Investigation of thermally stimulated conductivity of cobalt silicide

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Abstract. Mono- and disilicide of cobalt were obtained in the near-surface region of diffusion-doped silicon by cobalt atoms. The thermally stimulated conductivity (TSC) of cobalt disilicide was investigated. The energy of the adhesion levels of 0.32 eV was determined for the structures of cobalt disilicide–doped silicon–cobalt disilicide. The influence of the illumination intensity on the TSC curves is investigated and it is shown that the illumination intensity does not affect the shape of the curve and weakly affects the magnitude of the maximum of the current peak.

1 Introduction

One of the urgent problems of today is the study of the physical processes occurring in the surface and near-surface regions of single-crystal silicon, diffusive doped with impurities that create deep levels. In diffusion-doped silicon crystals, a surface layer with a thickness of 30–40 microns is formed with a concentration of impurity carriers exceeding their solubility by 2–4 orders of magnitude and with other electrophysical parameters, namely, with high specific conductivity and low mobility relative to the parameters of the bulk part [1–4].

The attention of most researchers focused on the bulk part of the crystal obtained by removing the near-surface region, so the near-surface layer was considered to be disturbed and not of practical interest. However, for a deep study of the process of diffusion doping of silicon with metals and rare-earth atoms, it is necessary to consider such important issues as the physics of the formation of a strongly doped near-surface region, the nature of the formation of metal silicides, which are very different from metal and semiconductor, as well as physical and chemical processes occurring in the near-surface region (mutual diffusion, solid-phase reactions, etc.)

Currently, transition metal silicides are becoming the basic materials for new promising technologic schemes of future generations due to their resistance to aggressive environments and high-temperature treatments [5–9]. Therefore, a comprehensive study of the mechanism of impurity entry into the crystal volume and their interaction with both matrix atoms of the crystal and technological impurities is relevant.
From this point of view, the study of the formation of silicides in the surface region of silicon during diffusion doping and the development of new semiconductor devices based on them is of particular scientific importance in the context of creating new materials for micro- and nanoelectronics.

In this connection, we have investigated the thermally stimulated conductivities (TSC) of chromium silicides.

2 Experimental method

Cobalt has a large diffusion coefficient in silicon, so we used the diffusion doping method. This method has a number of other advantages: 1) the relative simplicity of the technology; 2) the possibility of studying the effect of annealing temperature on the initial crystal parameters; 3) the possibility of controlling the concentration of electrically active chromium atoms by changing the temperature.

For silicon doping with cobalt, ingots of both p-type KDB-10 and n-type KEF-20 silicon single crystals grow by the Chokhralsky method were used. The initial parameters are as follows: for n-type silicon - resistivity $p=20 \Omega \cdot cm$, electron mobility $\mu_n=1430 \text{ cm}^2/V \cdot \text{s}$, electron concentration $n=2.4 \times 10^{15} \text{ cm}^{-3}$, for p-type silicon - resistivity $p=10 \Omega \cdot cm$, hole mobility $\mu_p=430 \text{ cm}^2/V \cdot \text{s}$, hole concentration $p=1.5 \times 10^{15} \text{ cm}^{-3}$, oxygen concentration $\leq 1 \times 10^{17} \text{ cm}^{-3}$.

Samples in the form of a parallelepiped measuring (1-2) x (2-5) x (10-30) mm$^3$ were cut out of silicon single crystal ingots with a diamond disk. The samples were ground using silicon carbide micro-powder M-5, M-10 and subjected to chemical etching in a solution of 1HF:5HNO$_3$ for 1-2 minutes, washed in deionized water and dried at a temperature of not more than 1000°C. Silicon samples were placed in a quantity of 3 pieces in quartz ampoules, previously washed in a solution of HNO$_3$:3HCl and boiled in distilled water.

The mass of the alloying metal atoms was determined from the Mendeleev-Clapeyron equation:

$$pV = mRT\mu^{-1}$$

$$m = pV\mu^{-1}T^{-1}\mu$$

Hence, $m = pV\mu^{-1}T^{-1}$, where $p$ is the vapor pressure of the metal in the ampoule, which is equal to $1 \cdot 10^{-2} \div 2 \cdot 10^{-5}$ mm Hg at $T=1000 \div 1250 ^\circ C$. The weight of the metal determined in this way was 3 mg. The weight of the metal is not limited in the larger direction, i.e. at least 3 mg is used. A metal powder of frequency 99.999 in the amount of 3-5 mg was placed in the ampoule. Ampoules with samples and diffusant were pumped out to a vacuum of ~10$^{-3}$ mm Hg (1.33·10$^{-1}$ Pa) and sealed. Then the ampoules were placed in a horizontal furnace and annealed at a temperature of 1050 ÷ 1070°C for 20 minutes to 2 hours. Temperature fluctuations in the working area of the furnace did not exceed ±5°C. After annealing, the samples were quenched by cooling at a rate of 100-150 deg/s by dropping the ampoules into water and kept to the crystal temperature $T=15-20 ^\circ C$. After opening the ampoules, the surface of the samples had a p-type conductivity.

3 Results and discussion

Before studying the conductivity distribution over the thickness of the samples, the surface resistance was measured on all crystal surfaces using the four-probe method. The measurements showed that the surface resistances of all sides of the doped crystals were low in resistance, compared to the surface resistances of the original crystals. In order to remove the surface layer broken during grinding, the samples were degreased in toluene at the temperature of the initial crystals (that is, they were subjected to, and also not subjected to, heat treatment of crystals without admixture).
Due to the fact that the samples had a surface layer with high conductivity, to exclude its shunt effect, the samples were ground from three sides to a depth of about 40-50 microns. Electrical contacts were connected to two opposite unpolished ends, and measurements were made on the unpolished surface lying between them with successive removal of thin layers. It turned out that the conductivity profiles have two sections: a near-surface one with increased conductivity and a volume one with a conductivity close to its own.

