OPTO-ELECTRONICS REVIEW **8**(4), 410–413 (2000)

Development of gettering processes for the preparation of the solar silicon material

A.A. EFREMOV, N.I. KLYUI, V.G. LITOVCHENKO, V.G. POPOV,
A.B. ROMANYUK, and B.N. ROMANYUK*

Institute of Semiconductor Physics, National Academy of Sciences
45 Prospect Nauki Str., 252028 Kiev, Ukraine

A number of gettering treatments of Cz-Si wafers have been investigated. The characteristic parameters of the wafers have been measured. Among the procedures used, the gettering treatment, which included deposition of Ge film, followed by ion beam mixing and thermal annealing was preferred. This treatment allows to increase the diffusion length (L_d) of non-equilibrium carriers from 25–30 µm to 100–300 µm. The subsequent thermal treatments did not lead to deterioration of L_d as it took place for the wafers without gettering treatments.

Keywords: gettering, solar cell, ion implantation, silicon, diamond-like film.

1. Introduction

It is well known that oxygen in Si can beneficially or adversely influence material properties in dependence on growth technology, temperature treatments, and presence of carbon [1]. We have shown [2] that some thermal treatments of Cz-Si result in change of the state of dissolved in crystal oxygen and influence recombination properties of the material. The effect revealed is especially interesting for application to material that is destined for solar energy converters. In this material the large carrier lifetime τ_v increases the collection coefficient of carriers generated by light of infrared spectral range.

In this work, the investigations of evolution of the diffusion length (L_d) of non-equilibrium carriers, that characterises recombination activity of materials subjected to different thermal and gettering treatments, have been carried out. In various gettering methods the different mechanisms of removal and capture of recombination centres occurred, namely, segregation, injection of point defects, passivation of recombination centres [3].

2. Investigated samples and experimental methods

The investigated Si material was grown by the Czochralski method. From the available Si samples the (100) boron-doped wafers with a diameter of 100 mm were chosen for experiments. Two batches of wafers were used:

- initial wafers, that were not passed through preliminary technology treatments,
- wafers after epitaxial growth and removal of surface layer.

For the samples from the second batch the thickness of the removed layer was 20 µm. The operations of chemical-mechanical polishing and chemical etching using conventional technology procedures were performed. The wafers additionally passed through thermal annealing at the temperatures ranged from 750 to 1200°C for 30 min., rapid thermal annealing at the same temperatures for 10–50 s, and thermal oxidation at T = 1050°C in O_2 ambient.

The effect of different getter layers formed on the backside of the wafers was studied. The following treatments were used:

#1 – H^+ implantation ($E = 150$ keV, $D = 3\times10^{16}$ cm^{-2}),
#2 – Ar^+ implantation ($E = 150$ keV, $D = 3.6\times10^{16}$ cm^{-2}),
#3 – C^+ implantation ($E = 100$ keV, $D = 1.8\times10^{16}$ cm^{-2}),
#4 – deposition of Al layer (d = 100 nm),
#5 – deposition of Al layer followed by Ar^+ implantation,
#6 – deposition of Ge layer (d = 100 nm),
#7 – deposition of Ge layer followed by Ar^+ implantation,
#8 – doping by phosphorus;
#9 – growth of the porous silicon layer followed by Al layer deposition.

For the front-side gettering the CVD deposition of diamond-like carbon film have been used (treatment #10). After the getter layer forming the samples were annealed in Ar ambient at T = 900 C for 2 hours (for treatments #9 and #10 the temperatures have been varied, see Figs. 1 and 2). The L_d parameter was measured using spectral dependence of surface photovoltage [4].

