

# Electronic properties of semiconducting poly(ferrocenylsilane) thin films with vapor-phase iodine diffusion doping

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We report diffusion doping of the semiconducting polymer poly(ferrocenylsilanes), or PFS. We have obtained a steady-state conductivity change of greater than eight orders of magnitude effected through iodine vapor doping of PFS. The sign of thermoelectric power measurements indicates p-type conductivity. The conductivity exhibits an activation energy of  $\Delta E = (0.45\text{--}0.65)$  eV for moderately-doped samples and  $\Delta E = (0.8\text{--}0.99)$  eV for heavily-doped samples. We report sample photoconductivity, which we find to be principally of bolometric origin. We also study the evolution of electrical properties over time: during several days after fabrication, the samples exhibit an irreversible decrease in conductivity which may be attributable to partial iodine desorption. After this aging process, especially noticeable in heavily doped material, the sample properties stabilize, suggesting promise in a range of prospective device applications.

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## 1. Introduction

Conducting polymers, which possess physical flexibility, spin-on processability, and diverse functionality through molecular engineering, hold promise in applications such as displays [1–3], radio-frequency identification tags [4–6], and optical communications networks [7, 8]. Common to these diverse areas of application is the need for monolithic or hybrid integration of multiple devices – millions of transistors in VLSI, or only a few devices in some optoelectronic applications – onto a single substrate. Due to the wide range of functional potential, polymers of this type are prospective enablers of low-cost integration and interconnection into a variety of functional circuits – such as electrical, thermal, chemical, mechanical, linear optical and non-linear photonic devices.

One process fundamental to many existing planar integration technologies is the strong modification of electrical conductivity, both type and magnitude, through laterally selective, surface-based doping processes such as ion implantation and solid-phase and vapor-phase diffusion. Surface diffusion has already been exploited in:

- integration of complementary electronic logic devices [9];
- integration of optoelectronic devices with silicon electronics [10] and other compound semiconductor devices [11, 12];

- all-photonic integration [13];
- integration of micromechanical actuators and sensors [14, 15] with electronic signal-processing elements.

The tremendous benefits of polymer-enabled integration, together with the critical role of selective surface diffusion technologies throughout integration processes, motivate the search for and investigation of new conducting polymers which can be readily doped from the vapor phase.

In the present work we focus in particular on one class of semiconducting polymer, poly(ferrocenylsilane), or PFS, whose general features are described in Section 2. We report a steady-state conductivity change of greater than eight orders of magnitude effected through iodine vapor doping of PFS. We report measurement of key electrical characteristics of PFS and their correlation with the technological parameters describing synthesis and doping of the samples.

## 2. Material description

Polymers with backbones containing main group transition elements, in particular, PFS, represent an important class of conducting polymers promising for optoelectronic applications [16]. They have molecular weights of the order of  $10^4\text{--}10^5$  g/mol and are soluble. Many other widely used conducting polymers, such as

poly(thiophene), poly(para-phenylene), poly(phenylene vinylene), poly(acetylene), poly(phenylacetylene) are highly intractable at these molecular weights.

PFS represents an easily accessible and well-defined example of a processable organometallic polymer which contains redox active ferrocene moieties in the polymer backbone. In contrast, the processable analog of poly(thiophene), poly(octadecylthiophene)), is difficult to fabricate and the degree of electrical conductivity possessed by this material as well as other analogs of conducting organic polymers depends on the nature of substituents. For example, in the case of poly(thiophene)s, the conductivity is maximized when the individual thiophene units are coplanar. When the thiophene units are functionalized, the individual thiophene moieties twist away from a coplanar arrangement, thereby reducing the effective conjugation length and therefore the bulk conductivity [17].

One further advantage of PFS is its relative stability to ambient environmental conditions. Many of the above-mentioned alternative materials, while stable in the intrinsic form, become reactive after the doping procedure.

