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≪Original≫ Comparative Study on Two Types of Silicon p-n Junction for Photovoltaic and Electronvoltaic Cells

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Abstract

The photovoltaic and the electronvoltaic cells have been obtained by forming Sb-implanted n- on p-type and In-implanted p- on n-type silicon p-n junctions Such shallow implantations into silicon wafers due to each dopant were done by the VDH-Implanter. The two types of the silicon p-n junction for these cells have shown special features on their various characteristics to be fitted for the direct energy conversions. The results of the comparative study on both of these cells are described in this article.

요 약

p型의 시리콘基板위에서 n型의 안티모니를 注入시킨 것과 n型의 시리콘基板위에서 p型의 인듐을 注入시킨 두 種類의 시리콘 p-n接合을 形成시키므로서 光에 依해서 起電力을 내는 電池와 電子照射에 依해서 起電力을 내는 두 種類의 電池를 얻었다 시리콘基板속에 各注入子를 이와같이 엷게 注入시키기 爲해서 VDH注入機를 使用하였다. 이들 電池를 爲한 두 種類의 p-n接合은 에너지의 直接變換에 適合한 諸特性上의 特徵을 나타내었다. 本 論文에는 이 두 種類의 電池에 關한 比較硏究의 結果가 나타나 있다.

1. Introduction

It has been reported[1,2] that solar energy and radioactive beta energy can be directly converted into useful electrical power by means of silicon p-n junction.

When sufficient electromagnetic radiation in the spectral region from 0.4μ to 1.2μ is incident upon silicon p-n junction, electron-hole pairs are created in both of p- and n-type regions of the crystal. The electric field of the junction separates them, pushing the holes into the p-region and the elcetrons into the n-region, building up the plus and minus charges on both sides of the transition region of the junction to generate external voltage on the device as a solar cell.

On the other hand, when a silicon p-n junction is irradiated by a radioactive beta source, electric voltage can be generated on the device by the similar process as aforementioned. This is called as electronvoltaic effect

(EVE)[2].

For both of these cells, the junction depth of each cell should be shallower the better and moreover the state of impurity concentration in each type of the p-n junction is different.

The purpose of this article is in clarifying the special features on both types of the p-n junction for the solar cell and the EVE cell by comparing the various different characteristics of both cells.

2. Experimental Procdures

(1) General Description of the Apparatus for Forming the p-n Junctions

It is very difficult to form a shallow p-n junction having its uniform projected range in average by means of thermal diffusion technique. In order to meet with these stringent requirements, we attempted to use the VDH-Implanter(Vacuum Discharge and Heating) which was recently invented by one of the authors, and the description of the implanter in detail is to be found elsewhere[3]. It has been experimentally proven that the implantability of the VDH-Implanter is equivalent to that of an ion implanter of high voltage accelerator type. The brief explanation of the implanter is as follows.

The vacuum discharge is to be taken place in an evacuated glass bell jar having four electrodes in it as shown in Fig. 1.

The positive heavy ions due to the rarefied air plasma is to be accelerated toward the cathode of mesh type. When the ions pass through the mesh electrode, neutralizing action of the ions occurs by tangential touching (grazing incidence) with the matrix wires of the mesh electrode.

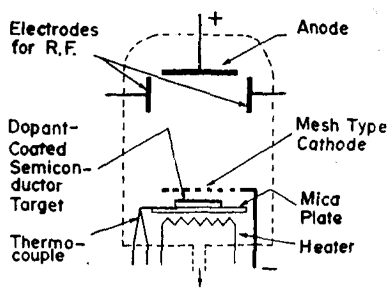

Fig. 1. Schematic illustration of the VDH-Implanter.

Since the dopant-coated silicon wafer which is placed underneath the mesh electrode is preheated to the temperature of about 400°C, dopant atoms can be easily implanted into the silicon target by the process of radiation enhanced diffusion[4].

During the impact of the neutralized ions with the stationary atoms, the energy loss at the surface layer due to the nuclear stopping is greatly alleviated. The influence due to the electronic stopping is negligible for such low energy particles. The junction depth can be easily controlled by varying accelerating voltage, heating temperature, and implanting time.

(2) Forming Methods of the p-n Junctions

The two types of the p-n junction were formed by the VDH-Implanter. In each case, the dopant-coated silicon substrate was bombarded and annealed in the implanter, and after the implanting the remaining dopant film was removed by an etchant. Since the accelerating voltage of only 1,000 volts order was applied to the main electrodes, each junction depth was very shallow.

As for the p-n junction for a solar cell, antimony as an n-type dopant was implanted in a p-type silicon base, because the mobility of an electron as a minority carrier in the p-type region is higher than that of a hole in the n-type region(Ref. 5).

