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ELECTRONIC PROPERTIES OF SEMICONDUCTORS

Effect of Alkali Metals on the Electronic Properties of Grain Boundaries on a Polycrystalline Silicon Surface

L. O. Olimov

Babur Andizhan State University, ul. Universiteta 129, Andizhan, 710000 Uzbekistan
e-mail: O.Lut@mail.ru; O.Lut@rambler.ru

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Abstract—The effect of alkali metals on carrier drift from grain boundaries to a polycrystalline silicon surface is experimentally studied. The results obtained show that an increase in the dopant concentration during the diffusion, desorption, and adsorption of alkali metals along grain boundaries leads to an increase in the potential barrier.

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At present, the effect of alkali metals (AM) on the electronic properties of polycrystalline silicon (PS) [1, 2] and its adsorption properties can be considered studied well enough from both experimental and theoretical points of view [2–4]. The interaction of AMs with radiation defects with energy levels of ≈0.15, ~0.17, ~0.3, and ~0.36 eV, which results in a decrease in the density of states at grain boundaries (GB) and an increase in the radiation resistance of solar cells (SC), is reliably identified [1, 2]. The potential barrier increases during the diffusion and adsorption of AM atoms along GBs [4]. As for the effect of AMs on the electronic properties of GBs on the PS surface during doping, it is still an unsolved problem, although the effect of such impurities on PS's electrical properties [1, 2] and the effect of adsorption on the electrical properties of GBs in the PS bulk [4] are relatively well studied. An urgent problem concerns study of the effect of AMs on the electrical properties of GBs on the PS surface during the development of SCs and other semiconductor devices on it. This work is devoted to study of the effect of AMs on the electrical properties of GBs on the PS surface.

It is known that, among the methods for determining a GB's electrical properties, carrier concentration variation by doping (see, e.g., [5] and references therein) is the most attractive when studying polycrystalline elemental semiconductors. This method makes it possible to obtain information in a wide energy range, especially, when using n-type and p-type samples.

Samples were prepared as polished wafers 300 μm thick from cast p-type PS with the resistivity $\rho \approx 1\ \Omega$ cm and grain sizes of 100–300 μm [6]. Rapidly diffusing AMs, i.e., Li, Na, K, and Cs were chosen as dopants. Doping was performed by ion implantation (II). After II, samples were annealed in vacuum of 6–10 Torr in the temperature range from 300 to 1000 K. To estimate the effect of AMs on the GB's electrical properties, the sample conductivity σ was measured by the four-point probe and Van der Pauw methods before and after II and after each heat treatment performed with a step of 50 K.

It is known [5] that the conductivity expanded in Taylor series is given by

$$\sigma = \frac{e}{k}\langle a\rangle AT\exp\left(-\frac{e\varphi}{kT}\right), \quad (1)$$

where e is the electron charge, k is the Boltzmann constant, $\langle a\rangle$ is the grain size, A is the effective Richardson constant, T is the temperature, and φ is the potential barrier height at the GBs. The quantity φ is related to depletion layer thicknesses W on both sides of the GB and the concentration of electrically active dopants N_G. If grains are not completely depleted, the potential barrier height is written as [5]

$$\varphi = \frac{eN_GW^2}{2\varepsilon}, \quad (2)$$

where ε is the permittivity.

It is known from the doping method [5] that the concentration N_G of the electrically active dopant is related to the concentrations N_D of implanted impurities. The implanted impurity concentration N_D decreases during heat treatment either due to direct evaporation or segregation on oxide layers which are etched in the next stages. Then N_G can become significantly lower than N_D due to losses and segregation on the GB. However, the active dopant concentration N_G before treatment can be comparable with the implanted impurity concentrations N_D.

