Optical and structural effects of ion implantation in polymer waveguides

Pierre Cottin [a], Roger A. Lessard [a], Émile J. Knystautas [b], and Sjoerd Roorda [c]

[a] Centre d'optique, photonique et laser, Département de physique, Université Laval
[b] Département de physique, Université Laval
[c] Département de physique, Université de Montréal

ABSTRACT

Our work consists in the study of ion implantation effects on the linear and nonlinear optical properties of polymer thin films. This project started with developing good quality planar waveguides based on a well-known photoconductor polymer, the polyvinylcarbazole. This polymer, which has no nonlinear properties, is deposited by spin coating on a BK7 substrate. A diffraction grating etched on the substrate surface, will act as an input coupler for the waveguide.

We present here our latest results concerning the study of these polymer waveguides exposed to energetic ion beam. We are using the grating coupler method to characterize the linear and nonlinear optical properties of these 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 electronic nonlinear refractive index.

Concerning the structural modifications, the implanted polymer films are studied by infrared and UV/visible spectroscopy. We will lay emphasis on the new structures created as well as on the important destruction caused by implantation.

Keywords: Ion implantation, polymer, waveguide, optical effect, IR spectroscopy, polyvinylcarbazole

INTRODUCTION

The last decades have seen growing the ion implantation fields of applications. More specifically, polymers are materials of special interest with their great versatility. Chemically customizable, their properties could be modified by ion implantation too. Increasing the conductivity of polymer[1] takes probably the most important share of the research work in this field. Concerning pristine polymers, a lot of work has been done for integrated optics applications. The photolithographic technique allows the very well-controlled design of passive devices like channel waveguides or beam dividers. Concurrently, we can obtain similar results with the ion beam technique[2] as well as more complex structures such as buried waveguides inside a bulk polymer[3] and, more generally, three-dimensional devices.

On the other hand, nonlinear optical polymer devices seem far to be market-ready and a lot of more fundamental research remains to be done to find more efficient nonlinear polymer materials. Here, ion beam technique has probably an important role to play[4]. Rare-earth implanted polymer[5] can lead to gain devices and electroluminescence phenomenon can be improved by ion bombardment[6].

Work presented here focuses on third-order nonlinear optical phenomenon that is needed in all-optical switches. We intend to interpret the analysis of the structural modification of implanted polymer, keeping in mind how they influence nonlinear processes. Optical spectroscopy was used to analyze the structural modification of copper and carbon implanted polyvinylcarbazole (PVK) thin films. Concerning optical effects of ion implantation, we developed good quality PVK planar waveguide and characterized them by linear and nonlinear grating coupler technique.

Further author information -
[1] P.C.(correspondence): Email: pcottin@phy.ulaval.ca; WWW: http://gabor.phy.ulaval.ca/cottin_en.html
[2] R.A.L.: Email: ralessard@phy.ulaval.ca; WWW: http://gabor.phy.ulaval.ca/lessard_en.html
[3] É.J.K.: Email: ejknyst@phy.ulaval.ca
[4] S.R.: Email: roorda@lps.umontreal.ca

POLYMER SAMPLE PREPARATION

Polycarbazole (Figure 1) powder commercially obtained from Aldrich is dissolved in chlorobenzene to get a 5%wt concentration solution. After passing through a 0.2 μm porosity Teflon syringe filter, the PVK solution is spin-coated and gives, after post-baking, a layer of 0.25 and 0.75 μm thickness. For spectroscopic measurements, films are coated on IR transparent CaF_2 substrates. Characterization by differential scanning calorimetry (DSC) gives a vitreous glass transition temperature of 225 °C. This quite high temperature of stability for a polymer will delay and prevent the thermal degradation due to ion bombardment.
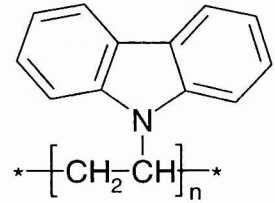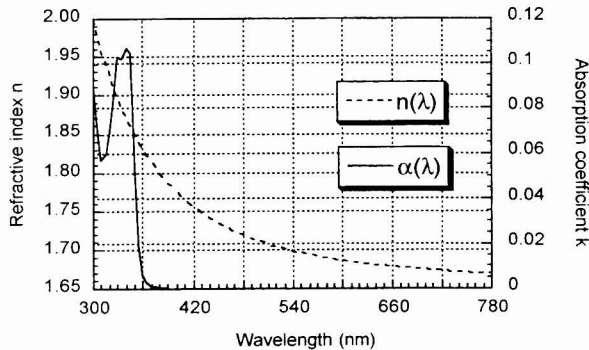
Figure 1. Polyvinylcarbazole