PFS was synthesized as described in Rulkens *et al.* [16], Roncali [18], and Manners [19] and was processed into films several micrometer thick on mylar substrates. Vapor-phase doping was performed by treatment in an iodine atmosphere. To reveal correlations between fabrication technology and electrical properties of the samples, samples with different iodine concentrations, as well as undoped samples, were prepared. For each doping regime, two polymer modifications were explored: semicrystalline poly(ferrocenyldimethylsilane) (PFDMS) and amorphous poly(ferrocenylmethylphenylsilane) (PFMPS). We consider herein samples subjected to 2-, 4- and 24-hour treatment, as well as undoped samples.

One type of contact was realized using vacuum evaporation of gold onto selected areas of the samples. Gold evaporation was performed prior to the iodine treatment in order to eliminate unintended iodine desorption in the presence of the heated metallization species. Another type of contact was created using a silver paste applied following the iodine treatment. For four-probe measurements at various points on the samples, a contact frame with a system of metallic springs was used to provide reproducible mechanical contact.

The test measurements demonstrated that samples with all types of contacts had a symmetric, linear

current–voltage characteristic consistent with their ohmic character. Two-probe and four-probe resistance measurements therefore yield consistent results.

### 3. Electrical characteristics of the samples

Measurements of electrical resistance confirmed the dielectric character of the untreated samples: their resistivity exceeded  $10^{12} \Omega \text{ cm}$ . Undoped PFS is clearly well-suited to provide excellent inter-device isolation required of a platform material for integration.

The doped samples had room temperature resistivity  $\rho_{300}$  in the interval  $(7 \times 10^4 - 10^8) \Omega \text{ cm}$  (see Table I). Local measurements using the four-probe technique described in the text indicate a strong spatial dependence to the observed sample resistance. In a given sample, resistivity at points not very close to the sample edge may vary by a factor of two. The edge regions of 1–2 mm size, where additional iodine absorption is expected, have a strongly reduced resistivity differing from that in the central region by an order of magnitude. All values of  $\rho_{300}$  given in Table I represent averaged values from the central part of samples.

Since  $I_2$  acts as a single electron acceptor in PFS [16], the doped material is expected to exhibit p-type conductivity. We sought to confirm this expectation using direct electrical measurements. In view of the low carrier mobility ( $4 \times 10^{-6} \text{ cm}^2/\text{Vs}$ ) [16], Hall effect measurements will be too weak to allow reliable determination of carrier density and type, so we used thermoelectric power measurements. Using this method, we found all samples to have p-type conductivity. The values of thermoelectric power in different samples measured at room temperature for the same temperature gradient are also presented in Table I. There exists a good correlation between  $\rho_{300}$  and  $\alpha$ : the larger the resistivity, the smaller is  $\alpha$ . If we assume that  $\rho_{300}$  is inversely proportional to the hole concentration  $p$  (not necessarily the case in polymer samples with hopping conductivity, but a useful starting-point in analysis), then this correlation suggests the  $\alpha \sim \ln p$  dependence typical in crystalline semiconductors.

For undoped samples,  $\alpha$  under the same conditions was more than an order of magnitude lower but typically exhibited a positive sign as well. Due to a very high resistance of the undoped samples, the measured data are somewhat uncertain, whereas the doped samples are consistently confirmed to have a p-type character.

To determine the activation energy of resistivity  $\Delta E$  in the doped samples, the temperature dependence of this

TABLE I

Sample	Material	$I_2$ treatment (h)	$\rho_{300}$ ( $\Omega \text{ cm}$ )	$\alpha$ (mV)	$\Delta E$ (eV)
B-2(18)	PFMPS	2	$10^6$	6.5	0.50
G-2(18)	PFDMS	2	$10^8$	4.1	0.54
B-4(19)	PFDMS	4	$5 \times 10^5$		0.45–0.64 <sup>a</sup>
B-4(20)	PFMPS	4	$10^6$		0.5–0.62 <sup>a</sup>
G-4(18)	PFMPS	4	$10^6$	7.0	0.5 (0.5) <sup>b</sup>
B-24(18)	PFMPS	24	$2 \times 10^7$	4.6	0.99
G-24(20)	PFDMS	24	$7 \times 10^4$	17	0.80 (0.64) <sup>b</sup>

<sup>a</sup>Activation energy varies in the experimental temperature interval.

