Polyferrocenylsilanes as Protective Charge Migration Coatings for Dielectrics*

Alexandra Bartole-Scott,[1] **Andrea Berenbaum,**[1] **Rui Resendes,**[1] **Ian Manners,**[1] **Gerald Dubois,**[2] **and Keith G. Balmain**[2]

Polyferrocenylsilanes $[Fe(\eta\text{-}C_5H_4)_2SiMePh]_n$ (**3**) and $[Fe(\eta\text{-}C_5H_4)_2SiMe_2]_n$ (**4**) were prepared by transition metal-catalyzed ring-opening polymerization (ROP) and thin films of these materials were studied to investigate their potential utility as protective charge migration coatings for dielectrics. Films (>15 μm) of **3** or **4** cast from a concentrated toluene solution coated on Mylar did not experience any arc discharging when exposed to a beam of low energy (20 keV) electrons for a 1 h time period. In order to further investigate the charge migration properties of polyferrocenylsilanes, thick shapes and films of **3** were prepared by mold-extrusion and solution-casting onto a Teflon substrate, respectively. Charge accumulation measurements on **3** using a nonintrusive electrostatic probe showed that even after a 1 h exposure to a 25 keV electron flux, no appreciable charge accumulation existed. The direction of current flow was explored by constructing a device consisting of a film (thickness ca. 100–130 μm) of polymer **3** coating a layer of copper. When positioned beneath a circular mask and exposed to a low energy electron flux (5–25 keV), measurements of the current at the surface of the polymer film either exposed to or not exposed to the electron flux were not significantly different, and the current recorded from the bare copper connection to the ground was significantly (100–1000 times) higher. Although the mechanism of charge migration in polyferrocenylsilanes is not fully understood, these experiments indicated it may arise from a conduction mechanism, however electron scattering may also be involved.

KEY WORDS: Polyferrocenylsilanes; charge migration; negative charge accumulation; arc discharge

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1. INTRODUCTION

Orbiting at altitudes of 3–6 earth radii, numerous satellites that provide defense, communication, and meteorological services are currently circling the Earth. They are under the influence of the "solar wind" which consists of charged particles (electrons, protons, and helium nuclei) originating from the surface of the sun. Satellites immersed in this ambient plasma attain electrical equilibrium via the deposition of charges. However, in regions of low sunlight intensity or during periods of intense solar activity, negative charge accumulation can occur near the surface (from low energy electrons) and deep within the interior (from high energy electrons) of the dielectrics comprising the satellite's thermal blankets, cable coatings, and microelectronic devices [1]. When the differential charge between the satellite's dielectrics and the surrounding environment becomes sufficiently large, this charge accumulation gives rise

to an electrical field and may lead to a high energy arc discharge of sufficient energy to generate electromagnetic interference, material breakdown, and device failure [2]. The failures of the synchronous-orbit ANIK satellites in January 1994 and March 1996 are attributed to such arc discharges. To date, a number of studies aimed at understanding the interaction of dielectrics with high and low energy electrons have been undertaken [3].

It would be highly desirable to develop a robust polymeric coating which, if applied to the surface of a dielectric would remove or prevent the formation of charge accumulation. Importantly, this coating would need to permit charge migration without having high intrinsic electrical conductivity since the presence of induced electric currents might lead to undesirable interference with any nearby radio frequency devices. Thus, we have investigated polyferrocenylsilane polymers as viable candidates for improved charge migration coatings for dielectrics.

The thermal [4], anionic [5, 6], and transition metal-catalyzed [7, 8] ring-opening polymerization (ROP) of silicon-bridged [1] ferrocenophanes **1** has proven to be a valuable route to a variety of high molecular weight polyferrocenylsilanes (PFSs), **2** [9].

These novel, readily available, and processable metal-containing polymers can be either crystalline or amorphous [10–13] and are attracting attention with respect to applications as magnetic ceramic precursors [14–17], redox-active gels [18], variable refractive index materials [19], and etch resists [20–22] for nanolithographic applications [23]. The ROP methodology can be extended to other [1]- and [2] metallocenophanes to yield other classes of metal-containing polymers [24].

Electrochemical studies of PFSs **2** have revealed the presence of significant Fe$\cdots$Fe interactions along the polymer backbone. When doped, hole conductivities in the semiconductor range (ca. 10^{-4} S·cm^{-1}) have been established [25, 26]. However, the polyferrocenes in their pristine state are insulating (conductivities less than 1×10^{-14} S·cm^{-1}) [26]. We were therefore interested in investigating additional properties of
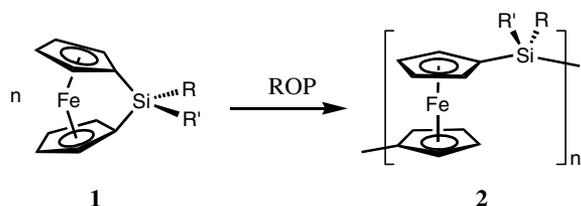
polyferrocenylsilanes including their dielectric properties in comparison with other commercially available organic polymers.

In a preliminary communication [27] we reported our initial studies on the ability of thin polyferrocenylsilane films to act as protective charge migration coatings for dielectrics when exposed to low energy electrons. In this follow-up paper we describe full details of our investigations of this phenomenon and also report on experiments using thick films (>100 μm) and fabricated shapes aimed at further exploring the charge migration properties of this organometallic polymer.

