

POLYMER DIODES MADE OF ION IMPLANTED POLYACETYLENE FILMS*

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ABSTRACT

Polyacetylene films were doped with FeCl_3 and implanted with 30 keV K^+ ions. Physical changes to the films were examined by a series of measurements, which include the four-probe test, infrared ray absorption and 2 MeV He^+ particle elastic recoil detection and Rutherford backscattering. The chemical dopants (Fe^{+++} and Cl^-) were redistributed after the implantation and the different species (K^+ , Fe^{+++} and Cl^- ions) formed p-n junctions at the implantation depths. The implanted films exhibited desirable I-V characteristics, with current densities as high as 600 mA/cm² at 3V and back-to-forward ratio of current over 300. The polymer diodes kept their behavior for over 60 days. Discussions on the results were given in detail.

Keywords: Ion implantation Dopant depth profiling Polyacetylene diodes

I. INTRODUCTION

For the past years people have been interested in developing new polymeric materials that are electrically conductive or semiconductive^[1-4]. Polyacetylene (PA), the simplest linear polymer, has caught researchers' attention because it can be doped with ease by a number of chemical substances into n-type or p-type semiconductors. And modifying polyacetylene films with chemical doping and ion implantation has provided ways to create p-n junctions underneath the films' surface^[5-6]. We present here our work on low energy ion implantation (30 keV K^+) of FeCl_3 doped PA films to make better p-n junctions.

II. EXPERIMENTAL

Large area of free standing PA films were synthesized at room temperature using an improved Zeigler-Natta catalyst technique^[7]. The catalyst solution was a mixture of tetralutoxytitanium (3ml) and triethylaluminum (4ml) suspended in 5ml of silicone oil. It was aged for two hours at 120°C and cooled down slowly to room temperature while degassing. Purified acetylene gas was allowed to pass through the catalyst solution, completing the polymerization in about one hour. The synthesized films were washed for several times in solvent to remove the catalyst. The films, about 50

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micrometer thick and $0.5\text{g}/\text{cm}^3$ in density, contained about equal amount of trans- and cis-PA, as was revealed by IR measurements.

Chemical doping was undertaken immediately after the polymerization. The films were immersed into nitromethane solution of anhydrous ferric chloride. Dopant concentrations were adjusted by controlling the time of immersion. Generally, several minutes of immersion would result in dopant concentrations of 1–2 mol percent, which would lower the resistance of the films to 1–100 $\Omega\text{-cm}$ (p-type semiconductive) and would be just enough to accomplish their ion implantation in reasonable times. Washes were nevertheless needed, with nitromethane and other agents, to remove the residual catalyst.

The films were implanted with 30 keV K^+ ions on the isotope separator at SINR. The beam currents were kept below $2\ \mu\text{A}/\text{cm}^2$ so as to avoid overheating effect. The K^+ beams were scanning across a $60 \times 60\ \text{mm}^2$ area of the target holder which could hold up to 12 PA film samples, each was 14mm in diameter and masked to give a $50\ \text{mm}^2$ implanting area. The implantation dose varied from 1×10^{17} to 3×10^{17} ions/ cm^2 , depending upon the amount of the FeCl_3 dopant in a film.

III. RESULTS AND DISCUSSION

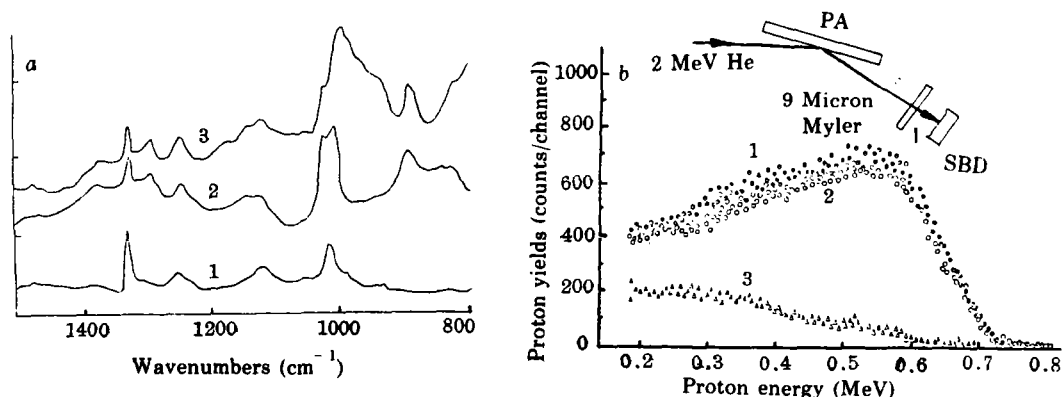


Fig. 1 Observations of ion-implantation induced damages to the surface of PA films