Figure 1 shows the dependences of φ on the implanted impurity concentration N_D. We can see that an increase in N_D results in an increase the potential barrier height. In [7], it was ascertained that the height

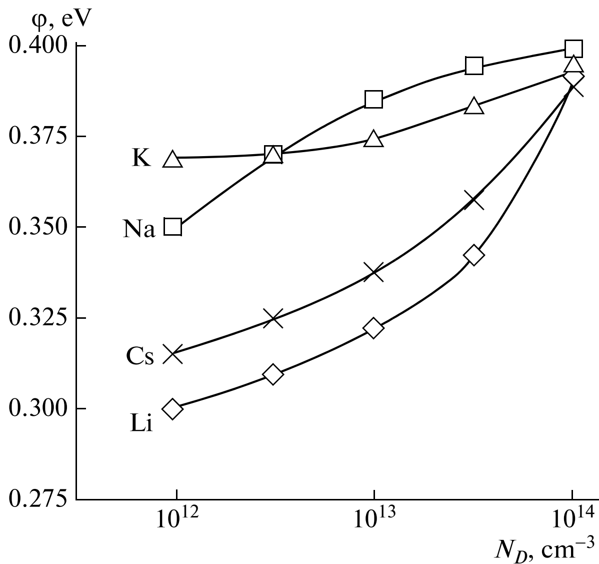

Fig. 1. Potential barrier heights of the grain boundaries of polycrystalline silicon as functions of the concentration of active dopants.

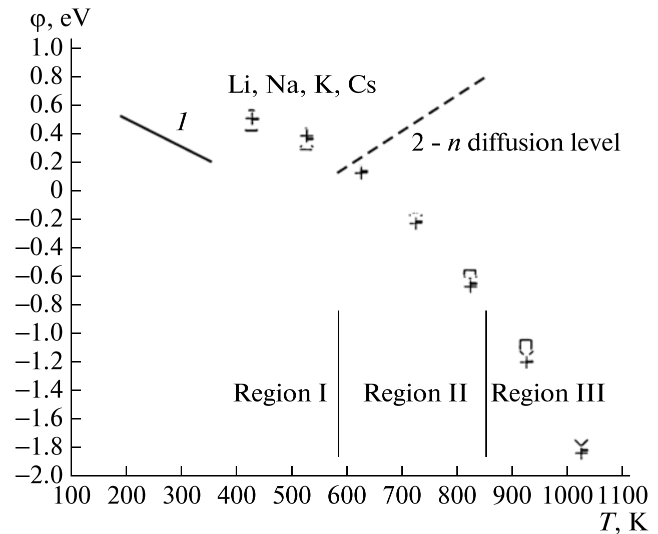

Fig. 2. Potential barrier heights of the grain boundaries of polycrystalline silicon as functions of heat treatment. Line *1* presents the results of [7].

of most barriers in PS at $N_D < 10^{14}$ cm^{-3} is $\varphi = 0.55$ eV. The barrier height depends on the doping level, and the trap and dopant concentrations (see, e.g., [7] and references therein). This change in height is caused by a double charge layer formed by ionized impurities and filled with traps. The width of this layer increases with the impurity concentration. In the case at hand, the potential barrier height is in satisfactory agreement with the results of [7], i.e., an increase in N_D results in simultaneous increases in N_G, and also W, and φ.

The data obtained in these studies show that the model with a double depletion layer and thermal excitation of charge carriers interprets well enough the nature of GBs in silicon [7]. The main conclusion of this study is that the barrier height depends also on temperature. The GB barrier height in PS varies linearly with temperature (as shown in Fig. 2, line *1*). The double layer's width and barrier height begin to decrease as traps are filled or passivated, whereas the total charge in this region remains unchanged [7]. In the case at hand, linear changes in the barrier height are identical to the results for region I at $T \leq 600$ K [7]. However, as the temperature increases (regions II and III at $T \geq 600$ K), the barrier height's sign changes.

