

## The Effect of Ion / Electron Irradiation on Polymer Based Organic Optoelectronic Devices

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The use of conjugated polymers in optoelectronic devices is getting increasingly attractive for industrial applications. They can be utilized as the active medium in organic light emitting devices (OLEDs), solar cells and organic field effect transistors (OFETs). Since most of these devices are assembled into thin film multilayered structures, electron microscopy offers a convenient tool for probing the metal-polymer interfaces. However, due to the low melting point of organic materials, it is commonly a difficult and challenging task to carry out electron microscopic investigations, because both electron and ion irradiation will generally result in the degradation of the structures. Especially, during the sample preparation for Transmission Electron Microscopy (TEM) of these multi-layered devices with Focused Ion Beam (FIB) milling, the samples are exposed to high doses of ion irradiation, which can alter the chemical structure of the conjugated polymers, leading to a change in the electronic and optical properties.

The occurrence of irradiation damage in organic materials is very common and already well known [1]. Special focus in this investigation was put on the conjugated bonds. In the study, samples of poly-(3-hexylthiophene) (P3HT) and polyfluorene (PF) based optoelectronic devices were examined. Polyfluorene is an electroluminescent polymer, with an emission maximum at about 440 nm and a glass transition temperature of 70°C, which is often used for blue OLEDs. P3HT is a common material used for OFET applications. It has high a charge carrier mobility due to its nanocrystalline structure, and it experiences a phase transition to an amorphous state at temperatures higher than 220°C. Polyfluorene and P3HT are both conjugated polymers, and the uninterrupted conjugation is crucial for the optical and electronic properties. Most conjugated polymers lose their electronic properties due to structural degradation when heated above ~220°C. Additionally, glass transitions (TG) and melting can occur during FIB treatment, hampering preparation. It has been shown that similar polymers are prone to electron irradiation damage already at very low electron energies and low electron doses [2].

A potential ion and electron irradiation damage of the polymers was investigated by Raman spectroscopy, which is a convenient method to determine the alterations in chemical structures with a lateral resolution down to 1 µm. The effects of sputtering and electron and ion assisted chemical vapor deposition (CVD) of protective metal coatings were also analyzed. Alternatively, both FIB milling and ultramicrotomy were applied for the preparation of the polyfluorene sample; and irradiation artifacts of FIB based nanomachining were compared to mechanical sectioning. Ultramicrotomy is a common sample preparation technique that allows cutting very thin sections of embedded samples using diamond knives without causing any irradiation damage to the material. However, ultramicrotomy cutting requires suitable “soft” substrates and, thus, can not be applied to the organic devices fabricated on silicon substrates. In a control experiment, a corresponding bulk polyfluorene specimen was used for ultramicrotomy sectioning. Concerning the Raman spectra, the peak indicating the double bonds

vanishes during both the electron irradiation and the FIB milling, with the amount of damage being dose- and time- dependent. This clearly demonstrates the loss of chemical stability of the investigated materials. On the contrary, sputter coating with the diode sputter coater has left the specimen undamaged.

## References

- [1] R.F. Egerton et al., *Micron*, 35 (2004) 399.
- [2] H. Ahn et al., *Macromolecules*, 37 (2004) 3381.
- [3] This work was performed within the "ISOTEC" project funded by the Austrian NANO initiative (project DevAna 0706). The aid of Dr.E. Ingolić is gratefully acknowledged.

