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A Review of Research on the Conductivity Mechanism and Performance Effects of N-type and P-type Doping in Silicon Materials

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Abstract

Due to the extremely limited number of electrons that cross its band gap at room temperature, it is unsuitable for direct application in semiconductors and other electronic devices. However, its conductivity can be altered through effective doping. This paper analyzes the impact of n-type and p-type doping on the conductivity of pure silicon. In n-type doping, the majority carriers are free electrons, while in p-type doping, they are holes. The former increases conductivity by adding free electrons, while the latter increases the hole concentration. Although the principles differ, the effects are similar; both hybridization methods can increase carrier concentration by several orders of magnitude. To further improve conductivity, heavy doping can be achieved by scientifically increasing carrier concentration. Conversely, deep-level impurities can have a compensating effect, reducing conductivity. The limitations of this paper are: the cited literature primarily focuses on bulk silicon and nanowires/nanotubes, with insufficient discussion of doping behavior at the nanoscale; and most experimental studies lack direct, systematic comparisons of n-type and p-type doping under identical conditions. Future research could delve deeper into areas such as systematic comparisons of carrier mobilities, synergistic effects of co-doping, and the application of novel doping techniques, such as self-assembled monolayers, in ultra-shallow junctions.

Keywords

doping, n-type silicon, p-type silicon, electrical conductivity, carrier concentration

1. Introduction

Silicon is now widely used in semiconductors, chips, solar cells, and other fields and is an important part of the manufacturing industry. PN junctions, MOSFETs, solar cells, and power devices all rely on precise doping to control the type and concentration of charge carriers. However, the charge-carrier concentration in pure silicon at room temperature is only 1.5×10^{10} cm^{-3}, which is far from meeting the requirements of hardware applications [1]. Therefore, it is necessary to control the doping to change the conductivity of silicon. Doping can be divided into two categories: n-type semiconductors are obtained by doping with pentavalent elements such as phosphorus, and p-type semiconductors are obtained by doping with trivalent elements such as boron [1]. The main objective of this paper is to analyze the mechanism of influence of n-type and p-type doping on

the conductivity of silicon materials. n-type doping uses electrons as the majority carriers and conducts current through the electron conduction mechanism; p-type doping uses holes as the majority carriers and conducts current through the hole conduction mechanism. n-type doping (of Group V elements) introduces donor levels near the bottom of the conduction band in silicon's bandgap, providing free electrons to the conduction band and increasing the electron concentration from the intrinsic value of 10^{10} cm^{-3} to 10^{15}-10^{20} cm^{-3}. p-type doping (of Group III elements) introduces acceptor levels near the top of the valence band, generating holes in the valence band and increasing the hole concentration by the same order of magnitude. Both types of doping shift the Fermi level to the conduction or valence band, thereby determining the material's type of conductivity.

2. Theoretical Background

2.1 Band Theory

In band theory, the bands of silicon consist of a valence band, a conduction band, and a band gap. The band gap is about 1.12 eV. At room temperature, it is difficult for electrons to obtain enough energy to transition from the valence band to the conduction band. Therefore, for intrinsic silicon, the carrier density is very low, and the conductivity is also very low.[1]

Impurity energy levels are divided into two categories: donor and acceptor levels. Donor energy levels can be doped with pentavalent elements such as phosphorus, located at the bottom of the conduction band, forming n-type conductivity. Acceptor energy levels can be doped with trivalent elements such as boron, located at the top of the valence band, forming p-type conductivity. Impurity energy levels can reduce the energy of electron transitions, thereby making non-conductive silicon conductive [1]. In the study by Zhang Jiahong et al., density functional theory was used to show that vacancy doping and element doping both introduced impurity energy levels into the band gap of silicon nanowires and formed N-type and P-type semiconductors, respectively. Both types of doping improved the conductivity of silicon nanowires. The research results confirmed the influence of impurity energy levels on the conductivity of silicon materials [2].

