ANALYSIS OF DOPING ELEMENTS FOR PHOTO DIODE

Prabakaran Balakrishnan
Sri Shakthi Institute of Engineering and Technology, EEE, L&T By-Pass, Chinniyampalayam post,Coimbatore, India, 641062, Email: bp.siet@gmail.com

Vivekanandan Chenniappan
SNS College of Engineering, EEE,Kurumbapalayam,Coimbatore,India,641107,Email:vp.snsce@gmail.com

Abstract: *An analysis was done on the type of doping elements which can be added with Silicon material. Pure Silicon has four electrons in valence band. If pure Silicon is doped with bivalent element like Calcium as acceptor impurity, this provides two free protons in the conduction band of the Si Crystal and this can be used as p-type material for the photo diode. If pure Silicon is doped with hexavalent element like Sulfur as donor impurity, this forms two electron in the conduction band of the Si Crystal and this can be used as n-type material for the photo diode. By this method, the number of pairs of free electron and free proton can be increased in the photo diode.*

Key words: *Silicon, valence band, conduction band, photo diode, impurities, doping.*

1. Introduction

In the present day, the attention of the science world is turned towards Autonomous systems, which are used to provide situational awareness and long-term environment monitoring. In this line, Photovoltaics is one such system favored as a dependable long term power source for many applications [1]. Photovoltaics (PV) are a term which covers the conversion of light into electricity using a device called photodiodes. These Photodiodes are manufactured using some specific semiconducting materials choosed in accordance with their inherent properties best suited for this purpose. Photodiodes are operated at high reverse bias voltages [2]. The common solar cell which is used to generate electric power is a large area photodiode. In Solar cell, the longer a photo generated carrier exists, the greater are its chances of being collected by the electric field at the junction and of contributing to the photocurrent [3].

2. Theory of Photodiodes

A photodiode consists of P-Type Silicon, N-Type Silicon and P-N junction (Depletion layer of p and n). The photodiode is shown to be suitable for real-time second-order autocorrelation measurements of pulses [4]. Four inversion layer photo diode was discussed in article [5]. Avalanche photodiode (APD) detectors were described in article [6]. Highly efficient photovoltaic devices were discussed in reference [7]. High speed operation of avalanche photodiodes was achieved in reference [8]. Fabrication of an InP-InGaAs uni-travelling-carrier photodiode was discussed in [9]. Results on Limited Geiger-mode Microcell Silicon Photodiode (LGP) were described in [10]. Ultra compact 45 GHz CMOS compatible Germanium waveguide photodiode was discussed in [11]. A random access photodiode array for intelligent image capture was discussed in [12].

P-Type Silicon

The best conductors have one valence electron. The best insulators have eight valence electrons. Therefore a semiconductor is an element which has the property of a conductor and an insulator i.e. it has valence electron between 2 and Seven. Trivalent means three electrons in valence band of that element's atom. In the case of Silicon, if the doping atom is trivalent, one electron vacancy (proton) will remain after sharing its three electrons with the four Silicon atoms in the Silicon. This doped Silicon is p-type Silicon. Here, the trivalent element is known as acceptor. The P-Type Semiconductor is shown in Fig.1.

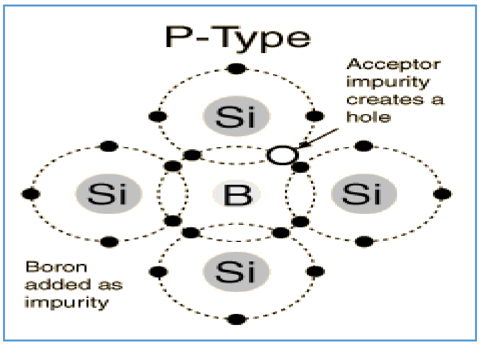

Fig.1.P-Type Semiconductor

N-Type Silicon

Pentavalent means five electrons in the valence band of that element's atom. In the case of Silicon, if the doping atom is pentavalent, one extra electron will remain after sharing its four electrons with the four Silicon atoms in the Silicon. Here the pentavalent element is known as donor. In p-type, out of four Silicon atoms, only one free proton is produced. In n-type, out of four Silicon atoms, only one free electron is produced. The N-Type Semiconductor is shown in Fig.2.