2. EXPERIMENTAL

2.1. Materials

Polyferrocenylsilanes [Fe(η-C$_5$H$_4$)$_2$SiMePh]$_n$ **3** and [Fe(η-C$_5$H$_4$)$_2$SiMe$_2$]$_n$ **4** were prepared using Pt-catalyzed ROP according to literature procedures [8, 28]. Molecular weights were estimated by gel permeation chromatography (GPC) calibrated to polystyrene standards. For **3**: $M_w = 4.3 \times 10^5$ (PDI = 1.9), for **4**: $M_w = 2.9 \times 10^5$ (PDI = 1.6).

2.2. Arc Discharge Simulations

Devices based on **3** and **4** were prepared by coating a 50μm thick Mylar film with 1.5 mL of a 15 % (weight/weight) solution of **3** or **4** in toluene. Film applications were accomplished with the use of a motor driven blade applicator built in-house. Mylar films (type A Mylar–Dupont) were purchased from Cadillac Plastics. Films of **3** and **4** supported on Mylar were placed underneath a copper mask possessing a 4.5 cm diameter circular aperture. The electron beam was generated using a modified SEM operating at variable filament currents. Discharge images were captured with a Tektronix model C1002 CCD video camera which was fed into a Sony model EVO-9800 Hi8 videocassette recorder. Discharge current pulses were measured using a Tektronix model 72500 transient digitizing oscilloscope.

2.3. Deep Charging Simulations

The charge measuring device containing the sample of **4** was placed in one arm of a vacuum system consisting of a 10 cm diameter stainless steel cross with the sample facing a ^{90}Sr source inserted at

Scheme 1.

Table I. Summary of Current Recorded at Each Ammeter of a Thick Film Sample of **3** on a Copper-clad FR4 Substrate

	Current recorded		
Acceleration voltage	Ammeter A (Bare copper connection under polymer film)	Ammeter B (Surface of polymer film not in electron beam)	Ammeter C (Surface of polymer film directly in electron beam)
5 keV	9.7–10.1 nA	0.017 nA	0.01 nA
10 keV	9.8–10.3 nA	0.043 nA	0.012 nA
25 keV	9.2–10 nA	0.096–0.1 nA	0.021–0.044 nA

the opposite arm. Signal cables from the charge-measuring device were connected to the outside of the chamber through a connection feedthrough. The cross was evacuated using a Boc Edwards EXPB8 turbomolecular pumping system attached to a third arm of the cross with a Boc Edwards ion gauge attached to the fourth arm. The ^{90}Sr Beta source was a 100 millicurie source sealed in a X112 capsule from Amersham/Searle. The main Beta particle emissions are at 0.546 and 2.274 MeV. The charge on the various probes were measured at regular intervals and recorded in a file on a PC. The experiment was conducted over a period of approximately 475 h.

2.4. Charge Accumulation Measurements

Charge accumulation measurements were accomplished with the use of a Trek Model 341 Noncontacting Electrostatic Voltmeter. The measurements involved rastering an electromechanical modulating tip (housed within a conducting probe at a fixed potential) over the film surface both before and after exposure to a 25 keV electron flux. Differences between the surface (resulting from negative charge accumulation) and probe voltages results in the development of an electric field (E_f) proportional to the voltage difference and inversely proportional to the distance between surface and the probe. As the probe scans the surface, the electric field (E_f) induces an AC signal that is related to the amount of accumulated surface charge.

2.5. Charge Migration of Thick Film Samples of PFS 3 on a Copper Substrate

A film of **3** approximately 100–130 μm thick was applied to a piece of copper-clad FR4 approximately 10 cm by 10 cm using a motor-driven blade applicator. Three electrical connections were made on the copper-clad material using a conductive silver epoxy, one connection was made to a section of the bare

copper on the polymer coated side, a second connection was made on the top surface of the polymer coating itself in an area that would be covered by a mask and the third connection was made on the surface of the polymer in an area that would not be covered by a mask. The polymer coated sample was then attached to the substrate plate of a vacuum chamber using Velcro. The electrical connections on the polymer coated sample were attached to wires leading to coaxial feedthroughs to the outside of the vacuum chamber. These coaxial connections were connected to three microammeters to measure the current at each area. A grounded mask with aperture 5 cm in diameter was placed approximately 3–4 mm over the polymer coated sample, resulting in an area of 19.6 cm^2 exposed to the electron beam. The chamber was evacuated to a pressure of 2×10^{-6} Torr. The vacuum chamber has an electron gun installed which has a variable filament current and acceleration voltage which gives the capability of variable current density over a range of charging voltages. In the experiment a current density of 0.5 nA/cm^2 was used with acceleration voltages of 5, 10, and 25 keV (see Table I).

