

Polymer PN Junction by low Energy Double Implantation Technique

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Abstract— Polymer base organic PN junction with various ion types was studied. Low-energy ion implantation technique (~keV) is very useful in physical doping on PPP (Polyparaphenylene) polymer. By double implantation, effective organic PN junction was achieved. The best obtained electrical I-V property was rectification ratio which was about 10000. However, still have problems in low junction current density.

Index Terms— Ion Implantation, polyparaphenylene, Polymer PN Junction,

I. INTRODUCTION

THE conjugated polymers, known as conducting polymer, are widely used in electronics and optoelectronics. Generally has semiconducting properties from its single and double carbon bonding of aromatic benzene ring in polymer chains. Polyparaphenylene (PPP) is one of these conjugated polymers. Simple structure and good thermal stability of PPP makes it possible as a good model for theoretical study of doping [1]. But PPP itself has a very weak electrical conductivity. Thus different doping techniques are needed for organic conducting or semiconducting device.

By chemical doping, polymer n-type semiconductor or p-type semiconductor are possible [2~3]. As physical doping technique, there are ion implantation technique. Ion implantation technique is already used as a standard technique in conventional semiconductor industries for doping. For inorganic semiconductor such as Si, implantation energy is sometimes higher than ~MeV.

But the high energy of ~MeV makes severe damage to the polymer chains and even several hundreds keV could make a same damage due to the strong kinetic energy of accelerated ions. Broken bondings caused by these damages should have a role as carriers or particles in the implanted polymer material. Therefore conductivity could be enhanced after high energy implantation. However severe degradation of polymer properties enhanced simultaneously. This is why we try to use low energy ion implantation. Recently, many different research groups

are concentrated on the subject of OTFT. This OTFT (Organic Thin Film Transistor) is actually based on the technique of Field Effect Transistor in conventional inorganic semiconductor. It is composed of one organic or polymeric semiconductor and metallic electrodes. In natural or doped p-type or n-type organic semiconductor, carrier concentration is induced by applying electrical field between two electrodes. For the operation of OTFT, we only need one type of semiconducting material. On the other hand, PN junction is achieved by making a junction interface of two different types of semiconducting properties in one body. Therefore it is more complicated and needs sophisticated process. This is one of the reason why there are not many research groups on organic PN Junction.

In this paper, low energy ion implantation technique on PPP polymer film was challenged in order to prevent damage by high implantation energy. Various ion types and different implantation energies were tested. Thermoelectric power of implanted polymer films was measured and verified its semiconducting properties. Then organic polymer PN junction was obtained by double ion implantation technique

II. EXPERIMENTS AND DISCUSSION

Experimental procedure was launched with preparing the PPP (polyparaphenylene) film by pyrolyzation of PPP/PS block copolymer [4]. More than 20 specimens of spin-coated PPP/PS specimens on glass substrate and also 10 specimens on KBr substrate were simultaneously pyrolyzed for each series in order to have uniformity of each specimen. Electrical properties were measured with specimens on glass substrate and specimens on KBr substrate were used for optical properties like IR and UV/Vis spectra. The Specimen was spin coated for 30 seconds with 2500rpm. ECR type ion gun is mounted on our custom-built ion accelerator.

Ion implantation with various ion types and different conditions were finished and then its DC conductivity was measured. We used Four-point probe method with 4-point head on MS-TECH probe station MST-5000A in dark box and Keithley 2400 source meter.

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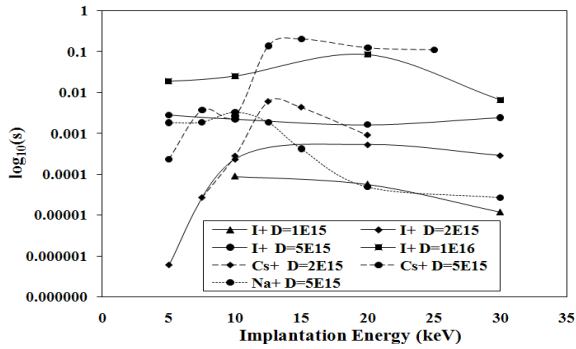


Fig. 1. DC conductivities of implanted PPPs.

In figure 1, DC conductivities for different implantation energy were showed. In general consideration, conductivity of implanted polymer is increased with higher implantation energy. This enhancement was originated from the generation of defects in polymer chains. For Na^+ , conductivity gave significant meaning compared to other heavy ions. In low energy between 10keV and 15keV, higher conductivity value was possible than in 30keV. Also Cs^+ had similar trend. However for I^+ , conductivity did not show significant value in different conditions.