Figure 2. Ellipsometric dispersion curves of a PVK thin film

For photo-ellipsometric characterization, PVK film is deposited on a 1 mm thick BK7 substrate. The dispersion curves of the refractive index and the absorption coefficient are presented in Figure 2. As PVK refractive index is much higher than that of the glass is, it gives more flexibility in the design of the waveguide thickness versus ion implantation energy.

To carry out our waveguiding experiments, we need to deposit the polymer film on a special substrate comprising a diffraction grating. The fabrication of this type of substrate needs the following steps (graphically summarized in Figure 3). A 25 mm diameter BK7 disc is coated with positive photoresist. Next, it is exposed to the sinusoidal pattern of intensity generated by the interference of two wide 413 nm krypton laser beams. The angle between the two beams fixes the period of modulation. After exposure and development, the resist is used as a mask in a reactive ion beam etching process. The thickness modulation in the photoresist layer is transferred into the glass substrate and the remaining resist is removed with an organic solvent.
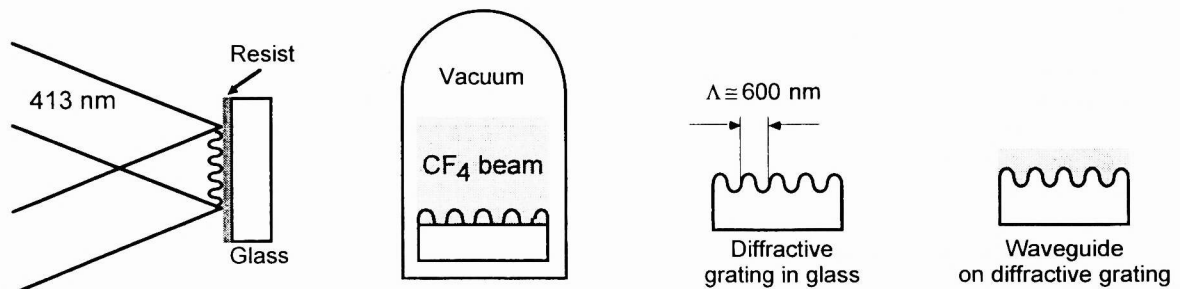

Figure 3. Grating coupler fabrication process

## ION IMPLANTATION PARAMETERS AND WAVEGUIDING CONSIDERATION

Our goal is to modify waveguides by ion vacuum implantation, so one of the most important parameters we have to control is the depth of penetration of the accelerated ions and consequently, the profile of modifications. Moreover, these modifications will be probed by a guided wave to display effects, which are intensity dependent. So, the most interesting part of the guide is where the intensity is the highest. In Figure 4, we show a comparison between the shape of the fundamental guided mode for a PVK waveguide (0.5 μm thickness) on a glass substrate and the distribution profile of carbon ions accelerated at 80 keV. It is clear that effect of ion doping will affect only a small part of the guided mode. To increase this influence, we choose to implant ions at several energies and then improve the overlap between ions profile and mode profile (Figure 5). Based on TRIM95[7] calculated ranges and stragglings and with choosing a reasonable set of energies (five for the example of carbon),

we optimized the dose at each energy to get an almost constant profile. During a multiple energy implantation, ions are implanted with decreasing energy to avoid the influence of the following implantation on the already implanted profile.