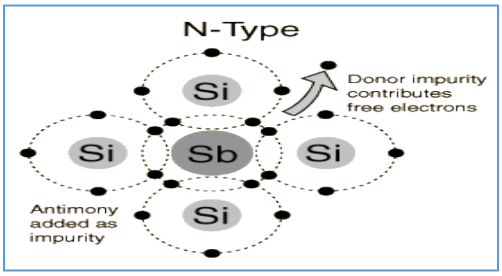

Fig.2. N-Type Semiconductor

P-N junction:
When a junction between a p and n type material is formed, the free electrons diffuse from a higher concentration side (n) to a lower concentration side (p). Similarly, the free protons diffuse from p-type to n-type. Soon after crossing the junction, the free electrons combine with the free protons and vice-versa. This flow of proton and electron leads to the formation of depletion region, which has the accumulated mobile charges. This region is also called space charge region or transition region. Mobile charges exist only outside the depletion region. The PN Junction is shown in Fig.3.An abrupt junction is an idealization because the p side cannot suddenly end where the n side begins. In a more realistic on junction there is a gradual change from one type of material to another. Such a junction is known as graded junction. When a junction between a p and n type material is formed, the free electrons and protons diffuse from a high-concentration side to a lower-concentration side. Soon after crossing the junction, these carriers recombine with the other types of majority carriers on the other side.

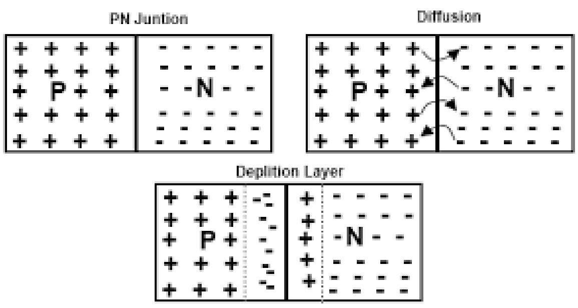

Fig.3. PN Junction

3. Working principle of photodiode

The photo diode has p-side, n-side and junction. The depletion layer is formed when PN junction is made. When the depletion layer is illuminated, the free protons are formed when p-type material is made. The free electrons are formed when n-type material is made. When connected to the load these free electrons move through the n-side and the free protons move through the p-side. The free electrons in the n-side of the PN Junction move towards the p-side and the free protons in the p-side move towards n-side in the depletion layer. During this movement, some of these electrons and protons recombine and form the depletion layer. This layer acts as a barrier for further movement of free electrons and free protons through the depletion layer.

4. Analysis

In the doping process, the evolution of free electron/proton production is analyzed. Silicon has four electrons in the valence band of its atom. When a trivalent element which has three electrons in the valence band of its atom, is added with the Silicon, one free proton is produced. When a pentavalent element which has five electrons in the valence band of its atom, is added with the Silicon, one free electron is produced. The main purpose of doping is to increase the free electrons in the n-type Silicon and to increase the free protons in the p-type Silicon.
To increase the efficiency of photo diodes, the PN junction of the photo diode is analyzed.

From the analysis of P-type material formation, it is derived that if the doping element is bivalent, two extra protons will remain after sharing its two electrons with the four tetravalent Silicon atoms. This can be used as p-type material. For example, Calcium is taken as bivalent element and Silicon is taken as tetravalent element. The Fig.4 shows the P-type material using these elements.
As Calcium is naturally available, this is the best suited element for doping with pure silicon.
From the analysis of N-type material formation, it is derived that if the doping element is hexavalent, two extra electrons will remain after sharing its six electrons with the four tetravalent Silicon atoms. This can be used as n-type material. For example, Sulfur, the hexavalent element, which is available in nature in crystal form, is taken and Silicon is taken as tetravalent element. The Fig.5 shows the N-type material using these elements.
This can increase more number of free electron-proton pairs in the case of p-n junction formation in the photo conducting diode.

