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MODEL OF BORON CLUSTERING IN SILICON

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The model of formation and dissolution of neutral boron clusters in silicon has been developed. Numerical calculations showed that the model proposed describes well the experimental data obtained for rapid thermal annealing. Agreement with experiment is observed for clusters incorporating a small number (2-3) of boron atoms. The assumption about the increasing rate of the reaction of cluster formation allows one to explain the experimentally observed phenomenon of the hole concentration saturation at a high doping level. The increase in the reaction rate is a result of the crystalline lattice deformation due to the mismatch between the boron and silicon atomic radii.

Keywords: boron, silicon, clustering, stresses, annealing.

Introduction

It is well known that low-energy high-dose ion implantation with the subsequent rapid thermal annealing is widely used for manufacturing modern ultra-large-scale integrated microcircuits (ULSI). During annealing, the defects created by ion implantation are avoided. Simultaneously, the redistribution of implanted impurity atoms occurs. It means that the final distribution of impurity atoms is determined by both the parameters of ion implantation and characteristics of impurity diffusion. Using ion implantation allows one to form highly doped layers with impurity concentration far above the solubility limit of impurity in silicon. It is worth noting that the formation of the clusters that incorporate impurity atoms occurs during thermal treatment of such implanted layers [1]. In the papers [2,3] the model of the charged cluster formation was proposed. It allows explaining the phenomenon of electron concentration saturation in silicon heavily doped with arsenic or phosphorus. It also explains why the saturation value of electron concentration n_e is significantly below the limit of impurity solubility in silicon C_{sol} [1]. It was shown in addition that this phenomenon could not be explained within the framework of the model of neutral cluster formation. On the other hand, according to the experimental data of [1], clustering of boron and antimony is also characterized by the saturation of concentration of charge carriers, namely, holes. However, it is impossible to explain this phenomenon by using the model of charged clusters, since the value of saturation for concentration of holes p_e is equal to the impurity solubility limit C_{sol} [1]. The goal of this investigation is to develop a model of the formation of neutral boron clusters that can explain the phenomenon of saturation of holes under the condition $p_e = C_{sol}$.

Model

Let us consider the formation of neutral clusters incorporating boron atoms and point defect. Then, the generalized equation of cluster formation and dissolution proposed in [2, 3] takes the following form:

$$mB^- + m_1 \mathrm{D}_1^{r_1} + ke^- \leftrightarrow \Phi + m_2 \mathrm{D}_2^{r_2}, \quad (1)$$

where D_1 is the point defect participating in the formation of the neutral cluster Φ and D_2 is another point defect generated in clustering; m, m_1, and m_2 are respectively the numbers of boron atoms and point defects D_1 and D_2 participating in cluster formation; k is the number of the electrons participating in reaction (1); r_1 and r_2 are the charge states of defects D_1 and D_2, respectively.

It is worth noting that the charge conservation law is valid for the reaction of neutral cluster formation (1):

$$m_1 z_1 - m - k = m_2 z_2 , \tag{2}$$

where z_1 and z_2 are respectively the charges of defects D_1 and D_2 in terms of the elementary charge.

For a quantitative description of boron clustering mediated by silicon self-interstitials, let us use reaction (1) in which the defect D_1 is silicon interstitial atom I. For simplicity, let us also assume that there is no generation of defects D_2 in the course of cluster formation. Then, it follows from the mass action law that

$$K_1 C^m \left(C^{Dr1}\right)^{m_1} p^{-k} = K_2 C^{AC} , \tag{3}$$

where C is the concentration of substitutionally dissolved boron atoms; C^{Dr1} is the concentration of defects D_1 in the charge state r_1; p is the concentration of holes; K_1 and K_2 are the rates of the direct and reverse reactions (1), respectively; C^{AC} is the concentration of impurity atoms incorporated into the clusters.

Let us determine the concentration of holes p from a local charge neutrality and the relationship $pn = n_i^2$. Then, the normalized concentration of charge carriers (holes) χ can be expressed as

$$\chi = \frac{p}{n_i} = \frac{C - C^B + \sqrt{\left(C - C^B\right)^2 + 4n_i^2}}{2n_i} , \tag{4}$$

where C^B is the concentration of donors; n_i is the intrinsic carrier concentration.

