DIFFUSION OF HYDROGEN FROM PLASMA SOURCE BY GRAIN BOUNDARIES IN EFG SILICON

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Diffusion of atomized hydrogen along grain boundaries (GBs) studied by transformation of their electrical activity in p-type silicon bicrystalline samples cut from EFG silicon crystals was investigated. The changes in electrical activity of GBs was estimated relative to both minority (MiC) and majority (MaC) carriers and demonstrated the correlation between the type, structure and thermal pre-history of GBs. It was shown on the base of this study that diffusion along GBs depends essentially on three factors: type of GBs, state of ribbons (as-grown or annealed) and concurrence of grain boundary dangling bonds and boron passivation effects. The model of the longitudinal hydrogen diffusion that explains these results is proposed.

Introduction

The performance of devices manufactured on the base of polycrystailine silicon is strongly dependent on the electrical activity of GBs. A great effort has been dedicated to the passivation of GBs in order to improve electronic properties of poly-Si. Heat treatment in different ambients and hydrogenation, typically from a plasma sources, are usually used for this goal. Recently almost all research works related to hydrogen passivation of GBs were focused on optimization of the hydrogenation conditions. And GBs were believed to act as diffusion pipes for hydrogen causing enhanced GB diffusion (e.g. [1]). However when comparing hydrogen diffusion in silicon single crystals with its diffusion in poly-Si it has been often found that GBs act as efficient sinks for hydrogen effectively reducing the GB diffusivity [2,3]. So, all these observations indicate that hydrogen diffusion in poly-Si is a very complex phenomenon. In particular, the consequences of hydrogenation of poly-Si should greatly depend on the relation between hydrogen diffusivities along GBs and in the grain bulk. We believe that this relation in turn should depend on such factors as the state of poly-Si (growing technique and thermal pre-history), type of GBs (their atomic structure and density of deep interfacial traps), nature of interfacial states and their distribution over GB plane, etc. [4]. To understand diffusion in poly-Si and its effect on passivation of GBs in poly-Si, we should subdivide all the above mentioned factors by their relative influence. Here we present the results of study which can shed a new light on the problem of hydrogen diffusion along GBs in poly-Si and changes in their electrical activity under subjection to the low-energy hydrogen plasma treatment.

I. Experimental

The studied bicrystalline samples with GBs of different types were cut from boron-doped 0.8-1.2 Ω·cm silicon ribbons grown by the Edge-defined Film-fed Growth (EFG) technique [4-6]. The large-grained structure of such polycrystals permitted cutting samples with selected (single) tilt GBs of different types. To study a role of thermal pre-history on the diffusion of hydrogen along such GBs, a part of every as-grown ribbon was annealed in air at 1200 °C for 1 hour with subsequent cooling in the furnace.

All the studied GBs were nomenclatured by special X-ray analysis [5,6]. According to [5,6], in EFG crystals all tilt GBs could be divided by their structure into the special (mainly Σ3,9), weakly-deviated and highly-deviated from special orientations. Procedures of sample preparation for electric measurements were the same as in [4-6]. Electrical activity of GBs relative to MiC assessed by the recombinational contrast that was measured in the Electron Beam Induced Current (EBIC) regime. The activity of GBs relative to MaC was estimated by the transversal carrier transport properties such as equilibrium DC conductance and current-voltage (I-V) characteristics.

Hydrogenation of samples was carried out by the dc glow discharge hydrogen plasma [4]. An exposure to hydrogen plasma was at 100 °C with the electrode voltage of 500 V and current density of 50 μA/cm^2. The changes in GBs activity relative to MaC under the effect of hydrogen diffusion were estimated by the shape of transversal I-V characteristics when current passed across GB plane. Their linearity after hydrogenation indicated the inactivity (the lack of intergrain barrier) of GBs and therefore the enhanced diffusion along them. Nonlinearity of transversal I-Vs demonstrated the activity of GB due to the presence of the intergrain barrier (owing to the availability of interfacial traps) and low GB diffusivity. To characterize quantitatively the changes in the electrical activity of GBs we have also used the dependencies of transversal equilibrium GB conductance $\sigma = (dI/dV)_{V\to 0}$ and conductance of the grain bulk on exposure time t. In the hydrogenation experiments we have studied the weakly-deviated boundary Σ19(320)/<110> (see GB N7 in Table 1 in [6]) and highly-deviated boundary Σ13(111)/<100> (see GB N12 in Table 1 in [6]).

