Optimum technological modes of ion implantation and subsequent annealing for formation of thin nanosized silicide films

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Abstract. Using the methods of electron spectroscopy and slow electron diffraction, we studied the processes of the formation of nanosized metal silicide films in the near-surface region of Si (111) and Si (100) during low-energy implantation of Ba ions and alkaline elements. The optimal technological modes of ion implantation and subsequent annealing for the formation of thin nanoscale films of silicides were determined. The type of surface superstructures of thin silicide films has been established.

1 Introduction

The processes of formation of nanoscale films of metal silicides in the near-surface region of Si (111) and Si (100) during low-energy implantation of Ba^+ ions and alkaline elements have been studied by electron spectroscopy and low-energy electron diffraction. The optimal technological modes of ion implantation and subsequent annealing for the formation of thin nanosized silicide films have been determined. The type of surface superstructures of thin silicide films has been established.

In recent years, considerable attention has been paid to the formation of thin monocrystalline silicide films of Li, K, Na, Rb, Cs, Ba in silicon in connection with the prospect of their use in thermogenerators, thermoelectric batteries, thermal radiation receivers, various sensors, as elements of functional integrated circuits for high-speed micro- and nanoelectronic devices, as well as plasmon waveguides for optoelectronic devices.

2 Methods

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 [1-4]. 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). The experimental technique is described in [5].

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3 Results and Discussion

Systematic studies of changes in the Si surface region occurring during the implantation of Li, K, Na, Rb, Cs, and Ba ions with different energies and radiation doses have been carried out by the methods of low-energy electron diffraction Auger electron spectroscopy, and high-resolution scanning electron microscopy. Based on these studies, we have determined the optimal modes of ion implantation (type, energy, dose) and subsequent thermal annealing (temperature, time) for the formation of thin nanosized films of metal silicides (Table).

Table 1 shows the modes of formation and types of surface superstructures of Ba silicides and alkaline elements formed after short-term annealing of silicon samples implanted with ions with an energy of 1 keV [6-12]. Note that we also observed the indicated surface superstructures after annealing of samples implanted with high-energy ions (E_0 = 2-5 keV). The only difference was that the formation of surface structures required a longer (the more, the higher the ion energy) annealing at the corresponding temperatures [13-20].

Table 1. Optimal modes for the formation of thin nanosized films barium silicides and alkaline elements

Silicide type / Options	LiSi	NaSi	KSi	RbSi	CsSi	BaSi
Initial Si structure	111	100 111	100	100 111	100 111	100 111
Ion energy, keV	0.5-5	0.5-5	0.5-5	0.5-5	0.5-5	0.5-5
Annealing temperature, K	900-1000	600-700	800-850	800-850	500-600	800-900
Silicide thickness, Å	50-110	45-100	35-95	30-90	40-90	35-85
Superstructure type	4x4	4x4 1x1	2x1	2x4 2x2	2x8 2x2	2x2 1x1
Electron energy E_P, eV	42	35 43	49	35 42	39 30	38 43
Recovery temperature initial structure, K	1400	1100	1200	1200	1000	1300

Depending on the type of the initial face of the silicon surface and the type of implanted ions of alkaline and alkaline-earth elements, the formation of various types of surface superstructures is observed. We have found that starting from a certain dose of implantation of low-energy ions (which depends on the energy and type of ions), amorphization of the near-surface region of Si (111) and Si (100) is observed. The critical doses of Si amorphization have been determined. It was also found that starting from doses exceeding the dose of amorphization, partial formation of new chemical compounds is observed. Subsequent short-term thermal annealing of ion-implanted Si samples leads to the formation of thin nanosized silicide films with new surface structures: Si (111)-4x4Li, Si (111)-2x2Rb, Si (111)-1x1Na, Si (111)-2x2Cs, Si (111)-1x1Ba, Si (100)-2x2Ba, Si (100)-4x4Na, Si (100)-2x4Rb, Si (100)-2x1K, Si (100)-2x8Cs. The appearance of new surface superstructures is an additional confirmation of the formation of thin silicide films with a single crystal structure.

