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POST-IMPLANTATION ANNEALING OF SILICON IMPLANTED WITH ALKALI METAL IONS

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Abstract
The base of the ion implantation method has been studied, where the energy of ions can vary from several hundred electron volts to gigaelectron volts. It has been shown that ion bombardment allows for the modification of almost all properties of the near-surface region of a solid, resulting in the formation of homogeneous, continuous films. These processes are carried out in ultra-high vacuum conditions ($P \leq 10-8$ Pa). Low-energy ions implanted at shallow depths create surface defects at the early stage of epitaxial film growth, which later act as centers of crystal nucleation.

Keywords: Ion implantation, energy, ion, electronvolt, giga, vacuum, implantation, defect, nucleation, formation, annealing, run.

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Introduction

Post-implantation annealing is a process during which the crystal structure, elemental and chemical composition of the surface layers of silicon implanted with alkali metal ions changes.

The ion implantation method is based on the implantation of ionized atoms and molecules accelerated in an electrostatic field into a solid. Any ion-target combination is possible.

Ion energies can range from several hundred electronvolts to gigaelectronvolts (i.e., billions of electronvolts). The ion penetration depth depends on the energy and mass of the ions and atoms of the solid, as well as the density of the target material. For example, the average range of 10-keV phosphorus ions in silicon is approximately 14 nm, while that of 1-MeV boron ions is approximately 1756 nm.

Ion bombardment allows for the modification of virtually all properties of the near-surface region of a solid: electrophysical, mechanical (strength, hardness, friction coefficient, wear resistance), corrosion, catalytic, optical, and emission properties. Ion implantation has now become one of the primary methods for introducing impurities into semiconductor crystals.

Previously, the most common methods were epitaxy (the introduction of impurities during crystal growth), diffusion, and fusion. Epitaxy allows layers with a specified impurity concentration to be grown on the original crystal.

The diffusion method is based on the diffusion of impurity atoms from the surface layer into the semiconductor. Finally, during alloying, the semiconductor layer adjacent to the surface is melted and, during subsequent recrystallization (solidification), enriched with impurity atoms. Unlike these methods of introducing impurities into crystals, the ion implantation method is primarily independent of chemical solubility limits, the temperature during

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implantation, and the concentration of the impurity material on the semiconductor surface.

Since implantation is a thermodynamically nonequilibrium process, it can be used to create compounds and alloys that cannot be obtained by traditional methods, and also achieve concentrations of the implanted impurity that significantly exceed the solubility limit of the impurity in the target material. Naturally, under favorable conditions, the implanted atoms can also form chemical bonds with atoms of the solid. This is possible both during irradiation and during subsequent processing.

The concentration of implanted impurity atoms has a certain distribution over depth, which in the general case can be approximately described by a Gaussian (normal) distribution with an average projected range Rp and a standard deviation ΔRp.

The ion implantation method has a number of advantages that are important both from a technological point of view and from the point of view of designing and creating new types of electronic devices and integrated circuits (IC):

- reduction in the duration of the impurity introduction process by 10^{2}–10^{4} times, uniform distribution over the surface and reproducibility of parameters;
- the ability to precisely control the number of introduced impurity atoms by simply integrating the ion current onto the target, which is especially important at low concentrations (for example, shifting the threshold voltage in MOS transistors);
- high process purity, since in accelerators ions are separated by mass using mass separators;

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- low process temperature; y simplicity of methods for masking areas on the crystal surface that should or should not be doped by using thick oxide, nitride, metal or photoresist layers;
- the possibility of doping through thin passivation layers (for example, SiO2 or Si3N4); y small ion penetration depth (usually less than a few microns, and sometimes up to tens and units of nanometers), which makes it possible to dope thin surface layers with a very steep impurity concentration gradient (for example, for VLSI with submicron or nanometer element sizes, avalanche-transit diodes, etc.);
- the possibility of creating a distribution profile of implanted atoms of any given shape using multi-stage implantation by changing the accelerating voltage (polyenergetic implantation);
- the possibility of manufacturing particularly miniature devices (submicron and nanometer technology) with low parasitic capacitances due to insignificant lateral scattering.

The advantages of the method also include its versatility, ease of control of ion beams using a computer, i.e. the possibility of complete automation, and, as noted, the possibility of creating nonequilibrium metastable systems, compatibility with planar technology processes.

