The development and application of silicon Neutron Transmutation Doping (NTD) technology in China

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Abstract: The research and development history of silicon Neutron Transmutation Doping (NTD) technology and its applications at home and abroad are introduced in this paper. The advantages of NTD, compared with conventional technology of doping, are narrated. The principle of NTD as well as the implementation of the main procedures related to Si NTD is explained. The market demand tendency is prospected, and the advanced measures on NTD quality control are described.

Key words: monocrystal silicon; Neutron Transmutation Doing (NTD); uniformity; doping accuracy; application; design

1 Introduction

Monocrystal silicon is widely used in semiconductor device production. As the polycrystalline used to produce monocrystal silicon has a high resistivity (> 2 000 Ω · cm), it does not meet the requirements of different levels of resistivity. In order to obtain silicon with the required resistivity (120 ~ 30 Ω · cm), a certain amount of phosphorus as donor element must be doped in a controlled manner. Prior to NTD technique, incorporation of phosphorus is achieved by the means of conventional gas diffusion.

The NTD principle is brought forward by K. lark-Horovitz in the early 1950s. In 1960s, Tano-nbaum, C. N. Klahr and others had done some silicon doping process verification experiments and device experiments in the laboratory. However, due to the irradiation damage mechanism was not clear as well as the actual demand for high-power devices was not very urgent , people did not connect the new NTD technology with the production of silicon thyristor at that time.

In 1970s, with the development of high-voltage large-power direct current transmission of electricity, the high voltage, large-power thyristor was needed urgently. Influenced by uneven thermal field, segregation, evaporation and contamination of impurities, etc, the conventional float-zoned silicon has the defects of doping inaccuracy, uneven distribution of radial and axial resistivity . Moreover, the intrinsic quality is not good, which affects the voltage-tolerance characteristics of the device, thus it is unable to meet the high power requirements. All of that largely drives NTD technology developing and maturing.

The conventional doping method has to introduce the impurities from outside of silicon crystal, but NTD method does not have this disadvantage. Compared with conventional silicon doping method, NTD has some obvious advantages such as narrow resistivity tolerances, uniform radial and axial resistivity, no micro-zone structure, good mechanical strength, etc.

The performance comparisons between NTD silicon and Conventional Doping Silicon (CDS) are shown in Fig. 1 and Table 1.

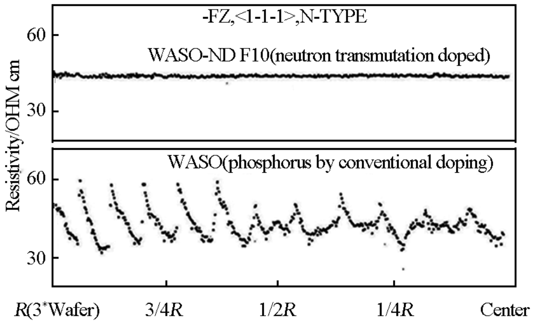

Fig. 1 Comparison of the spreading resistance profiles between conventionally doped FZ and NTD FZ

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Table 1 The performance comparisons between NTD and CDS

Item	Performance	NTD	CDS
1	Resistance tolerance (< 100 Ω· cm)	± 10 %	± 25 %
2	Center-$R/2$	5 %	25 %
3	Center-edge	5 %	18 %
4	Spreading resistivity (peak/valley) (typical)	7 % ~ 10 %	30 % ~ 50 %
5	Minority-carrier lifetime (minimum/typical)	100/500	200/6500

2 The principle of NTD

Silicon NTD is based on the following nuclear reaction:

$$^{30}\mathrm{Si}(n,\gamma)^{31}\mathrm{Si} \rightarrow {}^{31}\mathrm{P} + \beta \qquad (1)$$

In natural, there are three kinds of stable silicon isotopes, which are uniformly distributed in the silicon material. Moreover, they almost are transparent to the neutrons, i. e., their macro cross sections are very small. So if a uniform neutron irradiation field is provided, the phosphorus impurities produced in silicon will be very uniform The more accurate the neutron fluence is controlled, the higher accuracy of the target resistivity can be achieved. The concentration of ^{31}P doped in the process of NTD can be calculated by the following equation:

$$^{31}N = {}^{30}N\sigma_r\phi \qquad (2)$$

In the equation, ^{31}N is the concentration of doped ^{31}P, atoms/ cm^3, ^{30}N is the atomic density of isotope ^{30}Si, atoms/ cm^3, σ_r is neutron capture cross-section, barn, ϕ is the neutron fluence, n/ cm^2.

