Polymer waveguides under ion implantation: optical and chemical aspects

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Abstract

The effects of ion implantation on the linear and nonlinear optical properties of polymer thin films are studied. In the first step, good quality planar waveguides were made in a well known photoconducting polymer, polyvinylcarbazole (PVK), which has no intrinsic nonlinear optical properties. The polymer is deposited by spin-coating onto a BK7 glass substrate. A diffraction grating, etched on the substrate surface, acts as an input coupler for the waveguide. We present our results from the study of these polymer waveguides, following exposure to an energetic ion beam. The grating coupler method was used to characterize the linear and nonlinear optical properties of the waveguides before and after ion implantation. Due to the conjugated chains created by the implantation, we expect $\chi^{(3)}$ type nonlinear properties and more specifically, an electronic nonlinear refractive index. The implanted polymer films are characterized by infrared and UV/visible spectroscopy to study structural modifications. The new structures created and the significant damage caused by the implantation are discussed. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Optical applications of ion implantation in polymers focus mainly on passive devices [1,2]. Despite the fact that nonlinear properties of optical polymers can be improved by chemical means, they are not yet widely used in applications, suggesting that other techniques merit study.

Work presented here focuses on the third-order nonlinear optical susceptibility. We interpret the analysis of the structural modification of implanted polymer, with a view to understanding how it influences nonlinear processes [3]. Optical spectroscopy was used to analyze the structural modification of implanted polyvinylcarbazole (PVK) thin films. Planar PVK waveguides were developed, implanted and characterized for their nonlinear optical properties by linear and nonlinear grating coupler techniques.

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2. Polymer structure and nonlinear optical effects

Before studying the effects of ion implantation, one must first understand how nonlinear effects occur in chemically designed nonlinear polymers. A common characteristic links all these materials: they are conjugated polymers. Conjugation of polymer backbones consists of sequences of double or triple carbon bonds, so-called π bonds. These bonds share π electrons that are delocalized along the polymer backbone. In an intense electric field E, these electrons are highly polarizable, which gives to these materials a strong Kerr effect. This effect, described by the hyperpolarizability tensor $\chi^{(3)}$, leads to an intensity-dependent refractive index: $n = n_0 + n_2 I$ where I, the light intensity, is proportional to E^2, n_0 is the refractive index at low intensity and n_2, the nonlinear refractive index, is related to a term of the $\chi^{(3)}$ tensor.

3. Experimental considerations

Thin films of polyvinylcarbazole (Fig. 1) are spin-coated from a 4–6% wt concentration solution in chlorobenzene. To carry out the waveguiding experiments, a glass slab with a diffraction grating etched onto its surface is used as substrate.

Since nonlinear effects are intensity-dependent, one must ensure that the region of maximum wave intensity overlaps as much as possible the implanted region. Fig. 2 displays the shape of the
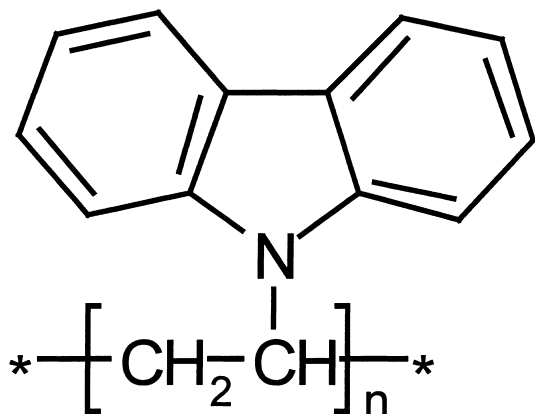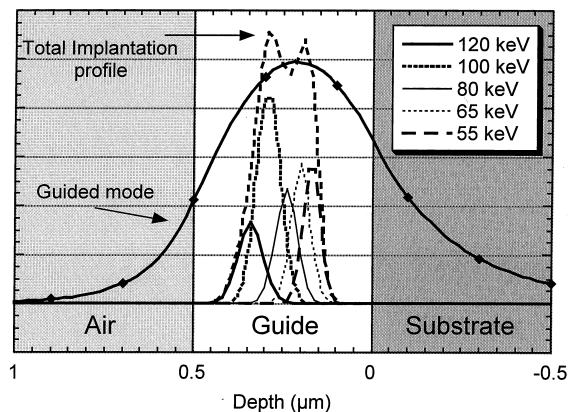

