CONDUCTIVITY REVERSAL IN SILICON DOPED WITH S AND Zn

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Abstract—Based on experimental results of investigation of type of conductivity of silicon samples doped with sulfur at \( T = 1250^\circ C \), and thereafter with zinc at \( T = 1200^\circ C \), the authors put forward the hypothesis about self-assembly of “binary” elementary cells where atoms of elements of group II (Zn) and IV (S) allegedly form ZnS-type compounds in Si. The thermodynamic conditions required for buildup of such elementary cells and assembly of various associations in the basic lattice of silicon including self-assembly of ZnS clusters were theoretically determined and experimentally justified.

Keywords— resistivity, silicon, sulfur, bonds, impurity atoms, chemical complex, binary complex, diffusion doping, cluster.

I INTRODUCTION

The phenomenon of self-buildup of clusters of alien atoms that interact with lattice defects in the crystal lattice of silicon is expected to be one of the likeliest techniques for the development of nanoscale structures.

The possibility of formation of clusters of impurity atoms in silicon is presently actively investigated by many researchers worldwide. The interest in engineering clusters of impurity atoms in silicon is pervasively motivated by the desire to develop nanosize structures, which in turn will have given the possibility to develop novel elements for micro- and nanoelectronics. Engineering clusters of various nature significantly depends on solubility, diffusion parameters of impurity atoms and thermodynamic conditions as well. However, virtually no significant research has been conducted over lately on the possibility to vary the parameters of such clusters.

Thus, of particular interest is the possibility to engineer impurity atoms in a Si crystal lattice, particularly, binary clusters of impurity atoms, being a new \( \text{Si}_2^3 \text{A}^n \text{B}^{8-n} \) unit cell (where A and B are impurity atoms which substitute the adjacent sites in the Si lattice and n is the number of the valence electrons).

Moreover, the formation of such unit cells in the silicon lattice could help engineer novel materials with novel parameters for electronics.

To be able to form “binary” unit cells in silicon the following conditions are to be met:

1. The sum of valence electrons of atoms A and B must be 8 to prevent the violation of the tetrahedral partially ion-covalent bond in the silicon lattice.
2. One of the A or B impurity atoms must have a sufficiently high diffusion coefficient; i.e., it must predominate to diffuse across interstitial positions thus rising probability of formation of the \( \text{A}^- \text{mB}^{+m} \) compound.
3. Both impurity atoms have to exhibit sufficient chemical activity to ensure buildup of compounds such as \( \text{A}^- \text{mB}^{+m} \).

Selecting proper elements from these groups and in view of their negativity, atomic size, solubility, and diffusion coefficients, Si\( \text{A}^n \text{B}^{8-n} \) unit cells could be assembled in Si lattice with changeable fundamental parameters which in turn could generate photon carriers for both \( h\nu < E_\text{g} \) and \( h\nu > E_\text{g} \) diapasons of light emission. This would considerably increase the spectral sensitivity range of silicon.

The production of photo cells based on these materials could help to replace “sandwich” \( \text{A}^{III}\text{B}^{V} \) and \( \text{A}^{II}\text{B}^{VI} \) photo cells and they can be called “silicon integral photo cells”.

II MAIN PART AND THE EXPERIMENT

With the aim to investigate peculiarities of the interimpurity interaction of sulfur with zinc in silicon, the silicon samples were doped with sulfur at \( T = 1250^\circ C \), and then sequentially doped with zinc at a temperature of 1200°C, while the same duplicate samples of Si \( <\text{P},\text{S}> \) and Si \( <\text{P},\text{Zn}> \) were also annealed for further comparative analysis of parameters (Table 1). These data show the exclusively acceptor nature of zinc in silicon at a low concentration of its electroactive atoms, which confirms the literature data [1, 2].
Zinc-doped Si<P,S> samples and Si<P,S> and Si<P,Zn> samples alike were subjected to annealing up to $T = 900^\circ$C and shortly thereafter had manifested practically the same properties and were of n-type conductivity with specific resistance almost $\rho \approx 100$ Ohm-cm. This trend manifests itself up to the annealing temperature $= 850^\circ$C (Table 1). These data can be explained by the decay of electroactive sulfur atoms and the low concentration of electroactive atoms of zinc in silicon. The samples of Si<P,S> ($= 1200^\circ$C), additionally doped with zinc at $= 720^\circ$C remain of p-type conductivity with $\rho \approx 28$ Ohm-cm. At the same time, the Si<P,S> samples annealed under the same temperature converse the conductivity type and become of n-type with a resistivity of $\rho \approx 1.45$ Ohm.cm. And at $T = 1200^\circ$C the Si<B,S,Zn> samples also change the type of conductivity and $\rho$ of these samples is 332 Ohm.cm, whereas $\rho$ of samples Si<P,S> begins to decrease, and only at $1250^\circ$C Si<P,S> and Si<B,S,Zn> samples manifest practically the same properties. Such significant changes in the properties of Si<P,S> at $T = 850^\circ$C could be explained by a sharp increase in the concentration of electroactive sulfur atoms in silicon, which was observed earlier in [3, 4]. However, it is not quite clear why such an effect does not happen in Si<B,S,Zn>. Moreover, in Si<B,S,Zn> samples (Table 1), the concentration of electroactive atoms of zinc, even at higher temperatures, is quite low and cannot compensate for the donor states of sulfur in silicon. And a further increase in the annealing temperature leads to an increase in the concentration of electroactive sulfur atoms and this concentration is greater than the total number of Zn atoms in Si, which will determine the properties of the material [5]. Thus, it could be believed that some sort of electrically neutral complexes form between zinc and sulfur whereby their concentration peaks at $T = 850^\circ$C.

