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Investigation on the Electronic Structure of Nanosized Barium Monosilicide Films Produced by Low-energy Implantation of Ba^+ Ions in Si

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Abstract: The processes of formation of nanoscale silicide films during the implantation of Ba^+ ions into Si (111) and Si (100) and subsequent thermal annealing were studied by electron spectroscopy. It is shown that implantation of ions with a high dose D > 10^{16} cm^{-2} and short-term heating leads to the formation of thin films of barium monosilicide with new surface superstructures. The optimal modes of formation and band-energy parameters of BaSi films obtained by low-energy high-dose implantation of barium ions in Si are determined. It is shown that BaSi films are a narrow-gap semiconductor with a band gap of 0.7 eV and have good emission and thermoelectric properties corresponding to the solar spectrum and have high photoelectric and thermoelectric characteristics. It should be noted that, in addition to the formation of a chemical compound, the narrowing of the Si band gap upon implantation of large doses of Ba^+ ions also contributes to defects formed as a result of strong disordering of the crystal lattice.

Keywords: Low-Energy High-Dose Ion Implantation, Films of Barium Monosilicide, Optimal Modes of Film Formation, Energy-Band Parameters

1. Introduction

In recent years, high-dose ion implantation has been used to modify surface properties and synthesize new materials, which in some cases have unique properties [1–6]. At the same time, high-dose implantation of low-energy ions (E0≤5 keV) in Si and subsequent short-term annealing can produce continuous silicide films. The authors of [7] propose to use low-energy (up to 5 keV) and high-dose (D > 10^{16} cm^{-2}) ion implantation and subsequent short-term thermal heating at a temperature close to the temperature of formation of silicide compounds to obtain silicide films. Si (111) and Si (100) monocrystals of p-type with resistivity ρ = 3000 Ω·cm were chosen as the substrate. Cleaning of the initial crystal was carried out by thermal heating in ultrahigh vacuum p = 10^{-7} Pa in two stages: long-term (for 60-120 minutes) at T = 900 K and short-term (for 30-60 seconds) at T = 1500 K. The purpose of this work is to study the change in the electronic structure of the silicon surface during the implantation of Ba^+ ions and subsequent thermal annealing. The surface electronic properties of semiconductors, in particular Si, are the focus of attention of many researchers. It should be noted that intrinsic surface states are inherent in the free surface of the crystal, in contrast to improper surface states due to the presence of foreign atoms on the surface or edge surface states caused by the presence of a defect structure in the near-surface region of the crystal. Defects occur in ion-implanted silicon layers at low doses of ion implantation. In this case, one should expect the appearance of donor or acceptor impurity levels in the band gap of silicon. Ion implantation leads to a violation of the crystal structure of the original silicon up to amorphization. Of all the variety of processes that occur during the implantation of ions into silicon, our main attention was paid to the study of the effect of implantation of high-dose ions on the electron- band structure of silicon [20-22].

2. Materials and Methods

Implantation of Ba^{+} ions, sample heating, study of their composition and parameters of energy bands using AES methods and measuring the intensity of light passing through the sample were carried out in the same device under ultrahigh vacuum conditions ($P = 10^{-7}$ Pa). Si (111) and Si (100) monocrystals of *p*-type with specific resistance $\rho = 3000\ \Omega\cdot$cm were chosen as the substrate. Cleaning of the initial crystal was carried out by thermal heating in ultrahigh vacuum $P = 10^{-7}$ Pa in two stages: long-term (for 60-120 min.) at a temperature of T = 900 K and short-term (for 30-60 s) at T = 1500 K. The Si surface was also cleaned by a new method developed by the authors of this article [8].

The experiments were carried out in a device that allows cleaning, ion implantation of Si samples and studying the surface using the following methods: Auger electron spectrometry (AES), photoelectron spectroscopy (PES).

The main methods for forming silicide films are thermal deposition, solid-phase, and molecular beam epitaxy. Although the first two methods are generally available, they are rarely used recently due to the low quality of the films obtained. Molecular beam epitaxy allows to obtain very thin films with good quality but requires expensive equipment. In this work, to obtain thin silicide films, a method is proposed for the implantation of Li, K, Na, Rb, Cs, Ba ions in Si under ultrahigh vacuum conditions (10^{-7} Pa).