Fig. 2. Comparison between the implantation profile of C^+ ions at 80 keV (TRIM simulation) and the energy profile of the fundamental guided mode.

fundamental guided mode for a PVK waveguide as well as concentration profiles of carbon ions implanted at several energies. It is clear from the figure that ion doping at a single energy will affect only a small fraction of the guided mode. Hence several energies were used in order to maximize the overlap between the doped region and the mode profile. Ion profiles were calculated using the TRIM95 [4] code.

4. UV-visible spectroscopic analysis

The structural and chemical modifications of the polymer were investigated by spectroscopic analysis. Fig. 3 displays the UV-visible absorption spectrum as a function of implanted dose for 100 keV C^+ ions; similar curves are obtained with 500 keV Cu^+ ions. Increasing absorption at the shorter wavelengths, which also spreads towards the red end with increasing doses, is characteristic of a global conjugation increase in the polymer. Unlike intrinsic conjugated polymers, such as polydiacetylene-4-BCMU, where the absorption band is narrower, this spreading is interpreted as the superposition of multiple absorption bands, each one characteristic of a particular type of conjugated structure. As already observed [5–7], the induced coloration varies with increasing dose from a light
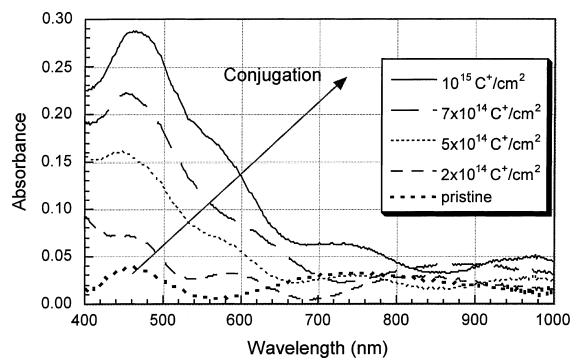

Fig. 1. Structural formula of polyvinylcarbazole.

Fig. 3. Absorption spectra of a PVK thin film implanted with 110 keV C$^+$ ions.

Fig. 4. IR spectra of a PVK thin film implanted with 500 keV Cu$^+$ ions.

brown for doses near 10^{14} C$^+$/cm^2, to a metallic black for doses greater than 5×10^{15} C$^+$/cm^2.

Even if the conjugated structures of our implanted polymer chains have not been characterized, we may assume that their lengths are much shorter than the backbone chain length of intrinsic nonlinear polymers. Nevertheless, theoretical studies of polymer nonlinearities have shown that the influence of the conjugated backbone chain length saturates for more than ten carbon units. Therefore, this parameter should not hinder the possible observation of nonlinear effects.

5. Infrared spectroscopic analysis

To carry out the analysis of the implanted polymer films, Fourier transform infrared spectroscopy is used. First, a significant degradation, which increases with increasing doses, is indicated by the broadening of all resonance peaks of the polymer (Fig. 4). This phenomenon is common to all implanted polymers, and it is interpreted as a carbonization process [5,6,8]. As in visible spectroscopy, the broadening of each IR resonance can be seen as the breaking of a certain number of a particular bond type (thereby decreasing the absorption), and the creation of a multitude of new types of bonds (with overlapping resonances), hence of complete disorder in the material.

