THE SURFACE LAYER MORPHOLOGY OF Si<Cr> SAMPLES

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In this work, the electrical and photoelectric properties of the near-surface and surface layers of silicon doped by diffusion with chromium atoms were investigated. The formation of an anomalous concentration of charge carriers in these regions, as well as an anomalously low mobility, was revealed. The specific conductivity of the near-surface layer with a thickness of $1 \div 5$ µm turned out to be equal to $(1.6 \div 9.9) \cdot 10^3$ Ohm$^{-1} \cdot$cm^{-1}. The inhomogeneity of the crystal under study was determined by the light probe method.
Keywords: *Silicon; Chromium; Surface; Subsurface; Conductivity; Hall mobilty; Inhomogeneity; Silicide*
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INTRODUCTION

Modern world scientific and technical progress is largely determined by the development of microelectronics and nanoelectronics, the achievements of which directly depend on the successes of fundamental sciences, primarily solid state physics and semiconductor physics. The latest achievements in these areas are related to the physics of doped semiconductors and the creation of technologies for obtaining micro- and nanostructures with fundamentally new functional capabilities for computer and measuring equipment, communications, etc. In this regard, studies of physical processes occurring both in the volume and on the surface, and in the near-surface layers of a single-crystal semiconductor, in particular, silicon in the process of diffusion doping with impurities, creating deep levels and obtaining compensated materials with specified electrophysical, tensoelectric, photoelectric and optical properties are urgent tasks of today [1-6].

The observed increased interest in the development of new materials with improved thermoelectric properties is due to the ever-expanding needs for the use of such materials in the national economy as thermal sensors and active elements [7-8].

Traditional materials used as effective thermoelectric converters of thermal energy, in particular solar energy, into electrical energy are various compounds of bismuth and lead with tellurium and selenium, as well as binary compounds in the form of alloys and solutions based on isovalent elements of germanium and silicon [9-11]. Along with the existing materials listed above, manganese silicide can also find an equally important application as a base material for creating highly effective thermoelectric power sensors.

The thermoelectric properties of a number of silicides have been considered in sufficient detail [12, 13], where, in particular, the possibility of creating a thermoelectric generator with a semiconductor nature of electrical conductivity based on manganese silicide was demonstrated. Thermoelectric properties were studied on samples of manganese silicide obtained by the method [14].

At the global level, the use of diffusion-doped monocrystalline silicon to obtain compensated materials with specified electrophysical, photoelectric and optical properties in modern microelectronics is an urgent task. Well-developed technology for growing monocrystalline silicon, planar technology for creating integrated devices based on it, a fundamentally new technology for creating low-dimensional objects in silicon, modification of properties by various methods, as well as the discovery of new physical phenomena that are not characteristic of bulk silicon, attracts the close attention of researchers as an active material for the needs of micro- and nanotechnology [15].

Currently, transition metal silicides are becoming the base material for new, promising technological schemes of future generations due to their resistance to aggressive environments and high-temperature treatments. Therefore, a comprehensive study of the mechanism of impurity entry into the crystal volume and their interaction with both the 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.

The purpose of this work is to study the heterogeneity of the near-surface and surface layer within the formation of chromium silicides of diffusion-doped silicon with chromium atoms.

EXPERIMENTAL METHODS

Chromium has a high diffusion coefficient in silicon, so we used the diffusion alloying method. This method has a number of other advantages: 1) relative simplicity of the technology; 2) the ability to study the effect of annealing

temperature on the initial parameters of the crystal; 3) the ability to regulate the concentration of electrically active chromium atoms by changing the temperature.

For alloying silicon with chromium, we used ingots of both *p*-type KDB-10 and *n*-type KEF-20 silicon monocrystals grown by the Czochralski method. Their initial parameters are as follows: for n-type silicon, the resistivity is $\rho = 20$ Ohm·cm, the electron mobility is $\mu_n = 1430$ cm^2/V s, the electron concentration is $n=2.2\cdot10^{14}$ cm^{-3}; for *p*-type silicon, the resistivity is $\rho=10$ Ohm·cm, the hole mobility is $\mu_p = 430$ cm^2/V s, the hole concentration is $p = 1.5\cdot10^{15}$ cm^{-3}, the oxygen concentration is $1 \cdot 10^{17}$cm^{-3}.

Parallelepiped-shaped samples measuring $(1\div2)\times(2\div5)\times(10\div30)$ mm^3 were cut out from silicon single-crystal ingots using a diamond disk. The samples were ground using silicon carbide micropowder M-5, M-10. In order to remove the surface layer damaged during grinding, the samples were degreased in toluene at a temperature of 40-50°C and chemically etched in a 1HF:5HNO$_3$ solution for $1\div2$ minutes, washed in deionized water and dried at a temperature of no more than 100°C. Silicon samples were placed in a quantity of 3 pcs. in quartz ampoules, pre-washed in a solution of HNO$_3\div$3HCl and boiled in distilled water.