3. RESULTS AND DISCUSSION

3.1. Charge Migration Properties of Polyferrocenylsilane Thin Films

Our initial experiments involved coating a 50 μm thick Mylar sheet with a 30 μm thick coating of the amorphous PFS **3** ($T_g = 90°C$) [9]. The coated Mylar was then exposed to a 20 keV electron beam at current densities of 1, 5, and 10 nA·cm^{-2} using the experimental set-up depicted in Fig. 1(a). No discharges were observed over a 1 h period at each current density. For comparison, a 50 μm thick sample of uncoated Mylar was exposed to similar conditions. At a current density of 5 nA·cm^{-2}, a discharge was observed after 7 min of exposure and
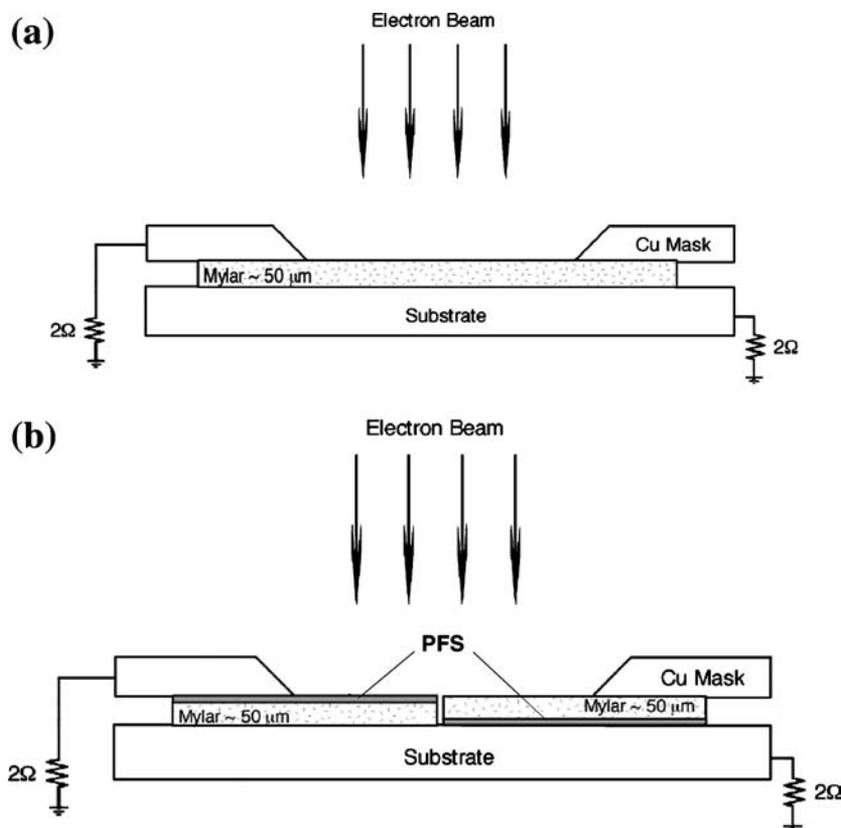
Fig. 1. Schematic representation of experimental set-up for surface charging experiments (a) 50 μm thick Mylar sample and (b) 50 μm thick Mylar sample, half (left) of which has been coated with PFS.

repeated discharges were observed thereafter (Fig. 2(a)). Experiments were repeated with a thinner 15 μm coating of PFS **3** and, again, no discharges were observed after a 1 h exposure at all three current densities.

In order to further substantiate our observations, Mylar samples coated with a 15 μm coating of **3** were cut in half, and one half inverted (Fig. 1(b)) thereby exposing the Mylar side of the sample to the electron beam. At a current density of 1 nA·cm^{-2} a

3:R = Me, R' = Ph
4:R =R' = Me

Scheme 2.

single discharge was observed on the uncoated side during a 1 h period (Fig. 2(b)). At a current density of 5 nA·cm^{-2} five discharges were observed on the uncoated side, and one discharge was observed on the PFS-coated side. Discharging on the side coated by the PFS became more frequent with thinner (10 μm) coatings. Importantly, in all cases where a discharge was observed on the PFS-coated side, discharging appeared to originate on the Mylar half, or at the coated–uncoated junction.