The relation between resistivity and the impurity concentration in monocrystal silicon is listed as following:

$$\rho = \frac{1}{N_D \cdot \mu_e \cdot e} \qquad (3)$$

In the equation, N_D is the concentration of doped ^{31}P, atoms/ cm^3, μ_e is migration rate of doped ^{31}P, cm^2/ V· s, e is the electron charge quantity, C.

Based on the above equations and parameters, the relationships among neutron irradiation fluence ϕ, the target resistivity ρ_t and the original (pre-doping) resistivity can be determined as following.

$\phi = 1/K(1/\rho_t - 1/\rho_0)$ for original n-type silicon

$\phi = 1/K(1/\rho_t + 3/\rho_0)$ for original p-type silicon

In the equation, K is doping coefficient, and it is about 3.91×10^{20} according to theoretical arithmetic. However, the suitable K to each reactor is obtained statistically through irradiated silicon samples. It can be seen from the above equations that the neutron irradiation fluence is determined as long as the target resistivity ρ_t and the original resistivity ρ_0 are determined.

It is known that neutron fluence is the product of neutron flux and irradiation time. So there are two methods can be adopted to control the irradiation fluence, one is to control the irradiation time which can be calculated while the neutron flux has been already measured. The other is to take the advantage of Self Power Neutron Detector (SPND) so as to control the irradiation fluence directly.

3 Domestic current status and the applications of silicon NTD

3.1 Domestic current status

The development of NTD silicon in China started in 1979. At that time, Doctor Dai Chuanzeng, a famous physicist and an academician of Chinese Academy of Sciences (CAS), organized and developed successfully the NTD silicon technology in China Institute of Atomic Energy (CIAE). This technology was used in small scale commercial production in 1980. The commercial irradiation of NTD silicon is developed continuously in several reactors, such as SPR and HWRR in CIAE, SRR in Tsinghua University, SPRR-300 in China Academy of Engineering Physics (CAEP), and HFETR and MJTR of Nuclear Power Institute of China (NPIC). After a long research period, technology of NTD silicon in China has approached or reached the international level, related information of NTD silicon on research reactor in China is listed in Table 2.

Table 2 Information of NTD silicon in research reactor of China

Reactor	Owner	Type	Power /MW	$\Phi_{th,max}$ in tubes /(10^{13} cm^{-2}s^{-1})	Max diameter of Si ingots /inch	Annual output /t	Status
HWRR	CIAE	Pressure pipe	10	3.0	4	30	
HFTR	NPIC	Pressure pipe	125	5.0	5	10	OPER
SPR	CIAE	Pool	3.5	2.0	4	5	OPER
MJTR	NPIC	Pool	5.0	0.8	5	20	OPER
SRR	TSINGHUA	Pool	1.0	0.6	4	1	SHUT
SPRR-300	CAEP	Pool	3	0.86	3	2	SHUT
CARR	CIAE	Pool tank	60	8	5	35 (estimate)	Critical in 2009

3.2 Applications

Based on the production methods, there are two kinds of Monocrystal Silicon, Czochralski Si (Cz-Si) and float-zoned Si(FZ-Si), The latter is more suitable for NTD technology.

Because of it's high purity and more perfect lattice structure, FZ-Si is used as main material of high-power equipment and detector. It is traditionally used for the production of electric and electronic devices such as SCR, GTR, GTO, MOSFET, IGBT and PIC. In recent years, FZ-Si has been used to produce high efficiency solar battery (photoelectric transformation efficiency up to 20 %), and the ratio of performance-to-price of such battery is better than that of Cz-Si solar battery, which extends the market of FZ-Si. In addition, new markets are formed step by step, such as radio-frequency molectron, microwave monolithic integrated circuit, photoelectric detector, etc.

The application field of FZ-Si devices are green illuminating facilities (power saving lamps and electronic ballasts), the high frequency speed regulations of electric drive equipments (engines, military vehicles and marines), solidification of high-power oscillating tube of high or middle frequency furnace, driving engine speed regulations in large-scale industry blower, large distance extra high voltage AC&DC power transmission and transformation in power plant, high-tech field on defense, infrared optical devices, motor electron fields and high efficiency solar batteries, etc

According to the statistics, the world market scale of FZ-Si is about 1 000 t, almost 10 % of the whole monocrystal silicon market, while its annual increment speed is 15 % ~20 %. The domestic market demand of FZ-Si is 50 t, annual production capacity is around 40 t, and annual increment speed 25 %.