<sup>b</sup>Figures in brackets correspond to  $\Delta E$  after 7-day aging (see Section 4).

quantity was measured in the temperature interval from 205 K to 312 K. This interval provided a resistivity range over three orders of magnitude, sufficient for reliable determination of  $\Delta E$ . Measurement over a wider temperature range was prevented by sample cracking, resulting from mismatched thermal expansion coefficients of polymer and substrate.

We present in Fig. 1 the results of resistivity measurements over a range of sample temperatures. The activation energies determined from these plots are given in Table I. For all of the samples which were subjected to 2- and 4-hour  $I_2$  treatment,  $\Delta E$  had values (0.45–0.64) eV, with results clustered around 0.5 eV. An interesting and unusual result is the increase of  $\Delta E$  in those samples which had the largest iodine concentration (24-hour treatment in  $I_2$ ). No noticeable difference in the activation energies of semi-crystalline (S) and amorphous (A) materials with comparable doping levels was observed.

#### 4. Photoconductivity and sample aging

Preliminary measurements show that the doped samples are photosensitive to both visible and UV radiation. As seen in Fig. 2, a transient response under a step change in illumination exhibits very slow photoconductivity kinetics. The characteristic time of the response varies noticeably from sample to sample and occurs on timescales of seconds to minutes. Similar long-term photoconductivity relaxations have also been reported in non-uniform crystalline semiconductors: in this case, they are the result of non-equilibrium carrier separation due to built-in electric fields in the presence of inhomogeneities [20].

We investigated further the physical nature of the observed photoconductivity. We sought to determine whether this was the result of a light-induced excitation of free carriers which in turn participated in conduction; or whether the effect had a bolometric character associated with sample heating and the observed strong

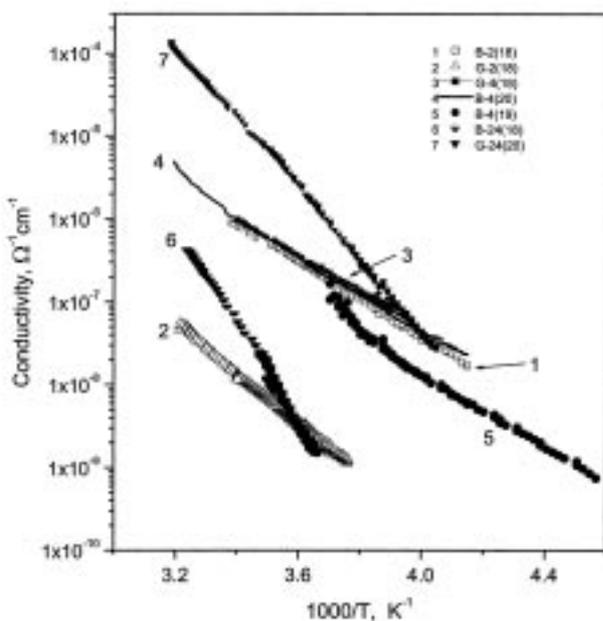
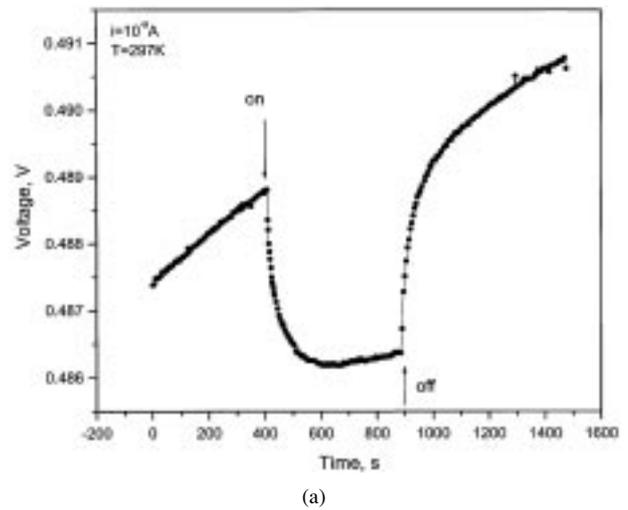
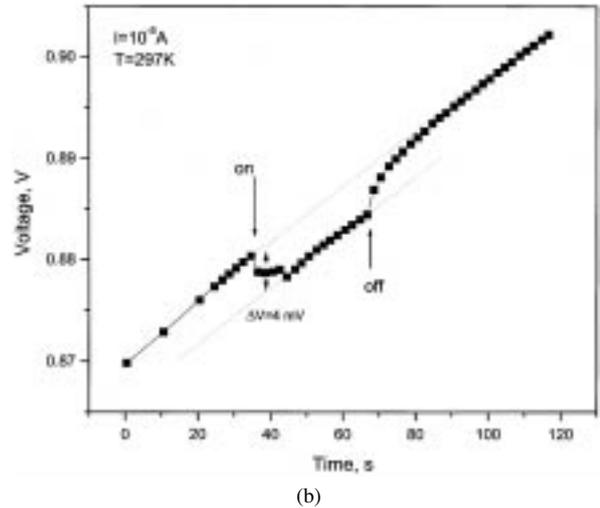