In efforts to determine whether this phenomenon was limited to amorphous samples of PFS, semicrystalline PFS **4** ($T_g = 34°C$, $T_m = 120–145°C$) [9] was investigated under analogous conditions. When a Mylar sample coated with a 15 μm layer of **4** was exposed to current densities of 1, 2.5, and 5 nA·cm^{-2} for a 1 h period, no discharges were observed. In order to investigate the effect of film thickness on the charge migrating properties, devices composed of a 5 μm thick coating of **4** on 50 μm thick Mylar were also investigated. While no discharging was observed at a current density of 1 nA·cm^{-2} over a 1 h period,
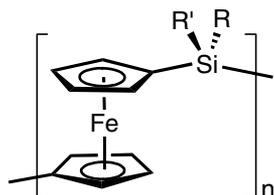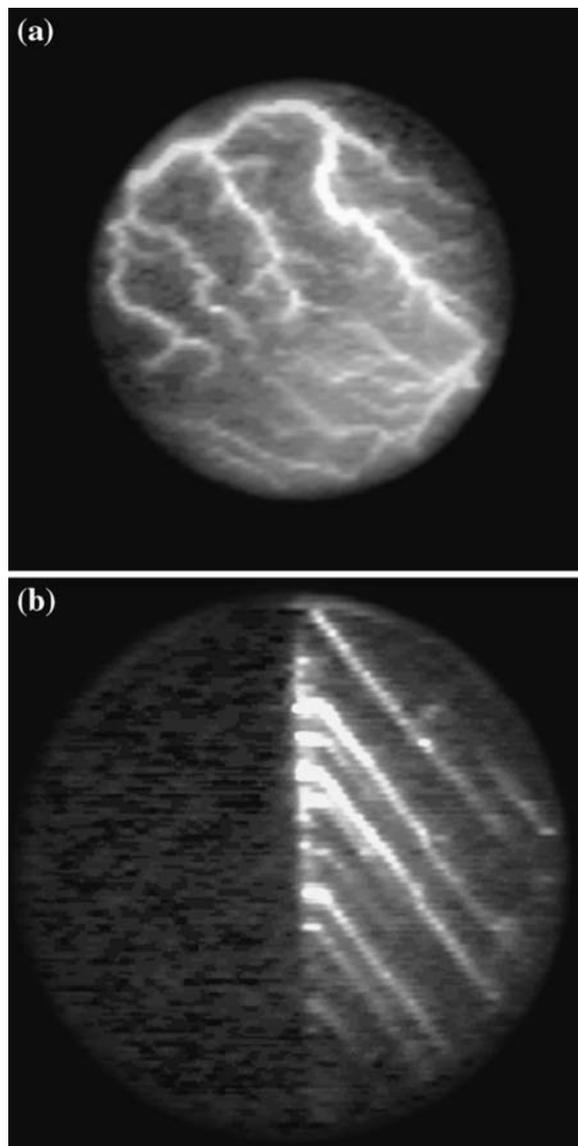
Fig. 2. Arc discharge tracks as seen in (a) 50 μm thick Mylar sample and (b) 50 μm thick Mylar sample, half (left) of which has been coated with a 15 μm thick layer of **3**.

discharge tracks appeared to have originated on the uncoated half or at the junction between the halves. It is highly probable that the discharges originate from sites at which the PFS coating had flaked away as part of the cutting process. The fact that discharging appeared more prevalent in the halved devices constructed with the semicrystalline PFS **4** than with the amorphous analog **3** is in agreement with the observation that films of **4** are much more brittle than **3** and tend, therefore to flake away much more during the splicing process.

3.2. Deep Charging Experiments

Given the potentially significant advantages of incorporating coatings of this type into the components of geosynchronous orbit satellites, it became desirable to further understand the charge migration phenomenon. The low energy (20 keV) electrons utilized in the aforementioned studies are known to penetrate materials by ca. 10 μm [3]. In order to examine the charge migration properties of these materials in more detail, deep charging (using a ^{90}Sr source, ca. up to 2 MeV in energy) simulations with the semicrystalline PFS **4** ($M_w = 2.9 \times 10^5$, $PDI = 1.6$) were undertaken. Deep charging simulations were conducted with the use of a triangular sample of **4** prepared through a melt fabrication (ca. 150°C) route (Fig. 3).
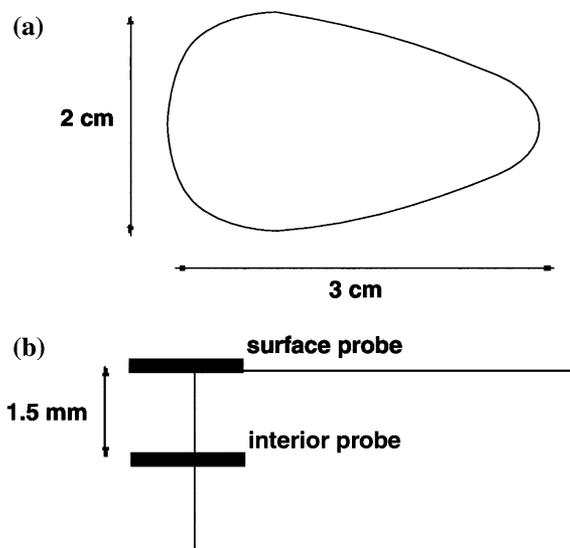
at higher current densities (2.5 and 5 nA·cm^{-2}) discharging was observed. This result is consistent with the fact that a 20 keV electron beam is known to penetrate materials by ca. 10 μm [3].

When the devices with a 15 μm coating of the PFS **4** were cut in half, and one half inverted so as to expose the underlying Mylar to the electron beam (Fig. 1(b)) discharges were observed consistently on both the coated and uncoated halves. Interestingly, similar to the analogous trials with **3**, when discharges were observed on the coated half, the

Fig. 3. Schematic representation of (a) top view and (b) side view of PFS sample **4** used for deep-charging experiments. Note: (a) and (b) are not drawn to scale.

With this experimental setup, the floating potential of inserted metallic probes at the surface and at a depth of 1.5 mm was monitored as a function of time (0–500 h). Under these conditions, the charging profiles measured for a typical dielectric, poly(methylmethacrylate) (PMMA) (*Plexiglass*[TM]) (Figs. 4(a) and 5(a)) show repeated negative charge accumulation followed by rapid discharging as a function of time (0–160 h). This is in striking contrast to PFS **4** whereby no accumulated charge was observed at either the surface (Fig. 4(b)) or within the interior of the sample (Fig. 5(b)). These results further illustrate the charge migration properties associated with PFSs.

