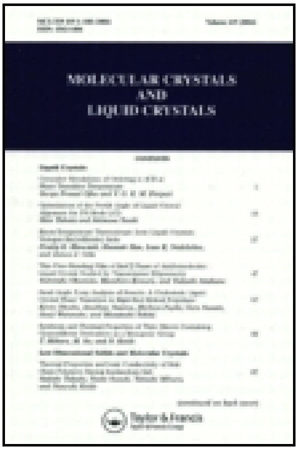

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Dual Mode Laser Treatment of Poly(Bis-Alkylthio-Acetylene)

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DUAL MODE LASER TREATMENT OF POLY(BIS-ALKYLTHIO-ACETYLENE)

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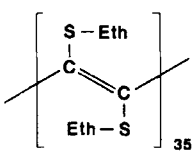
Abstract The irradiation of thin layers of insulating poly(bis-alkylthio-acetylene) with 488 nm Ar^+-laser or 351 nm XeF excimer laser radiation yields a conducting material in the treated regions, whereas the nonirradiated material remains insulating. The polymers can also be photodecomposed (i.e. ablated) by the same excimer wavelength but at higher fluences. The excimer laser patterned insulating polymer can be made conductive by an Ar^+-laser afterwards.

INTRODUCTION

Lasers provide intense light that can be focused onto a very small spot of a target. The combination of a laser with a positioning system results in a setup for polymer patterning. Using special polymers as the target and well defined irradiation conditions these patterns can be made electrically conducting. Recently it has been shown that laser irradiation of different polymers leads to highly conducting materials[1-4]. For polyvinylchloride[1] and for polyimide[2] graphitization processes are discussed. In previous papers we reported on the laser induced conversion of poly(bis-alkylthio-acetylene) into a conducting material and on some aspects of its application[3-5].

This paper discusses the possibility of generating an electrically conducting material by irradiating thin layers of the insulating polymer poly(bis-ethylthio-acetylene) with the beam of a 351 nm XeF-excimer laser.

LASER INDUCED CONVERSION



The preparation of the poly(bis-alkylthio-acetylene) has been previously described[6]. The polymers are soluble in common organic solvents and can be spin coated on sheets of glass in layers of about 3 μm thickness. The nonirradiated layers have a conductivity of 10^{-14} S cm^{-1}, which is common for polymers.

The UV-VIS spectrum (Fig.1) shows a broad absorption band with decreasing intensity up to 600 nm, and indicates a twisted polymer backbone with no extended conjugated π-electron system. This is one reason for the insulating properties of the initial polymer. From the absorption spectrum it is plausible that the polymer can be converted by both, ultraviolet and visible laser radiation.

When poly(bis-ethylthio-acetylene) is irradiated with 488 nm laser radiation, a conversion of the initially insulating material into an electrical conducting form is observed. The mainly gaseous conversion products as identified by mass spectrometry are alkyl disulfides and alkyl sulfides. Although numerous thioalkyl sidegroups are removed from the polymer backbone by laser induced cleavage of the C-S-bond, we found a considerable amount of sulfur remaining within the conducting material by X-ray fluorescence.

The conductivity of the polymer depends on the laser power and the scan velocity in a nonlinear manner. For example a scan velocity of 5 mm/s and a laser intensity of 15 kW cm^{-2} gives a conductivity of about 100 S cm^{-1}, as does a conversion with 2 m/s at 4 kW cm^{-2}. In experiments using 351 nm XeF excimer laser radiation we obtained a conductivity of $1.5 \cdot 10^{-1}$ S cm^{-1} at an integral fluence of 3 J cm^{-2}. In