---

* e-mail: romb@isp.kiev.ua

3. Experimental results

Initial samples of Cz-Si had the mean L_d value of 200 μm, while the wafers after the epitaxial growth stage have L_d = 30 μm. After oxidation of the wafers from batches 1 and 2, the L_d value falls down to about 70 μm (1st batch) and 25 μm (2nd batch). The L_d value also decreases after rapid and slow thermal annealing in the neutral ambient. At the temperature 900°C, small increase in L_d is observed whereas at other temperatures we observe the effect of L_d decrease. The mean L_d values for wafers, before the gettering and after different getter treatments, followed by additional thermal annealing at 900°C (30 min.) are presented in Table 1. It can be seen that the presence of the getter layer as a rule leads to increase in L_d value the for batch 2 samples and prevents L_d degradation after the subsequent annealing for the wafers with a large L_d value (batch 1).

The samples with getter of "por-Si + Al", are of special interest because of the relatively low gettering temperature (~750°C) (see Fig. 1). The temperatures like that are used nowadays in the modern technologies of the IC and solar cell manufacturing.

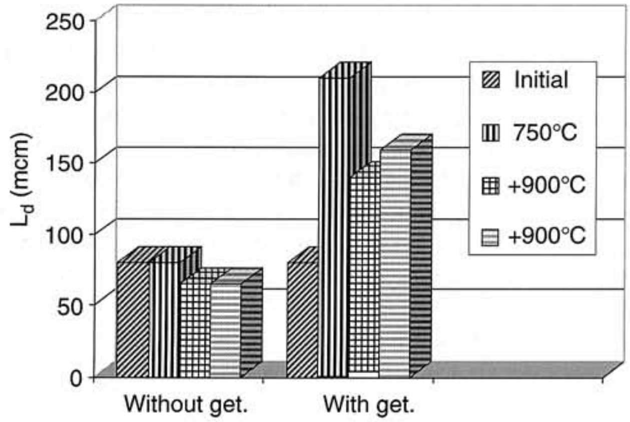

Fig. 1. L_d values for gettering by por-Si + Al, for the consecutive (30 min.) thermal annealing, compared with initial (without getter) samples.

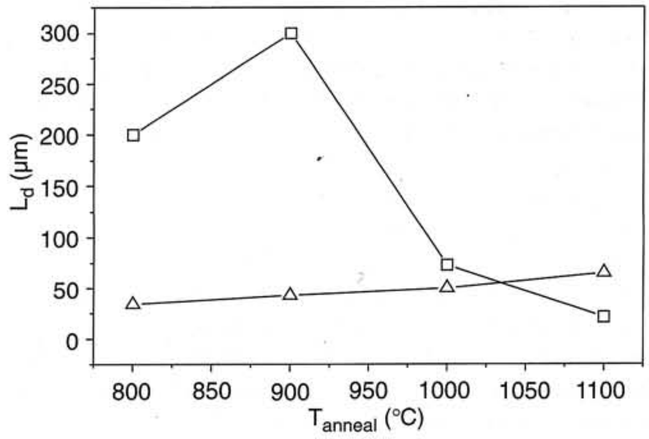

Fig. 2. Dependence of diffusion length on temperature of thermal annealing in the wafers covered by DLC film. Triangles – initial wafer with low L_d; squares – initial wafer with high L_d.

The L_d values for Si wafers with DLC front getter and subjected to post growth thermal annealing are presented in Fig. 2. It can be seen that for the wafers with the low initial L_d value (subjected to thermal annealing prior to the DLC deposition process) only slightly depends on the annealing temperature (triangles in Fig. 2). At the same time, for the wafers with the high initial L_d value marked gettering effect is observed being dependant on the annealing temperature (squares in Fig. 2).

4. Discussion

The L_d value is determined by:

- recombination-active impurities,
- microprecipitates of impurities and oxygen,
- defects of various characters.

Recombination processes in Si related to SiO_x precipitates intricately depend on annealing conditions and wafer characteristics [1]. They are determined by the availability of recombination centers at "SiO_2- Si precipitate" interfaces and positive charge built in the SiO_2 phase.