Semiconducting property of implanted PPP films was also verified. Thermoelectric powers of implanted PPP films were represented in figure 2.

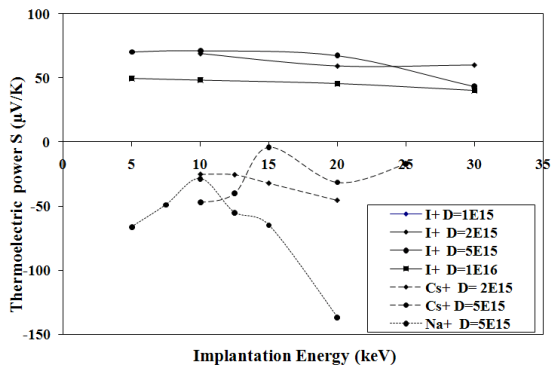


Fig. 2. Thermoelectric power S for various ions and energies.

Since thermoelectric power S of I^+ did not so much change much in all energy band, S of Cs^+ implanted specimen changed by itself extremely. The amplitude S of Cs^+ had minimum values in 10keV or 15keV compared to maximum value of DC conductivity of 15keV. Thus we supposed that better semiconducting property was possible with *low implantation energy*. Also from the sign of thermoelectric power S, doping effects were well certified (p type doping for Iodine and n type doping by Cesium or Sodium).

During implantation procedure, polymer network could be damaged by kinetic energy of accelerated ion. Therefore spectroscopy of UV/Vis and IR were carried out in order to check out these damages.

Absorption spectra of implanted PPP films were showed in figure 3 and figure 4.

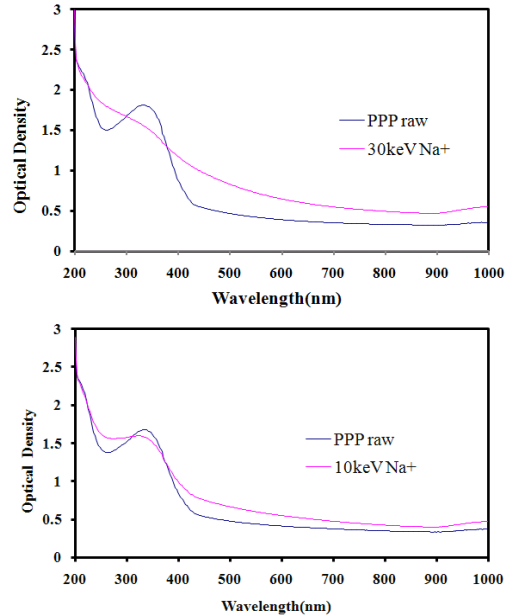


Fig. 3. UV/Vis spectra with Cs^+ implantation

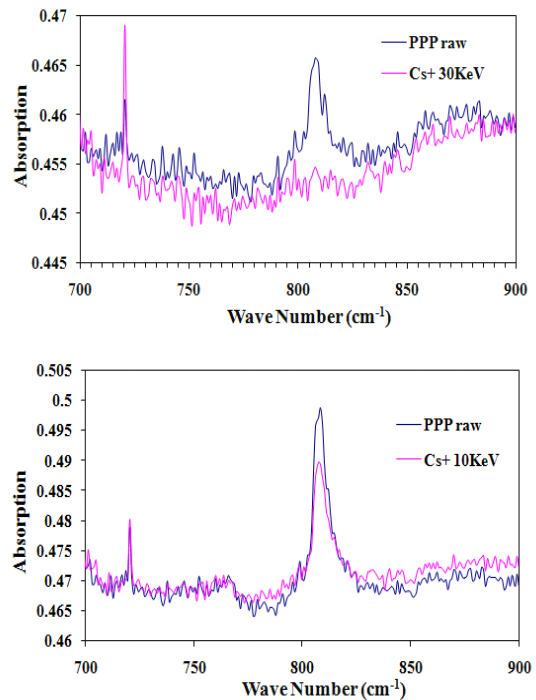


Fig. 4. IR spectra with Cs^+ implantation.

For relative high energy of 30keV, two UV absorption peaks of raw PPP film were totally disappeared, even with the small ion size such as Sodium Na^+ . These 220nm(5.9eV) and 350nm(3.5eV) peaks were attributed on resonance of benzene ring

and π - π^* transition respectively. For low implantation energy inferior to 30keV, here we demonstrated the case for 10keV, these two peaks (220nm and 350nm) were clearly seen, regardless of defects by implantation energy. It means that low energy should be extremely effective to prevent the damage on polymer chains. A similar significance was found in IR spectra between 700cm^{-1} and 900cm^{-1} in Cs^+ implanted PPP polymer. In IR spectrum of 30keV, we could not see the peaks of 760cm^{-1} and 810cm^{-1} , which were seen in raw material. These peaks were related to the conjugation length of polymer. In IR spectrum of 10keV implanted PPP, these two peaks were still remained. It means, even with heavier, low implantation energy made relative a few damage on polymer chains.