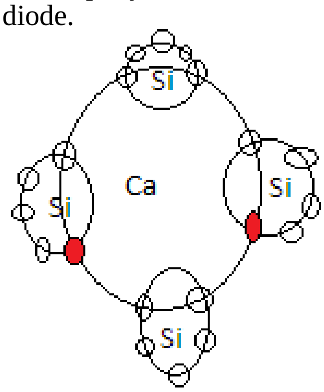

Fig.4.Acceptor impurity (Calcium) creates two free protons

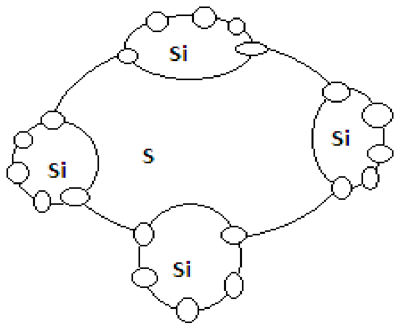

Fig.5.Donor impurity (Sulfur) contributes two free electrons

5. Manufacture of Photodiodes

Photodiodes are manufactured using naturally available materials. Silicon is used as basic element. Calcium is chosen as donor impurity for producing p-type material and Sulphur is selected as accepter impurity to produce n-type material.

The impurities are added to produce free protons/free electrons and the addition of these impurities into Silicon is called doping.

6. Semiconductors

The best conductors have one valence electron where as the best insulators have eight valence electrons. The best semiconductors have four valence electrons. Various favorable characteristics of Si have made it the semiconductor of choice. It is the element which is available in plenty on earth after oxygen. Each silicon atom shares its electrons with four adjacent atoms such that it has eight electrons in its valence orbit. Thus, each pair of electrons belongs to two adjacent atoms and is attracted by them with equal and opposite forces, which keeps them bonded together. Such a chemical bond is called as a covalent bond. This covalent bond keeps the crystal together and gives it solidity.

At absolute zero temperature, a semiconductor is an insulator with no charge carriers available for conduction of current. When temperature is increased, the vibration of atoms can sometimes dislodge an electron from the valence orbit. The dislodged electron is known as free electron and the vacancy thus created in the valence orbit is known as proton. Thus, with breaking of a covalent bond a free electron-proton pair is produced. Occasionally, a free electron will get attracted to a proton and fall into it. This merging of free electrons and a proton is known as recombination. The amount of time between creation and disappearance of an electron-proton pair is known as lifetime. It varies depending on how perfect the crystal is and also some other factors. At any instant, the following conditions exist within the Si crystal:

1. Some free electron-protons are being created.
2. Some free electrons-protons are being recombined.
3. Some free electron and protons exist temporarily, awaiting recombination.

7. Intrinsic silicon

Isolated Silicon has 14 protons and 14 electrons. The outermost orbit contains four electrons. Intrinsic Silicon crystal has every atom as Silicon atom. Each Silicon atom shares its electrons with four neighboring atoms to form a crystal. The crystal has got eight electrons in its valence orbit.

An isolated Silicon atom's behavior is explained here. The total energy of an electron depends on the size of its orbit. The orbit's radius determines its energy level. Nucleus attracts electrons. So, extra energy is needed to lift an electron into a larger orbit.

As shown in Fig.6, there are different energy levels of various electrons by respective lines. Energy levels are extended as energy bands when atoms of the intrinsic Silicon are considered. These energy bands are shown in Fig.7.

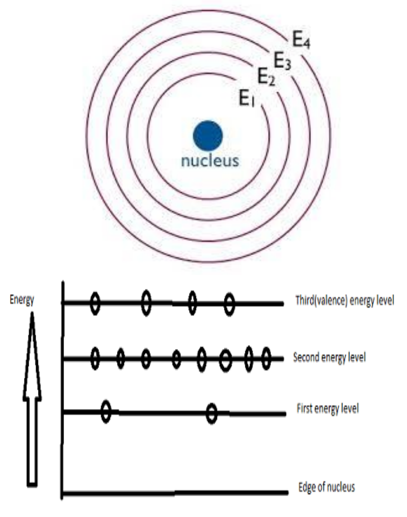

Fig.6. Orbits and Energy Levels

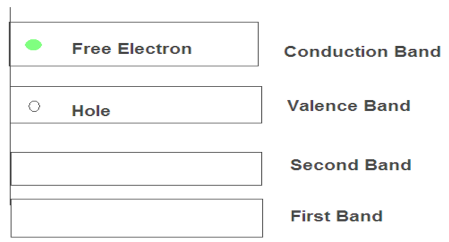

Fig.7.Energy Bands in Intrinsic Silicon Crystal

Extrinsic Semiconductor

The process of addition of an impurity in an intrinsic semiconductor material in order to produce majority of free electrons and free protons is known as doping. The doped semiconductor is called extrinsic semiconductor. The behavior of a semiconductor can be best explained with the help of quantum theory. Approximately, the total energy of an electron with the size of its orbit can be identified. That is, each radius of an orbit is considered as equivalent to an energy level. Since an electron is attracted by the nucleus, extra energy is needed to lift an electron into a larger orbit. Some of the external energy sources that can lift the electron to higher energy levels are heat and light.