If we want to study the effect of energy deposition and not the effect of ion doping, we have to consider the distribution of energies deposited in the PVK matrix given by TRIM95 (Figure 4). In this case, one implantation is enough but at a higher energy to get a more constant energy deposition.

These implantation parameters need a quite versatile system to be achieved. To be able to study effects of light ions as well as heavy ions, we used two implanters. Light ions implantations (C^+) were performed at Université Laval with a Kevatron type accelerator. Energy range available is limited between 40 and 130 keV. In each experiment, an electrostatic scanning system was used to improve the dose uniformity over 1 cm^2. Heavy ions implantations (Cu^+) were performed at Université de Montréal with a Tandetron type accelerator. Energy range available is limited between 0.4 and 1.7 MeV. In each experiment, an electrostatic scanning system was used to improve the dose uniformity over 1 cm^2.
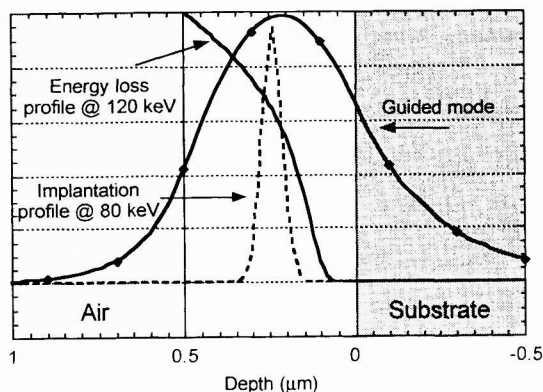
Figure 4. Comparison between implantation profile of C^+ ions at 80 keV, energy loss profile of C^+ ions at 120 keV (TRIM simulation), and the energy profile of the fundamental guided mode
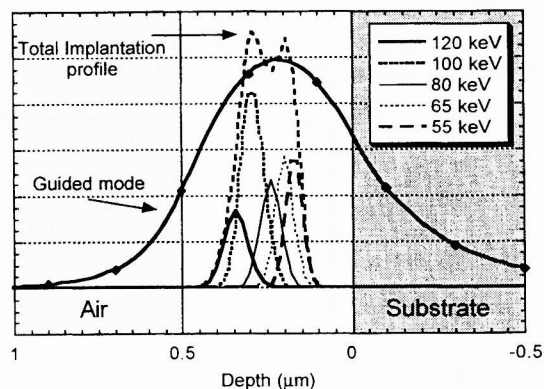
Figure 5. Comparison between implantation profile of C^+ ions at 80 keV (TRIM simulation) and the energy profile of the fundamental guided mode

POLYMER STRUCTURE AND NONLINEAR OPTICAL EFFECTS

As we are interested by improving nonlinear optical properties of polymers by ion implantation, we have first to understand how the nonlinear effects occur in general and especially in chemically designed nonlinear polymers.

When electrons of a medium are submitted to an intense electric field, they are perturbed and their oscillations become anharmonic. It leads to an induced nonlinear polarization that can be expressed as a power series of the electric field. Each term can be associated to an optical nonlinear effect[8]. In a non-centrosymetric medium, the first nonlinear effect is of the third order. Its value is described by a tensor of fourth rank $\chi^{(3)}$. After simplification, it can be interpreted as a nonlinear refractive index n_2 (in cm^2/GW) and the refractive index of the material becomes $n=n_0+n_2I$ where I is the intensity of the laser field (in MW/cm^2) and n_0 is the refractive index of the material at low intensity. It is called the Kerr effect.

The huge family of third order nonlinear polymers is growing non-stop. A common point links all these materials: they are conjugated polymers. Among them, DANS and polydiacetylene (PDA) are probably the most studied. These conjugations are backbones constituted by sequences of carbon multiple bonds (double or triple) called π bonds. These bonds share π electrons that are delocalized along the polymer backbone. These electrons have the property to be highly polarizable which gives to these materials such a strong Kerr effect.