2.2 Compensation Effect

In semiconductor doping engineering, the final conductivity type and effective carrier concentration of a material are determined by the compensation effect of donors and acceptors. When donor and acceptor impurities coexist in silicon, the electrons and holes they provide cancel each other out [3]. The charge neutrality condition determines the effective carrier concentration: when the donor concentration ND is greater than the acceptor concentration NA, the material is n-type and the effective electron concentration $n0 \approx ND-NA$; when the acceptor concentration NA is greater than the donor concentration ND, the material is p-type and the effective hole concentration $p0 \approx NA-ND$. The compensation effect is a double-edged sword in device engineering [3]. On the one hand, a high degree of compensation will seriously reduce the carrier mobility and effective carrier concentration, damaging device performance; on the other hand, precise compensation control can be used to manufacture high-resistance regions or achieve special doping distributions, such as forming a withstand voltage layer in power devices or a minority carrier lifetime control region required for high-speed switching.

If impurities (such as Au and Ni) are doped simultaneously in the same piece of silicon, a deep energy level will be formed in the center of the band gap. The deep energy level will adsorb electrons and holes, resulting in a decrease in the material's conductivity. This phenomenon is called the compensation effect. According to the research of Dong Maojin et al., after doping Au and Ni in n-type single crystal silicon wafers, their resistivity changed from the initial 1 Ω·cm to 64~416 Ω·cm, which shows the existence of the compensation effect [4].

3. Literature Review

3.1 Shallow-level Doping (Typical Doping)

Shallow-level doping is the primary means of improving the conductivity of silicon. The more traditional method is ion diffusion, but it can cause irreversible damage to the material. The arsenic-containing self-

assembled monolayer studied by Li Yunyao is better suited to silicon-based CMOS. The method is to graft arsenic-containing organic molecules onto the silicon surface to form a monolayer, and then anneal at high temperature to allow arsenic atoms to diffuse into the silicon substrate, thereby achieving ultra-shallow doping. This method can more effectively reduce the resistivity of silicon materials. [5]

Based on the distinct optical properties of P-type and n-type silicon, the doping type can be identified by terahertz time-domain spectroscopy. At the same resistivity, the refractive index of p-type silicon is greater than that of n-type silicon. This is because free carriers in P-type and N-type silicon respond differently to terahertz radiation, leading to systematic differences in their polarization responses to electromagnetic waves [6].

The variable temperature Hall effect can also distinguish it. The main carriers of N-type doped semiconductors are electrons, and the Hall coefficient is negative[7]. The main carriers of P-type semiconductors are holes, and the Hall effect is positive. In practical applications, p-type and n-type silicon wafers exhibit different electrical performance characteristics during the same battery preparation process, so the choice of doping type will also directly affect performance [8].

3.2 Deep-level Impurities and Compensation Effects

The addition of deep-level impurities will cause the material's resistivity to soar. As shown in the study by Dong Maojin et al. on the effect of Au and Ni doping on the conductivity of n-type silicon, Au and Ni, as deep-level impurities, can adsorb electrons and holes, thereby producing a compensation effect. The study also shows that under such conditions, the material can still maintain n-type conductivity and exhibit typical negative-temperature-coefficient thermistor characteristics, suitable for thermistor devices. [4] Therefore, doping should not be limited to improving conductivity; it should involve adding different impurities to obtain silicon materials with distinct effects.

In addition to being used in thermistor devices, EMM Maanzo et al. found that when Gd is doped into silicon diodes, it exhibits a consistent generation-recombination (gr) process across the entire voltage range, indicating nearly consistent performance. Because of its relative stability, the durability of this device under radiation conditions can be investigated. [9]