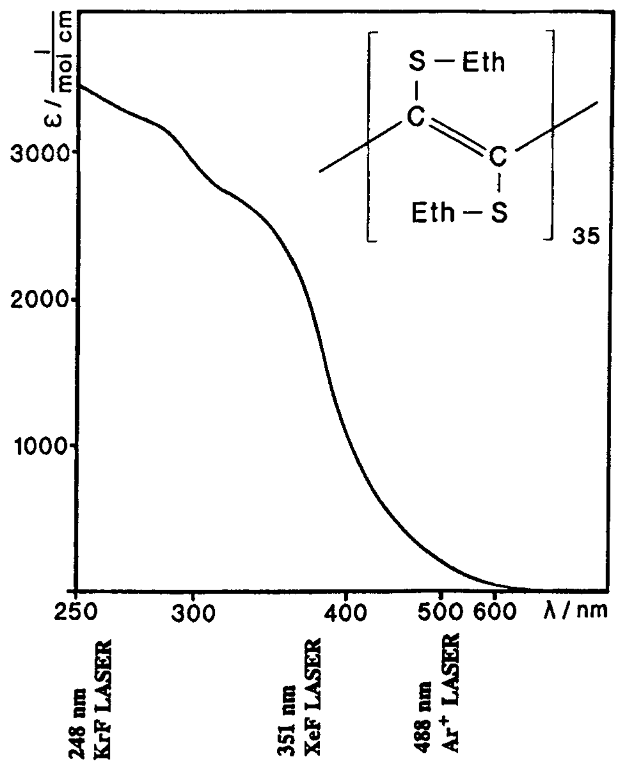


FIGURE 1 : UV-VIS absorption spectrum of poly(bis-ethylthio-acetylene) in chloroform with corresponding laser wavelengths

both cases the polymer was converted in normal atmosphere.

The different conductivities are considered due to the strong difference of the absorption of the polymer at the different laser wavelengths (see Fig. 1). Accordingly, the conversion happens in the case of VIS radiation in the bulk, whereas in the case of UV radiation only a thin layer at the surface of the polymer film is being converted. In the case of Ar+-laser irradiation the conducting polymer is a black-blue porous sulfur containing material. This residue may be formed together with gaseous compounds produced by the laser induced cleavage of the sulfur containing sidegroups of the polyacetylene backbone. Using the excimer laser radiation for conversion we found a velvet like structure of the conducting material[5].

The electrical resistance of the conducting material is stable for at least half a year, even without protection against air, and has a low temperature coefficient.

PHOTOABLATION OF POLY(BIS-ETHYLTHIO-ACETYLENE)

Excimer laser photoablation provides for an efficient and technologically useful type of patterning organic polymer surfaces. Poly(bis-ethylthio-acethylene) permits patterning by ablation with 351 nm XeF excimer laser radiation, the same waveleghth at which electrical conductivity can also be achieved, but at higher fluences. Figure 2 shows the linear dependence of the ablation depth on the intrinsic fluence per laser pulse. The ablation threshold energy is about 15 mJ cm^{-2}. The ablation rate was measured via a very sensitive quartz microbalance. To remove a polymer layer of 1 μm thickness with the 351 nm XeF line, an integral energy density of about 1 J cm^{-2} is necessary.