UV-VISIBLE SPECTROSCOPY ANALYSIS

Before undertaking nonlinear optical experiments to probe the effects of ion implantation on the optical behavior of PVK films, we investigated through spectroscopic analysis the structural and chemical modifications of the polymer. The UV-visible spectroscopy gives us information about the electronic configuration of the polymer chains in the matrix.

To be consistent with future waveguide analysis, we chose the same range of thickness, between 0.5 and 1.0 μm. This choice leads to étalon effect and artificial oscillations that appear in the absorption spectra must be disregarded.

The pristine PVK as shown in Figure 1 is perfectly transparent from 400 to 1100 nm. Figure 6 displays the evolution of the absorption spectra with increasing doses of implanted 100 keV C^+ ions. Similar curve shapes are obtained with Cu^+ ions accelerated at 500 keV. Absorption rising at the beginning of the spectra which shifts toward longer wavelengths with increasing doses is characteristic of a global conjugation increase in the polymer. Unlike intrinsic conjugated polymer like polydiacetylene-4-BCMU (PDA-4BCMU) where absorption band is narrower (Figure 7), this spreading is interpreted as the superposition of multiple absorption bands, each being characteristic of one type of conjugated structure. As already observed[9,10,11], the induced coloration varies with an increasing dose from brown light for doses near 10^{14} C^+/cm^2 to metallic black for doses greater than 5×10^{15} C^+/cm^2.
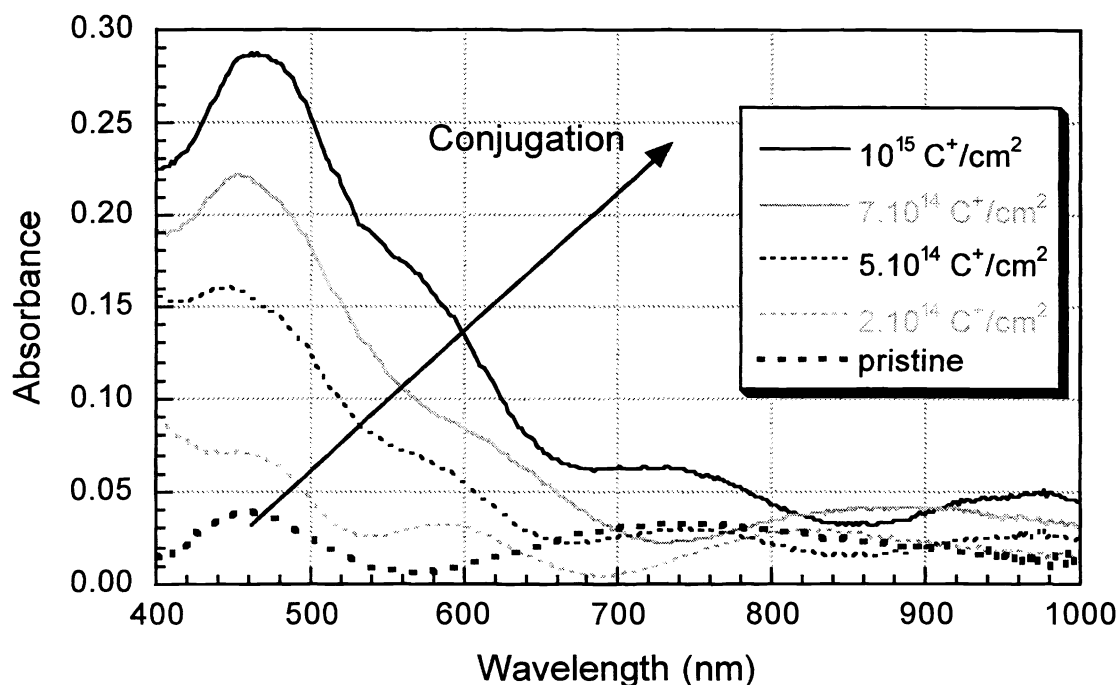
Figure 6. Absorption spectra of a PVK thin film implanted with 110 keV C^+ ions