II. Characterization of bicrystals before hydrogenation

According to our works [4-7], special GBs in as-grown EFG silicon crystals were inactive both to MiC and MaC displaying linear I-V characteristics, lack of EBIC contrast (GB barrier) and minimal (close to the grain) level of low-frequency current noise. Weakly-deviated GB Σ19 in as-grown samples was active

both in relation to MiC and MaC showing non-linear I-Vs, spot-like EBIC contrast (see Fig. 2b in [4]) and intermediate noise [7]. All this suggests that interfacial deep traps are distributed over the plane of Σ19 boundary very inhomogeneously. This, in particular, results in lack of continuous intergrain barrier for such boundary. Accordingly [4,6], the studied highly-deviated boundary Σ13 was active to MiC in as-grown samples showing a somewhat lower level of induced current than for Σ19 boundary but continuous EBIC contrast (see 2a in [4]). In contrast to recombination activity, Σ19 boundary has very low activity to MaC revealing weakly nonlinear transversal I-V and intermediate level of current noise [7]. This points to the fact that the density of interfacial states for Σ13 boundary is lower than for the weakly-deviated Σ19 boundary, while traps are distributed over the plane of Σ13 boundary more homogeneously.

Annealed EFG bicrystals exhibited a decrease in the recombination activity (see [4]) of the weakly-deviated Σ19 GB also transforming its I-V from highly non-linear into weakly non-linear. At the same time, EBIC contrast (see [4]) and non-linearity of I-Vs for the Σ13 boundary was increased after the heat treatment.

III. Characterization of bicrystals after hydrogenation

Hydrogenation experiments have shown that, on the one hand, for all crystal states (as-grown and annealed) and types (Σ19 and Σ13) of GBs reduced conductance $S(t)=\sigma(t)/\sigma(0)$ increases at exposure times less than 100 min (Fig. 1) demonstrating a decrease of GBs electrical activity (lowering of the barrier height) due to the passivation of deep interfacial states due to enhanced diffusion of hydrogen along the boundary. In so doing, the greatest longitudinal diffusivity and passivation effect (the largest increment of $S(t)$ with the exposure time t) is observed for Σ13 GB (curves 2 and 4 in Fig. 1). On the other hand, a subsequent increase of the exposure time over 100-120 min causes saturation of $S(t)$ for annealed crystals (curves 3 and 4) and its relative decrease for as-grown ones (curves 1 and 2) with a pronounced maximum for the latter case.

As the equilibrium conductance measurements show, for the exposure time over 120 min incorporation of atomic hydrogen in as-grown crystals is accompanied not only the decrease of $S(t)$ values for GBs but also the decrease of the grain-bulk conductance. It means that apart from passivation of GB electrical activity (due to the enhanced hydrogen diffusion along GB), in as-grown ribbons a decrease of the hole concentration (due to neutralization of boron atoms [4]) is exhibited in the grain bulk. This may be an indication of higher hydrogen diffusivity in the bulk of as-grown crystals as compared to the bulk of annealed ones. The latter is in good agreement with the conclusions of [4,8] that the bulk diffusivity of hydrogen is higher for materials fabricated in more non-equilibrium conditions (such as EFG crystals, for example).