The above experimental results suggest that sulfur and zinc atoms are located in adjacent sites of the silicon lattice, forming new unit cells like Si,ZnS (Fig. 1). In this case, the tetrahedral $sp^3$ hybrid bond is practically not broken, with new unit cells they will have a partially ionic-covalent bond, while the sulfur and zinc atoms in the silicon lattice do not act as classical impurity atoms, creating two donor and acceptor energy levels but instead morphing into $S^0$-e-$S^+/S^+/e-S^{++}$, $Zn^0$+e-$Zn^-/Zn^-+e-Zn^{--}$ thus generating sufficiently strong electric field and deformation around itself. The authors assume that assembly of Si-Zn$^{--}$S$^{++}$ unit cell is more propitious and beneficial in terms of thermodynamics of the process thus stimulating the buildup of such binary lattices in basic matrix [6].

The above hypothesis implies that we deal with somewhat two elementary cells in the silicon lattice (those of genuine silicon and those of Si-Zn$^{--}$S$^{++}$) which have starkly different properties, fundamental parameters, as well as a
band gap, etc. An increase in the concentration of S and Zn dopant atoms and thermal annealing at $T = 850^\circ C$ makes it possible not only to vary the concentration of new Si-Zn–S++sublattices, but also to form their various associations up to the formation of $Zn^-S^{2+}$ nanoclusters. This demonstrates that on the basis of such technological methods it is practically possible to obtain new materials based on silicon with tunable fundamental parameters. This is a practically new scientific direction in the field of semiconductor materials science. Therefore, the next task is to develop a technology that makes it possible to increase the concentration of impurities of Zn and S atoms in silicon (either by increasing their solubility or by inciting binds between atoms), as well as to develop optimal thermodynamic conditions that ensure participation of all introduced impurity atoms in the formation of binary unit cells, which make it possible to change their electro-physical and optical properties.

III Conclusion

Calculation of the electrostatic potential of the base matrix of Si and Si with an impurity cluster consisting of 3 tetrahedral Si2ZnS cells could help to reveal whether there is a noticeable change in the potential intensity at cell sites. Evidently, in the Si2ZnS cell itself, one could anticipate a charge transfer from S atoms to Zn atoms. Calculations might have proved that the Zn atoms at the sites eventually acquire a negative charge, and the S atoms acquire a positive charge, as a result of which the ionic component of the interatomic bond might arise, which would lead to a deviation of the angles and bond lengths from the correct geometric ones. In practice, the numerical calculation would confirm the hypothesis that instead of completing its structure to the most stable electronic configuration ... s2p6, in certain cases the chalcogen atom can also donate some of its electrons to form a quasi-stable configuration ... sp3. Also, due to the appearance of the ionic component of the bond, a noticeable change is expected to be building up in the form of the electrostatic potential of the structure with the Si2ZnS cell, which is caused by a change in the potential energy of the cell due to the appearance of a strong Coulomb field inside the cell.

If and when such a model calculation of the lattice parameters could be done, later study of such parameters as the charge state, and electrostatic potential in the silicon lattice of the diamond structure with a Si2ZnS cell could make it possible to predict somewhat different properties of crystalline silicon with various concentrations of such cells in the basic matrix.

REFERENCES


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