A totally different phenomenon occurs when PDA-4BCMU is implanted in the same conditions. In this case, we got the opposite effect: the absorption band totally disappear under ion implantation, even at a dose as low as 2×10^{14} C^+/cm^2. The film that is initially bright red becomes completely transparent and even the light brown coloration commonly observed is missing. Such a bleaching effect[12] is an evidence of the complete loss of conjugation of the polymer backbone.

For the PVK case, we can conclude that ion implantation (C^+ as well as Cu^+) strongly develops the conjugated structures in the polymer. Even if the characterization of the conjugated structures of our implanted polymer has not
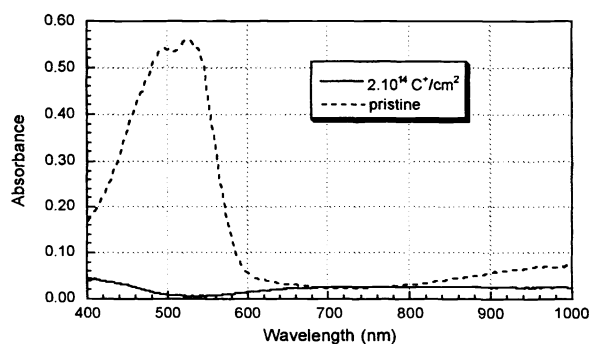

Figure 7. Absorption spectra of a pristine and a 110 keV C^+ implanted polydiacetylene-4BCMU film

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been undertaken, we could assume that their lengths are probably much shorter than the backbone length of intrinsic nonlinear polymers. But theoretical studies of polymer nonlinearities have shown that the influence of the conjugated backbone length saturates for more than ten carbon units. So, this parameter has no reason to negatively influence the observation of nonlinear effects. Furthermore, the spreading of the absorption band toward red could be used to two-photon resonantly enhance the $\chi^{(3)}$ effect.