9. Generation of Electron-Proton Pair by Photon Absorption

Photon is defined as a bundle of electromagnetic energy. This is the basic unit that makes up all light.

The energy available in a photon is given by

$E=hv=hc/\lambda$ Joules

Where
h is Planck's constant (h=6.63x10-34 joules-second)
c is the speed of light (2.988x108 m/s)
v is frequency of photons in Hz
λ is the wavelength of photons in meters
Expressing in m, and energy in eV (1eV=1.6x10-19 joules),

The expression becomes

$$E=1.24/\lambda \ \text{eV}$$

The energy in a photon must exceed the semiconductor band-gap energy E_g so that to get absorbed and generate electron-hole pair. For energies less than the band gap energy, absorption does not take place. The semiconductor material appears transparent to these low-energy photons. If a photon has energy much greater than the band gap, it still produces a single electron-proton pair, but the excess photon energy is lost to the material as heat. Since, the semiconductor used for photon absorption should have band-gap energy such that the maximum percentage of solar spectrum is efficiently absorbed.

10. Photo Conduction

Once the light energy is acted upon the depletion layer, electron-proton pairs are generated. Both electron and proton will be acted upon. It will cause the protons to be swept quickly towards the p-side and electrons to be swept quickly towards the n-side. Once out of the depletion region, these electrons and protons become part of the mobile charges in the respective regions. This addition of excess majority mobile charges on each side of the junction results in a voltage across external terminals of the junction. If a load is connected across the terminals, the photon-generated current will flow through this external circuit. This current will be proportional to the number of electron-proton pairs generated. Thus, an illuminated PN junction becomes a photovoltaic cell. It is shown in Fig.8.

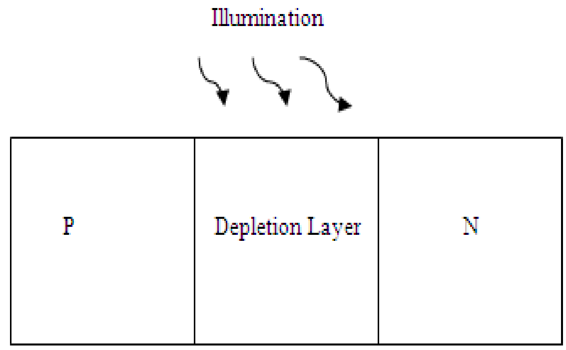

Fig.8.Illuminated PN Junction (Photovoltaic cell)

- ✓ The monovalent elements are Hydrogen (H), Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Caesium (Cs), Francium (Fr).
- ✓ The bivalent elements are Beryllium (Be), Magnesium (Mg),Calcium(Ca), Strontium (Sr),Barium(Ba),Radium(Ra).
- ✓ The trivalent elements are Boron (B), Aluminum (Al), Gallium (Ga), Indium(In).
- ✓ The tetravalent elements are Carbon(C),Silicon(Si),Germanium(Ge),Tin(Sn),Lead(Pb).
- ✓ The pentavalent elements are Nitrogen (N),phosphorus (P), arsenic (As),Antimony(Sb).
- ✓ The hexavalent elements are Oxygen(O),Sulfur(S),Selenium(Se),Tellurium(Te), Potassium(Po).
- ✓ The heptavalent elements are Fluorine(F),Chlorine(Cl),Bromine(Br),Iodine(I).
- ✓ The number of free electrons in the valence band of the elements is shown in the Fig.9.