3.3 The Effect of Heavy Doping on Defects

Under heavy doping, oxygen precipitation in silicon depends on whether the silicon is n-type or p-type. Dr. Gao Chao studied the effects of heavy doping on oxygen diffusion and precipitation in Czochralski silicon single crystals. The results showed that boron atoms and oxygen atoms in p-type heavy-doped boron combine to form BO pairs, which promote oxygen precipitation and lead to abnormal oxygen diffusion. In contrast, phosphorus atoms in n-type heavy doping will form PO pairs, thereby inhibiting oxygen diffusion, indicating that different doping levels have distinct effects on defects [10]. Heavy doping has a dual effect on the conductivity of silicon: Positive effect: The doping concentration directly determines the carrier concentration. Under heavy doping conditions, the carrier concentration can reach the order of 10^{19}-10^{20} cm^{-3}, which is 9-10 orders of magnitude higher than that of intrinsic silicon (about 10^{10} cm^{-3}). Negative effect: The increase in carrier concentration is accompanied by a significant degradation in mobility. The large number of ionized impurities introduced by heavy doping enhances Coulomb scattering of carriers, causing mobility to decrease with increasing doping concentration. As the doping concentration increases from 10^{15} cm^{-3} to 10^{20} cm^{-3}, the electron mobility in silicon decreases from approximately 1350 $cm^2/(V\cdot s)$ to the order of approximately 100 $cm^2/(V\cdot s)$, with a more significant degradation in hole mobility. This decrease in mobility partially offsets the increase in conductivity resulting from the increased carrier concentration; therefore, conductivity does not increase linearly with doping concentration, but rather, there exists an optimal range for doping concentration.

Heavy doping introduces a large number of ionized impurities and high concentrations of charge carriers. The many-body interaction leads to an effective narrowing of the semiconductor bandgap, known as bandgap shrinkage (BGN), which is one of the key physical mechanisms by which heavy doping affects device performance. Yan systematically studied the BGN problem in heavily doped silicon and found that BGN is not negligible for doping concentrations exceeding 10^{18} cm^{-3}. In equilibrium, p_0n_0 increases, which restricts device performance. Based on extensive experimental data, updated empirical expressions for the BGN of n-type and p-type silicon were derived. The key finding is that the BGN value of p-type silicon is slightly larger

than that of n-type silicon, which is due to the difference in the contribution of many-body interaction caused by the different majority carrier types [11].

BGN increases intrinsic carrier concentration, leading to increased leakage current at high temperatures and limiting key performance indicators such as open-circuit voltage and gain. Schenk's theoretical models often underestimate the recombination current; empirical expressions based on experimental data are more practically meaningful for quantifying performance losses due to heavy doping.

4. Discussion & Synthesis

4.1 The Core Differences Between N-type and P-type

Table 1: Comparison of key parameters between n-type and p-type doped silicon

Comparison Dimensions	n-type silicon	p-type silicon
Typical doping elements	Phosphorus, arsenic, and antimony (Group V)	Boron, aluminum, gallium (Group III)
Impurity level type majority carriers	Donor level (near conduction band) electronic	Acceptor level (near the valence band) Hole
Electrical conduction mechanism	Electron conductivity	Hole conduction
Heavy doping defect behavior	Oxygen precipitation is suppressed, inducing stacking faults [12]	Oxygen precipitation is promoted, and stacking faults are absent. [12]
Optical properties	Smaller refractive index for the same resistivity	A larger refractive index at the same resistivity[6]

As can be clearly seen from Table 1, the differences between n-type and p-type doping run through multiple levels from electronic structure to macroscopic properties and fabrication technology. These differences together determine the applicability of the two doping methods in different device applications. N-type silicon is superior in most high-speed devices due to its higher electron mobility. In contrast, p-type silicon occupies an irreplaceable position in certain structures (such as the anode region of a pn junction and the base region of a BJT). Furthermore, gallium-doped p-type silicon exhibits unique advantages in resisting photo-induced degradation [8].

4.2 Application-level Doping Strategies

P-type (boron-doped) silicon wafers have long dominated crystalline silicon solar cells due to the relatively simple, low-cost boron-doping process. However, p-type silicon wafers suffer from light-induced degradation (LID) caused by boron-oxygen recombination centers. Under illumination, the BO complex formed by boron and interstitial oxygen significantly reduces the minority-carrier lifetime, thereby decreasing cell conversion efficiency.

N-type silicon wafers have a higher tolerance to metal impurities and lack BO recombination centers, thus exhibiting greater resistance to light-induced degradation. Yang Aijing et al. studied the effects of different types of silicon wafers on battery electrical performance. They found that p-type gallium-doped silicon wafers and n-type silicon wafers exhibit different electrical performance characteristics in the same battery fabrication process [8]. In recent years, the efficiency record of n-type TOPCon cells has significantly surpassed that of p-type PERC cells, making n-type TOPCon cells the mainstream development direction for high-efficiency photovoltaic devices.