On the other hand, the p-n junction for the electronvoltaic cell was formed on an n-type silicon base by indium as a p-type dopant.

The data for the implanting factors in both cases are shown on the Table 1.

Table 1

Samples	Vdc volts	Timp °c	timp min.	Tann °c	tann min.	THc Å	D
Solar cell	1, 500	400	10	400	20	270	Sb
EVE cell	1, 000	150 300 400	3 3 4	450	10	400	In

Vdc; dc voltage, Timp: implanting temperature,
timp: implanting time,
Tann: annealing temperature,
tann: annealing time, THc: coated thickness,
D: dopant

(3) Method of Device Fabrication

Methdos[6] are known to make good ohmic contacts to both of p- and n-type silicon, but the actual technique is very difficult.

In any method of impurity doping, it is difficult to get a uniformly doped p-n junction over the whole size of a silicon wafer on account of the projected range straggling[7] caused by the defects of the silicon wafer, so that generally the wafer is cut into many segments after a metal coating for the electrodes.

In this research, both sides of each dopant-implanted silicon wafers were sputtered by Au-Cu alloy to the thickness of about 200Å, and each cell having the size of about 5mm× 7mm was obtained by cutting the wafers.

Copper was coated on a spot size of each sputtered film of each cell through a window of a mica mask, and a lead-wire was soldered on each copper spot by using a low temperature solder(120°C). Each suttered film was protected from the soldering by the copper film.

After attaching each lead-wire, each cell was coated by transparent lacquer for reinforcing the metal films and the passivation of uncoated surface of the silicon.

(4) Measurements of Both Types of Cell

Various characteristics of each cell such as I-V characteristic, spectral response, open *circuit output voltage vs.* illumination were

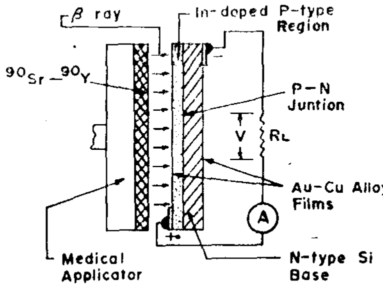

Fig. 2. Experimental arrangement for measuring the electronvoltaic effect.

measured by using the instruments such as Tektronix 575 spectrophotometer, Toshiba No. 5 type lux meter, H. P. model 425A microvoltammeter, and H. P. model 412A VTVM.

For the measurements of output voltage *vs.* output current through load resistances due to the electronvoltaic cell, the arrangement coupled with a radioactive source as shown in Fig. 2 was used. The radioactive source having 50 mCi is a disk type medical applicator which is coated by the activated $SrTiO_3$ as the Sr90-Y90 beta source, and can emit the beta-rays having their energies of 0.61 MeV and 2.26 MeV as well as their Bremsstrahlung.

3. Results and Discussion

(1) I-V Characteristics of the Solar Cell and the EVE Cell

Fig. 3-(a) shows the I-V characteristic of the solar cell having Sb-implanted silicon p-n junction, and Fig. 3-(b) shows that of the EVE cell having In-implanted silicon p-n junction. When we compare these two characteristics we can find following different points.

The characteristic of forward direction shows an almost straight line and that of reverse direction shows a harder curve in the Fig. 3-(b), whereas that of forward direction shows an exponential rise and that of reverse direction shows a softer curve in the Fig. 3-(a).

In the Fig. 3-(a), it is shown that the

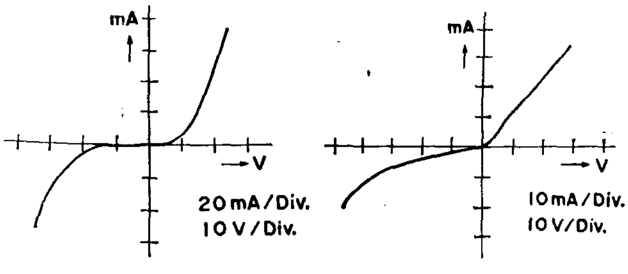

Fig. 3. I-V characteristics of the p-n junctions for the solar cell and the EVE cell.
(a) for the solar cell (b) for the EVE cell

forward curve rises exponentially in accordance with the increasing rate of the probability exp(eV/kT) by the electrons which are climbing on the increasing potential from n-region toward p-region, where V is the forward bias potential. In this case, the barrier potential is decreased by the forward bias, and the forword current can be given as I_o exp(eV/kT).

The reverse curve in Fig. 3-(a) shows that the decreasing rate of the probability exp(-eV/kT) by the electrons which are climbing on the increasing potential from n-region toward p-region. In this case, the barrier potential is increased by the reverse bias, and the reverse current can be given as $I_o$exp(-eV/kT).

