Abstract. In this work, the gettering process in the multicrystalline Si wafers by the combined getter structures of the porous Si and Al layers during annealings at temperatures 600 up to 750 °C has been theoretically studied. A kinetic model based on the diffusion equation has been developed, and the characteristics of increase in the minority charge carrier diffusion length as a result of gettering annealings have been determined. The obtained results are useful for technology of multicrystalline Si solar cells to improve their properties.

Keywords: gettering, multicrystalline Si, diffusion problem, combined getter.

1. Introduction

In crystalline Si solar cell technology, a great attention is given to the control over the recombination active metal impurities that cause degradation of the lifetime inherent to minority charge carriers in Si wafers. These impurities are present in initial Si material as well as can be additionally incorporated during technological wafer processing [1]. Among especially deteriorating metal impurities, there are transient metals, namely: iron, chromium, gold as well as heavy metals such as vanadium, molybdenum, wolfram, and titanium, which affect the characteristics of p-type Si used for solar cell production already at the concentrations as low as $10^{12}$ – $10^{14}$ cm$^{-3}$ [2, 3].

To reduce the concentration of metal impurities in Si wafers, the gettering procedures are included in technological routes of solar cell production. Increase of the lifetime of minority charge carriers is required over the entire Si wafer thickness. Therefore, external getters are mostly used in solar cell technology, in particular, the Al layer getters deposited onto the back side of Si wafers [1]. The gettering effect is obtained due to the several orders of magnitude higher solubility of metals in Al than in crystalline Si. A decrease in the metal concentration in Si takes place due to metal diffusion in the wafer and its capture by the getter during annealings at elevated temperatures.

Earlier, we have suggested the modified getter structure that consists of porous Si with Al layer deposited on its top (combined getter) [4, 5]. For multicrystalline Si wafers, this structure has demonstrated better performance as for the improvement of the recombination properties of minority charge carriers (increase in their diffusion length and lifetime) comparing to the traditional Al getters. In this work, we theoretically analyze the kinetics of gettering by the combined getter structures in the multicrystalline Si wafers in the framework of diffusion model and determine the respective process characteristics.

2. Experimental

We used the p-type multicrystalline Si wafers with the resistivity of 10 Ohm·cm and the average grain size of 10 µm. Bilayer getter structures were formed on the back side of wafers by using the stain chemical etching in the decorating solution HF:HNO$_3$:H$_2$O=1:X:1 (X ranging from 0.001 to 10% by volume) with subsequent Al deposition onto the etched porous Si surface by vacuum thermal evaporation. The thicknesses of porous Si and Al layers were within the range 0.5 up to 1 µm.

Si wafers with created getter structures were annealed in Ar atmosphere at the temperatures 600 up to 950 °C for 30 min. The gettering effect was controlled by measuring the diffusion length of minority charge carriers.
carriers by using the capacitor photovoltage method [6] before and after annealings. Shown in Fig. 1 is the experimental temperature dependence of the relative diffusion length for minority charge carriers in the multicrystalline Si wafers. As can be seen from the figure, there are two branches of this dependence. The gettering effect is enhanced with increasing the annealing temperature up to about 750 °C (increase in the minority carrier diffusion length) and is weaker at higher temperatures due to saturation of getter and its decreasing capacity with respect to Si wafer [1, 7]. We used the low temperature data of this dependence \( T \leq 750 \, ^{\circ} \text{C} \) for the description in the framework of theoretical model and determination of the characteristics of gettering process in the multicrystalline Si wafers with the combined getter structures of porous Si and Al layers.

3. Model

In the framework of diffusion model, the kinetics of evolution of the concentration of recombination active metal impurity in Si wafer during gettering annealings is described by the equation of the second Fick law as follows:

\[
\frac{\partial C_{\text{imp}}}{\partial t} = D_{\text{imp}} \frac{\partial^2 C_{\text{imp}}}{\partial x^2}. \tag{1}
\]

Here, \( C_{\text{imp}} = C_{\text{imp}}(x, t) \) is the concentration of recombination active metal impurity in the Si wafer and \( D_{\text{imp}} \) is its diffusivity.