Precipitation kinetic depends on many factors, namely, oxygen concentration, presence of nucleation centres (carbon, vacancy-related clusters), temperature and sequence of annealing, concentration of point and linear defects, value of mechanical stress. Microprecipitate growth/decay processes are determined by the value of precipitate critical radius R_c, that is a complex function of the factors mentioned above [5]. Precipitates of $R < R_c$ will decay while those of $R > R_c$ will grow at a given temperature. Let us consider at first the results on gettering for the wafers of the batch 1.

Table 1. Values of L_d parameter (in μm) for gettering treatments, followed by the subsequent thermal annealing (excepted the #10 getter; these data are without additional annealing). The L_d values for the samples before gettering and heat treatments are in parentheses.

Treatment	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	Without getter
Batch 1	190 (180)	170 (190)	50 (170)	260 (200)	270 (200)	50 (180)	200 (180)	30 (190)	180 (80)	300 (100)	70 (200)
Batch 2	47 (30)	55 (30)	60 (34)	48 (28)	60 (28)	25 (30)	100 (26)	25 (25)	–	60 (31)	25 (23)

As it is known, after implantation of Ar^+ ions and thermal annealing of Si structures, the extended defects are created, that actively getter metal impurities [6]. So, the L_d increasing for Ar^+ implanted samples is a consequence of the metal impurity gettering, entered into Si during annealing.

Implanted hydrogen creates microvoids which getter metal impurities [7]. Moreover, hydrogen diffusing inside a crystal passivates inner "SiO_2 precipitate-Si" interfaces. The L_d increase (comparing to oxidised samples without getter) after H^+ implantation is a result of passivation of these interfaces. It, in its turn, prevents the metal impurity accumulation at interfaces. Besides, hydrogen can substitute metal atoms at the "SiO_2 precipitate-Si" interfaces, that enhances recombination activity as well.

Aluminium getters metal impurity owing to Al-Si eutectics formation, which enables ones to obtain the high L_d values. Germanium, introduced in Si by ion mixing leads to Si_i generation and prevents the SiO_2 precipitate growth as well as stimulates precipitate decay. Precipitate decay is accompanied by their release from an impurity atmosphere. Metal atoms, releasing from microprecipitates are gettered by the defects, which arise at the Si-SiGe interface. Effect of gettering is vanished without ion mixing because of SiGe solid solution absence. The absence of interstitial-type point and gettering defects is responsible for low gettering efficiency as well.

As it is known, carbon is not effective for the metal gettering because of its passivation by oxygen in Cz-Si [8]. At the same time it is possible to getter oxygen to decrease its supersaturation in Si volume and to retard the precipitate growth using this method. However, it demands the special thermal treatments [9], that were not used in this work.

The main mechanisms of the "por-Si+Al" getter action, as our results (Fig. 1), and computer modeling show, are the mechanical stresses and the inner interfaces action. Only for the temperatures above 900°C the Al-Si eutectics takes place in the recombination-active impurity immobilisation.

Let us now consider the results of gettering for the 2nd batch samples. These wafers were oxidised before gettering to imitate the solar cell fabrication technological process. This resulted in a decrease in L_d value which remained practically unaltered for the wafers without getters after subsequent annealing at $T = 900°C$. Low L_d values obtained after this process are connected with dissolution of the most of precipitates and releasing of metal impurities trapped by them. It enhances the recombination activity of metal atoms.

Nonequilibrium charge carriers recombine both at "SiO_2 precipitate-Si" interfaces and at deep centres formed by metal impurities. Since duration of gettering annealing is relatively low, the precipitate dimensions are small. So, in spite of their interaction with metal atoms, the latter does not lose recombination activity, but only decrease their mobility. Only the largest precipitates surrounded by dislocation loops can act as effective gettering centres.

Similarity in the $L_d(T)$ dependencies for rapid and "slow" annealings indicates that recombination activity is controlled by the SiO_2 precipitate growth/decay processes and by interaction of precipitates with metal impurities, but not by possible gettering at the surface of a wafer or impurity contamination from the atmosphere.