INFRARED SPECTROSCOPY ANALYSIS

To carry on the analysis of our implanted polymer films, Fourier transform infrared (FTIR) spectroscopy has been used. Vibrational absorption bands in the 4000-1000 cm^{-1} domain can give us complementary information on the structure of the damage inflicted to the matrix as well as the emergence of new bonds.
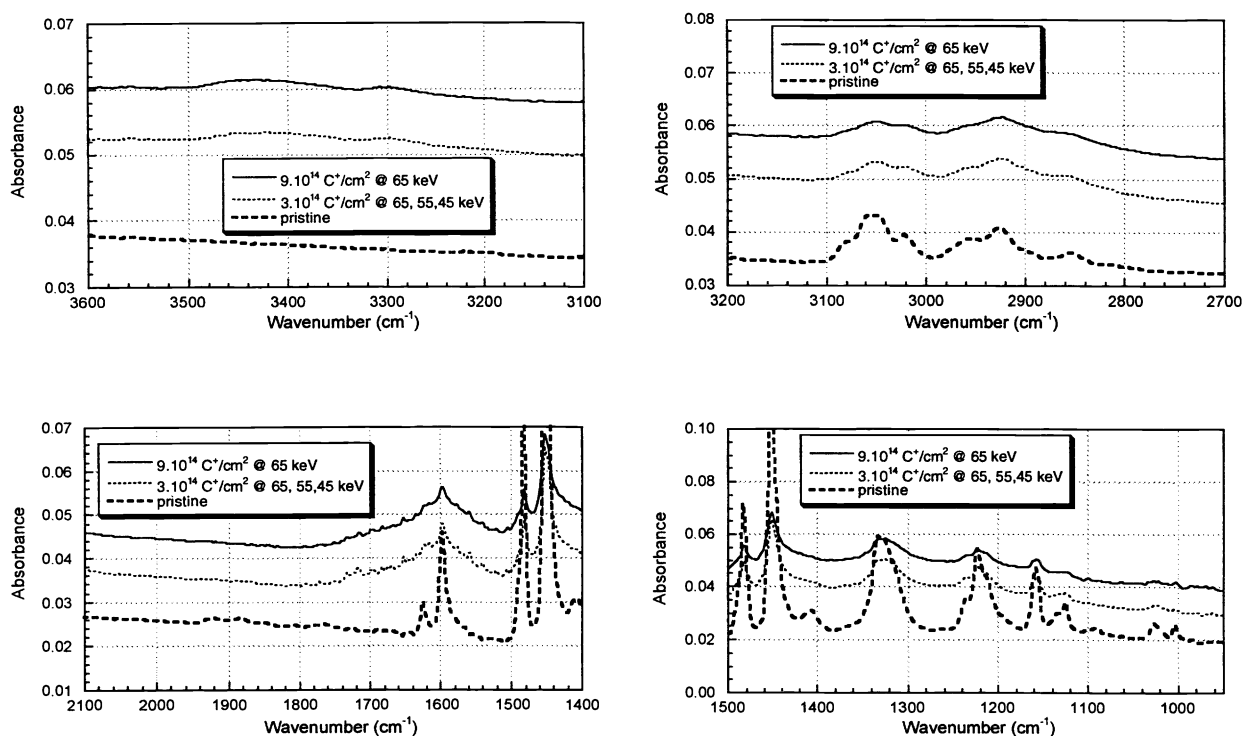
Figure 8. FTIR spectra of C$^+$ implanted PVK films; for the same implanted dose, comparison between implantation at one energy versus multiple energy

A glance at Figure 8 is enough to isolate the two main modifications of the PVK. First, a major degradation process is highlighted by the flattening of all resonance peaks of the pristine polymer. This alteration is a proof of a disorder that increases with increasing doses (Figure 8 and 9). This phenomenon is common to all implanted polymers and is interpreted as carbonization process[9,10,13]. As for visible spectroscopy, the broadening of each resonance can be seen as the destruction of a certain amount of one bond (decreasing its absorption) and the emergence of a multitude of new bonds (which resonances overlap) creating quickly a complete disorder in the material.

Despite of all this destruction, new resonances are rising at 3440 cm^{-1} and 3300 cm^{-1}. Because of their weakness, one of them could be attributed to an alkyne group (3300 cm^{-1}). But more probably, they could have appeared following an oxidation process (alcohol or phenol group).

Other information given by these graphs of Figure 8 is the influence of the energy of implantation. They display the comparison between a sample implanted at one energy (65 keV) and one implanted successively at three different energies

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(in this order: 65, 55, 45 keV). We note that shape and amplitude of resonances are not modified with changing the implantation energy. For small energy variation, only the implanted dose is influencing the matrix structure.
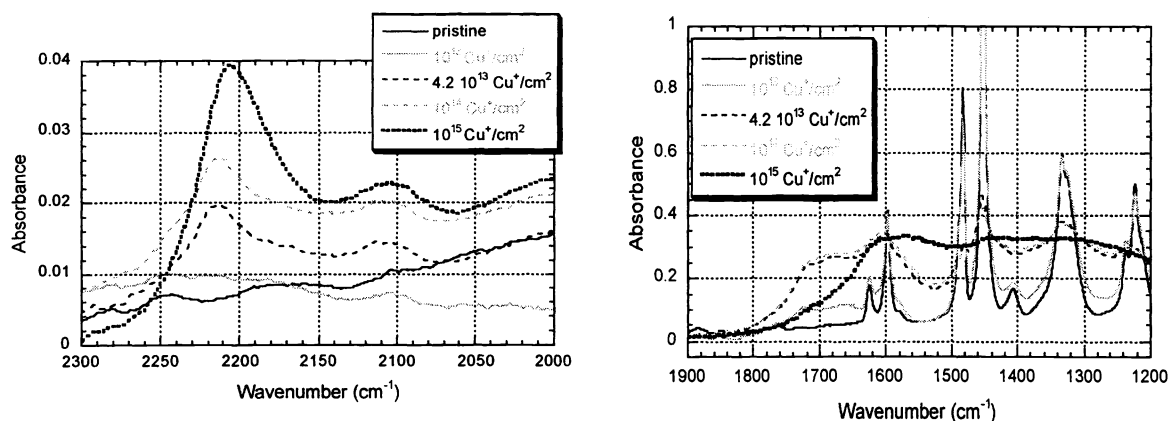