The mass of the alloying metal atoms was determined from the Mendeleev-Clapeyron equation: $pV = mRT\mu^{-1}$. Hence $m = pV\mu R^{-1}T^{-1}$, where p is the metal vapor pressure in the ampoule, which is equal to $1 \cdot 10^{-2} \div 2 \cdot 10^{-5}$ mm Hg at T=1000÷1250°C. The mass of the metal determined in this way was 3 mg. The mass of the metal is not limited upwards, i.e. not less than 3 mg is used. Metal powder of 99.999 purity was placed in the ampoule in an amount of 3÷5 mg. The ampoules with samples and diffusant were pumped out to a vacuum of ~10^{-3} mmHg (1.33÷10^{-1} Pa) and sealed. Then the ampoules were placed in a horizontal furnace and annealed at a temperature of 950÷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 until the crystal temperature T=15-20°C. After opening the ampoules, the surface of the samples had p-type conductivity [14,16,17].

Since the samples had a highly conductive surface layer, to eliminate its shunting effect, the samples were ground on three sides to a depth of about 40-50 μm. Electrical contacts were connected to two opposite unground ends, and measurements were taken on the unground surface lying between them with successive removal of thin layers. It turned out that the conductivity profiles have two sections - a near-surface section with increased conductivity and a volume section with conductivity close to the intrinsic one. Parallel measurements of conductivity and the Hall effect at temperatures T = -196÷27°C showed that the surface layer has *p*-type conductivity with a carrier concentration of $\sim10^{20} \div 10^{21}$ cm^{-3} and a Hall mobility of $\mu_H = 2 - 6 cm^2/V \cdot s$, while the bulk layer has *i*-type conductivity with a carrier concentration of $10^{10} \div 10^{12}$ cm^{-3} and a mobility of $\mu_H = 300 - 700$ cm^2/V·s. The same conductivity distribution (*p*-type with a concentration of $p \approx 10^{20} \div 10^{21}$ cm^{-3}) was obtained in the surface layer also when doping the initial n-type silicon with chromium. However, the bulk carrier concentration in the bulk of the sample remained almost unchanged (relative to the initial silicon).

The measurement results showed that the near-surface anomalous layer has a current carrier concentration of ~10^{20}÷10^{21} cm^{-3} and a Hall mobility of 1÷17 cm^2/V·s. Calculations showed that the near-surface Si<Cr> layers with a thickness of 1÷5 μm have a specific conductivity of ~(1.6÷9.9)×10^3 Ohm^{-1}×cm^{-1}.

RESULT AND DISCUSSION

To analyze the obtained thermoelectric properties of samples with higher chromium silicides (HCS), we will use generally accepted criteria.
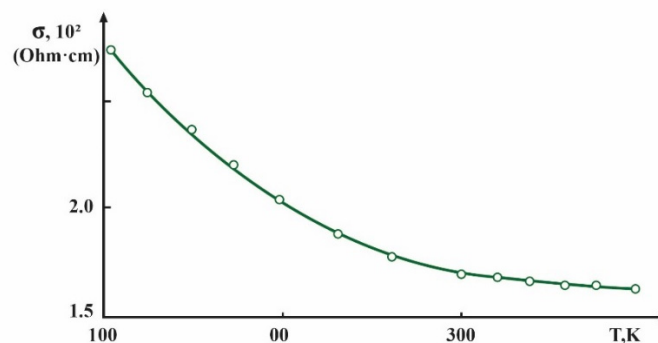

Figure 1. Temperature dependence of conductivity of HCS

It is known that the total efficiency of the Carnot cycle is determined by the thermoelectric figure of merit, the value of which for a particular material is determined as [18]

$$Z = \frac{\alpha^2 \sigma}{\varkappa} \qquad (1)$$

where α, σ and $\varkappa$ —electrical conductivity, differential thermoEMF, thermal conductivity, respectively.

The figure of merit is the only parameter that determines the characteristics of a thermoelectric device, and therefore it is desirable to have a material with the maximum value of α and, accordingly, the minimum ρ and $\varkappa$. The parameters that determine the thermoelectric figure of merit are interdependent and, in addition, they depend on the temperature, since $\varkappa$ and ρ depend on the concentration and mobility of carriers. With some degree of assumption, it can be assumed that the thermal conductivity of semiconductors $\varkappa = \varkappa_e + \varkappa_p$, where $\varkappa_e$ is the electron component, and $\varkappa_p$ is the phonon component of thermal conductivity.

Photoconductivity and photo-EMF measurements were performed at room temperature on Si<Cr> samples in which the bulk part of the crystal was overcompensated, i.e. *n*-type. The sample sizes were as follows: after doping with metal atoms – 0.3×0.4×0.5 cm³ and 0.4×1.6×1.6 cm³, after cutting for photo-EMF studies – 0.15×0.13×0.5 cm³ and 0.3×1.5×1.6 cm³.