Figure 1 Temperature dependence of conductivity for as-grown doped PFS samples with the parameters listed in Table I.



(a)



(b)

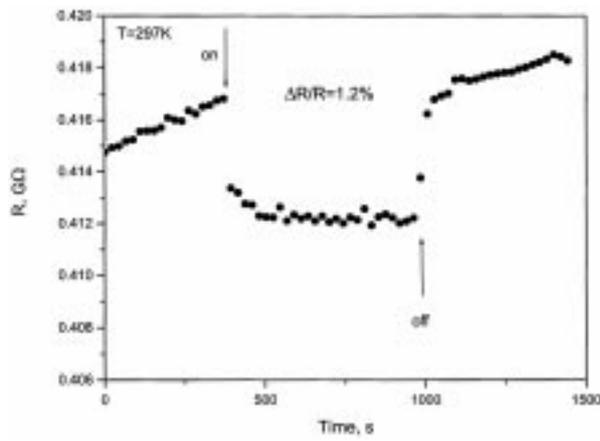
Figure 2 Photoresistance kinetics for two different samples: (a) G-4(18); (b) B-4(20).

temperature dependence of conductivity. For this purpose, we measured photoconductivity for samples which were identical except in their heat exchange conditions. A polymer layer on mylar film was subjected to photoconductivity measurements under three experimental configurations:

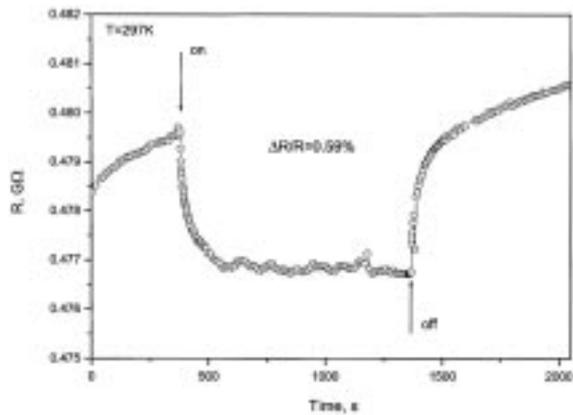
1. As a suspended sample;
2. Attached to a glass substrate;
3. Attached to a small copper plate using vacuum grease.