When creating nanoscale two- and multilayer heterostructures that provide the necessary combinations of materials for obtaining the basic elements of modern nano-, micro- and optoelectronics, methods of molecular and solid-phase epitaxy [1–6] are widely used, as well as the method of low-energy ($E_0 \leq 5$ keV) ion implantation in combination with annealing [7–12].

Among these methods, only the ion implantation method allows for the production of homogeneous continuous films with a thickness $h \leq 40-50\ ^0A$. To obtain such structures, the main requirements are the preparation of an

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atomically clean substrate surface and ensuring high purity of the deposited (implanted) substances.

All these processes are performed under ultra-high vacuum conditions (P ≤ 10−8 Pa). When cleaning Si single crystals, it is crucial to find a reliable way to minimize the presence of oxygen and carbon atoms on the surface.

In [13], optimal modes of ion-plasma and chemical-thermal cleaning of the silicon surface were determined, which make it possible to reduce the concentrations of C and O to zero (within the sensitivity of the Auger spectrometer ~ 0.1 at.%). Low-energy ions implanted at shallow depths at the early stage of epitaxial film growth create surface defects that subsequently act as centers of crystalline nucleation.

Ion energy stimulates chemical reactions on the surface, particularly the formation of thin transition layers [14–18]. Under certain conditions, ion bombardment promotes ion-stimulated desorption of C, O, and other contaminants from the surface. However, reliable data on the dynamics of changes in the morphology, composition, and structure of ion-implanted Si during stepwise annealing over a wide temperature range are still lacking.

This work is devoted to the study of changes in the composition and structure of the surface layers of Si(111) implanted with alkali metal ions during annealing at different temperature conditions.

The objects of study were single-crystal n-type Si(111) samples with a diameter of 10 mm and a thickness of 0.5 mm. Ion implantation, heating, and all other studies were carried out on the same experimental setup under a vacuum no worse than (P = 10^{-7} Pa). The ion energy varied from 1 to 5 keV, and their dose D ≈ 1014−1017 cm^{-2} . Standard chloride salts of the corresponding alkali elements with a purity of ~ 99.99% served as ion sources.

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Before ion implantation, the ion sources were cleaned by prolonged heating. After source cleaning, the O concentration on the Si surface remained unchanged during the formation of alkali metal vapor. A combination of methods was used to study the composition and structure: Auger electron spectroscopy (AES), high-energy electron diffraction (HEED) and low-energy electron diffraction (LEED), and secondary ion mass spectrometry (SIMS).

Scanning electron microscopy (SEM) images were obtained on a standard ISM-6490 setup with a resolution of 5–6 nm, and RHEED patterns were obtained on an EMR-2 setup. The formation of chemical bonds between the matrix and implanted element atoms was assessed based on changes in the shape and position of XVVa Auger peaks of the Si atom concentration, and impurity and alloying element concentrations, respectively, based on changes in the intensity of high-energy peaks.

Atomic depth distribution profiles were determined using EOS combined with layer-by-layer argon ion etching. For comparison, the surface structure of Si with a monolayer MeSi2 coating, obtained by sputtering Me onto Si and subsequent annealing, was examined.

Upon formation of a monolayer MeSi2 coating, the work function e_{ϕ} of the Si surface decreases to a minimum. The surface work function was monitored using the contact potential difference method. The experimental technique is described in detail in [1-17]. During ion implantation, disordering of the near-surface layer and the incorporation of alloying element atoms occur. The degree of surface disorder can be determined with high accuracy from LEED patterns.

The change in diffraction intensity will be determined by the sum of two effects: disruption of the atomic arrangement and a change in surface

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composition. To account for the combined effect, it is convenient to monitor the change in surface defectivity as a function of the ratio of the intensities of the diffraction reflection and the elastic background [15].

The measured quantities are the reflex current and the background current, which are proportional to the first power of the area occupied by order and the area occupied by disorder, respectively. Therefore, the dependence of the change in the ratio of the reflex (Ir) and background (Ib) currents on the irradiation dose, according to [15], has the form:

$$Ir/Ib = (Ir0/Ib0)\exp(-aD),$$

where Ir0/Ib0 is the value of the ratio of the reflex and background currents before irradiation;

a — average area of damage per ion;

D is the radiation dose.

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