The mentioned difference in hydrogen diffusivities means that for the same exposure times the hydrogen penetration into the grain bulk in as-grown samples should be greater than in the annealed ones. Then, provided the diffusivity of hydrogen along GBs is at least not lower than that in the grain bulk, fast decrease of the $S(t)$ observed in as-grown samples for hydrogenation times over 100 minutes would be associated with the creation of a thicker layer of reduced conductance in the grain bulk (due to neutralization of charged boron atoms) unlike a more thin layer in the annealed samples. However, our estimates of possible hydrogen diffusion depths based on the temperature dependencies of the bulk hydrogen diffusivities in silicon from [2] show that for the used exposure times they will not exceed 30 to 50 μm, being much lower than thickness of the samples. Taking into account that by no means all hydrogen atoms diffusing into the material will neutralize boron ions near the surface, admittedly the direct penetration of hydrogen from the surface into the sample depth had to be regarded insufficient to give a 2-3-fold decrease of $S(t)$ attained in our experiments after reaching maximal passivation of GBs (see initial portions of curves 1 and 2 in Fig. 1).

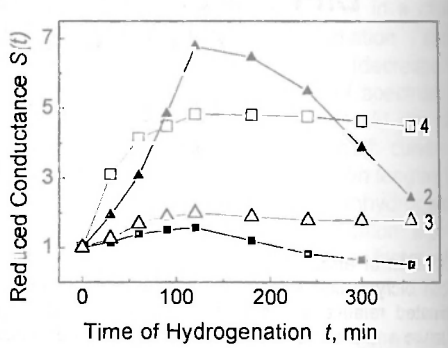

Fig. 1. Dependence of reduced transversal conductance $S(t)$ measured at 77 K on hydrogen plasma exposure time t for weakly-deviated Σ19 (1,3) and highly-deviated Σ13 (2,4) grain boundaries in as-grown (1,2) and annealed (3,4) EFG silicon bicrystals

The above analysis stands for the presence of any additional (non surface!!) channel of boron passivation in the process of hydrogenation. In our opinion, this additional channel may be associated with the enhanced diffusion of hydrogen along GBs and its fast accumulation in the GB "core", followed by diffusion from the "core" into the grain bulk, giving rise to additional neutralization of boron in the vicinity of boundary. In its turn, this lowering of the charged acceptors concentration will result in decrease of the screening charge density at the boundary (due to redistribution of holes in space charge region), increase of intergrain barrier height and, as a consequence, decrease of $S(t)$. This means the presence of GB depassivation effect which is developed for exposure times over 100-120 min to a greater extent for as-grown crystals than for annealed ones due to higher values of hydrogen diffusivity in as-grown poly-Si.

Hence the reasoning above is an evidence for the presence of two competitive processes during hydrogen diffusion in poly-Si under hydrogenation – passivation and depassivation that oppositely govern the electrical properties of GBs. A qualitative model

which illustrates the influence of enhanced diffusion of hydrogen along GB and its pushing-out into the grain bulk on redistribution of charges between interfacial deep centers and shallow acceptors in the space charge region (SCR) and change of barrier height in the vicinity of boundary is presented in Fig. 2.

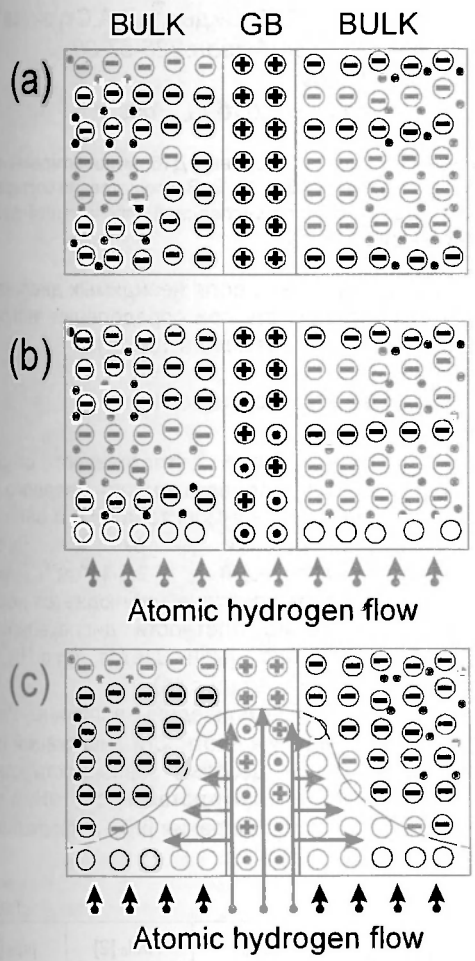

Fig. 2. Model illustrating effect of passivation and depassivation of grain boundaries in EFG polycrystals under influence of hydrogen exposure for different times *t*:
a – distributions of charged ⊕ and passivated ○ GB deep centers, ionized ⊖ and neutralized ○ acceptors, free holes ● before hydrogenation;
b – the same after hydrogenation for $t < 100$ min on the stage of GB passivation;
c - the same after hydrogenation for $t > 100$ min on the stage of GB depassivation