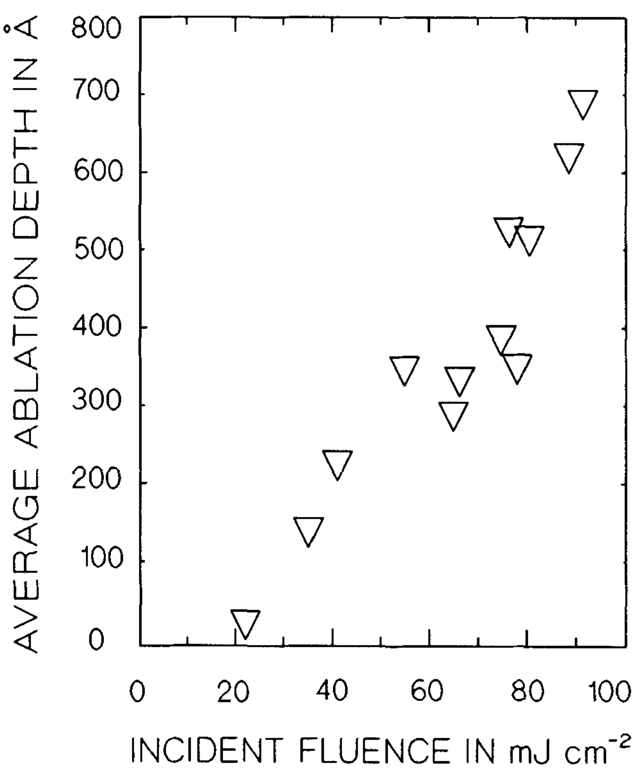


FIGURE 2 : Plot of the average ablation depth per pulse ("ablation rate") versus the incident single pulse fluence; ablation of poly(bis-ethylthio-acetylene) with 351 nm XeF laser radiation

CONDUCTING PATTERNS

Due to the fact that poly(bis-alkylthio-acetylene) is sensitive to radiation at more than one wavelength a variety of variants to realize conducting polymer patterns can be imagined. One way is to pattern the polymer by cw-exposure using a computer controlled two axial positioning system coupled with a 2W-Ar^+-laser (488 nm) in a line-by-line mode[5].

Another feasible approach is to use two different laser wavelengths . Figure 4 shows an ablated polymer pattern obtained upon exposure after 351 nm laser radiation through a stainless steel mask. After an initial ablation process parts of the insulating polymer pattern has been made conducting in a subsequent step using the 488 nm Ar^+-laser line in a scanning exposure apparatus.

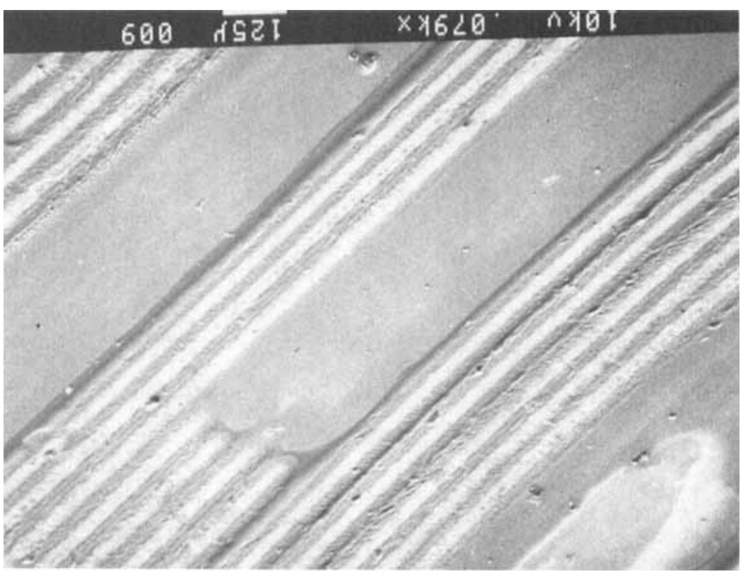


FIGURE 3: Conducting pattern in two laser wavelengths processed poly(bis-ethylthio-acetylene); the initial polymer was patterned using a 351 nm XeF excimer laser for ablation, and the remaining unreacted polymer was subsequently converted into a conducting form using a 488 nm Ar^+-laser

APPLICATION

Poly(bis-alkylthio-acetylenes) open up new ways for manufacturing passive electonic components on a printed circuit board. We realized capacitors by converting the polymer in comb like structures into its conducting form. Using unconverted PATAC as the dielectric spacer material we obtained capacitors with a specific capacity of more than 20 pF per cm^2. In a comparable procedure resistors can be manufactured by writing the conducting tracks in a meandering form, thereby tuning the irradiation conditions to result in a lower conductivity of the laser converted polymer. From the conducting material we fabricated small printed circuit boards without any wet processing steps, using laser induced patterning only, for example a small multivibrator circuit using SMD components mounted on the conducting polymer tracks by means of a conducting adhesive[5].

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