4 Processing technology of silicon NTD

The technology of NTD silicon has been maturely applied to commercial production. Although small difference in specific operational methods is there from reactor to reactor, the basic processing of NTD Si production is almost the same, including calculation and scheduling, target preparation, pre-irradiation transportation and storage, irradiation, cooling, cleaning, annealing, electric parameter measurement.

1) Calculation and scheduling. The needed neutron fluence of each silicon ingot is calculated according to the original resistivity and the target resistivity. The axial neutron flux in reactor irradiation hole is of cosine distribution, to improve the axial doping homogeneity and to utilize the irradiation space adequately, one ingot is installed above the flux vertex and another is below the vertex. The two ingots are transposed mutually or reversed severally at half irradiation time; of course, the precondition is that the doping neutron flounce of two targets is consistent or similar. So, the irradiation scheme is settled

2) Target preparation. The ingots are loaded into irradiation vessel according to the irradiation scheme. In order to reduce the radioactive contamination to the ingot surface during irradiation, the silicon ingots should be cleaned and enwrapped with aluminum foil and then marked.

3) Pre-irradiation transportation and storage. Before the startup of reactor or at a proper time, ingots are transported to a place where is convenient for handling remotely. In this way, the continuous work of doping irradiation is ensured and the exposure to radiation of personnel is reduced.

4) Irradiation. According to the irradiation scheme, the ingots are put into the reactor tubes for irradiation in turns by remote control, at the same time, the irradiation monitoring (time or count) is started, the ingots are took out from the irradiation tube when reaching the predetermined value. For the situation of two targets irradiated in the same tube simultaneously it needs to transpose mutually or reverse severally at half irradiation time. Recording of irradiation states is necessary for subsequent analysis.

5) Cooling. The radioactivity of ingots which are just out of the reactor is strong. It needs to store in cooling location to decay for three to five days.

6) Cleaning. After cooling aluminum foil should be peeled and dealt as radwaste, the irradiation vessel is used repeatedly. the radioactivity decontamination cleaning and radioactivity detection are needed. Because the NTD silicon is basic materials of semiconductor industry and it will be processed and circulated in market as nonradioactive materials, so this working procedure is very important.

7) Annealing. Severe crystal defect will induced during irradiation, and the crystalline and semiconductor characteristics are bankrupt. It's needed for special heat treatment to renew the crystal lattice. After many years' research and test, The annealing technology has been maturely applied to NTD silicon production.

8) Electricity parameter measurement. Minority-carrier lifetime and resistivity are two important electricity parameters necessary to examine. It can be shown that crystal defect has been removed by annealing if minority-carrier lifetime is larger than a certain value, otherwise, annealing needs to be done again. NDT silicon is used to be a basic material producing

semiconductor device, so its resistivity is a very important electricity parameter. in addition, the doping accuracy can be increased efficiently by means of comparing the measured resistivity with the target resistivity and succedent neutron flux correcting, monitoring device calibration, etc..

5 Technical design and control

5.1 Irradiation requirements

NTD silicon is irradiated in reactor, in order to meet the operational and safe requirements of the reactor, some analysis related to reactor should be done before the silicon ingots are put in reactor tubes. Generally, two aspects should be considered.

1) In order to get good quality of resistivity uniformity and doping accuracy, the neutron flux distribution in ingots should be considered. In addition, the reactor needs not to be shutdown while the ingots are put into or take out from the irradiation tube, so the analyses of impact on reactor safety should be conducted, e. g. the reactivity influence on reactor operation should be deliberated.

2) During the NTD silicon irradiation, nuclear heat will be produced due to the reactions between silicon and neutron or photon. So the cooling of the ingots should be analyzed to ensure that the temperature of ingots is acceptable for the silicon quality and the reactor safety.

5.2 Irradiation control

The resistivity uniformity control is very important. Usually, the radial uniformity is ensured by rotating the silicon ingots and the axial uniformity is ensured by upside-down or position-exchange at the half time of irradiation(Fig. 2).

The other importance is the doping accuracy control. The early control method is to determine the irradiation time based on the neutron flux which is measured previously, but this method is not good because of the neutron flux fluctuation during reactor operation. Current method is to install self powered neutron detectors (SPND) to monitor the neutron fluence, obviously, this real-time control method is better.

