

## Fabrication of a Stable p-n Junction in a Polyacetylene Film by Ion Implantation

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A stable p-n junction has been fabricated in high-density p-type polyacetylene film by sodium ion implantation.

The semiconductor characteristics (*i.e.*, n- or p-type) of polyacetylene (CH)<sub>x</sub> can be controlled by changing the dopant or the doping level.<sup>1</sup> However, stable p-n junctions have not been obtained, because p and n dopants easily migrate and compensate each other at the junction in the case of chemical doping.<sup>2</sup> Recently, the ion implantation technique has been applied to modify electroactive polymers<sup>3-5</sup> and improve their stability towards oxygen.<sup>6</sup> By this technique we have found an enhancement of the conductivity of (CH)<sub>x</sub>, which we assume is not caused by the carbonization (or degradation) of the polymer but by the doping effect.† Herein we report device fabrication by sodium ion implantation into high density (CH)<sub>x</sub> films (*ca.* 1 g/cm<sup>3</sup>; 200 μm thick).

† Resonance Raman spectra show that carbonization only occurs near the surface under the conditions of a high ion beam energy and a high fluence ( $\geq 1 \times 10^{17}$  Na<sup>+</sup>/cm<sup>2</sup> at 150 keV). The depth profile of the sheet resistance for implanted (CH)<sub>x</sub> has a complementary relationship with that of the Na ions.

The RIKEN 200 kV Low Current Implanter was used for implantation and the target holder was cooled with cold water during implantation. The conditions for sodium implantation are: ion beam energy 50–150 keV, fluence  $1 \times 10^{15}$ – $3 \times 10^{17}$  ions/cm<sup>2</sup>, and beam current *ca.* 5 μA. Implanted (CH)<sub>x</sub> films (diameter 0.6 cm) were characterized by i.r. and u.v.–visible spectroscopy, secondary ion mass spectroscopy (S.I.M.S.), and Rutherford backscattering (R.B.S.). A sandwich type cell was used for the measurement of current–voltage (*I*–*V*) characteristics. Gold electrodes were evaporated onto both sides of the implanted (CH)<sub>x</sub> films.

The pristine (CH)<sub>x</sub> was a p-type semiconductor doped with residual catalyst or oxygen.‡ Implanted sodium ions as n-type dopants were located near the surface and only this region was doped with Na. A p-n junction can be formed between a Na-implanted region and the substrate. The *I*–*V* curves of

‡ By means of R.B.S. and S.I.M.S., it was shown that the Al atoms of the residual catalyst are distributed uniformly in (CH)<sub>x</sub>. The conductivity of (CH)<sub>x</sub> was  $2.1 \times 10^{-5}$  S/cm.

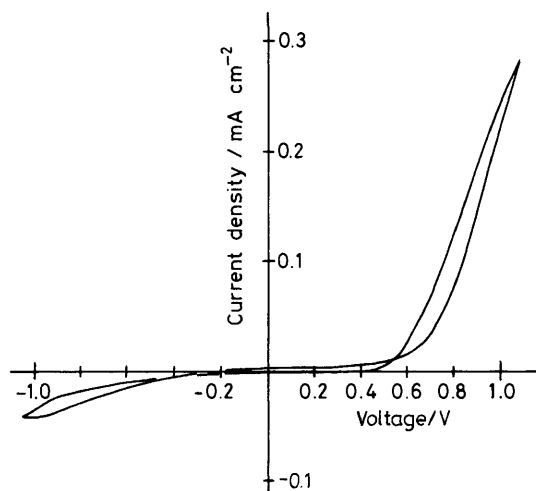


Figure 1.  $I$ - $V$  characteristics of  $\text{Na}^+$  implanted  $(\text{CHI}_y)_x$  ( $3 \times 10^{17}$  ions/cm $^2$  at 50 keV).

$(\text{CH})_x$  implanted with a fluence of  $1 \times 10^{17}$  ions/cm $^2$  at an energy of 100 and 150 keV show good diode characteristics. The back-to-forward ratio was  $\sim 12$  for  $(\text{CH})_x$  implanted with a fluence of  $1 \times 10^{17}$   $\text{Na}^+$ /cm $^2$  at 150 keV. After three days in the open air, the unimplanted region turned black and the conductivity decreased. However, the implanted region remained shiny, and the conductivity did not change. The back-to-forward ratio decreased to 7 mainly because of the degradation of unimplanted  $(\text{CH})_x$  by oxygen. Under an Ar atmosphere, the  $I$ - $V$  curve did not change over a month.

For high density  $(\text{CH})_x$  lightly doped with iodine [ $(\text{CHI}_y)_x$ ] (0.05%;  $\sigma = 3.8 \times 10^{-2}$  S/cm), quite a large fluence was necessary to obtain rectifying properties. At fluences less than this critical dose [ $10^{17}$  ions/cm $^2$  for  $(\text{CH})_x$  and  $3 \times 10^{17}$  ions/cm $^2$  for  $(\text{CHI}_y)_x$ ],  $I$ - $V$  characteristics were almost ohmic. Figure 1 shows typical  $I$ - $V$  characteristics of  $(\text{CHI}_y)_x$  implanted with a fluence of  $3 \times 10^{17}$   $\text{Na}^+$ /cm $^2$  at 50 keV. In contrast to the usual chemical doping, the compensation effect is very

small, and the resulting diode characteristics are stable for more than a week *in the open air*. The implanted ions will hardly diffuse in the polymer matrix, and a stable distribution of implanted ions (atoms) would be expected. The depth profile of implanted Na atoms in the high-density  $(\text{CH})_x$  films obtained by secondary ion mass spectrometry (S.I.M.S.) follows the Lindhard-Scharff-Schiott theory $^7$  and shows a Gaussian distribution centred around a few thousand Å. The stability of  $(\text{CH})_x$  in the open air may thus arise from the stable distribution of implanted ions in the film. In the case of the implanted  $(\text{CHI}_y)_x$  film, the concentration maximum is 1700 Å from the surface. When about 3000 Å of the surface of the film was removed by sputtering with an Ar ion beam of 7 keV, a depth which is much greater than the concentration maximum of  $\text{Na}^+$ , the diode characteristics disappeared and the  $I$ - $V$  curve was almost ohmic. These results strongly suggest that the highly implanted region became an n-type semiconductor and a p-n junction was formed between these regions and the substrate.

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