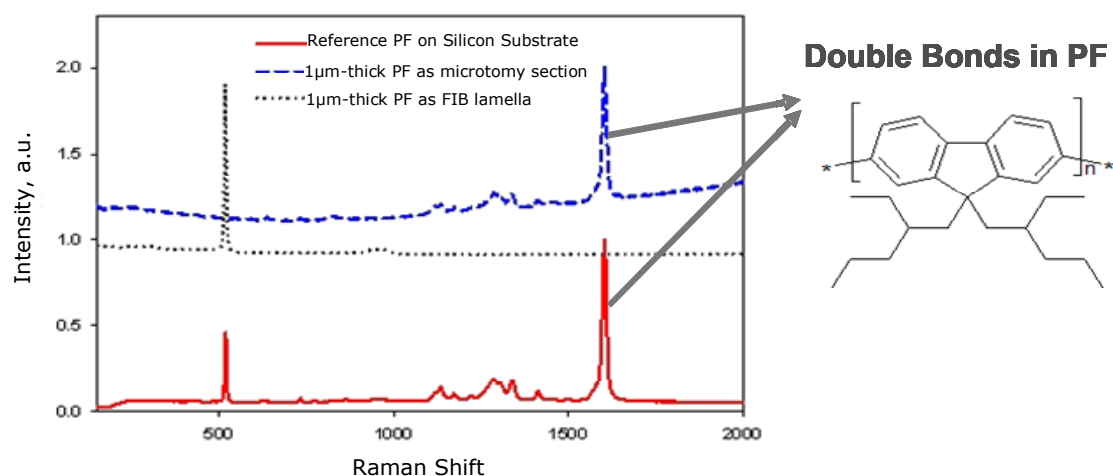


FIG.1. A comparison of Raman spectra, showing the effect of two TEM sample preparation techniques on the chemical stability of polyfluorene. The band at  $520\text{ cm}^{-1}$  originates from the silicon substrate. The spectrum of the reference PF sample has a higher intensity compared to that of the microtomy section because of the highly refractive silicon substrate. The signal/noise ratios, however, are similar for both spectra.

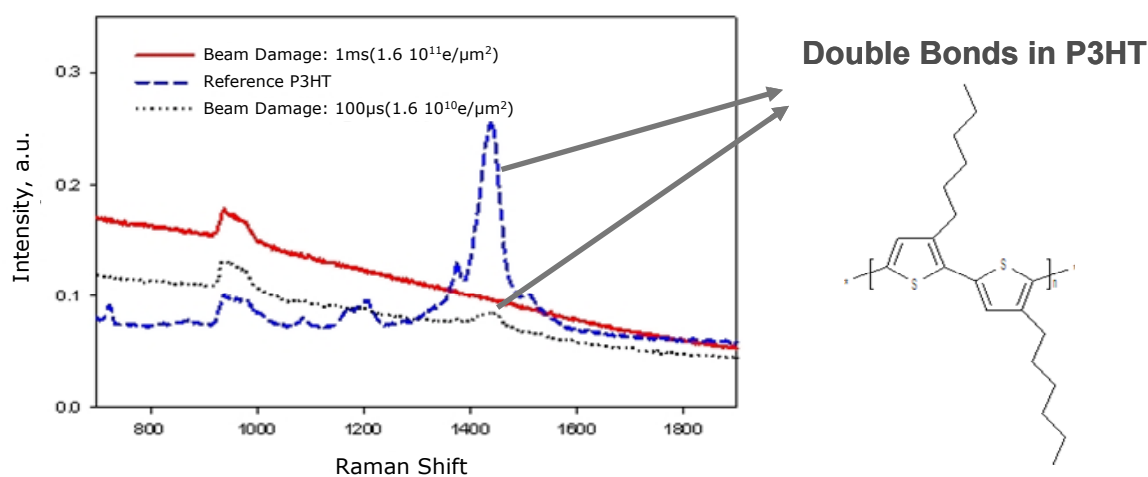


FIG.2. Raman spectra from P3HT samples irradiated with electrons at dwell times of  $100\ \mu\text{s}$  and  $1\ \text{ms}$  per pixel, with total irradiation times of  $58\ \text{sec.}$  and  $9:42\ \text{min.}$  respectively, [ $E_0$ :  $5\ \text{keV}$ ; total area:  $100\ \mu\text{m}^2$ ]. The peak at  $1439\ \text{cm}^{-1}$  corresponds to the double bonds. The background differences are due to sample fluorescence, presumably generated by the products of polymer degradation.