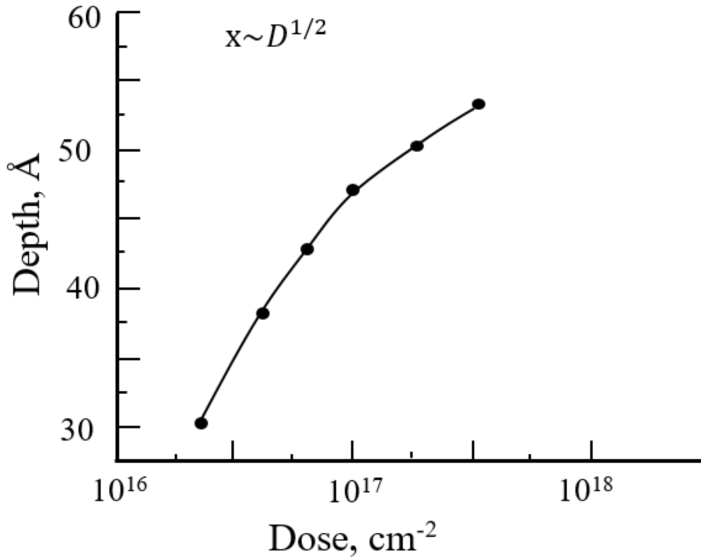

Fig.1. Dependences of the thickness of the RbSi silicide film x on the dose of ions D.

Thus, as a result of ion implantation and subsequent annealing, films of the following silicides are formed in the near-surface region of Si: LiSi, KSi, RbSi, CsSi, NaSi, and BaSi.

Experimental measurements of the thickness of silicide films showed that it grows with an increase in the energy of implanted ions; at fixed ion energy, it also grows with an increase in the dose, approximately as $D^{1/2}$ (Fig. 1). Figure 1 shows the dependences of the thickness of the RbSi silicide film on the dose of D ions.

Measurement of the maximum range of Ba^+ ions and alkaline elements in Si (111) on the energy of implanted ions showed that the range of ions increases almost linearly with increasing E_0 (Fig. 2).

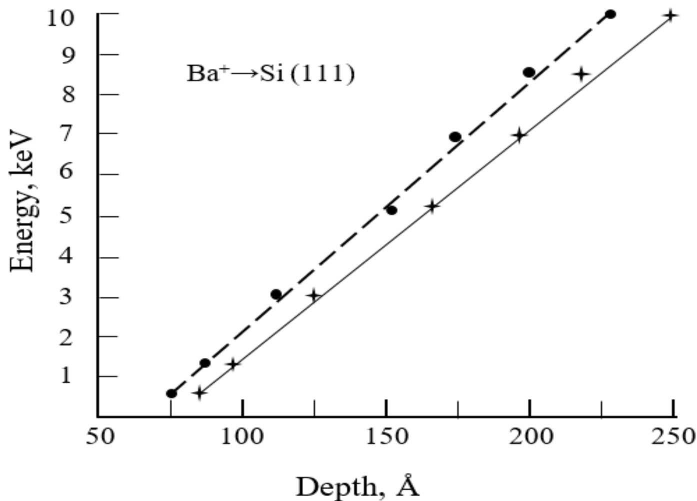

Fig.2. Dependences of the maximum range on the energy of the implanted barium ions E_0 (solid curve is experiment, dashed curve is calculation).

It is shown that the implantation of Na^+, Rb^+, Cs^+, Li^+ ions with E_0 = 1 keV, with a large dose in Si (111) and subsequent short-term heating at 600, 800, 500, 900 K, respectively, leads to the formation of silicide films in the near-surface layer with the following structures: Si (111)-4x4 Na; Si (111)-2x2 Rb; Si (111)-4x4Cs; Si (111)-4x4 Li, and heating of Si (100) samples implanted with Na^+, Rb^+, K^+, and Cs^+ ions with E_0 = 1 keV leads to the formation of silicides with surface superstructures: Si (100)-4x4Na; Si (100)-2x4Rb; Si (100)-2x1K; Si (100)-2x8Cs.

It has been established in the course of studies of changes in the specific electrical conductivity of the n-type Si (111) surface during the implantation of Ba^+, Na^+, and Li^+ ions with an energy of 1 keV with various doses that the implantation of ions (regardless of the type of ions) up to a dose of $8 \cdot 10^{14}$ cm^{-2} is practically not led to a change in σ (Figure 3) [4]. The result is probably associated with deep penetration due to the channeling of implanted ions and their small contribution to the surface conductivity. It should be noted that the implantation of Ba^+ ions and alkaline elements with a dose of ~10^{14} cm^{-2} leads to an increase in the concentration of electrons at donor levels and to the beginning of the splitting of donor levels, which should result in an increase in σ [4]. However, at these doses, the Si (111) surface region is significantly disordered, which leads to a decrease in the surface electrical conductivity, the latter compensating for the contribution of an increase in donor concentration to an increase in σ. An effective and similar mechanism is evidenced by the minima on the dose dependences of σ (Figure 3). With an increase in the dose of implanted ions, a sharp increase in σ is observed up to D = 10^{17} cm^{-2}.