Let us calculate the concentration of charged defects $D_1^{r_1}$ as a function of the concentration of these particles in the neutral charge state $D_1^{\times}$ using the mass action law [4]:

$$C^{Dr1} = h^{Dr_1} \chi^{-zz_1} C^{D1\times} = h^{Dr_1} \chi^{z_1} C_{eq}^{D1\times} \tilde{C}_D^{\times} , \tag{5}$$

where $\tilde{C}_D^{\times} = C^{D1\times} / C_{eq}^{D1\times}$ is the concentration of point defects D_1 in the neutral charge state normalized to the thermally equilibrium concentration of these particles $C_{eq}^{D1\times}$; h^{Dr_1} is a constant of local equilibrium for the reaction of conversion of defects D_1 from a neutral charge state to a charge state r_1.

Substituting (4) and (5) into (3) allows one to obtain the concentration of impurity atoms incorporated into clusters:

$$C^{AC} = \frac{K_1}{K_2} n_i^{-k} \left(h^{Dr_1} C_{eq}^{D1\times}\right)^{m_1} \left(\tilde{C}_D^{\times}\right)^{m_1} \chi^{-k} \left(\chi^{z_1}\right)^{m_1} C^m = K \left(\tilde{C}_D^{\times}\right)^{m_1} \chi^{\left(z_1 m_1 - k\right)} C^m , \tag{6}$$

or, taking into account the charge conservation law (2),

$$C^{AC} = K \left(\tilde{C}_D^{\times}\right)^{m_1} \chi^m C^m , \tag{7}$$

where the constant of local thermodynamic equilibrium for the reaction of clustering has the following form: $K = \frac{K_1}{K_2} n_i^{-k} \left(h^{Dr_1} C_{eq}^{D1\times}\right)^{m_1}$.

The parameter K represents a constant value depending on the annealing temperature. This value can be obtained by fitting to experimental data. The dimensionless function $\tilde{C}_D^{\times}$ takes into

account the nonuniformity of distribution of point defects D_1 participating in cluster formation. It is worth noting that due to the mathematical manipulations performed, only the nonuniformity of the distribution of point defects in the neutral charge state is involved in expressions (6) and (7). This is very convenient for calculating cluster concentration because the internal electric field does not exert a direct influence on the diffusion of neutral point defects. Moreover, the last fact allows one to widely use the assumption of uniform distribution of neutral mobile defects.

Numerical calculations

In Fig. 1 the results of modeling boron clustering during low temperature annealing are presented. The set of equations (4) and (7) has been employed for calculations. The experimental data obtained in [5] are used for comparison. In [5], the implantation of boron ions with an energy of 1.5 keV and a dose of 3×10^{15} cm^{-2} was carried out in a silicon layer preliminary amorphized by implantating of Ge ions with an energy of 12 keV and a dose of 1×10^{15} cm^{-2}. The annealing was performed for the time of 1 min at a temperature of 850 °C. Measurement of the total boron concentration was carried out by SIMS, and the carrier concentration was obtained by spreading resistance profiling. The treatment of the experimental data of [5] allows us to obtain the values of the concentration of holes p as a function of the total boron concentration $C^T = C + C^{AC}$. This dependence is presented in Fig. 1 by filled black circles. The experiment on transient enhanced diffusion of boron implanted into silicon [5] was performed at a very low temperature for a short time of annealing. Therefore, it is reasonable to assume that in the case under consideration the initial stage of boron clustering is observed. Then, the number of boron atoms incorporated into a cluster is not large. Therefore, calculations were performed only for the clusters IB_2, IB_3, and IB_4. It is evident from Fig. 1 that for the cluster IB_2 good agreement is observed between simulation and experimental data. The value of the constant K used in these calculations was equal to 3.0×10^{-10} μm^3.

