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Changing the Properties of Semiconductors by Introducing Copper Doping Into Semiconductor Materials

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Abstract
This article extensively discusses the process of introducing copper (Cu) doping into semiconductor materials and its effect on the crystal lattice, electrical conductivity, energy band structure, and carrier concentration. The position of copper atoms in the silicon or germanium lattice during the doping process, their participation as donors or acceptors, and the shift of energy levels are analyzed based on experimental and theoretical sources. The changes in the physical, electrical, and structural properties of semiconductors as a result of doping with copper are considered on the example of real practice. The article is aimed at analyzing the role of copper in semiconductor manufacturing technologies, its advantages, and properties.

Keywords: Semiconductors, copper doping, doping process, donor and acceptor levels, energy band, electrical conductivity, silicon, germanium, crystal lattice, defects, carrier particle concentration.

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Introduction. Semiconductor materials are one of the mainstays of modern electronics, microelectronics and device technology. Controlling their electrical and physical properties, especially through alloying, is important for creating high-performance semiconductor devices. The introduction of various metal and non-metal atoms into semiconductors significantly changes the energy band gap, electrical conductivity, lattice structure and carrier density of the material. From this point of view, the introduction of copper (Cu) dopants into semiconductor materials is of particular scientific interest. Copper atoms are characterized by the ability to form deep levels in basic semiconductors such as silicon (Si) and germanium (Ge), the formation of acceptor centers, and a high diffusion rate in the lattice. This creates broad opportunities for controlling the electro-physical properties of the material, but at the same time some technological limitations arise.

Dopants are foreign atoms that are added to the crystal lattice of the main semiconductor material in a certain amount, which radically changes its electrical properties. For example, pure silicon (Si) does not have a large number of free electrons or holes and behaves almost like an insulator. However, when we "pollute" it with certain atoms (for example, phosphorus P or boron B), it becomes a conductor. The main function of dopants is to increase the number of charge carriers

(electrons or holes) in the semiconductor and control their mobility. This process is the basis of electronics, and the operation of transistors, diodes, and microchips depends on it [1].

Methods. Dopants are divided into two main types: donor (n-type) and acceptor (p-type). Donor dopants are atoms that have an additional valence electron compared to the main semiconductor atoms. For example, a silicon atom has 4 valence electrons, while a phosphorus atom has 5 valence electrons. When phosphorus is introduced into a silicon crystal, 4 of its electrons are covalently bonded to neighboring silicon atoms, while the remaining 1 electron is free, helping to carry current. This increases the number of negatively charged electrons in the crystal, making the material an n-type semiconductor. Acceptor dopants, on the other hand, are atoms with fewer valence electrons than the base material. A boron atom has 3 valence electrons. When it enters a silicon crystal, even though all 3 of its electrons are bonded to their neighbors, one spot remains "empty" - this is called a hole. The hole plays the role of a positive charge carrier. Thus, silicon with boron dopants becomes a p-type semiconductor. Donor dopants include phosphorus (P), arsenic (As), antimony (Sb); acceptor dopants include boron (B), aluminum (Al), gallium (Ga). The most common methods of doping are diffusion and ion implantation. In the diffusion method, a semiconductor sample is heated to a high temperature (800–1200°C) and dopant atoms are introduced into it. At high temperatures, the dopant atoms penetrate the crystal lattice and slowly diffuse. This method is relatively simple, inexpensive, and has been used for many years. However, its disadvantage is that the distribution of dopant atoms is difficult to precisely control, as they penetrate "deeply" depending on temperature and time. Ion implantation is a more modern and precise method. In this method, dopant atoms are ionized and "thrown" onto the surface of the semiconductor with high energy (1–200 keV). In this method, the concentration and depth of the doping can be controlled very precisely, even to the atomic level. In addition, ion implantation can be carried out at low temperatures, which prevents the formation of additional defects in the material. However, the equipment is expensive and complex. Both methods are used in modern semiconductor production, often used in a complementary manner [2].

We will study the properties of the semiconductor materials silicon and germanium by introducing copper doping. Silicon is a basic material in the electronics industry, and dopants are added to control its electrical conductivity. When copper (Cu) is added to silicon, it acts as an acceptor and forms a p-type semiconductor. Copper is added to silicon to increase the concentration of holes, control recombination processes, reduce defects in the crystal lattice, and increase the sensitivity of sensor, thermoelectric, and microchip elements.

Copper atoms are located in the silicon lattice in two ways. In the substitutional arrangement, copper atoms are located in place of silicon atoms, giving them acceptor properties, the number of valence electrons decreases, and the concentration of holes increases. In the interstitial arrangement, copper atoms enter the vacant space in the lattice, causing strong deformation and the appearance of local energy levels [3].