6 Technique development tendency

The important development tendency of monocrystal silicon is to produce larger diameter (wafer), which is not only the requirements of semiconductor development but also optimal approach of increasing production efficiency and integrated management for manufacturing of semiconductor and semiconductor material. How to adapt with the development tendency of producing larger diameter monocrystal silicon and guarantee the NTD production capacity and quality is a new task for the further R&D on NTD technique and relevant equipments.

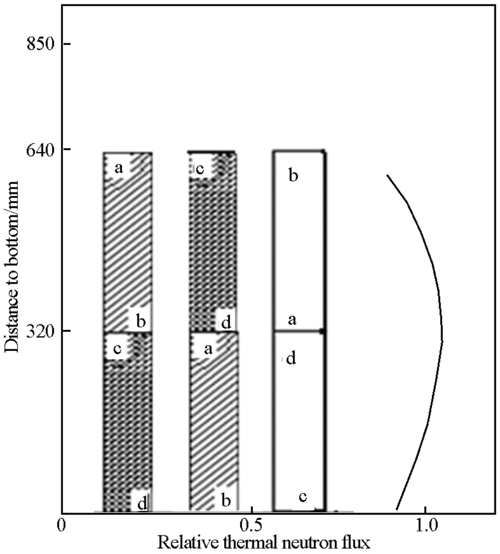

Fig. 2 Position-exchange and upside-down sketch map

The advantage of NTD silicon is its good behavior in resistivity uniformity and accuracy. In the other hand, the control of uniformity and accuracy becomes more difficult for larger dimension silicon ingots. To keep the competitiveness of NTD silicon depends on if this difficult can be adequately overcome.

The axial non-uniformity can easily be reduced less than 5 % by reversing the silicon ingots. for the radial uniformity, the only way that can be adopted now is rotating the ingots, and the radial non-uniformity will be larger along with diameter of Si ingots increasing, for example, the radial non-uniformity can be controlled within 5 % for 6 inch silicon ingots, but it will more than 10 % for 12 inch ingots. Using horizontal rather than vertical irradiation tubes maybe one of the feasible ways to deal with 12 inch silicon ingots.

For axial uniformity control, the ideal way is flatting the axial neutron flux distribution by neutron screen which is a combination of various materials with different thickness(Fig. 3). This method is especially effective for high neutron flux research reactor; it can save the manual work and reduce the human error so as to improve the irradiation efficiency.

It should be mentioned that during the reactor operation the control rods position are regulated to meet the fuel burn-up, and the neutron flux distribution is changed correspondingly. To accurately control the uniformity of NTD silicon, the neutron screen should be moved according to the position of the control rods.

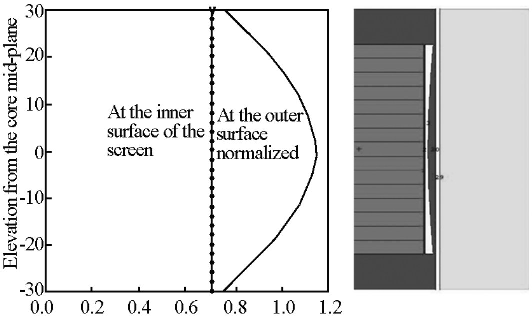

Fig. 3 Thermal neutron flux and new fashioned Si irradiation container

7 Introduction of silicon NTD facility

In order to provide a clear image about NTD technology, Silicon NTD facility developed in China Advanced Research Reactor (CARR) is introduced as an example.

CARR owned by China Institute of Atomic Energy (CIAE) is an inverse neutron trap tank-in-pool type reactor, cooled by light water and moderated by heavy water. The rated nuclear power of CARR is 60 MW. it will be critical at the end of 2009. Fig. 4 is the sketch of Si NTD system in CARR.