Figure 9. IR spectra of a PVK thin film implanted with 500 keV Cu^+ ions

As for carbon, copper implantation leads to a high degree of disorder in the polymer matrix. But, in the 1750-1650 cm^{-1} domain, the growth of absorption could not be assigned to the broadening of a neighboring resonance. Moreover, a saturation phenomenon appears for doses greater than 10^{15} Cu^+/cm^2. In this domain could be found resonances corresponding to carbon-carbon double bond, which confirms observation of visible absorption spectra. No satisfactory interpretation of this saturation effect has been yet proposed.

Comparing with carbon, we note here the emergence of two much stronger new resonances in the 2300-2000 cm^{-1} range. The first at 2210 cm^{-1}, probably too strong to be assigned to an alkyne group, is associated with a Cu—H stretching absorption. On the other hand, the weakness of the 2110 cm^{-1} band could be characteristic of a carbon-carbon triple bond vibration.
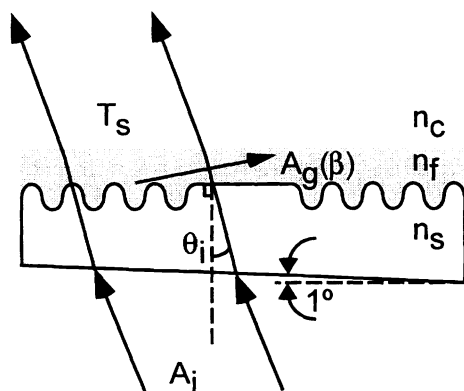
WAVEGUIDING EXPERIMENTS

Figure 10. Coupling configuration of the incident wave A_i into a guided wave A_g with propagation constant β. n_c, n_f, n_s are the refractive indices of, respectively the cladding (air), the film (PVK), and the substrate (BK7)

Waveguiding experiments intend to highlight the ion implantation effects on polymer waveguides and more specifically on their third-order nonlinear optical properties. A good method to probe these effects consists in monitoring the coupling efficiency between a free-space wave and a guided wave versus the wave intensity. This coupling is very sensitive to the different parameters of the waveguide and the coupling method. All these parameters being kept constant, if we have a Kerr medium, varying the intensity will affect the refractive index of the film through the expression $n_f=n_{f0}+n_2\times I$. Generally, if two-photon absorption occurs, each index of this formula becomes complex.

The most common coupling technique use a prism to couple a laser beam into a guided mode[14]. Due to a mechanical contact difficult to reproduce between a quite soft polymer film and the glass prism, we chose to use a grating coupler[15,16,17]. The grating etched into a BK7 glass substrate as previously described offers a reliable coupling. The coupling process is shown in Figure 10. A wave A_i (with a gaussian profile) incident on the grating is diffracted into a -1 order. With tuning the angle of incidence, it is possible to overlap the diffracted