It should be clarified that p-type silicon wafers have not been completely replaced. Gallium-doped p-type silicon wafers have significantly improved resistance to photo-induced degradation compared to traditional boron-doped p-type silicon wafers because they eliminate BO recombination centers [8]. Therefore, the choice of the doping element also significantly impacts device performance.

4.3 Consistency and Insufficiency

Both n-type doping and p-type doping can increase carrier concentration, thereby improving conductivity. The difference between the two lies in their different principles [1]. n-type doping brings the conduction band

bottom closer to the Fermi level, thus narrowing the band gap. p-type doping causes the impurity level to cross the Fermi level, thereby enhancing conductivity [2].

Doping can change the physical properties of silicon. Li Yunyao's research shows that ultra-shallow doping of silicon with arsenic self-assembled monolayers can enhance silicon conductivity [5]. Research by Zhang Jiahong et al. shows that elemental doping can effectively alter the dielectric constant, absorption coefficient, refractive index, and reflectivity of SiNWs [2]. According to the review by Tian Chun et al., the physical properties of silicon nanotubes are altered by doping with carbon, aluminum, carbon/germanium, boron/nitrogen, group III elements, and group V elements [13]. In addition, deep-level impurities generally have a compensating effect on the conductivity of silicon. As shown by the research of Dong Maojin et al. and EMManzo et al., whether it is transition metal elements (Au, Ni)[4] or rare earth elements (Gd)[9], they will introduce deep-level defects into the band gap, thereby capturing a large number of charge carriers and reducing the conductivity of the material. Heavy doping will affect the micro-defect behavior of silicon. Huang Xiaorong et al. comprehensively compared the effects of doping on oxygen precipitation across different dopants [12]. Dr. Gao Chao revealed the formation mechanism of PO atom pairs and their inhibitory effect on oxygen diffusion at the atomic level [10].

However, existing research also has some shortcomings. Existing experimental studies often focus on a single doping type and lack systematic comparisons across multiple doping types. Most studies focus on the electrical or defect behavior of a single dopant element at a specific concentration, rarely comparing n-type and p-type doping at the same concentration and under the same processing conditions on the same experimental platform. For key parameters such as ionization energy, impurity scattering intensity, and defect density in shallow-level doping, data for n-type and p-type doping often come from different laboratories, different sample batches, and even different measurement methods, making direct quantitative comparison difficult.

There are few studies on the compensation effect, and little research on the actual impact of multiple impurity elements on electronic devices. Most existing studies on the compensation effect focus on compensation between a single deep-level impurity and a single shallow-level dopant.

Data on carrier mobility are scattered, and no unified conclusion has been reached. Carrier mobility is a key parameter linking doping concentration and device performance, but mobility data in the existing literature come from scattered sources and are measured under varying conditions. A systematic comparison of the mobility of n-type and p-type silicon under the same doping concentration and temperature range has not yet been made.

Future research could delve deeper into areas such as comparative analysis of carrier mobility systems, synergistic effects of co-doping, and the application of novel doping techniques, such as self-assembled monolayers, in ultrashallow junctions.

5. Conclusion

This review systematically demonstrates the mechanisms by which n-type and p-type doping influence the conductivity of silicon materials. n-type doping mainly involves doping with pentavalent elements such as phosphorus, with free electrons as the majority carriers. It introduces donor levels in the band gap near the bottom of the conduction band, thereby increasing conductivity by increasing electron density [7]. p-type doping mainly involves doping with trivalent elements such as boron, with holes as the majority carriers. It introduces acceptor levels in the band gap near the top of the valence band, thereby increasing conductivity via hole conduction [1, 7].

Shallow-level doping generally increases the conductivity of materials [2, 5, 6]. However, deep-level doping can lead to a compensation effect due to deep-level impurities, thereby reducing conductivity.

Future research could focus on the synergistic effects of co-doping (where both n-type and p-type doping occur simultaneously), enabling different material properties by adjusting the n-type-to-p-type doping ratio.

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Conflicts of Interest

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