Germanium has a lower energy gap (Eg = 0.66 eV) than silicon, and is used as a sensitive semiconductor even at high temperatures. Copper (Cu) as an alloying element significantly changes the properties of germanium. Copper performs two functions in the germanium structure:

As an acceptor (p-type) dopant, it increases the number of holes by taking away electrons, and Ge becomes a p-type semiconductor.

As an element that forms recombination centers, it reduces the stability of electron-hole pairs and shortens the photocarrier lifetime. Therefore, Cu-doped Ge is mainly used in sensors, photodiodes, and fast electronics.

Copper atoms occupy two different positions in the germanium crystal lattice:

In the substitutional arrangement, the Cu atom takes the place of the Ge atom, which results in the formation of an acceptor level and an increase in p-type properties.

In the interstitial arrangement, the Cu atom is located in a vacant place in the lattice. As a result, energetic "trap" levels are formed, recombination is accelerated, and the stability of the conductivity may decrease. Since the Ge lattice is softer than the Si lattice, copper diffuses quickly [4].

Results and analysis. The exact position that copper occupies depends on the insertion temperature and the diffusion rate. When copper is introduced, silicon becomes a p-type semiconductor. This is because Cu^{1+} or Cu^{2+} ions create an electron deficiency in the 4-valence lattice of silicon. This increases the number of "holes" (positive charge carriers). The overall change in conductivity is given in the following table:

Cu concentration (ppm)	Conductivity (S/m)
10 ppm	2.3×10^{-3}
50 ppm	1.1×10^{-2}
100 ppm	6.4×10^{-2}
500 ppm	3.5×10^{-1}

As the copper concentration increases, the conductivity increases by 10–100 times. Due to copper ions, the electrical resistance of silicon decreases. This increases the efficiency of p-type silicon-based diodes and transistors. In the bandgap of silicon (Eg = 1.12 eV), copper forms the following levels:

- Acceptor level EA ≈ 0.15 – 0.23 eV close to the EV (valence band). Holes are easily formed here and the p-type is strengthened.
- Levels deep within the bandgap, these levels can enhance recombination, but are of great benefit for sensors and photodetectors.

The atomic radius of copper is larger than that of silicon, which leads to a lattice strain. As a result, local internal stress appears. Dislocation points increase, diffusion becomes easier. Copper diffuses very quickly in silicon. At a temperature of 700–900°C, it penetrates to a depth of one hundred nanometers in 1–2 minutes. This property makes copper a dominant alloying element [5].

The introduction of copper also affects the optical properties of silicon. The following changes occur: the absorption coefficient increases, photorecombination processes increase, and sensitivity to infrared rays increases. Therefore, Cu–Si compounds, i.e., photodiodes, thermosensors, and solar cell sensors, are widely used. As a result of copper and silicon compounds, the p-n transition in diodes increases, the reverse current decreases, and sensitivity increases. In transistors, the efficiency of p-type emitters increases. In photosensors, the quantum efficiency increases by 20–30%. In thermoelectric devices, the introduction of copper increases the ZT coefficient, and the efficiency of thermocouples improves.

As a result of the introduction of copper into silicon, the following changes occur in its electrical properties: conductivity increases, resistance decreases, and a p-type semiconductor is formed. In its structural properties, the crystal lattice is deformed, and defects and dislocations increase. The energetic properties exhibit the following changes: acceptor levels appear, and additional levels are formed within the forbidden band.

Its optical properties increase infrared sensitivity and increase absorption. As a result, Copper (Cu) is an effective alloying agent that significantly changes the electrical, optical, and structural properties of silicon, and is widely used in modern electronics and sensor devices [6].

After the introduction of copper, some changes are observed in germanium. Due to the acceptor properties of copper, the number of p-type carriers (holes) increases. The following is a change in conductivity depending on the copper concentration:

Cu concentration (ppm)	Conductivity (S/m)
5	1.7×10^{-3}
20	8.6×10^{-3}
50	2.4×10^{-2}
100	3.9×10^{-2}
300	1.2×10^{-1}

Therefore, the conductivity increases rapidly with increasing copper concentration.

When copper is added, the electrical resistivity of germanium decreases by a factor of 5–20. This increases the efficiency of p-type Ge diodes and transistors. Since the band gap of germanium is small (0.66 eV), the levels formed by copper have a strong effect. Cu forms an acceptor level 0.11–0.18 eV deep in the substitutional position. Cu forms trap states in the interstitial state. These levels enhance recombination and control the sensitivity of photoresistors and infrared sensors.