wave and a guided mode. Eventually, a second grating can be used to out-couple the guided wave into free space. When the angular position is far from the optimum coupling angle, the major part of the incident wave is transmitted into the zero order. The closer the optimum we are, the more the transmitted energy decreases and the more the guided energy rises. The zero order transmission curve versus angle gives a resonance curve. The depth of resonance and its width are mainly connected to the film absorption while its angular position depends on the real part of the film refractive index. The full-automated setup used to record resonance curves at different energies is presented in Figure 11.
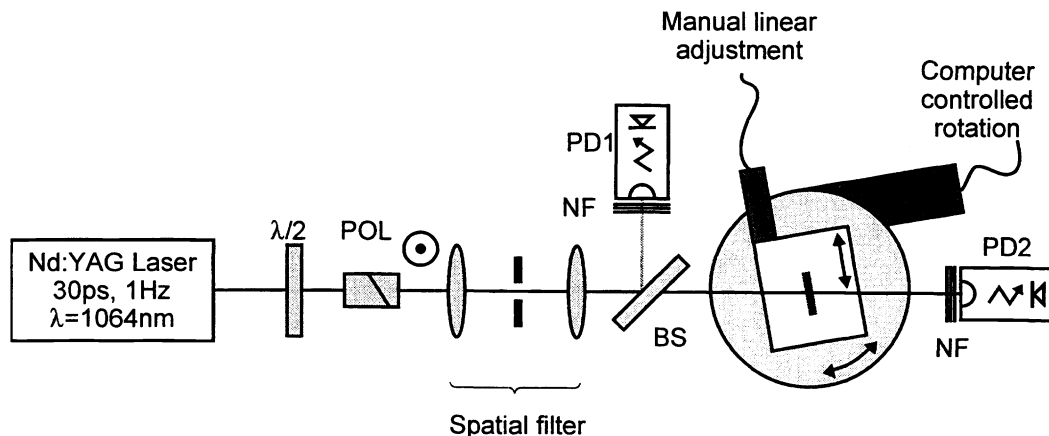
Figure 11. Linear and nonlinear grating coupler experimental setup. $\lambda/2$ is a half-wave plate, POL is a Glan-Laser polarizer cube, BS is a beam sampler, NF are neutral filters, PD1 and PD2 are two fast silicon photodiodes
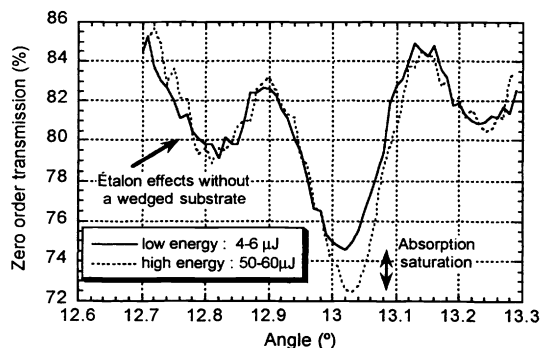
As is shown in Figure 12, when a parallel face substrate is used, it leads to étalon effects. They can be removed by using a wedge substrate (Figure 10).

Both resonance curves shown in Figure 12 are preliminary results that are not corresponding to our prediction in term of nonlinearities. Instead of observing an angular shift between resonances, the high-energy curve is deeper than low-energy one. It means that more energy is coupled into the waveguide: it is the opposite of two-photon absorption and then can be interpreted as an absorption saturation phenomenon.

Figure 12. 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.

CONCLUSION AND PERSPECTIVES

Far from being exhaustive, work presented here proposes a new approach of how it is possible to interpret and use ion implantation in polymer thin film. We have analyzed by visible and infrared spectroscopy the evolution of polyvinylcarbazole film upon light and heavy ion implantation. We can conclude as it was already observed in most polymers that a carbonization process occurs. It comes with the emergence of a conjugated structure that is highly favorable to third-order nonlinear optical processes. Future work will tend to determine how is evolving the conjugation, especially the

conjugated chain size. Concerning nonlinear measurements, the obtained results are quite disappointing but an OPO being recently available, we intend to probe the nonlinearities much closer from the resonance to enhance them. In the same way, chlorine and iodine that are known to improve molecular nonlinearities[18], will be implanted into our PVK films.

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