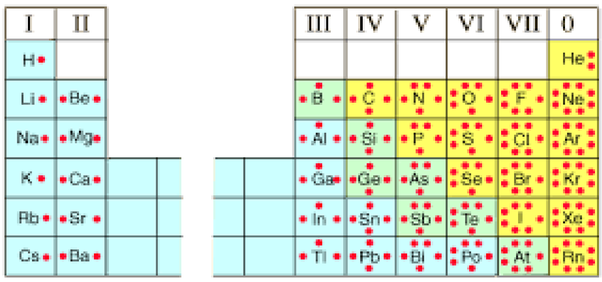

Fig.9. Free electrons in the valence band of the elements

11.Method to Increase the Electron-Proton Pair

Electron-hole pairs are generated within the junction (depletion layer) of photodiode. Both carriers (electrons, holes) will be subjected to the high intensity of illumination. This causes protons to be driven quickly towards the p-side and the electrons towards n-side. When the concentration near the junction increases they diffuse away from the junction. This additional excess charge carried on each side of the junction. This creates voltage difference across external terminals of the photodiode.

If electron-hole pairs are generated near the junction then depending on how far it is from the junction, it may or may not contribute to the photocurrent. Suppose that the electron-proton pairs are generated near the junction on the n side. If the generated protons which is minority carrier in the n region, manage to reach the junction before it gets recombined, it will be swept across the junction on p side and contribute to photocurrent. If they get recombined before reaching the junction, they are lost from the conduction process. Similarly, if the electron-proton pairs are generated near the junction on the p-side, the generated electrons must reach the junction before getting recombined in order to contribute in photocurrent. Thus, the minority carriers, generated outside the junction region due to optically generated electron-proton pairs, must reach the junction in a time less than the respective minority carrier lifetime to be able to contribute in the photocurrent.

8. Applications of Photo Diode

Some of the areas where Photodiodes used are listed below:

1. Cameras
2. Medical devices
3. Safety equipments
4. Optical communication devices
5. Position sensors
6. Bar code scanners
7. Automotive devices
8. Surveying instruments

9. Selection of Material for P-type Silicon

If the doping element is bivalent, two extra protons will remain after sharing its two electrons with the four tetravalent element Silicon atoms. This can be used as p-type material. The bivalent materials are Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba), Radium (Ra). The comparison of availability of these materials is mentioned below.

Table. 1
Selection of Material for P-type Silicon

S.No	Material	Availability
1	Beryllium (Be)	It is a relatively rare element in the universe.
2	Magnesium (Mg)	It is the ninth most abundant element in the universe.
3	Calcium (Ca)	It is the fifth most abundant element in Earth's crust and the third most abundant metal, after iron and aluminium.
4	Strontium (Sr)	It occurs naturally mainly in the minerals celestine, strontianite.
5	Barium (Ba)	Because of its high chemical reactivity, it is never found in nature as a free element
6	Radium (Ra)	In nature, it is found in uranium and (to a lesser extent) thorium ores.

Since Calcium is the fifth most abundant element in Earth's crust and the third most abundant metal, after iron and aluminium, it can be chosen as the bivalent element which can be doped with Silicon to form P-Type material of the photo diode.

14. Selection of Material for N-type Silicon

If the doping element is hexavalent, two extra electrons will remain after sharing its six electrons with the four tetravalent element Silicon atoms. This can be used as n-type material.
The hexavalent materials are Oxygen (O), Sulfur(S), Selenium (Se), Tellurium (Te), and Potassium (Po). The comparison of availability of these materials is mentioned below.

Table.2
Selection of Material for N-type Silicon

S.No	Material	Availability
1	Oxygen (O)	It is the third-most abundant element in the universe, after hydrogen and helium.
2	Sulfur(S)	It is abundant, multivalent, and nonmetallic.
3	Selenium (Se)	It rarely occurs in its elemental state or as pure ore compounds in the Earth's crust
4	Tellurium (Te)	It is occasionally found in native form as elemental crystals.
5	Potassium (Po)	It in nature occurs only in ionic salts.

Since Sulfur is the abundant element, it can be chosen as the hexavalent element which can be doped with Silicon to form N-Type Material of the photo diode.

15. Conclusion

In this paper, logic is derived to get the correct doping materials for the p-type and n-type silicon materials. If the doping element is bivalent, two extra protons will remain after sharing its two electrons with the four tetravalent element Silicon atoms. This can be used as p-type material. If the doping element is hexavalent, two extra electrons will remain after sharing its six electrons with the four tetravalent element Silicon atoms. This can be used as n-type material.