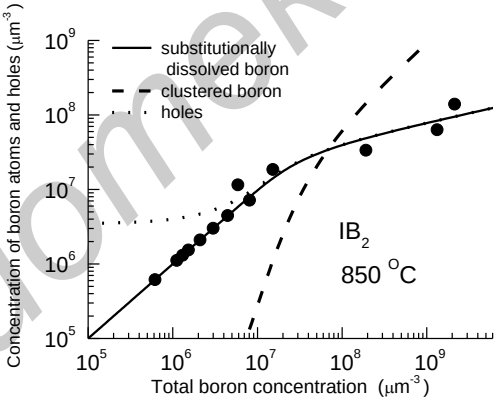

Fig. 1. Calculated concentrations of substitutionally dissolved boron atoms (solid line), clustered boron atoms (dashed line), and hole density (dotted line) against the total dopant concentration for the formation of neutral clusters, incorporating two boron atoms. The measured hole density (filled black circles) are obtained from Pawlak et al. [5] for diffusion at a temperature of 850 °C.

It is known from the experimental data [1] that the concentration of charge carriers (holes) increases with enhancement of boron doping level until saturation is reached at the value of $p_e = p_e(T) = C_{sol}(T)$. Thereafter, the density does not change with increasing impurity concentration. In the literature, it is attempted to explain the saturation of the concentration of holes by the formation of the neutral clusters incorporating a large number of boron atoms. Really, with increase in the number of impurity atoms incorporated into cluster, the curve $p = p(C^T)$, where C^T is the total boron concentration, become flatter. However, the saturation is not reached in principle. Therefore, to explain the hole density saturation for high boron concentrations, it is reasonable to analyze the crystalline lattice deformation that arises due to the substitutionally dissolved impurity atoms. Indeed, the atomic radius of the boron atom is equal to 0.095 nanometers (tetrahedral covalent

radius is equal to 0.089 nm), whereas for silicon the atomic and tetrahedral covalent radii are equal to 0.134 and to 0.117 nm, respectively. For arsenic and phosphorus, the atomic radii are equal to 0.140 and 0.130 nm, respectively (tetrahedral covalent radii are 0.117 and 0.110 nm, respectively). For antimony, the atomic radius is equal to 0.161 nm and the tetrahedral covalent radius is 0.135 nm [6]. It is evident from the data presented that the substitutionally dissolved boron and antimony atoms produce the greatest deformation in the crystalline lattice, although the generated stresses have an opposite sign. It is natural to explain the observed features of boron and antimony clustering based on the crystalline lattice deformation.

It is assumed in the paper that, as the concentration of impurity atoms approaches the solubility limit, the rate of direct reaction for cluster formation (1) increases. It means that the value of the quantity K in Eq. (7) increases significantly. It follows from [7] that the potential energy of a point defect in the field of elastic stresses is proportional to the concentration of impurity atoms. Then, taking into account [8], the constant of local equilibrium in expression (7) can be presented in the following form:

$$K = K_0 \exp\left[\frac{\alpha C}{C_{sol}}\right], \qquad (8)$$

where K_0 is the value of K in low-doped silicon; α is the dimensionless parameter.

In Fig. 2, the results of modeling boron clustering at a temperature of 1000 °C are presented. To calculate the presented curves, a set of Eqs. (4), (7), and (8) is used. It can be seen from Fig. 2 that there is good agreement between the results of calculation and experimentally obtained boron solubility limit. The following values of parameters were used for simulation: the number of boron atoms in a cluster $m = 3$; $K_0 = 5.0\times10^{-24}$ μm^6; $\alpha = 6$. The boron solubility limit in silicon at a temperature of 1000 °C $C_{sol} = 1.1857\times10^8$ μm^{-3} is taken from [1]. It is supposed that the cluster IB_3 under consideration is electrically neutral.