a. IR absorption spectra b. ERD spectra

The 30 keV K^+ ion implantation caused no visible damage to the film surface. There were just slight changes in color of the films' metal luster. Changes in physical properties of the implanted films were examined by a series of measurements. A four-probe system was used to measure the sheet resistance, which decreased up to 5 orders of magnitude after implantation. Infrared ray absorption measurements showed the PA films had been isomerized into trans-PA by the implantation. The increase of conductivity was mainly contributed by the isomerization (3–4 orders of magnitude). In Fig. 1a are typical IR absorption spectra of a PA film, derived from 1) the pristine, 2) implanted with $1 \times 10^{17}/\text{cm}^2$ of 30 keV K^+ ions, and 3) with $3 \times 10^{17}/\text{cm}^2$ of the ions.

Absorptions at the 1015 cm^{-1} band, a characteristic trans-PA absorption band, increased with the dose. The IR measurement also indicated, to some extent, damages to the C-H bonds of the polyacetylene, as some small absorption peaks appeared after implantation at the wavenumber band.

Ion implantation induced damages to the surface structure were detected, too, by 2 MeV He^+ elastic recoil detection (ERD), which provides hydrogen depth profiles of a surface^[6]. In Fig. 1b we give the ERD spectra of three PA films, 1) the pristine, 2) 30 keV K^+ ion-implanted to 1×10^{17} ions/cm², and 3), for comparison, implanted with 5×10^{16} /cm² of 180 keV Ar^+ ions. The experimental geometry is inserted in the figure. The high energy implantation gave rise to considerable hydrogen depletion throughout the range of the Ar^+ ions, indicating that the covalent bonds broke in large amount as the energetic particles were impinging on them. Hydrogen depletions could also be seen in 30 keV K^+ ion implantation. However, the process took place along the depths at a much lower rate, by which only about 5% of the hydrogen were taken apart from the C-H bonds, even though the K^+ ion dose was twice as large as that of the Ar^+ ions.

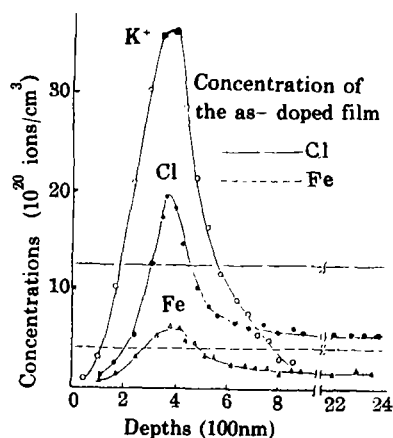


Fig.2 RBS depth profiling of K^+ , Fe^{+++} and Cl^- dopants in a PA film

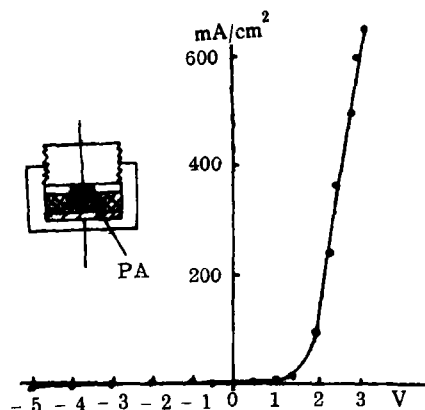


Fig.3 I - V characteristics of a PA film

Depth profile of the K^+ and FeCl_3 dopants were determined by means of Rutherford backscattering (RBS) with 2 MeV He^+ beams. The implanted species formed Gaussian-like distributions at 300 nm from the surface, with inward tails to depths of about 850nm. Typical RBS results are reported in Fig.2. What interested us the most was the redistribution of the chemically doped species. The film was doped with 1.2 mol percent FeCl_3 and implanted with 2.5×10^{17} K^+ ions/cm² at 30 keV. Upon the chemical doping, the Cl^- and Fe^{+++} ions distributed homogeneously throughout the depths (as far as a 2 MeV He particle could see). After implantation, however, some of the chemical dopants became concentrated at the depths where the K^+ ions were stopped. The ion-implantation induced dopants redistribution can be explained as follows. It is reasonable that the dopant concentrations decreased during the

implantation because much of the chemicals would flee from a film that had been placed in vacuum and bombarded by the ions. However, as the ingoing ions were creating broken C-H bonds, the radicals would capture the dopants that were fleeing from the implanted region or coming from inner depths. And some of the alkaline ions would combine with the halogen ions. The resulting redistribution of FeCl₃ suggests the formation of an interface where the implanted p-type carriers and the concentrated n-type carriers coexist, in other words, p-n junctions.