Solution of Eq. (1) requires additionally the boundary and the initial conditions. The boundary condition on the front (getter free) wafer surface \((x = 0)\) is composed taking into account zero impurity flow through the wafer surface:

\[
\frac{\partial C_{\text{imp}}(0, t)}{\partial x} = 0. \tag{2}
\]

The boundary condition on the back side of Si wafer \((x = d_{Si}, d_{Si} \text{ being the Si wafer thickness})\) describes the kinetics of impurity capture by the getter. We have simplified the problem for the actual experimental conditions. Fig. 2 shows the calculated temperature dependences of the residual iron concentration in Si wafers annealed for 30 min at different Al getter thicknesses [7]. One can see that the gettering effects caused by the 0.5 to 3 µm thick Al layers have almost no difference as compared to the effect from infinite getter in the temperature range 600 to 750 °C. The gettering process for a given annealing time and mentioned (and higher) Al layer thicknesses within the temperature range 600 to 750 °C is controlled by the kinetics of impurity supply to the getter and not by the getter capacity with respect to Si wafer. Therefore, the getter can be considered infinite in our problem and the boundary condition on the back side of Si wafer acquires the following form:

\[
C_{\text{imp}}(d_{Si}, t) = 0. \tag{3}
\]

It should be noted that the approximation used here is valid without restrictions for thicker getters and shorter annealing times, whereas its validity for thinner getters and longer annealing times has to be verified.

The initial condition determines the impurity concentration in every point of Si wafer before gettering annealings. Assuming the homogeneous impurity distribution \( C_{\text{imp}}(x, 0) = C_{\text{imp}}^0 \).

The solution of diffusion problem (1)–(3) is significantly simplified using the normalized quantities:

\[
\frac{\partial \nu}{\partial \theta} = \frac{\partial^2 \nu}{\partial \xi^2}, \tag{4}
\]

where \( \nu = \nu(\xi, 0) = \frac{C_{\text{imp}}}{C_{\text{imp}}^0} \) is the normalized impurity concentration.
concentration, \( \xi = \frac{x}{d_{Si}} \) coordinate, and \( \theta = \frac{D_{imp}}{d_{Si}} t \) time, respectively. The boundary conditions (2) and (3) for the normalized problem acquire the following form:

\[
\frac{\partial v(0, \theta)}{\partial \theta} = 0
\]

\[
v(1, \theta) = 0
\]

and the initial condition for the system (4)–(6) is written as \( v(\xi, 0) = 1 \).

To compare the calculation results with experimental data, the latter were transformed as follows. For the lifetime of minority charge carriers in Si wafers, the following relation is valid [8]:

\[
\frac{1}{\tau} = \frac{1}{\tau_g} + \frac{1}{\tau_{ng}}, \quad (7)
\]

where \( \tau, \tau_g, \) and \( \tau_{ng} \) are the determined minority charge carrier lifetime, the lifetimes in gettered and non-gettered samples, respectively. The lifetime in the gettered ones results from heavy metal impurities that can be removed by gettering. The lifetime in the non-gettered ones results from recombination of minority charge carriers with defects inside the Si wafer as well as on the front and back wafer sides. It cannot be improved by gettering.

The lifetime of minority charge carriers after gettering is inversely proportional to the heavy metal impurity concentration, capable of being removed (and, hence, to its normalized concentration), \( C_{imp} \sim v \sim \frac{1}{\tau_g} \).

From this

\[
C_{imp} = \text{const} \left( \frac{1}{\tau} - \frac{1}{\tau_{ng}} \right), \quad (8)
\]

Since \( \tau_g << \tau_{ng} \) in the multicrystalline Si, \( C_{imp} \sim v \sim \frac{1}{\tau_g} = \frac{D}{L_D^2} \), where \( D \) is the diffusivity and \( L_D \) is the diffusion length of minority charge carriers, respectively. So, the ratio of the concentrations of impurity atoms after and before gettering annealings of multicrystalline Si wafers can be considered as equal to the ratio of the squares of the diffusion lengths of minority charge carriers measured before and after gettering:

\[
\frac{C_{imp}}{C_{imp}^{\text{before}}} = v = \frac{L_{D0}^2}{L_D^2}, \quad (9)
\]

with \( L_{D0} \) and \( L_D \) being the diffusion lengths of minority charge carriers before and after gettering, respectively.