3.3. Surface Charge Accumulation Measurements

Given current knowledge of the charge transport properties of polyferrocenylsilanes, it is plausible to imagine of the coatings of PFSs **3** and **4** acting as semiconductors [25, 26]. In essence, the charge being directed at the surface of the coated sample might therefore be slowly drained to the ground by contact with the edges of the grounded mask aperture. While the hole mobilities and conductivities of **3** and **4** have been studied [25, 26], very little is known about the electron conductivities of these materials. In one example by Yamamoto *et al.* [29], a polyferrocene/poly(aryleneethynylene) type copolymer with electron withdrawing substituents has been observed to possess an electrical conductivity of 10^{-5} S·cm^{-1} when reduced with sodium metal. This would suggest that the narrow conduction bands of a polyferrocene are capable of permitting some degree of electron conductivity.

We performed charge accumulation measurements on thin films of **4** using a nonintrusive, surface electrostatic probe which showed that even after 1 h of exposure to a 25 keV electron flux, no appreciable charge accumulation was detected on the embedded probe (Fig. 6). In this type of measurement, an electrostatic probe is rastered across the surface of the sample before (Fig. 6(a)) and after (Fig. 6(b)) exposure to an electron flux and detects any accumulated charge. For typical dielectrics (e.g. *Plexiglass*[TM]), charge accumulation produces surface potential on the order of 10^3 V is typically observed [30]. The small voltages (ca. 30–50 V) detected on the surface of films of **4** (after exposure to an electron flux) confirmed the absence of any significant amount of accumulated negative charge.

In order to further investigate the ability of PFS films to allow charge migration, and to explore the direction of electron flow when irradiated, an additional experiment was performed. A film of **3** (100–130 μm in thickness, ca. 10× 10 cm in area) ($M_w = 4.3 \times 10^5$, *PDI* = 1.9) was coated on a sheet of copper-clad FR4 (printed circuit board), as shown in Fig. 7. Three electrical connections (ca 3 mm diameter contacts) were made on the copper-clad material using a conductive silver epoxy; one was made to a section of the underlying copper substrate (A), a second was made on the top surface of the polymer coating itself in an area that would be covered by a mask (B) and the third connection was made on the surface of the polymer in an area that would not be covered by the mask (C). This device was placed under a grounded mask 5 cm in diameter, and exposed to an electron flux. The exposed area was approximately 19.6 cm^2. A current density of 0.5 nA/cm^2 was utilized at three acceleration voltages; 5, 10 and 25 keV.

For all three acceleration voltages, the current recorded from the surface connection on the polymer that was not in the electron beam (read by ammeter B), and the current recorded from the surface connection in the electron beam (read by ammeter C) were not significantly different. In contrast, the current recorded at ammeter A from the bare copper connection to the ground was 100–1000 times that of the value measured at the surface of the polymer film. In addition the current measured at ammeter A is consistent with the current density × exposed area, which indicates that very little transverse conduction has occurred (See Table I).

These results indicate that significant charge conduction is being carried out by the PFS film in the direction normal to the copper substrate. As we are mainly familiar with doped samples of PFSs carrying charge through a hole-conducting mechanism [25, 26] this behavior was unexpected. However, given the results obtained by Yamamoto *et al.* [29] and the fact that an electron beam has the ability to act as a very strong reducing agent, this electron conduction mechanism is plausible.