It is known that AMs in silicon are donor impurities. In [1, 8], the formation of p–n structures based on PS and single-crystal silicon was experimentally determined using implanted AM atoms and heat treatment in the range of 700–800 K. In the case at hand, the possibility of the formation of p–n structures was estimated by measuring the current–voltage characteristic of the samples under study before and after II and after each heat treatment performed with a step of 50 K. The obtained results showed that the quality of electron–hole junctions depends strongly on the heat treatment temperature. Heat treatment causes a significant improvement of the rectifying property of the p–n junction at $T \leq 700$–800 K (Fig. 3). However, as the temperature was further increased, the diode characteristics of the samples under study deteriorated. This can be associated with AM diffusion along GBs; more specifically, metal–oxide or metal films are formed on the grain surface upon the adsorption of AM atoms on GBs in PS during diffusion, which causes grain growth and an increase in the potential barrier height [4]. Thus, in the case at hand, the change in the barrier height at $T \geq 600$ K (regions II

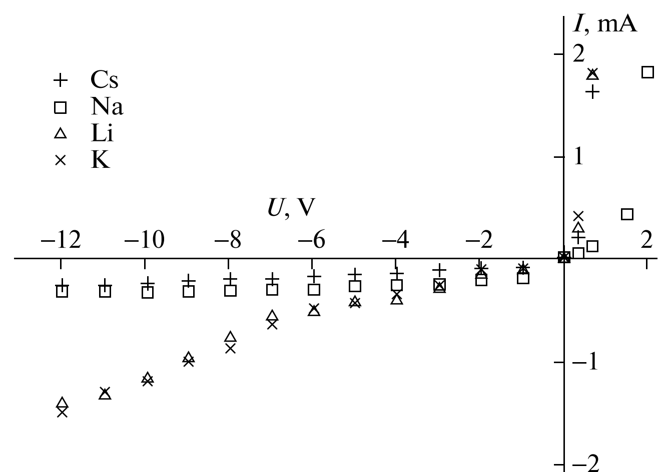

Fig. 3. Current–voltage characteristics of p–n junctions as functions of alkali metal types (heat treatment at $T = 750$ K).

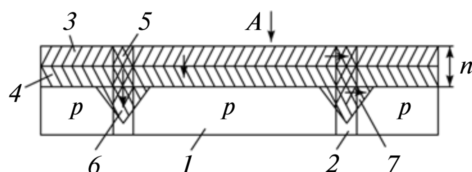

Fig. 4. Simplified representation of a sample portion: (*1*) *p*-type Si grains, (*2*) grain boundary regions, (*3*) ion-implanted layer of alkali metal atoms, (*4*) diffusion layer of alkali metal atoms, (*5*) desorption layer of alkali metal atoms in the GB region, (*6*) diffusion of alkali metals along grain boundaries, (*7*) adsorption layer of alkali metal atoms. *A* is the measured sample side.

and III) can be associated with the *n*-regions of *p*–*n* structures (Fig. 4, regions *3* and *4*), i.e., with the diffusion *n*-layers (Fig. 2, line *2*).

It is known that impurities in the bulk of PS-based structures diffuse over grains and GBs, as shown in Fig. 4 (regions *4* and *6*). Noteworthy are interesting phenomena: impurities in this process diffuse not only over grains and GB; simultaneously, as the temperature is increased to 800 K, the desorption of AM atoms from GB occurs, as is shown in Fig. 4 (region *5*). These processes result in an increase in the widths of the doped layers (regions *4* and *6*) and simultaneous AM segregation at the GB. In this case, dipole–dipole repulsion of impurities to the GB [3, 4] causes an increase in the potential barrier height of the *n*-region of the *p*–*n* structures. As the temperature is further increased, the change in the barrier height (region III in Fig. 2) is associated with the adsorption of AM atoms at GBs in the PS bulk, which we discussed in [4]. AM atoms mostly diffuse over GBs (Fig. 4, region *6*); this results in AM segregation at GBs and simultaneous adsorption on the grain surface (Fig. 4, region *7*).

Thus, an increase in the active dopant concentration, diffusion and desorption of AM atoms in the GB region on the PS surface leads to an increase in the potential barrier height. These results can be used to develop *p*–*n* structures based on polycrystalline semiconductors and to explain GBs' electrical properties.

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