3. Results

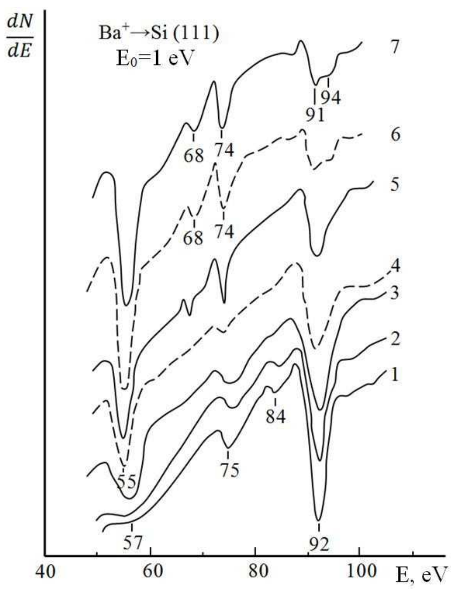

Figure 1. *Changes in the Auger spectrum of silicon upon implantation of Ba^{+} ions with E_0=1 keV with different irradiation dose D, cm^{-2}: 0-curve 1; $5x10^{13}$ - 2; $5x10^{14}$ - 3; $5x10^{15}$ - 4; 10^{16} - 5; $8x10^{16}$ - 6; $2x10^{17}$ -7. (Where dN/dE (E) is the derivative of the energy distribution of secondary electrons, in relative units).*

Let us note the main features of the changes in the AES spectra of silicon. Figure 1 shows the Auger electron spectroscopy (AES) spectra of pure silicon (curve 1) and Si implanted with Ba^{+} ions at various doses (curves 2–7). Barium implantation with a dose of $D > 5x10^{13}$ $см^{-2}$ leads only to a slight weakening of the $Si_{L2.3VV}$ peak at 92 eV, and there are no Auger peaks characteristic of the alloying element in the spectrum.

This indicates that, at low doses, dopant ions penetrate deep into the target to depths exceeding the exit zone of low-energy Auger electrons, and the dopant front is initially formed in the region of maximum range of ions with a given energy. With a further increase in the dose of ions, a barium peak appears in the spectrum at E = 55 eV, associated with an Auger transition of the $N_5O_2O_2$ type, and the amplitude of the $Si_{L2.3VV}$ peak strongly decreases. Another feature of the spectrum is that during ion implantation, starting from $D = 4x10^{15}$ $см^{-2}$, the shape of the $Si_{L2.3VV}$ peak changes - at E = 94 eV a small protrusion appears. Further, with an increase in the dose of Ba^{+} ions, the $Si_{L2.3VV}$ peak passes from the singlet form to the doublet form with a splitting of 3 eV. This behavior of the Auger peak $Si_{L2.3VV}$, due to the interaction between sp^{3} - electrons of silicon *s* and *d*-electrons of barium, indicates the appearance of a chemical compound of barium with silicon. To establish the quantitative chemical composition and determine the type of chemical bond between silicon and impurity atoms in the implanted layer, we used the AES method in combination with ion etching of the sample.

On figure 2 shows the curves of changes in the relative concentration of barium atoms in silicon with respect to the depth of the sample implanted with an energy of E_0 = 1 keV and with different irradiation doses. The concentration profiles of the distribution of atoms were calculated using the TRIM program. It can be seen from Figure 2 that, in the surface region of the ~40 Å thick sample, the concentration of barium is equal to the concentration of matrix atoms. If we take into account that Ba atoms even at room temperature have a large diffusion coefficient in silicon, then during ion implantation with an energy of E_0=1 keV, impurity atoms should penetrate to great depths (10^{2} Å). However, during layer- by-layer etching, the authors failed to detect Ba atoms in the Si volume deeper than 80 Å. This fact suggests that in the near-surface region of Si implanted with a high dose, almost all barium atoms enter into a chemical combination with silicon. Hence, it can be assumed that the plateau section on the *C(x)* curve (Figure 2) corresponds to barium monosilicide BaSi [9–12].

As a result of the implantation of Ba+ ions with a dose of $D < 5x10^{14}$ $см^{-2}$, when there is still no noticeable disordering of the near-surface layer in the Si band gap, separate shallow donor levels of barium appear, which partially compensate for the initial acceptor levels of boron (Figure 3). Such a picture can take place in the case of isolated impurity barium atoms, when their force fields and wave functions of electrons do not overlap, are localized at discrete levels, that is, if the barium concentration N_{Ba}, the Bohr radius in the crystal a_B and the screening radius r_0 satisfy the conditions: $N_{Ba}^{1/3} >> r_0$, $N_{Ba}^{1/3} >> a_B$, where $a_B = Bh^2/me^2$; e and m are the charge and mass of the electron, ε is the permittivity of the medium. At $D = 5x10^{14}$ $см^{-2}$, the electrically active acceptor levels of boron are almost completely compensated, and the EF level is set in the middle of the band gap. After this stage of ion implantation, the surface layer has the following parameters: electron work function eφ = 4.4 eV, electron affinity æ = 3.9 eV, band gap Eg = 1.1 eV. With a further increase in the dose D > $5x10^{14}$ $см^{-2}$, the number of donor levels sharply increases, overcompensation of acceptor levels and inversion of the Si conductivity type occur (Figure 3c).

