR video camera for optical measurements.](image1)

![Fig. 3. (a) Sample mount with four samples (A) in the corners of the sample holder and a centered copper pseudo Faraday cup (B) for monitoring the beam current. (b) Rotating sample cover, which allows only the sample under investigation to be exposed to the beam. (c) Sample (in red circle), while the electron beam is on. (d) The position of an arc on the sample (C).](image2)
Higher conductivity samples (275XC230 and 1100 Dun-Lam laminate) have similar arc rates and arc amplitudes/intensities for similar ranges of incident current, energy, power and temperature. Limited measurements at 22 keV and ~5 nA/cm² on lower conductivity (100XC10E7 and 100XC10E5) samples suggest that arc rates are ~2-10X higher than observed for higher conductivity (275XC230) samples at comparable energies and current densities.

Measurements were made from <40 K to 290 K. Lower temperature samples in general showed larger arc rates, although insufficient data have been acquired at different beam current densities and energies to establish a functional dependence. The dark current and radiation induced conductivities in polyimide are several orders of magnitude lower at the lower temperatures, leading to reduced charge dissipation and enhanced charging and electrostatic discharges at low temperatures.

Figs. 5 (b-e) show typical arc intensity curves as a function of time for electrometer, oscilloscope, CCD camera, and InGaAs camera measurements. Time constants for the exponential decays observed for many different arcs are fairly consistent for each individual instrument but vary substantially from instrument to instrument (electrometer: 10⁸ s; CCD camera: 10⁵ s; oscilloscope: 10² s; InGaAs camera: 10¹ s). In general, the oscilloscope data exhibit much faster response, with widths on the order of a few ms. The longer time constants exhibited in the other instruments are most likely the result of instrumental broadening. These response times longer than the arc duration cause the slower instruments to record a signal averaged over the slower response times; the different response times for different instruments makes cross-comparison of absolute peak amplitudes and power in the curves from different instruments difficult.

The generation of arcs in HCBK from incident electron flux at low temperatures and room temperatures and the approximate arc rates as reported here has been confirmed by limited measurements in independent studies [16, 17]. High frequency arc signatures, in radio frequencies, have also been observed with antennas near Black Kapton™ samples exposed to electron beams [18]. Additional investigations of how glow/arc/flare intensity, power and frequency scale with illuminated area are currently underway at USU and MSFC [16].

B. Sustained Glow

Sustained glow is long duration cathodoluminescence that turned on and off with the incident electron beam. It occurs over the full illuminated sample area when beam is on, as seen in Fig. 4. Fig. 5 shows that there is excellent temporal correlation between the electrometer data and the video camera spectral radiance curves. Sustained glow intensity or current takes a finite amount of time to reach a fairly steady equilibrium value. There is also a finite decay time seen in glow intensity and current curves after the beam is turned off. The exponential rise and decay time constants (10⁻¹ s) are roughly the same and are believed to be related to filling and release rates of the traps in the insulating polyimide.

The magnitude of the sample currents during beam on times was consistent with a displacement current that resulted as charge accumulated in the sample. The rate of surface charging was typically close to the incident beam current density, J₀, reduced by the total electron yield of the sample at the incident beam landing energy, \( \frac{d\Sigma}{dt} \propto J_0 [1 - \sigma_{yield}(E_b, \Sigma)] \). At higher incident power levels, equilibrium
glow intensity is sometimes seen to decrease ~2X due to long exposure of beam as the accumulated negative surface charge or reduced landing energy increased the electron yield, \( \sigma_{\text{yield}}(E_p, \Sigma) \), toward unity.

Negative currents result from displacement currents to the grounded rear sample electrode and the grounded sample holder, as negative charge from the electron beam accumulates in the sample. Increased negative currents during arcs result from accumulated electrons in the sample moving to the grounded sample holder.