Each of these forward and reverse currents should be composed of the drift current by the drift fields E=dV/dx and the diffusion current by the gradient of carrier concentration.

When the implanted impurities have a graded concentration, the gradient of carrier concentration should be obtained as well as a relevant drift fields to increase the mobility of carrier.

The p-n junction for the solar cell used here is made of Sb-implanted n- on p-type as aforementioned. We can easily understand the presence of graded impurity in the n-region, but in the p-region the situation is a little different from the n-region.

Let Nd be the donor concentration and Na the acceptor concentration. In the n-region, Nd is larger than Na: in the transition region, Nd=Na: and in the p-region, Nd<Na, but in a certain scope of the p-region, cancelling action between Nd and Na occurs by the graded Nd due to the deeply projected donor impurities having the range straggling[7], so that effectively graded layer of Na can exist in the p-region. The exponential reverse curve in Fig. 3-(a) shows the presence of impurity grading in the p-region.

Most commercially available solar cells are of the classical type, *i.e.*, are fabricated by making diffusion into a base material with constant impurity concentration.

When an n-type impurity is doped on a p-type silicon base for making a solar cell, generally a graded impurity concentration can not only be obtained in the n-type region, but also a graded p-type impurity layer should be formed effectively in the p-type base region as explained above.

Wolf[8] reports that, for an improved solar cell, it is necessary to diffuse n- and p-type impurities from both sides of an intrinsic silicon with proper parameters so as to obtain a junction in the desired distance below the surface and simultaneously obtain desired impurity grading.

Later, Overstraeten and Nuyts[9] obtained a drift-field type solar cell by making a graded base impurity concentration in accordance with Wolf' idea. The formation of a graded impurity concentration in the base layer should be the essential condition for a solar cell.

In the Fig. 3-(b), it is shown that the forward curve rises as an almost straight line while the reverse curve takes an harder characteristic of exponential rise. This means that an almost step junction is formed by the p-type indium dopant with the n-type base, and the harder reverse curve shows the presence of a steeply graded n-type dopant in the n-type region. It is known[2] that the indium dopant tends to make a step junction in group Ⅳ semiconductors by forming an alloy at low temperature less than 600°C. It can be pointed out that the formation of such a step-like junction is the essential condition for obtaining higher electronvoltaic effect by beta-ray irradiation on the p-n junction.

(2) Spectral Response of Both Cells

The spectral response against various light bands of the two types of p-n junction are compared as shown in Fig. 4. The curve (a) shows the spectral response of the solar cell while the curve (b) shows that of the EVE cell.

The p-n junction for the solar cell used in this article is n- on p-type, and the junction has a graded impurity concentration in both regions as aforementioned.

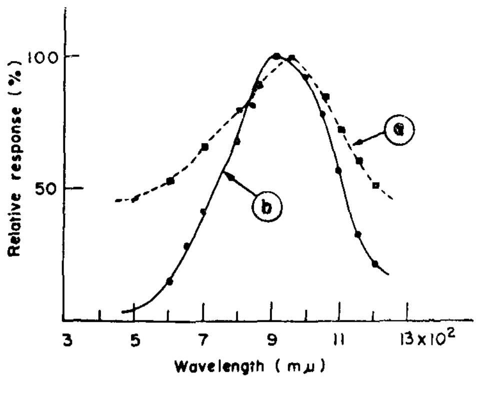

Fig. 4. **Spectral response by the solar cell and the EVE cell.**

The barrier height, which is equal to the maximum applicable forward voltage on the p-n junction, is determined by the difference in Fermi levels in the n- and the p-type region on both sides of the junction, These Fermi levels are a function of impurity concentration and the temperature of the silicon, and drift fields can be obtained by proper impurity grading which leads to a varying position of the Fermi level with regard to the band edges. Electron-hole pairs created by the incident photons can be separated into two kinds of minority carrier at both regions by the drift fields, pushing them into each opposite region for building up the plus and minus charges by the fields.

According the Shockley,[10] in a silicon p-n junction at forward bias, the current is carried by recombination through deathnium centers in the space charge layer and varies with voltage V as exp(eV/AkT), when A changes from 1 at low forward bias to 2 at high forward bias. In case of the photovoltaic effect by the two types of p-n junction, such conception of trapping center should be introduced.

When the impurites have a graded concentration in the n-type region of a silicon p-n junction, trap depth of each localized impurity center should be different, because the average electron demaraction level is a function of impurity concentration and the energy state of each impurity center, and besides the occupation of the shallow trapping states by electron is determined by thermal exchange with free carriers at their nearest band edge. For example, in a radiationless transition by the cluster state of impurities, recombination rate of electrons is greatly varied by the degree of the cluster state.