The atomic radius of copper is larger than that of germanium, which creates strain in the crystal lattice. As a result, the number of dislocations increases, local deformation of the crystal occurs, the diffusion rate increases, and the lattice periodic parameters change slightly. These changes also affect the thermal stability of the substance.

When copper is added, the optical properties of germanium change significantly: absorption in infrared rays increases, the photoabsorption spectrum broadens, the photorecombination process accelerates, and the sensitivity for IR sensors increases. Therefore, Cu–Ge compounds are very suitable for IR photodiodes, thermal sensors, and radiation sensors [7].

In diodes and transistors, p-type germanium is stronger and the reverse current is reduced, and the "switching speed" is increased. In photodiodes, the IR sensitivity increases by 20–40%. In thermoelectric devices, the thermoelectric power coefficient ZT increases. In sensors, temperature sensitivity increases, and they can operate at low voltage.

The introduction of copper changes the electrical properties of germanium, creating p-type conductivity, increasing conductivity, reducing resistance, creating acceptor levels, and creating deep energy traps. Structurally, lattice deformation and an increase in dislocations are observed.

The optical properties also change, i.e., infrared sensitivity increases and the absorption spectrum broadens. As a result, copper-doped germanium is a highly sensitive p-type semiconductor, which is a very convenient material for sensors, detectors, and fast electronics [8].

Conclusion. There are a number of methods for studying the properties of a material with doped elements. Among electrical measurements, the Hall effect measurement is the most important. The Hall effect is the phenomenon of the appearance of a voltage in a magnetic field in a sample with a current flowing through it, in a direction perpendicular to the current and the magnetic field. By measuring this voltage, the concentration of charge carriers, their type (electrons or holes), and their mobility (mobility) are determined. Mobility is a quantity that shows how easily electrons or holes move. Photoluminescence (light emission) spectroscopy is used among optical methods. When light of a certain wavelength is incident on a material, it emits light itself. The energy levels of the doped atoms, their concentration, and their position in the crystal are studied through the spectrum of this emitted light. Raman spectroscopy, on the other hand, allows us to determine the changes that occur in the lattice under the influence of doped atoms by studying the vibrational states of the crystal lattice.

The amount (concentration) of dopants has a dramatic effect on the properties of a material. In low-doped materials (10^{14}–10^{16} atoms/cm³), the number of free charge carriers is small, so the resistance is high. Such materials are used for high-voltage devices, large-area transistors or photodetectors. Materials with moderate dopants (10^{16}–10^{18} atoms/cm³) are optimal for many everyday electronic devices - microprocessors, memory chips. They have a good balance of speed and power consumption. In highly doped materials (above 10^{18} atoms/cm³), the number of free charge carriers is very large, and the resistance is very low. Such materials are usually used as contact layers, transition layers or low-resistance tracks. However, when too many dopants are introduced, the material "metallizes" - its properties become closer to those of a metal and its advantages as a semiconductor may be lost. Therefore, the input concentration for each device is carefully selected.

A number of problems can arise during the doping process. In the diffusion method, dopant atoms can be unevenly distributed, penetrate too deeply, or accumulate on the surface. In addition, at high temperatures, other undesirable atoms can also penetrate the material. In ion implantation, high-energy ions can damage the crystal lattice, that is, displace atoms and create defects. These defects can reduce the conductivity of the material. Various methods are used to eliminate these problems. After ion implantation, the material is processed (annealed) - heated to a certain temperature to restore the crystal lattice and reduce defects. In the RTA (rapid thermal processing) method, the material is heated to a high temperature for a very short time (seconds), which eliminates defects and prevents excessive diffusion of dopant atoms. In addition, strict control and monitoring systems are established during the production process.

With the development of nanoelectronics, doping technologies are also reaching a new level. Doping in nanomaterials such as quantum dots, carbon nanotubes, and graphene is much more difficult because their size is very small (a few nanometers). In such materials, each individual doping atom is important. Therefore, atomic-level manipulation methods are being developed, such as placing each atom in a specific location using a scanning tunneling microscope (STM). New materials, such as wide-bandgap semiconductors such as silicon carbide (SiC) or gallium nitride (GaN), are being used for high-power and high-temperature devices. Doping in them is also more difficult than in traditional silicon, because their crystal lattice is different and more rigid. Also, doping in organic semiconductors (such as polymers) is a new area that opens up the possibility of flexible and inexpensive electronics. In the future, doping methods will become more precise, efficient, and stable, which will allow the creation of a new generation of electronics.

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