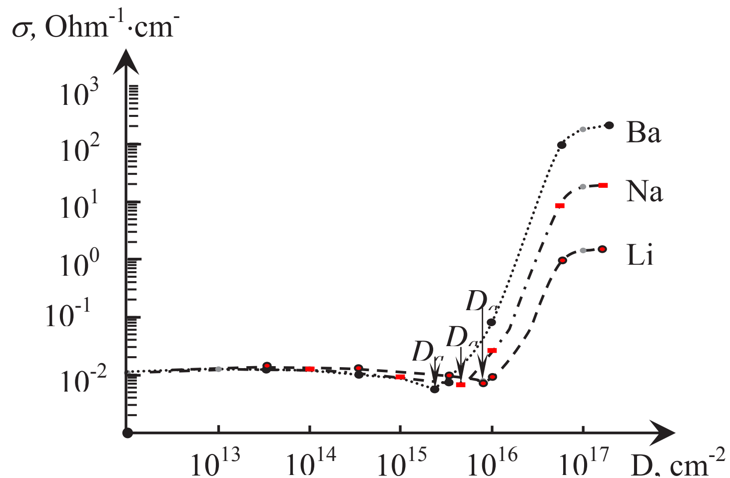

Fig.3. Dependences of the specific electrical conductivity σ of the Si (111) surface on the dose of implantation of ions (Li^+, Na^+, and Ba^+) with an energy of 1 keV [4].

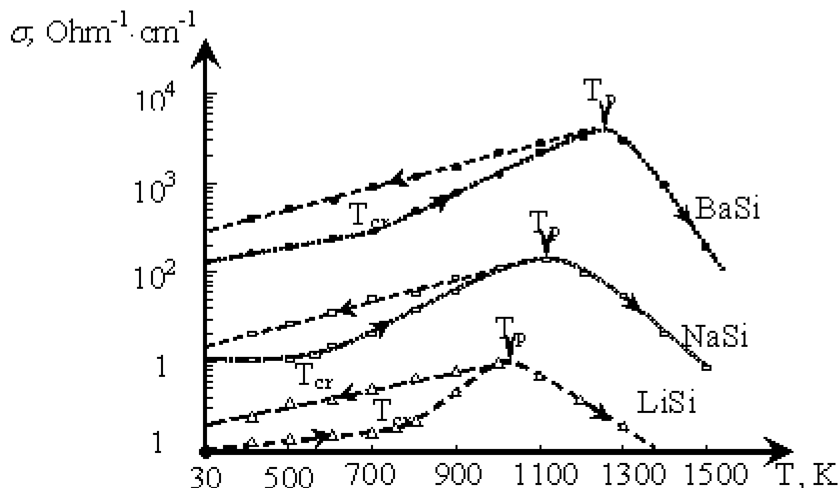

Fig.4. Dependences of the specific electrical conductivity σ of the Si (111) surface implanted with ions (Li^+, Na^+, and Ba^+) on the annealing temperature [4].

Figure 4 shows the dependences of the specific electrical conductivity σ of the Si (111) surface implanted with Li^+, Na^+, and Ba^+ ions with an energy of 1 keV with a dose of $2 \cdot 10^{17}$ cm^{-2} on the temperature of subsequent annealing [6]. It can be seen from the figure that, starting from the temperature T_{cr}, which corresponds to the recrystallization of the implanted area, a sharp increase in σ is observed. In our opinion, at $T = T_{cr}$, the formation of nanoscale films of LiSi, NaSi, BaSi is observed.

At a temperature $T > T_p$, the fracture of the silicide film σ decreases. Evaluation of the thickness of the silicide film by the method of layer-by-layer Auger analysis showed that at an ion energy of 1 keV, the thickness of the films is 5–6 nm (or 50–60 Å). When the silicide films are cooled from T_p to 300 K, the electrical conductivity of the silicide films decreases linearly, which is typical for degenerate semiconductors.

4 Conclusion

In this work, the optimal modes of formation of thin nanosized films of barium silicides and alkali elements are determined for the first time. It is shown that the thickness of the metal silicide films increases linearly with an increase in the energy of the implanted ions and, at fixed energy, increases with an increase in the dose as $D^{1/2}$.

It has been established that implantation of Ba^+, Na^+, and Li^+ ions with an energy of 1 keV (regardless of the type of ions) up to a dose of $8 \cdot 10^{14}$ cm^{-2} practically does not lead to a change in the specific electrical conductivity of the n-Si (111) surface. With a further increase in the dose of implanted ions, a sharp increase in σ is observed up to $D = 10^{17}$ cm^{-2}, then saturation occurs.

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