From these points of view, the impurities having a graded concentration should be localized at different trap depth, so that wider spectral response can be obtained.

The p-n junction for the solar cell having a proper grading of the impurity concentration has a wider spectral response as shown in the curve (a), whereas the p-n junction for the EVE cell having a poor grading of the impurity concentration has a narrower spectral response as shown in the curve (b).

(3) Photovoltaic Effect of Both Cells

The open circuit photovoltaic output voltage *vs.* the illusmination of the two types of the cell by an incandescent lamp is shown in Fig. 5.

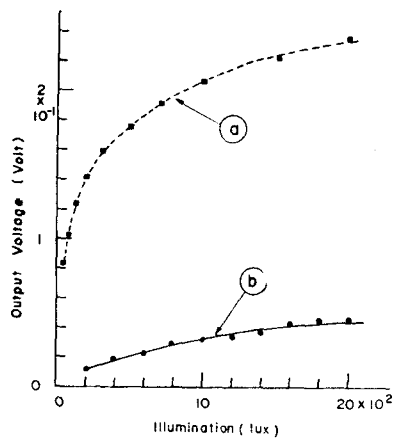

Fig. 5. Photovoltaic effect by the solar cell and the EVE cell.

The curve (a) and the curve (b) are due to the solar cell and the EVE cell respectively. It is shown that the photovoltaic effect of the solar cell is almost normal while that of the EVE cell is very poor.

It can be assumed that, the thinly implanted antimony layer and the opposite p-type layer of the solar cell have properly graded impurity concentrations so as to be able to bring the higher collection efficiency, whereas the thinly implanted indium layer and the opposite n-type layer of the EVE cell have poorly graded impurity concentrations.

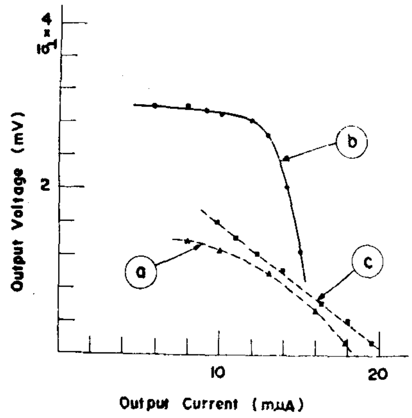

Fig. 6. Electronvolt effect by the solar cell and the EVE cell.

(4) Electronvoltaic Effect of Both Cells

The electronvoltaic output voltage *vs.* the output current through load resistances by two types of the cell is shown in Fig. 6. These measurements were done by the arrangement as shown in Fig. 2.

The curve (a) is due to the solar cell being directly irradiated by the beta-ray, the curve (b) the EVE cell irradiated by the beta-ray, and the curve (c) the solar cell on which the painted-ZnS: Ag is irradiated by the beta-ray.

The curves (a) and (c) show that the electronvoltaic effect by the solar cell is very poor though the result of double conversion due to the painted-ZnS:Ag on the solar cell is a little better than the direct conversion by the beta-ray.

On the other hand, the curve (b) shows that the result of the direct conversion by the EVE cell is fairly preferable. Such results can be explained as follows.

A beta-ray emitted from its source of bulk material has a continuous energy distribution in a certain scope on account of the ionized radiation in the bulk.

The beta source used in this experiment is made of the $SrTiO_3$ thin film coated on a metal disk for the use as a medical applicator, so that two kinds of almost monoenergetic beta-rays can be emitted from the source (0.61 MeV and 2.26 MeV).

Since the EVE cell has a step-like p-n junction of p-on n-type, the accepter impurity centers should have narrower variety of the trap depth, so that almost monoenergetic beta-rays can affect for the excitation of the impurity centers, hence for obtaining a better EVE, beta energy and its penetration depth should be taken into account.

It can be also understood about the reason that the solar cell having the graded impurity concentration should not be fitted for the EVE.

4. Conclusion

As has been already stated, an extremely thin doped layer is necessary on the p-n junction for the solar cell and the EVE cell respectively, but actually it is very difficult to form such a junction by conventional diffusion technique.

A new method of thin impurity doping has been atempted by inventing the VDH-Implanter as described briefly in Part II-(1). Each p-n junction for the solar cell and the EVE cell was the Sb-implanted n- on p-type and the In-implanted p- on n-type respectively as aforementioned.

It has been experimentally proven that, a p-n junction having a graded impurity concentration in the both regions is fitted for a solar cell, wheras a p-n junction having a steeply graded impurity concentration in the both regions is fitted for an EVE cell.

It should be emphasized that the results of such comparative study on the two types of the p-n junction for the solar cell and the EVE cell will be able to give a proper direction for the further studies of the silicon solar cell and the silicon p-n junction type nuclear battery.

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