It is seen in Fig. 3 that improved heat sinking is correlated with a reduction in observed photoconductivity under identical conditions of photoexcitation. This points to the dominance of the bolometric component of photoconductivity. The kinetics of photoconductivity are determined by heat flow and the resulting temperature distribution, an explanation consistent with the long observed characteristic times.

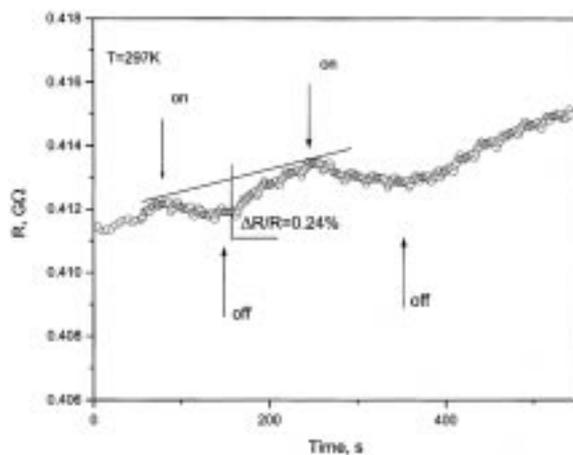
To corroborate further the bolometric origins of the observed photoconductivity, we carried out photoelectric measurements on high-resistivity undoped samples. No noticeable photoconductivity was observed. This is consistent with the bolometric model and is inconsistent with the hypothesis of dominant light-induced carrier generation.



(a)



(b)



(c)

Figure 3 Photoresistance in the sample G-4(18) for different experimental conditions. (a) suspended sample; (b) sample on a glass substrate; (c) sample on a metallic substrate.

Fig. 2 demonstrates one more important trend. The dark current and photocurrent are both characterized by a slow irreversible decrease. Fig. 2b shows that after turning off illumination, this long-term drift returns to the same trajectory which it began in the absence of illumination. The character of this irreversible process is independent of illumination. We attribute this observation to the gradual desorption of iodine. To verify this hypothesis, we measured the dependence of sample conductivity on the ambient atmosphere inside a controllable vacuum chamber. The experimental data are presented at Fig. 4. It is seen that, in vacuo, the sample resistance increased much faster than in normal ambient

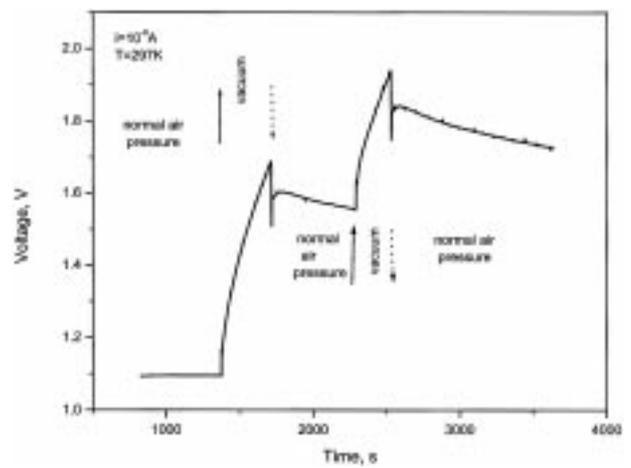
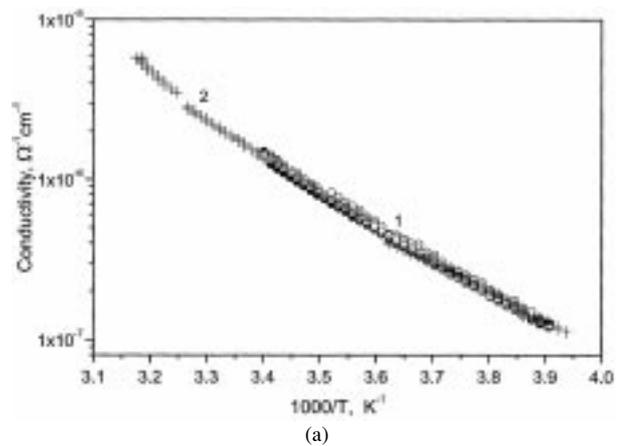