It is important to add that the charge migration properties of these materials may also involve an additional component. An electron scattering process, similar to that present in transmission electron microscopy (TEM) imaging experiments may be occurring concurrently with the possible electron conduction. Typical TEM experiments involve irra-
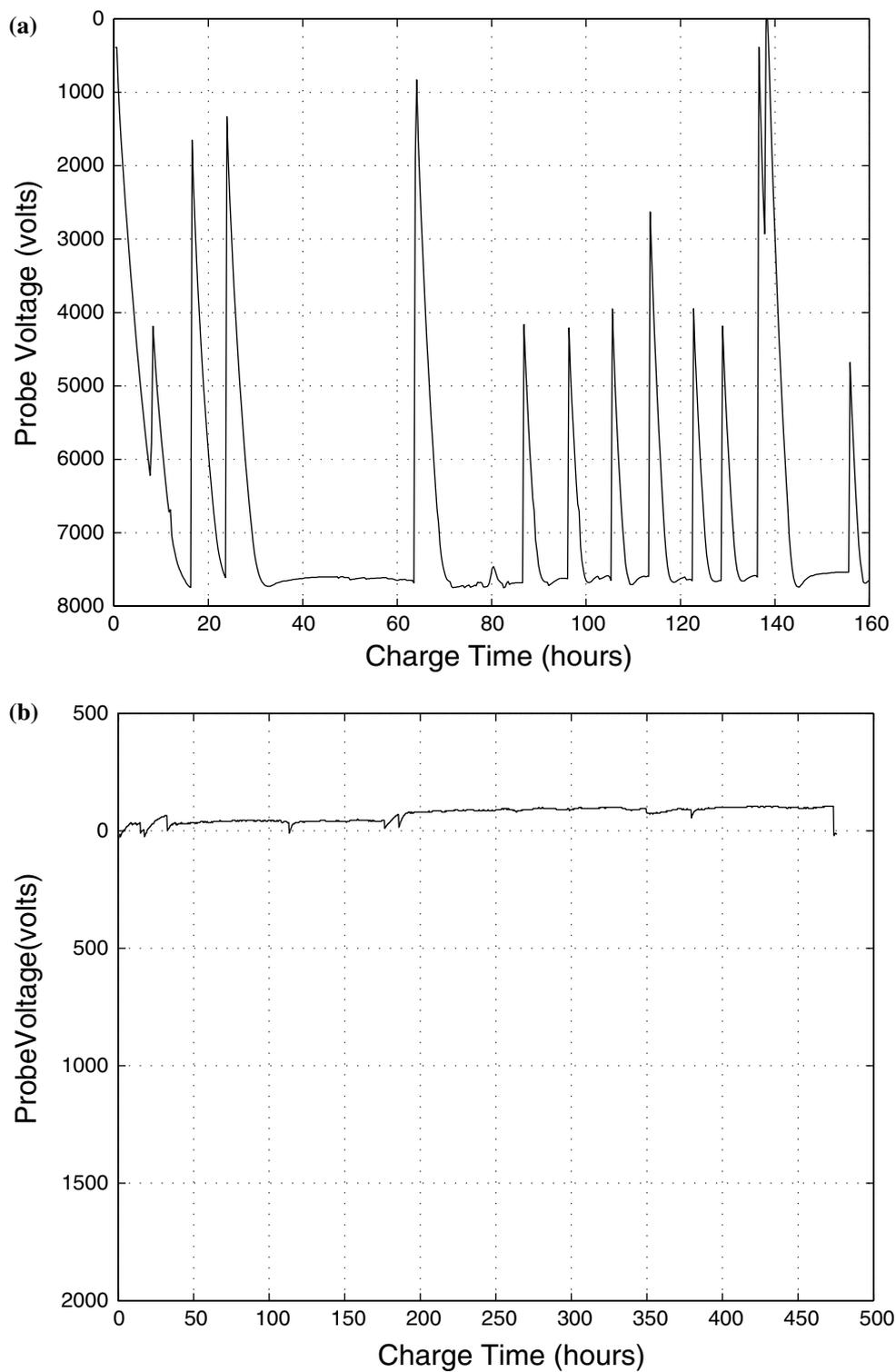
Fig. 4. Surface charging profiles for (a) PMMA and (b) **4** obtained through deep charging simulations.
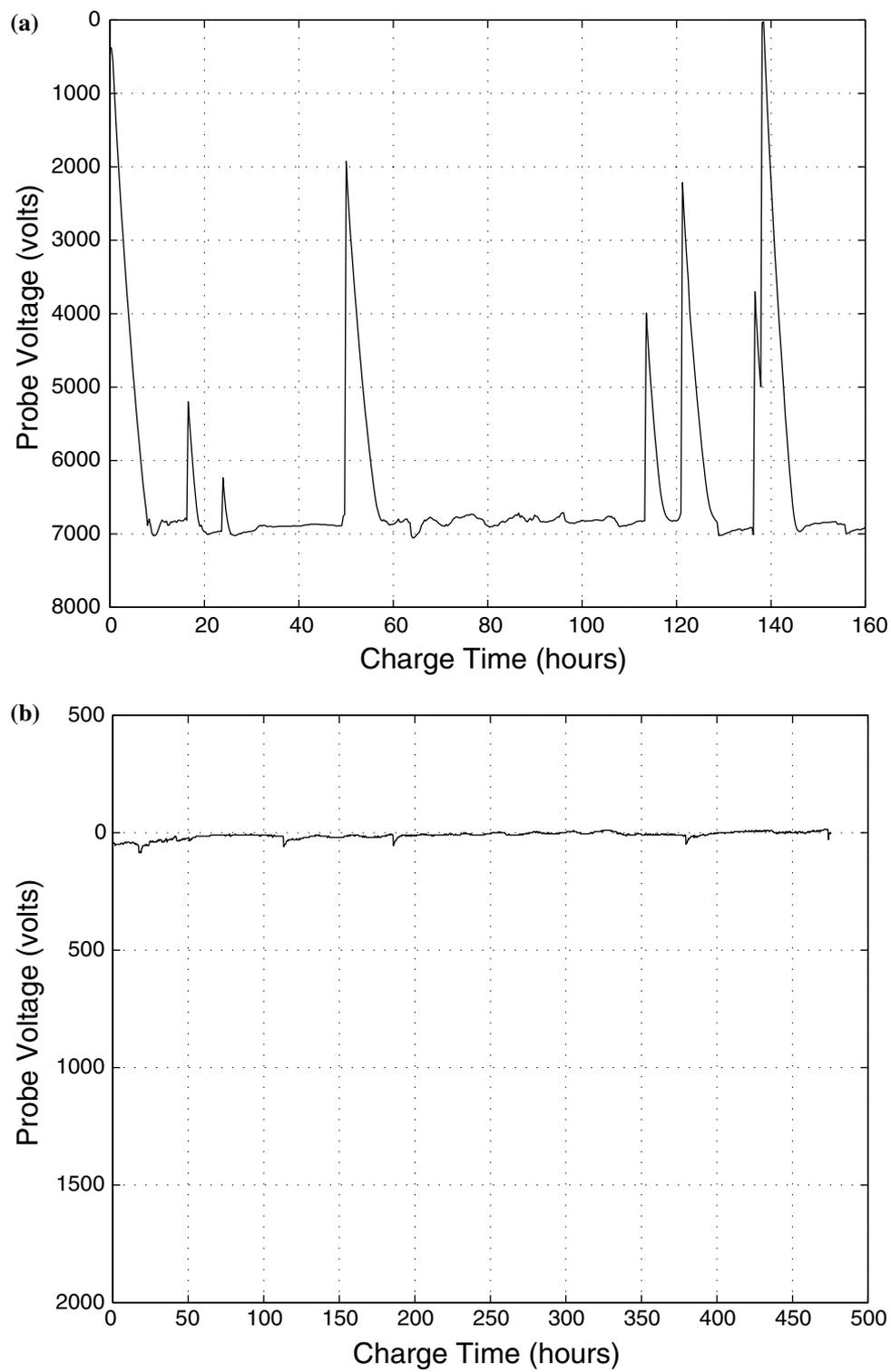
(a)