To measure the current-voltage response, an implanted PA film was placed between two gold-coated copper electrodes in a plastic cell. The FeCl₃-doped and K⁺ ion-implanted PA films showed diode-like I-V behavior. Fig.3 gives a typical I-V curve of a PA film treated with 1.5 mol percent FeCl₃ doping and 2.5×10^{17} K⁺ ions/cm² implantation at 30 keV. The backward-to-forward ratio of current was about 300 and the current density was 600 mA/cm² at 3V. Polyacetylene films such doped and implanted exhibited very good diode-like characteristics, with the best performance reaching more than 750 mA/cm² and 440, for the current and the ratio, respectively. Most of the polymer diodes functioned for weeks. Some lasted for over 60 days. The PA film diodes were kept in a N₂ ambience, but this did not protect them from oxidation. The diodes deteriorated with time by losing half level of the performance in several days. Systematic investigations are under way in an effort to gain better understanding of the phenomenon.

Controlling the implantation dose is a key problem to the study. We had been using I₂ doping and 15-30 keV K⁺ or Na⁺ ions to modify PA films. Some of the films did show diode-like behavior, and the iodine dopants redistributed similarly after implantation. However, iodine dopants lost in greater amount during implantation and one never knew how much alkaline ions were needed for the remaining halogen dopants. FeCl₃ is relatively stable. Tests showed FeCl₃ doped PA films could endure hours of heating at 150°C in vacuum, without losing greater than 20% of the dopant. If a PA film of 0.5 g/cm³ in density is doped with 2 mol percent FeCl₃, the density of Cl⁻ ions will be 1.4×10^{21} /cm³. A 30 keV K⁺ ion travels several hundred nanometers in polyacetylene. Therefore, one will have to implant at least 1×10^{17} /cm² of the K⁺ ions into the film to compensate⁽⁶⁾ the Cl⁻ ions in the implanted region, and still more for p-n junction formation. We have doped a PA film with 3.5 mol percent FeCl₃ and implanted 4×10^{17} K⁺ ions/cm² at 30 keV, and made a good PA diode with over 400 of the back-to-forward ratio of current.

IV. CONCLUSION

We have shown that the 30 keV K⁺ ion implantation of a few mol percent FeCl₃ doped PA films was an effective way to make PA film diodes of desirable performance. The films underwent little structural changes after large dose implantation of 30 keV

K^+ ions. RBS measurements revealed that the chemical dopants became concentrated in the implanted region. This indicates that some of the chemicals that were fleeing from the film were captured by the radicals created in the implantation as a result of energy deposition. The redistribution suggested the formation of p-n junctions at 300 nm from the surface. The PA film diodes produced in this way would function for a few months and gave as much as 600 mA/cm² of current density and 300 of the 'rectifying ratio' at 3V on the first day after implantation. The film diodes deteriorated because of oxidation related degradation of polyacetylene. And further investigations is needed to study the phenomenon and improve the performance of the PA film diodes.

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REFERENCES

- [1] H.Shirokawa, *Catalyst (in Japanese)*, **25** (1983), 12.
- [2] N.Basescu et al., *Nature*, **327** (1987),403.
- [3] Li S. et al., *Synth. Metals*, **20** (1987),141.
- [4] G.M.Holob and P.J.Ehrlich, *Polymer Science*, **150** (1977), 639.
- [5] N.Koshida and Y.Wachi, *Appl. Phys. Lett.*, **45** (1984), 436.
- [6] S.H.Lin et al., *Nucl. Instr. Meth.*, **B39** (1989), 778.
- [7] H.Naarmann and N.Theophilou, *Synth. Metals*, **22** (1987),1.
- [8] A.Turos and O.Meyer, *Nucl. Instr. Meth.*, **B4** (1984), 92.