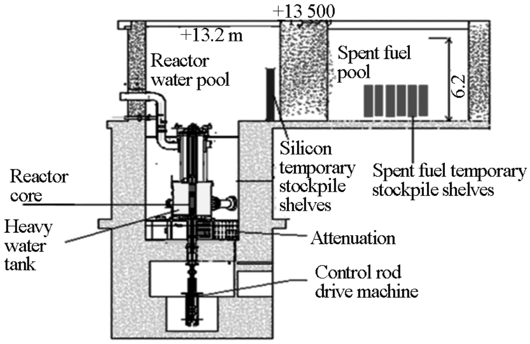

Fig. 4 Sketch of NTD system in CARR

There are 4 channels used to irradiate 3, 4 and 5 inches Si ingots and a hot neutron source channel which can be utilized to irradiate 6 and 8 inches. The 4 NTD silicon irradiation channels are placed in heavy tank where the neutron flux is about 9×10^{13} n/ cm^2 · s. The configuration of these channels is shown in Fig. 5.

The main hardware facilities are illustrated as follows.

1) Handle crane

It is used mainly for loading and unloading of fuel assembly, it can be used for transportation of silicon ingots also (Fig. 6).

2) Rotation equipment

It is used for rotating the irradiation channel, and it is driven by hydraulic power (Fig. 7).

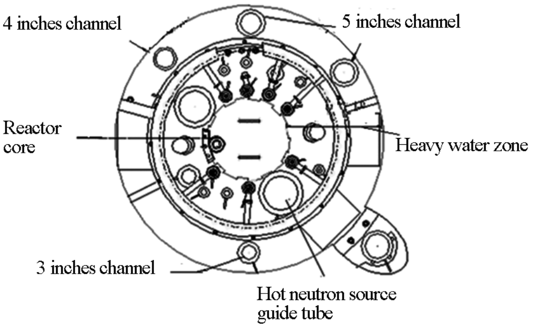

Fig. 5 Sketch map of Si irradiation tube

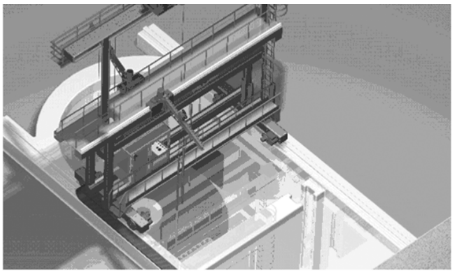

Fig. 6 Handle crane

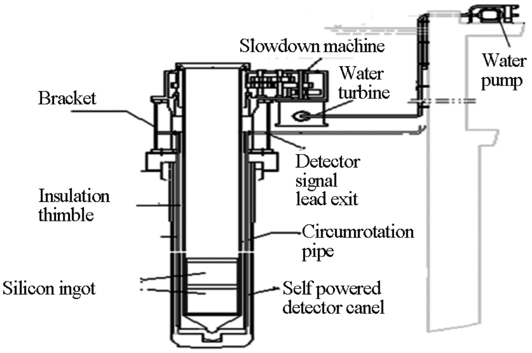

Fig. 7 Circumrotation equipment for Si irradiation

3) Storage shelf

It is located in the reactor pool and used for temporary storage of Si ingots before or after irradiation (Fig. 8).

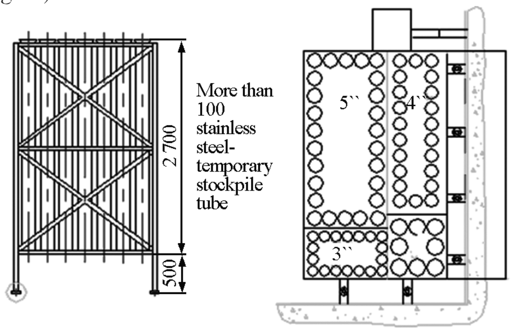

Fig. 8 Si temporary storage shelf

4) SPNDs

Every irradiation channel is equipped with a SPND to monitor neutron fluence.

5) Monitoring computer and under water monitor, etc.

CARR is expected to irradiate 30 t Si ingots per year. The radial and axial heterogeneity should be controlled below 5 %, and the detail value will be obtained in reactor operating practice.

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6 Discussion

From the first RR constructed in China, other several nuclear facilities had been constructed in short term. The tremendous achievements in nuclear field had been made and large number of nuclear specialists trained. RRs of China had made the great contributions to the starting and safe operation of China NPPs. The utilizations of RRs had made gigantic effect on many S&T fields. Generally, the RRs in China have made great contributions to many fields, such as society, economy, defense, agriculture, industrial, etc.

Looking back to the last several decades, the rapid development of RRs and their utilizations is benefited from the emphasis by the nuclear industrial field and from the national developments.

Along with China's rapid development in many fields and the requirement of creative S&T, the bright future of RRs and their utilizations could be anticipated.

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