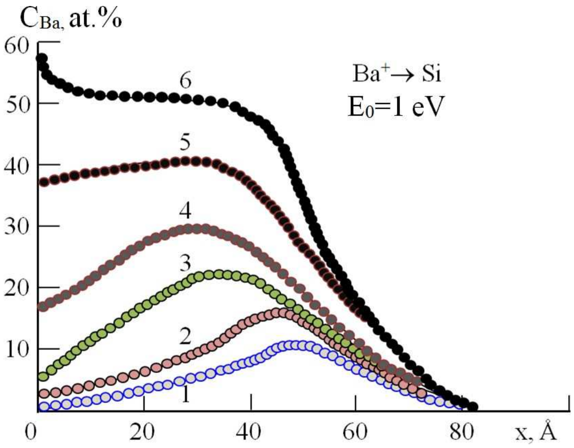

Figure 2. *Concentration distribution profiles of Ba atoms implanted in Si (111) with energy E_0=1 keV with different dose D, cm^{-2}: $5\cdot10^{13}$ (curve 1); $5\cdot10^{14}$ (2); $5\cdot10^{15}$ (3); $1\cdot10^{16}$ (4), $8\cdot10^{16}$ (5) u $2\cdot10^{17}$ (6).*

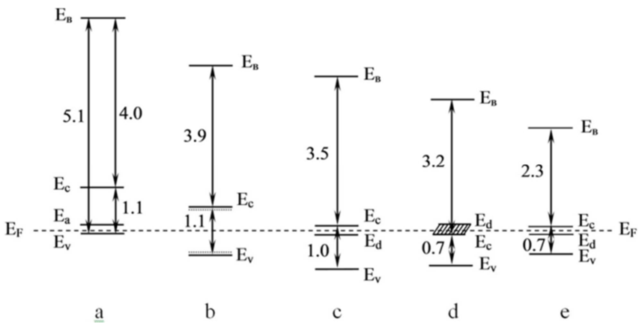

Figure 3. *Band diagram models of p-type Si (111) implanted with Ba^+ ions with E_0= 1 keV and different doses D, cm^{-2}: 0 – a; $5\cdot10^{14}$ – b; $5\cdot10^{15}$ – c; $6\cdot10^{16}$ – d; and after thermal annealing at T=900 K – e.*

As the N_{Ba} concentration increases, strong inequalities cease to hold. First of all, the first inequality is violated and an electron localized near one impurity atom will begin to experience the action of other impurity atoms. As a result, its energy level shifts in energy, and a certain discrete set appears in the band gap instead of one level, i.e. the well-known effect of the classical level broadening appears [13]. With a further increase in the dose D > $5x10^{15}$ cm^{-2}, the concentration of N_{Ba} increases and begins to be violated. In this case, the overlap of the wave functions of the electrons localized on different impurity atoms becomes noticeable, and the barium donor level turns into an impurity sub band. This effect is known as the quantum level broadening effect [14-16]. The optimal conditions for the formation of barium silicide films by the method of low-energy high-dose implantation of barium ions in Si (100), n - type are given in table 1.

Table 1. *Optimal Conditions for the Formation of Barium Silicide Films.*

Silicide type / Parameters	BaSi
Structure of initial Si	100
Ion energy, keV	0.5-5
T annealing, K	800-900
Silicide thickness, Å	35-85
Superstructure type	1x1
Electron energy E_P, eV	38

As a result, the band gap narrows. Recall that starting from this dose, a noticeable disordering of the near-surface layer and the formation of silicide phases occur [17-19]. At an irradiation dose D = $6x10^{16}$ cm^{-2}, the barium impurity band overlaps with the conduction band and the Fermi level E_F appears in the conduction band of ion-implanted Si. The band gap is E_g = 0.7 eV, eφ = æ = 3.2 eV. Those the band diagram of ion-implanted Si becomes similar to the diagram characteristic of a highly degenerate semiconductor (Figure 3d).

4. Conclusion

The optimal modes of formation and band-energy parameters of BaSi films obtained by low-energy high-dose implantation of barium ions in Si are determined. It is shown that BaSi films are a narrow-gap semiconductor with a band gap of 0.7 eV and have good emission and thermoelectric properties corresponding to the solar spectrum and have high photoelectric and thermoelectric characteristics. It should be noted that, in addition to the formation of a chemical compound, the narrowing of the Si band gap upon implantation of large doses of Ba^+ ions also contributes to defects formed as a result of strong disordering of the crystal lattice.

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