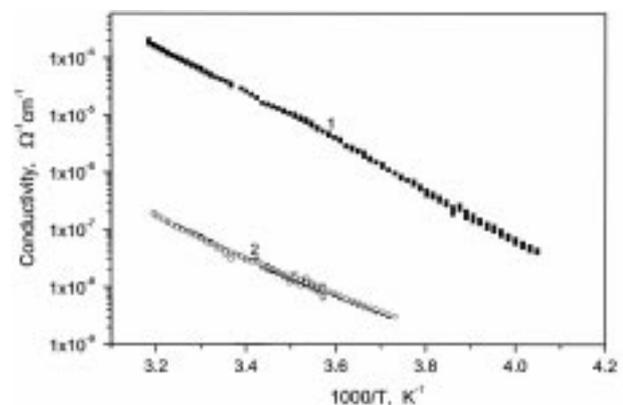
Figure 4 Atmosphere-dependent resistance changes for the sample G-24(20). Solid arrows mark the pump turn-on, dotted arrows mark the restoration of normal air pressure.

conditions. Subsequent restoration of normal air pressure did not restore the sample resistance. The samples with high  $I_2$  concentration (subjected to the 24-hour treatment) exhibited the most pronounced dependence on ambient pressure. The results point to the crucial role played by the ambient atmosphere. At the same time, the observation of partial restoration of sample conductivity in the normal ambient having both fast and slow components is not fully explained using a simple model which accounts only for iodine desorption.

After many days of conductivity change, the samples ultimately attain stable electrical properties. Fig. 5 illustrates this effect for two samples having different



(a)



(b)

Figure 5 Temperature dependence of conductivity in as-grown (1) and stabilized (2) samples. (a) sample G-4(18); (b) sample G-24(20).

iodine concentrations. For the sample subjected to a 4-hour iodine treatment (Fig. 5a), long-term steady-state conductivity is only some tens of per cent lower than the initial value. (In the logarithmic scale of the figure this difference is almost imperceptible.) The activation energy  $\Delta E$  shown in brackets in Table I was not influenced by aging. In contrast, in the sample with a 24-hour treatment, conductivity changed over three orders of magnitude. The activation energy decreased from 0.8 to 0.64 eV, approaching values typical for more stable samples with lower original iodine concentration (Fig. 5b).

In summary after aging over a period of days, the electrical properties of samples converge to a stationary, or perhaps quasi-stationary, state following which no further irreversible variations are observed. Ultimately, it will be necessary to determine the general character and origins of this state and to study its sensitivity to ambient conditions (atmospheric pressure and chemistry, temperature, etc.)

## 5. Conclusion

We have reported results of electrophysical measurements of semicrystalline and amorphous poly(ferrocenylsilane)s, PFDMS and PFMPs, subjected to a range of iodine treatments. These materials are of substantial applied interest in view of their potential to enable a single-layer spin-cast large-area low-cost integrated circuit process. We summarize our key conclusions as follows:

1. The iodine-doped samples possess p-type conductivity.
2. The conductivity exhibits an exponential temperature dependence with an activation energy close to 0.5 eV in moderately doped samples.
3. In the present examples, photoconductivity was largely the result of sample heating rather than through generation of non-equilibrium charge carriers.
4. Stationary properties of the samples are established after several days of aging. In moderately doped samples this initial "burn-in" process is accompanied by a slight growth in sample resistance.
5. Heavily doped samples are characterized by a much greater instability. During aging, their resistance

increases by several orders of magnitude. Their activation energy ultimately approaches the value typical for moderately doped samples.

In view of the promise of these materials and processes explored herein, the mechanisms of conduction, doping, photoconduction, and aging merit further detailed scientific investigation and technology development.

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