Fig. 2 shows the results of light scanning for typical Si<Cr> samples, irradiated with light of wavelength 0.63 μm, after removing a layer 3-5 μm thick from the surface. It is evident from the figures that the photo signal does not change monotonically from point to point.
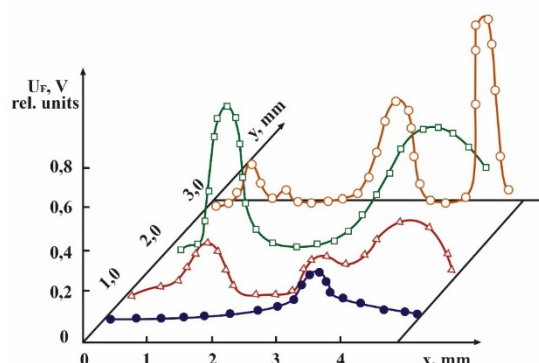
Figure 2. Results of light scanning for one n-Si<Cr> sample under irradiation with light with λ = 0.63 μm

It was found that the density of the photo-EMF spectrum decreases with increasing thickness of the layer being removed. The results of the study show that a new phase is formed on the surface of silicon diffusion-doped with chromium in the high-temperature process. Such a phase grows on the orienting substrate taking into account its atoms and regularly continues the crystal lattice of the substrate.

The formation of chromium mono- and disilicides was proven by X-ray diffraction [7].

Measurements showed that the areas of the photo-EMF spectra depend on the wavelength of light, and the shifts in the areas and their shape are apparently related to the depth of light penetration depending on λ. This shows that when using infrared radiation in the region of ~0.6 – 3.4 μm, it is possible to determine inhomogeneities inside the crystal.

A study of the dependence of the photo-EMF value on the thickness of the surface layer revealed that the photo-EMF signal increases as the layer is removed to a depth of ~25 μm, and then saturates in a narrow region and gradually decreases from ~30 μm and completely disappears after removal of more than 45÷50 μm [8].

To determine the internal electric field of a non-uniform region of a crystal, an external electric field of polarity E_e, opposite to the internal electric field E_i, was applied to it.

Research has shown that at E_e=0.9-1.2 V/cm, the volume photo-EMF current is zero when illuminated with modulated light. In this case, E_i can be determined according to the expression [19]:

$$E_i = \frac{1+b}{2} \cdot \frac{i}{s} \cdot p \qquad (2)$$

where s is the cross-section of the crystal, b is the ratio of the electron and hole mobilities, i is the compensating direct current, p is the specific resistance of the crystal.

When substituting the values $b = \mu_n/\mu_p = 3, p = 1.3 \cdot 10^4$ Ohm $\cdot$ cm, $i = 1.39 \cdot 10^{-6} A, s = 2 \cdot 10^{-2} cm^2$, the value $E_i = 1.8$ V/cm was obtained.

A model of the structure of the near-surface region of diffusion-doped silicon with chromium is proposed. The near-surface region of compensated silicon is a large number of Schottky diodes (pairs) connected in opposite directions, with a layer of silicon metal atoms compensated between them, connected in parallel and series. Such a model is determined by the island character of the second-phase inclusions located at a depth of ~3-45 μm from the surface. This is confirmed by the maximum photo-EMF value at a depth of ~25-30 μm, where there is apparently an optimal ratio between the number of islands (inclusions) and their surface, giving the maximum total surface of the silicon-second-phase inclusions boundary.

CONCLUSIONS

1. The local photo-EMF method was used to study inhomogeneities in the initial, heat-treated, and control silicon crystals and chromium-diffusion-doped silicon crystals. It was found that in the initial and control silicon samples of both n-type and p-type conductivity, inhomogeneous areas in photoconductivity and photo-EMF along the crystal and in depth

were not detected, while in chromium-doped *n*-type and *p*-type silicon crystals, photo-EMF and photo-conductivity signals were detected.

2. It was found that photo-conductivity and photo-EMF signals in chromium-diffusion-doped silicon samples are detected in the near-surface region with a depth of 3÷50 μm. It was shown that in these samples, photo-conductivity and photo-EMF signals are not detected in the near-surface region up to ~3 μm thick and in the bulk region more than ~50 μm from the surface.

3. It is shown that the photo signal in the inhomogeneous region of doped crystals changes from point to point non-monotonically. Measurements of layer-by-layer removal of layers have established that the sizes of the second-phase inclusions decrease deep into the crystal in the form of a cone.

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МОРФОЛОГІЯ ПОВЕРХНЕВОГО ШАРУ ЗРАЗКІВ Si<Cr>
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У роботі досліджено електричні та фотоелектричні властивості приповерхневого та поверхневого шарів кремнію, легованого дифузією атомів хрому. Виявлено формування аномальної концентрації носіїв заряду в цих областях, а також аномально низьку рухливість. Питома електропровідність приповерхневого шару товщиною 1÷5 мкм виявилася рівною $(1,6÷9,9)\cdot10^3\cdot$Ом$^{-1}\cdot$см$^{-1}$. Методом світлового зонду визначали неоднорідність досліджуваного кристала.
Ключові слова: *кремній; хром; поверхня; підповерхневий; провідність; Hall мобільність; неоднорідність; силіцид*