(b)

Fig. 5. Interior charging profiles for (a) PMMA and (b) **4** obtained through deep charging simulations.
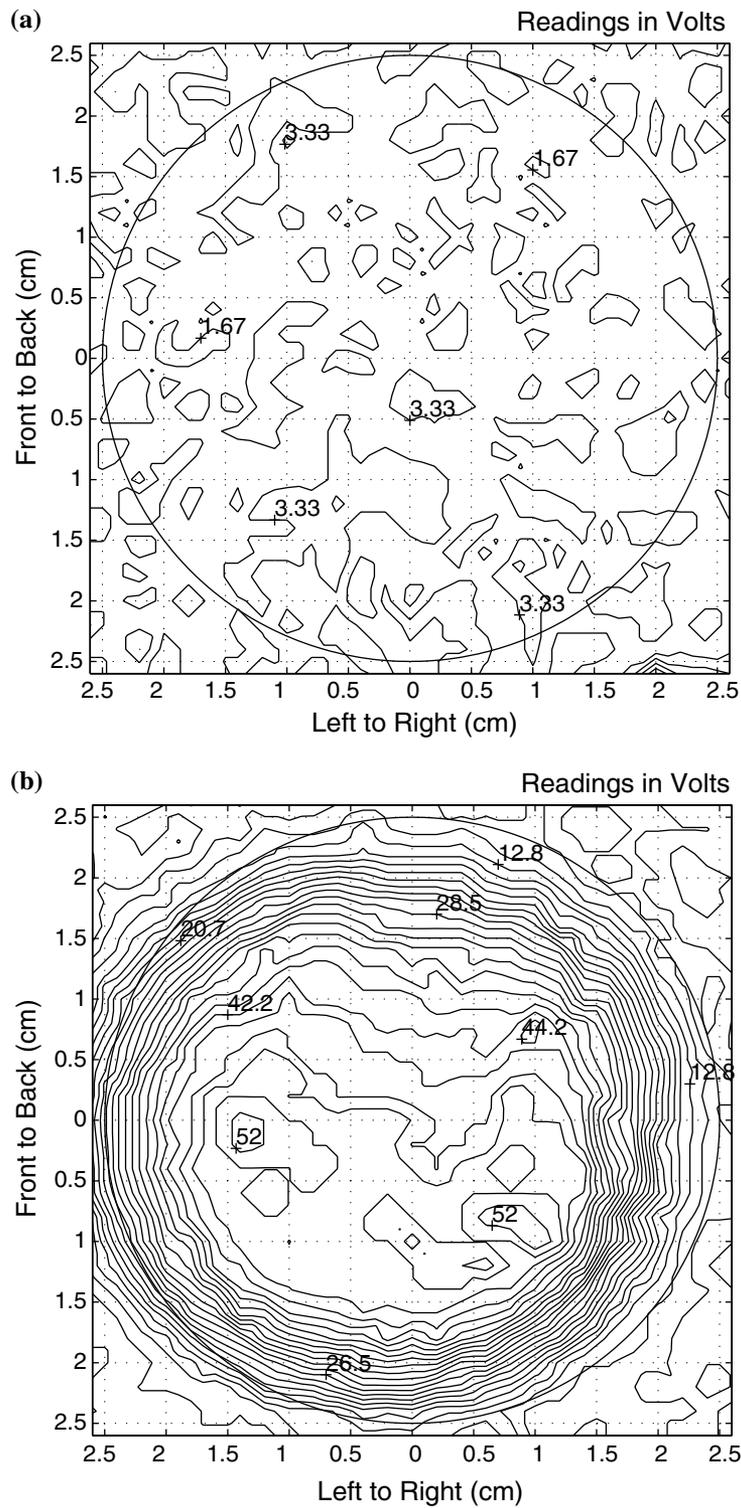
(a)

(b)