Mechanisms of the L_d value reduction due to oxygen precipitation may be various:

- decrease in specific component of internal interfaces when the size of SiO_2 precipitates increases,
- increase in positive charge, built in the SiO_2, that excludes a part of recombination-active centres,
- plastic processes that take place near the high-dimension precipitates.

Action of aluminium is connected with the gettering of a part of metal impurities, not bounded to dislocation loops.

Germanium film subjected to ion-beam mixing causes considerable compressive stresses in the bulk of a wafer, which can result in interaction of dislocation loops, coalescence, and sliding in the direction of stress gradient, up to attaining the surface. This mechanism should be analysed in more detail. Besides, this gettering treatment causes injection of interstitial Si atoms, which prevent growth of SiO_2 precipitates or enhance their dissolution.

In the wafers with high concentration of large SiO_2 precipitates significant mechanical stresses are generated at the SiO_2 precipitate/Si matrix interfaces. As a result partial dislocations arise being gettering centers for recombination active impurities. The impurities are accumulated at the precipitates and L_d value is determined by distance between the precipitates. In this case, the DLC getter is not effective (triangles in Fig. 2) because of passivation of dangling bonds by the impurities. Besides, for the wafers from the batch 2 the concentration of the impurities is much higher (low L_d) than that for the batch 1 (high L_d). For the wafers from the batch 1 due to low concentration of the impurities the recombination processes are probably determined by dangling bonds at the SiO_2 precipitate/Si matrix interface. In this case, the DLC getter is much more effective (squares in Fig. 2) due to hydrogen diffusion from the film into Si wafer and passivation of dangling bonds. It should be also noted that hydrogen diffusion from a DLC film is more effective than that from hydrogen ambient during conventional thermal annealing. It is likely connected with plasma removal of SiO_2 layer from the wafer surface during plasma etching before and during CVD process. The SiO_2 layer inhibits hydrogen diffusion into the wafer from hydrogen ambient during conventional thermal annealing in hydrogen atmosphere.

References

1. V.M. Babich, N.I. Bletskan, and E.F. Venger, *Oxygen in Silicon Monocrystals*, Interpress Ltd, Kiev, 1997.
2. I.P. Lisovski, V.G. Litovchenko, and V.B. Lozinski, "Properties of silicon monocrystals with oxygen impurity sub-

jected to long-time thermal treatments," *Ukr. Phys. Journ.* **39**, 68–73 (1994).

3. M.L. Polignono, G.F. Cerofolini, H. Benderx, and C. Claeys, "Gettering mechanisms in silicon," *J. Appl. Phys.* **64**, 869–876 (1988).
4. V.A. Zuev, A.V. Sachenko, and K.B. Tolpygo, *Nonequlibrium Near-Surface Processes in Semiconductors and Semiconductor Devices*, Sov. Radio, Moscow, 1977.
5. C. Claeys, and J. Vanhellemont, "A theoretical study of the critical radius of precipitates and its application to silicon oxide in silicon," *J. Appl. Phys.* **62**, 3960–3967 (1987).
6. T.E. Seidel, R.L. Meek, and A.G. Cullis, "Direct comparison of ion-damage gettering and phosphorus-diffusion gettering of Au in Si," *J. Appl. Phys.* **46**, 600–609 (1975).
7. J. Wong-Leung, C.E. Ascheron, and M. Petravic, "Gettering of copper to hydrogen-induced cavities in silicon," *Appl. Phys. Lett.* **66**, 1231–1233 (1995).
8. H. Wong, N.W. Cheung, and P.K. Chu, "Gettering of gold and copper with implanted carbon in silicon," *Appl. Phys. Lett.* **52**, 889–891 (1988).
9. B.N. Romanyuk, V.G. Popov, and L.G. Litovchenko, "Mechanisms for oxygen gettering in silicon plates with a nonuniform stress distribution," Semiconductors 29, 87–90 (1995).