The increase in absorption in the 1750–1650 cm^{-1} region could not be assigned to the broad-
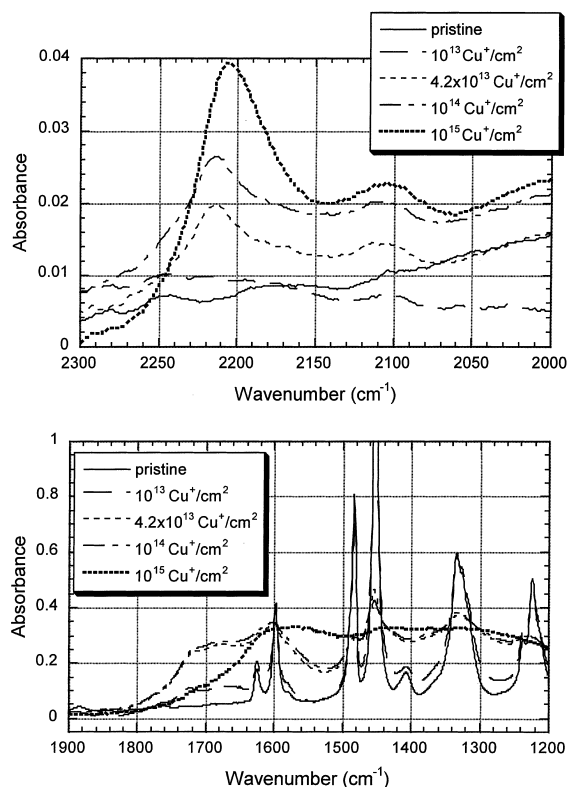
ening of a neighboring resonance. Moreover, the absorption saturates for doses greater than 10^{15} Cu$^+$/cm^2. This region corresponds to a carbon–carbon double bond, which is confirmed by the corresponding observation in the visible spectrum. No satisfactory interpretation of this saturation effect has been yet proposed.

The feature at 2210 cm^{-1}, probably too strong to be assigned to an alkyne group, is associated with a Cu–H stretching mode [9]. On the other hand, the weakness of the 2110 cm^{-1} band could be characteristic of a carbon–carbon triple-bond vibration [9].

6. Waveguiding experiments

These experiments study the effects of ion implantation on polymer waveguides and specifically,
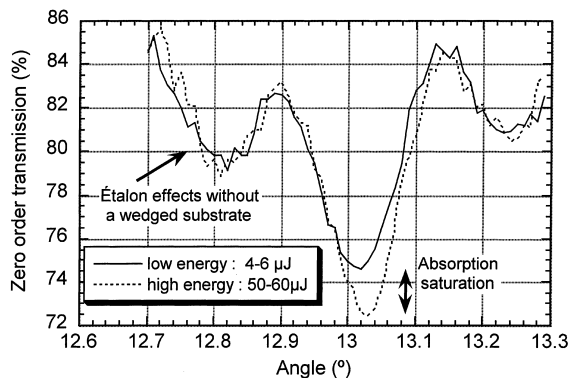
Fig. 5. Nonlinear grating coupler measurement showing absorption saturation effects due to Cu^+ implantation in a PVK waveguide. Implantation parameters: 3.5×10^{14} Cu^+/cm^2 @ 800 keV, 3.5×10^{14} Cu^+/cm^2 @ 650 keV, 3.5×10^{14} Cu^+/cm^2 @ 500 keV, 3.5×10^{14} Cu^+/cm^2 @ 350 keV, current density less than 40 nA/cm^2.

their third-order nonlinear optical properties. We used the nonlinear grating coupler technique, in which the zero-order transmission curve versus angle (near the optimum coupling angle) gives a resonance curve. The amplitude and width of the resonance are mainly related to the film's absorption (linear and nonlinear), while its angular position depends on the real part of the refractive index (linear and nonlinear).

Both resonance curves shown in Fig. 5 are preliminary results that do not correspond to our predictions in terms of nonlinearities: instead of observing an angular shift between resonances, the high-energy curve is deeper than low-energy one. This suggests nonlinear absorption. As there is more energy coupled into the waveguide, it means that absorption decreases with increasing intensity: the opposite of two-photon absorption. As a true nonlinear absorption (imaginary part of n_2) can not be negative, the observed phenomenon shows the nonlinear saturation of the absorption.

7. Conclusion and perspectives

This work aimed to understand the effects of ion implantation in thin polymer films on their nonlinear optical properties. From visible and infrared spectroscopic analysis, we conclude that a carbonization process occurs which results in a conjugated structure highly favorable to third-order nonlinear optical properties. Future work will study how the conjugated chain length evolves. Concerning nonlinear measurements, while these preliminary results are inconclusive, we will in future probe the nonlinearities at wavelengths much closer to the absorption band. In this way, nonlinearities will be resonantly enhanced and thereby easier to detect. In addition, chlorine and iodine ions, known to improve molecular nonlinearities [10], will be implanted.

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