The results of calculations were compared to the experimental data in the following way. Eq. (4) with the boundary conditions (5) and (6) was solved numerically. The values of normalized impurity concentrations in all spatial mesh points as well as its total value for all the points were calculated at every time step. The ratio of the total normalized impurity concentration at a given time step to its value before gettering was compared to the experimental value of the ratio of the squares of minority charge carrier diffusion lengths before and after annealing at a given temperature. The calculation process was continued until the coincidence of these mentioned values. The normalized time of this event was fixed for every annealing temperature. Using the values of \( \theta^0 \) as well as the experimental annealing time \( t^0 = 30 \) min and the Si wafer thickness \( d_{Si} = 300 \) \( \mu m \), the values of \( D_{imp} \) for each temperature were calculated using the formula:

\[
D_{imp} = \frac{d_{Si}^2}{t^0} \theta^0. \quad (10)
\]

The obtained values of \( D_{imp} \) were fitted using the typical Arrhenius dependence on the temperature:

\[
D_{imp} = D_{imp}^0 \exp \left( \frac{E_d}{kT} \right),
\]

and the values of \( D_{imp}^0 \) and \( E_d \) the pre-exponential term and the activation energy of diffusion process describing the kinetics of gettering in the multicrystalline Si wafers by the combined porous Si/Al structures were determined from this fitting.

The advantage in formulation of the diffusion problem in the form (4)–(6) is the independence of solution on the impurity type, its initial concentration, and the annealing temperature. The independence on the impurity type is stipulated by the absence in Eq. (4) of the terms that explicitly contain certain impurity characteristics (such as, e.g., the impurity diffusivity and solubility). By analogy, the absence of terms with explicit temperature dependence makes the solution to be independent of changes in the annealing temperature, and only one run of calculations is required. The independence of the initial impurity concentration is stipulated by that we deal with only the ratios of concentrations before and after the gettering and not with their absolute values.

4. Results and discussion

Modelling results enabled to determine the parameters of the diffusion problem describing the gettering process in the multicrystalline Si wafers by the combined getters of porous Si and Al layers during annealings at the temperatures 600 to 750 °C. Fig. 3 shows the temperature dependence of the values of diffusion coefficients in the problem calculated using the expression (10) as well as the result of approximation of these values by using the Arrhenius dependence. One may see that the calculated diffusivity values are well fitted by the straight line in the semilogarithmic coordinates that allows one to conclude that the gettering kinetics at the temperatures under consideration can be described by the diffusion process with the following
Fig. 3. Temperature dependences of diffusion coefficients of problem calculated by formula (10) (dots) and the dependences of the diffusion coefficients of main recombination active metal impurities in Si: 1 – titanium, 2 – vanadium, 3 – chromium, 4 – iron, 5 – manganese, and 6 – gold.

Fig. 4. Calculated temperature dependences of the relative diffusion length of minority charge carriers after various times of gettering annealings of multicrystalline Si wafers with porous Si/Al getter structures.

Besides, Fig. 3 also presents the temperature dependences of aromatic impurities in Si [9, 10]. As may be seen from this figure, the aromatic impurities of typical metals in Si do not correspond to $D_{imp}$. This means that the physical mechanism of gettering in the multicrystalline Si wafers with using the combined porous Si/Al getters cannot be regarded as plain diffusion of the interstitial impurity of one type but corresponds to a more complex process.

Secondary ion mass spectrometry found out several main types of metal impurities in the multicrystalline Si wafers at the concentrations that lead to significant deterioration of their recombination properties [3]. These impurities are titanium, vanadium, chromium, iron, manganese, and gold. The concentrations of them also exceed their solubilities at the gettering temperatures that leads to the impurity precipitation and formation of complexes with other atoms and defects (such as, e.g., Fe–B pairs). For the gettering effect, the metal atoms should be released from the complexes and precipitates in the interstitial state, in which they diffuse to the getter and are captured there. It is highly probable that in the multicrystalline Si wafers all the abovementioned impurities participate in the gettering process interacting with a number of capturing centres and precipitates. The modelling parameters determined in this work are therefore some effective parameters that do not characterize certain physical mechanism or impurity but the gettering process as a whole. They enable to predict the relative diffusion length of minority charge carriers for different thicknesses of porous Si/Al getters and annealing times of multicrystalline Si wafers. As the example, Fig. 4 shows the calculated temperature dependences of the relative diffusion length of minority charge carriers for different times of gettering, if assuming the condition (3) is valid. The obtained results can be used in technology of multicrystalline Si solar cells with improved performances.

5. Conclusion

In this work, we have theoretically studied the kinetics of the gettering process in the multicrystalline Si wafers by the combined getter structures of porous Si with Al layers as a result of annealings at the temperatures 600 to 950 °C. The gettering effect is enhanced for the temperatures up to about 750 °C when the process is governed by the impurity supply to the getter and not by the getter capacity. In this range, the process under consideration can be described using the diffusion model, which enables to determine its characteristics. The obtained results are important to improve recombination properties of multicrystalline Si solar cells.

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References