Parallel measurements of the conductivity and Hall effect at temperatures T=77 ÷ 300 K showed that the near-surface layer has a p-type conductivity with a carrier concentration of \( 10^{20} \div 10^{21} \text{cm}^{-3} \) and a Hall mobility \( \mu_H = 2 - 6 \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s} \). The bulk layer has an i-type conductivity with a carrier concentration of \( 10^{-12} \div 10^{-11} \text{cm}^{-3} \) and mobility \( \mu_H = 300 - 430 \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1} \). The same conductivity distribution (p-type with a concentration of \( p \approx 10^{20} \div 10^{21} \text{cm}^{-3} \)) was obtained in the near-surface layer and when the initial n-type silicon was doped with cobalt. However, the bulk carrier concentration in the sample depth remained almost unchanged (relative to the initial silicon).

The measurement results showed that the near-surface anomalous layer has a current carrier concentration of \( \sim 10^{20} \div 10^{21} \text{cm}^{-3} \) and a Hall mobility of \( 3 - 6 \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1} \). Calculations have shown that near-surface Si<Co> layers with a thickness of 1÷5 microns have a specific conductivity of \( \sim (1.7 \div 9.9) \cdot 10^{3} \Omega^{-1} \text{cm}^{-1} \).
Fig. 1. TSC of the CoSi$_2$–Si<sub>Co</sub>–CoSi$_2$ structure.

Analysis of the TST curves for cobalt-doped silicon crystals shows that monomolecular recombination occurs at these levels. The dependence of $I$ on the trap depth $E_t$ can be expressed by the relation:

$$I = c \cdot n \cdot \nu \cdot \exp(-E_t/kT),$$  

(1)

where $c$ is the geometric factor, $n$ is the concentration of carriers in the traps, and $\nu$ is the frequency factor, which can be related to the frequency of carriers leaving the traps $\xi$ by the following relation:

$$\xi = \nu \cdot \exp(-E_t/kT)$$  

(2)

The frequency $\xi$ is the inverse of the time spent by the carrier in the trap. On the TST curve, the trap depth $E_t$ is determined from the formula:

$$E_t = \frac{1.51T^*T'}{(T^*-T')}$$  

(3)

where $T^*$ is the critical temperature at the peak maximum, and $T'$ is the temperature at which the ordinate of the low-temperature branch of the TST curve reaches half the peak value. This formula can be used if the condition $E_t/kT^* \geq 20$.

Knowing the area under the TSC curve, it is possible to calculate the concentration of current carriers that contribute to the current during measurement. The area is obtained by integrating the net TSC:

$$S = \int_{t_1}^{t_2} I \, dt,$$  

(4)

where $t_1$ and $t_2$ are the start and end times.
\[ N_t = \frac{A}{eV_G} \]  

(5)

\[ G = \frac{\tau \mu U}{L^2} \]  

(6)

A is the area under the TST curve, \( V \) is the sample volume, and \( e \) is the electron charge.

To establish a correlation between the number of electrons that contribute to the thermally stimulated current and the trap concentration, we need to take into account the photoelectric gain factor \( G \), which is equal to:

\[ \tau, \mu \] are the lifetime and mobility of carriers, \( L \) is the sample length, \( U \) is the applied voltage, \( \mu \) is obtained from experimental measurements of electrical conductivity and Hall coefficient, and \( \tau \) is obtained from measurements of photoconductivity.

The 0.22 eV level has a state density of \( \sim 3 \times 10^{15} \text{cm}^{-3} \) and the 0.3 eV level has a state density of \( \sim 4 \times 10^{15} \text{cm}^{-3} \).

Fig. 2. Influence of light intensity on the TST curve of the structure CoSi – Si<Co> – CoSi.

As the intensity increases, the area under the TST curve increases, which indicates an increase in the concentration of impurity centers involved in thermally stimulated conductivity. The weak dependence on the illumination intensity is due to the fact that we are dealing with regions close to the saturation of impurity centers. The calculation shows that at an illumination intensity of 10%, the trap concentration is \( 6 \times 10^{-15} \text{cm}^{-3} \), the recombination capture cross-section is \( 5 \times 10^{-20} \text{cm}^{-2} \), at an intensity of 30%, \( N_t = 3 \times 10^{16} \text{cm}^{-3} \), \( \sigma_n = 4 \times 10^{-20} \text{cm}^{-2} \), at an intensity of 100%, \( N_t = 3.5 \times 10^{16} \text{cm}^{-3} \), \( \sigma_n = 4 \times 10^{-20} \text{cm}^{-2} \).
4 Conclusion

The formation of mono- and дисилицид cobalt disilicide in the near-surface and surface regions of diffusion-doped monocrystalline silicon by cobalt atoms is revealed. The concentrations of current carriers and Hall mobility in these regions are determined. To determine the depth of traps, the TSC was used as an independent technique. The energy of the adhesion levels of 0.32 eV is determined for the cobalt disilicide–doped silicon–cobalt disilicide structures. The influence of illumination intensity on the TSC curves is investigated and it is shown that the illumination intensity does not affect the shape of the curve and weakly affects the value of the current peak maximum.

References

9. K.V. Shalimova, Physics of semiconductors. (Moscow, 2010)