It is concluded that p-type and n-type material are to be made from Silicon, bivalent and hexavalent elements by doping. These materials can be diffused to form the photo diode. So, it is proposed that Silicon has to be doped with bivalent element like Calcium to form the p-type material and to form the N-type material Silicon has to be doped with hexavalent element like Sulfur.

Calcium is a reactive pale yellow metal which has two valence electrons. It can be used as a doping element to form the p-type material. It has atomic number 20.It has a symbol of Ca.

Sulfur is a non-metal which has six valence electrons. It can be used as a doping element to form the n-type material. It has atomic number 16.It has a symbol of S. It is a bright yellow crystalline solid reacts with all elements except nitrogen and the noble gases. It occurs naturally as an element.

Thus the efficiency of the photo diode can be increased by increasing the number of free electron-hole pairs.

References

1. Phillip P. Jenkins, et al, "*High-Band Gap Solar Cells for Underwater Photovoltaic App*lications", IEEE Journal of Photovoltaics Vol. 4(1), 202-207(2014).
2. H, Melchior, W.T.Lynch, "*Signal and Noise Response of High Speed -- Germanium Avalanche Photodiodes*", IEEE Transactions on Electron Devices, Vol. Ed-13, No. 12, 829-838(December 1966).
3. Daniel L. Meier, Jeong-Mo Hwang, And Robert B. Campbell, "*The Effect of Doping Density and Injection Level on Minority -Carrier Lifetime as Applied to Bifacial Dendritic Web Silicon Solar Cells*", IEEE Transactions On Electron Devices, Vol. Ed-35, No. I, 70-79(January 1988).
4. Jinendra K. Ranka, Alexander L. Gaeta, Andrius Baltuska, Maxim S. Pshenichnikov, and Douwe A. Wiersma ,"*Autocorrelation measurement of 6-fs pulses based on the two-photon-induced photocurrent in a GaAsP photodiode*", Optics Letters,Vol.22,Issue.17,pp.1344-1346(1997).
5. Edward F. Zalewski and C. Richard Duda, "*Silicon photodiode* device with 100% external quantum efficiency", Applied optics,Vol. 22, Issue 18, pp. 2867-2873 (1983).
6. R. Lecomte ; J. Cadorette ; S. Rodrigue ; D. Lapointe ; D. Rouleau ; M. Bentourkia ; R. Yao ; P. Msaki, "*Initial results from the Sherbrooke avalanche photodiode positron tomograph*", IEEE Transactions on Nuclear Science,Volume: 43, Issue: 3, Jun 1996.
7. PLucimara S. Roman, Mats R. Andersson,Teketel Yohannes, Olle Inganás, "*Photodiode performance and nanostructure of polythiophene/C60 blends*", 1997,Wiley Online Library.
8. J.C. Campbell,A.G. Dentai,W.S. Holden,B.L. Kasper,"*High-performance avalanche photodiode with separate absorption 'grading' and multiplication regions*", Electronics Letters, Volume, 29 September 1983, p. 818 – 82.
9. H. Ito ; T. Furuta ; S. Kodama ; T. Ishibashi, "*InP/InGaAs uni-travelling-carrier photodiode with 310 GHz bandwidth*", Electronics Letters, Volume: 36, Issue: 21, 12 Oct 2000.
10. G.Bondarenko,P.Buzhan,B.Dolgoshein,V.Golovin,E.Guschin,I.lyina,V.Kaplina,K.arakash,R.Klanner,V.Pokachalova,E.Popova,K.Smirnova,"*Limited Geiger-mode microcell silicon photodiode: new results", Nuclear Instruments and Methods* in Physics Research,Volume 442, Issues 1–3, 11 March 2000, Pages 187-192.
11. Christopher T. DeRose, Douglas C. Trotter, William A. Zortman, Andrew L. Starbuck, Moz Fisher, Michael R. Watts, and Paul S. Davids, "*Ultra compact 45 GHz CMOS compatible Germanium waveguide photodiode with low dark current*", Optics Express Vol. 19, Issue 25, pp. 24897-24904 (2011).
12. O. Yadid-Pecht, R. Ginosar , Y. Shacham-Diamand, "*A random access photodiode array for intelligent image capture*", IEEE Transactions on Electron Devices, Volume: 38, Issue: 8, Aug 1991.