In the next step, realization of polymer PN junction was followed. The first implantation (10keV, $0.2\mu\text{A}/\text{m}^2$) was made with Iodine ions(I^+), since it showed relative similar value of thermoelectric power S for different implantation energy. Specimens were then annealed for 100 minutes at 100°C . This process was done for even distribution of implanted I^+ ions (P type doping). On the P type doped PPP film, N type doping with Sodium ions(Na^+) was accomplished in various implantation energy. For obtained PN junctions, electrical property of I-V measurement was accompanied. We used precision probe station MS-TECH MST-5000A in dark box and Keithley 2400 Source meter. Junction current I-V curves were demonstrated in figure 4. The better result for Na^+ ion was in case of 5keV than in case of 10keV.

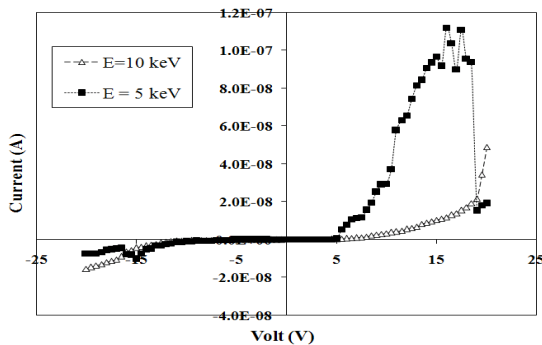


Fig. 5. I-V properties of Polymer PN-Junction

These results were verified by the ion concentration simulation program SRIM-2000[5]. Concentration profiles of implanted ions were different from ion type and energy. It is demonstrated in table 1. The higher the implantation energy is, the deeper penetration depth is possible. However with the smaller ion size, it is easier to penetrate into the polymer due to the decreased collision rate. Profile depth of Cs^+ is very similar with that of I^+ . Since atom numbers of two materials are very similar, 55 for

Cesium and 53 for Iodine respectively. We used I^+ and 10keV for first implantation. The measurement of penetration depth was about 150\AA . From table 1, Na^+ ions with 10keV could have deeper profile depth than Cs^+ 10keV.

TABLE I
PROFILE DEPTH(\AA) BY SIMULATION SRIM2000

	5keV	10keV	15keV	20keV	30keV
Na^+	~138	~240	~347	~462	~680
Cs^+	~110	~150	~188	~220	~214

On the contrary, Na^+ with 5keV had reverse tendency compared to Na^+ 10keV. So we proposed our junction models also in figure 6.

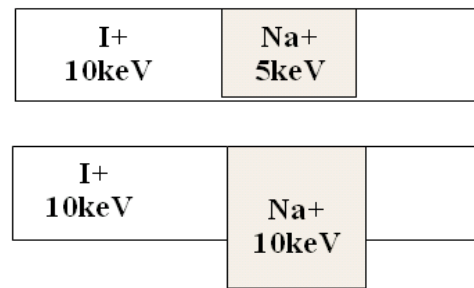


Fig. 6. Proposed Junction models.

For 10keV implantation, its deeper concentration depth made smaller junction interface. This was the reason why junction property in 10keV was poor than in 5keV against its good conductivity. However, thermoelectric power S was well matched to junction current results. These results were correspondence to other experiments with polythiophene[6~7], polyacetylene[8] and with pressed PPP[9]. The best rectification ratio was about 10000 between 5V and 10V apply voltage in 5keV implantation.

Otherwise it might be also possible with much smaller ion like Li^+ . We followed the exact procedure, but due to its strong reactivity of Li^+ , our apparatus should have encountered with severe problem of corrosion. Therefore we could not continue this procedure.

III. CONCLUSIONS

Polymer PN junction by double ion implantation on PPP films were successfully achieved. Low energy ion implantation with small ion size could make a little damage on implanted polymer surface. Thus enhancement

of conductivity was not from broken polymer chains but from implanted ions. And better semiconducting properties (type p and type n doping) were possible. Combination of Na^+ (5keV) and I^+ (10keV) had more wider junction interface. Rectification ratio of junction current was about 10000. It was better than any other research. However, we must ameliorate its weak junction current density.

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