Simple models propose that luminescence increases linearly with incident power density (beam energy times beam current density) for non-penetrating radiation (e.g., M55J carbon/epoxy composite data in Fig. 6(e)) and decreases in proportion to the range of incident electrons for penetrating radiation (e.g., fused silica coating data in Fig. 6(e)) [13]. As seen in Fig. 6(e), the spectral radiance of HCBK samples is largely independent of absorbed power. Bowers has proposed that a linear combination of thick polyimide regions (with non-penetrating radiation) and thin polyimide layers coating near-surface carbon particles (with penetrating radiation) can produce such a signature nearly independent of incident power [19]. The fraction of such regions can be approximated as the fraction of light (~36%) and dark (~64%) pixels in a binary image of the electron micrograph of Fig. 1 [20]. This simple luminescence model [13] for 10 nm (~0.4 keV penetration energy) and 50 \( \mu \)m (~60 keV penetration energy) in the ratio of thin to thick areas approximated by the SEM binary image [19] predicts the curve of spectral radiance versus energy shown in Fig. 6(e).

Higher conductivity samples (275XC230 and 1100 Dun-Lam laminate) have similar glow intensities for similar ranges of incident current, energy, power, and temperature. Limited measurements at 22 keV and ~5 nA/cm\(^2\) on lower conductivity (100XC10E7 and 100XC10E5) samples suggest that sustained
glow spectral radiance is ~2-10X lower than observed for higher conductivity (275X230) samples at comparable energies and current densities. The amplitudes of the sustained glow increased roughly linearly with decreasing temperature and was approximately 8X brighter at 100 K than at room temperature.

Fig. 7 shows a low resolution plot of the sustained glow spectra that is peaked in visible near ~550 nm and extends into NIR. Calibrated measurements of the absolute spectral radiance with the cameras were consistent with the spectral measurements and were used to scale the spectra. This observed spectra is somewhat similar to cathodoluminescence of epoxy resin composites [5] and fused silica [13] observed previously.

C. Flares

Features seen simultaneously in current and VIS and NIR spectral response curves of intermediate duration (~100 s) glow that dissipated exponentially with time have been termed flares (see Fig. 4). Flares are infrequent (~2 flares/hr) and were only observed in long runs after ≥20 min duration, which suggests the necessity for substantial charging within the sample before flares can occur.

Flares (usually) have an arc associated with their instigation, although the origin of such large arc triggers is not known. Flares have abrupt onset rise times (<0.1 s), believed to be associated with a rapid discharge. Flares also exhibit very long times (10^2 s) for the currents or spectral radiance to return to pre-flare equilibrium values associated with sustained glow. The response for individual flares between the abrupt onset and long term decay is complex and can vary from one flare to the next.

The spectral response and electrometer currents ~1-100 nA amplitude with <1-10 µJ) of flares are ~2-20X that observed for typical sustained glow. Only about a half a dozen flares have been observed in ~20 hrs of HCBK data, too few to accurately determine the flare dependence on current density, charge fluence, beam energy, or deposited power. Flares seem to occur mostly for higher energies or power density; this suggests a possible link with charge dissipation through RIC. RIC allows lateral charge motion and downward motion in penetration region.

IV. CONCLUSIONS

High conductivity carbon-loaded polyimide underwent electron irradiation experiments to investigate the electron transport, charging, discharging, cathodoluminescence and emission behavior. These experiments revealed that for many applications HCBK cannot be viewed as a macroscopic conductor; it is a nanodielectric. This composite material is comprised of an insulating polyimide matrix with imbedded nanoscale conducting regions. Because the size of these regions is comparable to the length scales of electron penetration and transport, the material exhibits profound changes in the conducting and dielectric properties. Upon electron beam bombardment, the material exhibited behaviors similar to other dielectric materials; these include long duration cathodoluminescence, short duration arc and intermediate duration flare behaviors. As shown here, these properties can only be understood quantitatively by considering the nanoscale structure.

ACKNOWLEDGMENT

We gratefully acknowledge: contributions to instrumentation and experimental efforts from members of the Materials Physics Group (Ryan Hoffmann, Jerilyn Brunson, Jennifer Albrehtsen Roth and Jodie Corbridge Gillespie); help with optical calibrations from James Peterson of the USU Space Dynamics Laboratory; SEM measurements by Len Wang at NASA GSFC; use of the infrared and CCD video

Jensen, et al.,
cameras from Michael Taylor; and useful discussions with Charles Bowers, Robert Meloy, Malcolm Niedner and Jim Heaney of NASA GSFC, Todd Schneider of NASA MSFC, and Nelson Green of NASA JPL.

REFERENCES