Fig. 6. Charge density profiles of **4** (a) before irradiation with 25 keV electron flux and (b) after 60 min exposure to 25 keV electron flux.
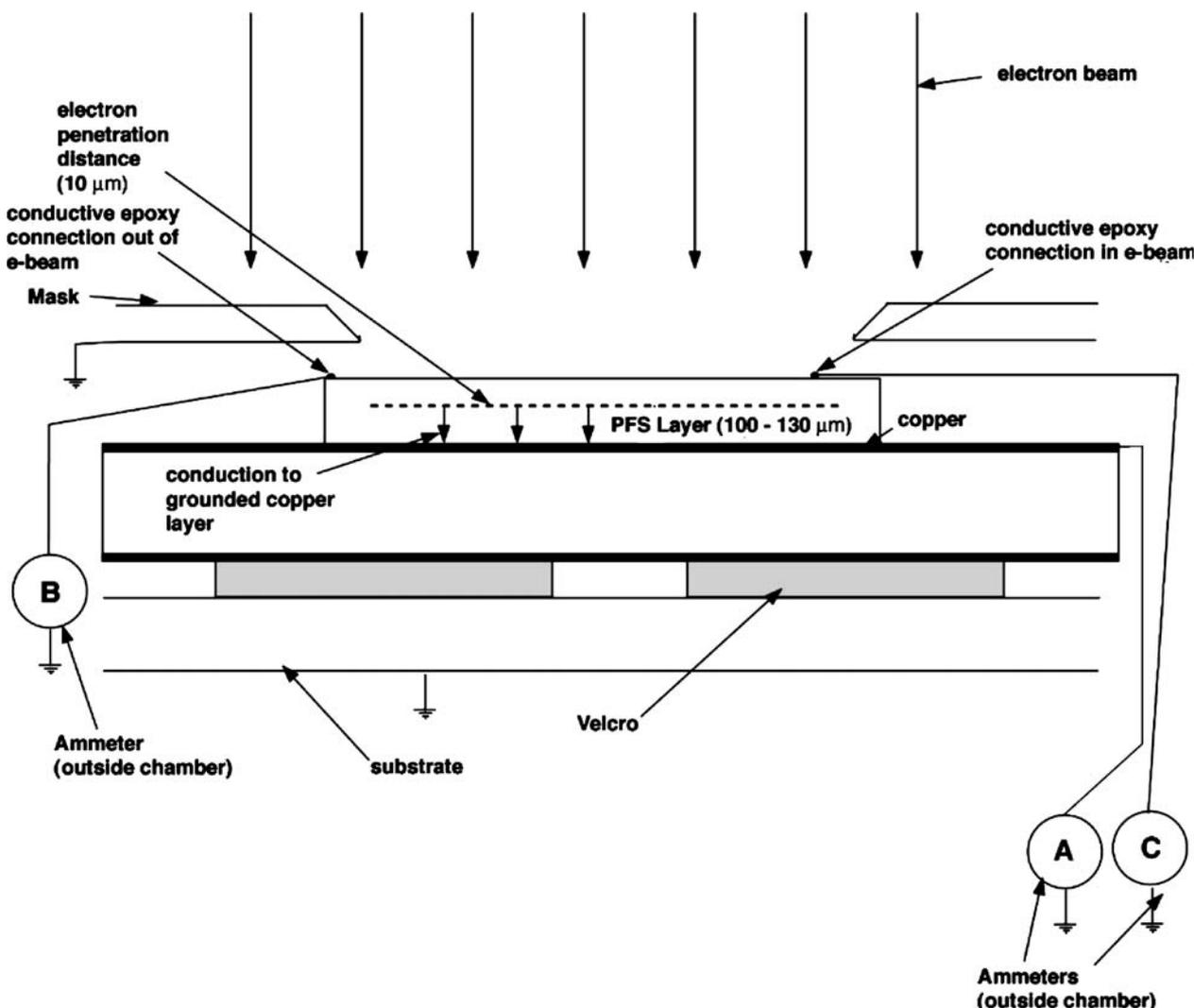
Fig. 7. Schematic representation of the experimental set-up used to measure conduction through a 100–130 μm layer of **3** under electron flux.

diating samples supported on thin carbon films with a 75–100 keV electron beam. The contrast obtained in the imaging process relies on differences in electron scattering arising from local differences in electron density. Recently, polyferrocene regions of phase-separated block copolymers derived from **1** (R = R′ = Me) have been imaged successfully by TEM without the use of any staining techniques [6, 31, 32]. This is a direct result of the presence of electron rich iron atoms in the polyferrocene backbone. Bearing this in mind, it is likely that part of the charge migration mechanism operating for PFSs **3** and **4** could involve electron scattering similar to that detected in TEM imaging.

4. CONCLUSIONS

The preparation of polyferrocenylsilanes via transition metal-catalyzed ring-opening polymerization yields high molecular weight, processable polymers that are suitable for film-formation and mold-extrusion. The results of this study demonstrate that coatings of PFSs **3** and **4** impart a high degree of protection to underlying dielectrics with respect to high energy arc discharges brought about by negative charge accumulation. Experiments involving the irradiation of a Mylar sample coated with thin (>15 μm) films of **3** or **4** with a 20 keV electron beam failed to incur an arc discharge in the underlying Mylar.

Similarly, deep-charging simulations failed to detect any appreciable amount of negative charge accumulation on the embedded probes. Studies aimed at elucidating the charge migration mechanism suggest that these materials may transport charge mainly through an electron conduction mechanism. An additional contribution may be provided by electron scattering due the unique iron-containing PFS structure. Studies aimed at furthering our understanding of the relative contribution of these two processes to the overall charge migration mechanism for PFS materials are ongoing. Additionally, studies focusing on the unexpected electron conduction of PFS under the influence of an electron beam will be undertaken. The results obtained in our studies to date suggest materials such as **3** and **4** have excellent potential as protective charge migration materials, and therefore merit these further investigations.

ACKNOWLEDGMENTS

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