According to the presented model for initial stage of exposure hydrogen diffuses predominantly along GBs in depth of the sample resulting in the passivation of interfacial states and formation of a highly resistive under-surface layer due to neutralization of boron ions (Fig. 2b), decrease in the density of GB states and narrowing of SCR, decrease of intergrain barrier height φ_b and thereby increase of initial portions of $S(t)$ (Fig. 1). Note that this process probably has a tendency to saturation with the hydrogenation time due to finiteness of deep interfacial states. As hydrogen is accumulated in a GB "core", process of hydrogen diffusion from this "core" into the grain bulk is beginning. The latter will initiate an additional (in relation to the surface one) neutralization of boron ions around GB core (Fig. 2c), expansion of SCR and increase of the barrier height φ_b. Just because of this process, for longer hydrogen exposures we observed either lowering of $S(t)$ (curves 1 and 2 in Fig. 1) or its saturation (curves 3 and 4) depending on the value of in-grain hydrogen diffusivity.

IV. Summary

The conducted study of GBs activity with exposure of EFG silicon to hydrogen plasma has demonstrated that the changes observed depend both on the state of polycrystals (as-grown or annealed) and type of GBs. It was explained on the basis of a phenomenological model put forward in assumption that GBs deviated from special orientations manifests itself as channels with enhanced diffusion of hydrogen. In so doing, the state of the crystal determines the relation of diffusivities along GB and in the grain bulk and hence the relation between the neutralization efficiency of deep interfacial traps and shallow acceptors (boron) in the vicinity of boundary. As has been shown, the near-boundary neutralization of boron ions is accompanied by an increase of SCR width and the barrier height (effect of boundary depassivation) at the GB. This points to the fact that in the annealed crystals whose hydrogen diffusivity is essentially lower than in as-grown ones the enhanced GB diffusion results in only passivation of their electrical activity. At the same time, in the as-grown crystals (where the grain-bulk diffusivity of hydrogen is much higher than in annealed ones) processes of passivation and depassivation are in progress simultaneously.

References

1. *W.B. Jackson, N.M. Johnson, C.C. Tsai, L.-W. Wu, A. Chiang, D. Smith //* Appl. Phys. Letters. – 1992. – v.61. – p.1670.
2. Hydrogen in Semiconductors II, *N.Nickel* (Ed.), In: Semiconductors and Semimetals, Academic Press, New York. -1999. - v.61.
3. *D. Balloted, L. Lesson, A. Boutry-Forveille //* Solid State Phenomena. - 1998. – v.69-70. – p.571.
4. *A. Fedotov, Yu. Ilyashuk,A. Mazanik, A. Ulyashin //* Phys. Stat. Solidi A. – 1999. – v.171. – p.353.
5. *A. Fedotov, B. Evtody, L. Fionova, E. Katz //* J. Cryst. Growth. – 1990. – v.104. – p.186.
6. *A. Fedotov, B. Evtody, L. Fionova, E. Katz //* Phys. Stat. Solidi A.. – 1990. – v.119. – p.523.
7. *N. Tkachenko, G.Kolomoetz, A.Fedotov, Yu.Ilyashuk //* Soviet Physics-Solid State. - 1991. – v.33. – p.1593.
8. *B.L. Sopori, X. Deng, J.P. Benner, A. Rohatgi, P. Sana, S.K. Estreiher, M.A. Robertson, Y.K. Park //* Solar Energy Materials and Solar Cells. – 1996. – v.41/42. – p.159.

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