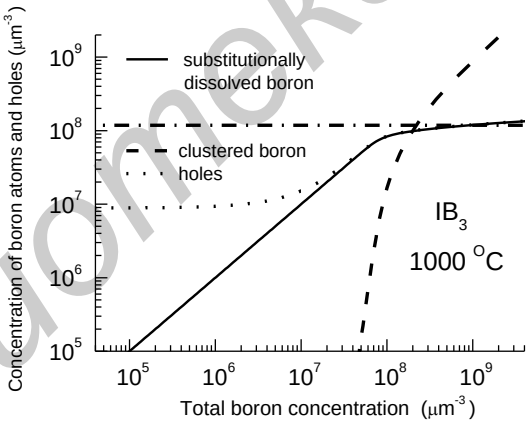

Fig. 2. Calculated concentrations of substitutionally dissolved boron atoms (solid line), clustered boron atoms (dashed line), and hole density (dotted line) against the total dopant concentration for the formation of neutral clusters, incorporating three boron atoms. The dash-dotted line is the boron solubility limit at a temperature of 1000 °C [1]

It is evident from the calculations performed that taking into account the deformation of the silicon crystal lattice as a result of doping with boron atoms allows one to describe the appearance of the boron solubility limit. It is possible to describe the boron solubility limit even under conditions of the formation of a cluster incorporating a few boron atoms. Thus, the developed model can be applied for modeling the doping processes used for shallow *p-n* formation by means of the low-energy high-dose ion implantation with the subsequent rapid thermal annealing when formation of small clusters occurs.

It is worth noting that the limit of boron solubility in silicon for a temperature of 850 °C is $C_{sol} = 4.88\times10^8$ μm^{-3} [1]. It can be seen from Fig. 1 that the concentration of electrically active boron and, respectively, the concentration of holes significantly exceeds the limit of boron solubility for the annealing temperature under consideration. Nevertheless, the phenomenon of the hole density

saturation is not observed. This contradiction can be easily explained within the framework of the clustering model proposed. Indeed, the formation of the preliminary amorphized layer due to the implantation of Ge ions does not only reduce the density of radiation defects and, respectively, the intensity of the transient enhanced diffusion but also results in the reduction of the crystalline lattice deformation in the layers doped with boron. It follows from the model proposed that the deformation reduction in turn increases the limit of boron solubility.

Conclusions

The model of formation and dissolution of neutral boron clusters in silicon has been developed. It is supposed in the model that the cluster formation occurs due to the interaction of impurity atoms with the intrinsic point defect. It follows from the calculations performed that the developed model describes well the experimental data in the case of rapid thermal annealing if the saturation of the hole density is not observed. It is interesting to note that numerical calculations agree well with experimental data for a cluster incorporating a small number of boron atoms. This fact is an additional evidence in favor of the correctness of the model proposed because the formation of large clusters during rapid thermal annealing is unlikely. To explain the saturation of the hole concentration in heavily doped layers, an additional assumption of the increasing rate of reaction of cluster formation is used in the model. This increase of the reaction rate results from the crystalline lattice deformation due to the mismatch between the boron and silicon atomic radii. The calculations performed clearly show that the account for the deformation allows one to explain the hole density saturation observed experimentally in ion implanted layers even for the formation of clusters incorporating a small number of boron atoms.

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References

1. *Solmi S.* Dopants in silicon: Activation and deactivation kinetics, in: Encyclopedia of Materials: Science and Technology / Ed. by K.H.J. Buschow Elsevier Science Ltd, 2001. P. 2331–2340.
2. *Komarov F.F., Velichko O.I., Dobrushkin V.A. et. al.* Mechanisms of arsenic clustering in silicon // Phys. Rev. B. 2006. Vol. 74 (3). Art. No. 035205.
3. *Velichko O.I., Sobolevskaya N.A.* // Nonlinear Phenom. Complex Syst. 2008. Vol. 11, № 3. P. 316–386.
4. *Velichko O.I., Fedotov A.K.* // Nonlinear Phenom. Complex Syst. 2003 Vol. 6, № 2. P. 607–618.
5. *Pawlak B.J., Lindsay R., Surdeanu R. et al.* // J. Vac. Sci. Technol. B. 2004. Vol. 22, № 1. P. 297–301.
6. *Ормонт Б.Ф.* Введение в физическую химию и кристаллохимию полупроводников / Под ред. В.М. Глазова. М., 1982.
7. *Landi E. Guimaraes S., Solmi S.* Influence of nucleation on the kinetics of boron precipitation in silicon // Appl. Phys. A. 1987. Vol. 44. P. 135–141.
8. *Höfler A., Feudel Th., Strecker N. et al.* // J. Appl. Phys. 1995. Vol. 78, № 6. P. 3671–3679.