

Segregation phenomena in large-size cast multicrystalline Si ingots

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Abstract

In cast multicrystalline silicon ingots impurity concentrations vary along the ingot height due to segregation phenomena during the directional solidification. It is expected that these concentrations are the highest at the top of the ingot which solidifies last. The bottom of the ingot which solidifies first, and which is longer in contact with the crucible floor is contaminated by solid state diffusion. As a consequence, lifetime (τ_n) and diffusion length (L_n) of minority carriers are the highest in the central part of the ingot and decrease strongly in the top as well as at the bottom. However, the impurity concentration is so high at the extremities of the ingot that additional solid state segregation phenomena occur at extended defects, which extract impurities from the adjacent grains. That is revealed at grain boundaries (GBs) by τ_n and L_n scan maps and also by the variation of the mobility of the majority carriers which cross GBs.

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1. Introduction

It is well known that in cast multicrystalline silicon (mc-Si) the interaction of extended defects and impurities control the values of lifetime (τ) and diffusion length (L) of minority carriers. Extended defects are essentially grain boundaries (GBs) and dislocations whose density and distribution are related to the ingot growth conditions, especially its high solidification rate. Impurities come from the feedstock (mostly waste of the microelectronic industry), from the walls of the crucible in which the ingots are casted and also from the atmosphere within the furnace. Metallic contaminants are Fe, Cr, Ni, Cu and Ti. During the directional solidification of the ingot, the melted silicon charge solidifies progressively from the bottom (i.e. the part which is in contact with the crucible floor and which solidifies first), to the top.

The metallic atoms whose solubility is higher in the liquid than in the solid phase are driven to the top of the ingot by a segregation phenomenon (in accordance with the Scheil law), because their segregation coefficients are extremely small.

This was well observed [1–4] in the central part of cast ingots where the concentration of impurities incorporated into the solid phase C_S during the crystallisation is given by

$$C_S = k_{\text{eff}} C_L \quad (1)$$

with C_L the impurity concentration in the liquid phase far from the interface, and k_{eff} an effective segregation coefficient which depends on the growth rate, the diffusivity of the impurities in the liquid and the thickness of the solid/liquid boundary layer at the interface [1]. Thus the Scheil law may be expressed by the equation

$$C_S = k_{\text{eff}} C_o (1 - f_s)_{\text{eff}}^{(k-1)}. \quad (2)$$

Often, the very top of the ingot is so concentrated in impurities that it must be discarded. The back solid state diffusion of fast diffusers from the very top of the ingot leads to a contamination of the lower top of the ingot, during the cooling down. During the growth of the ingot, its very bottom is continuously in contact with the floor of the crucible and is therefore contaminated through a solid state diffusion of impurities contained in the floor and the walls of the crucible. Since metal atoms diffuse slowly in solid silicon, this contamination of the very bottom of the ingot is less marked than that of the very top. Even so, this part of the ingot must also be discarded.

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These contamination phenomena are more marked when the ingot size and the solidification time increase. In large-size ingots, the Scheil law cannot explain the experimental results because additional segregation phenomena can occur at the extended defects of the bottom and top of the ingots, developing in the solid phase essentially during the cooling down of the ingot. If this cooling down is slow, equilibrium segregation occurs between solid homogeneous regions and extended defects. At these defects, the segregation is easier than in defect-free regions of the grains, because the free energy of metal atoms is lower due to the distortion of the lattice. Metal atoms which precipitate heterogeneously, like Fe, could be trapped by the extended defects, even if their concentrations are well below the solubility limit, as suggested in Ref. [1]. It is expected that a depletion of impurity concentrations may occur around extended defects and can be observed through minority carrier lifetime or diffusion length scan maps.

2. Experimental

We used an ingot with the following characteristics: 310 kg, 28 cm height, boron doped, 1 Ω cm in resistivity. Cost-effective silicon wastes were employed as feedstock. The ingot solidification time took 40 h. The ingot was cut into blocks, each with a base area of 12.5×12.5 cm². One of the central blocks was chosen for our investigations so that the influence of the crucible lateral walls can be neglected. Wafers were cut from the top (“T”), from the middle top (“MT”), from the middle (“M”), from the middle bottom (“MB”) and from the bottom (“B”) regions of the block. In the wafers, the mean grain size was about half a centimetre and the dislocation density, evaluated by the etch pits produced by Secco or Sirtl solution, was in the range 5×10^4 – 10^5 cm⁻². The wafers were characterised by the measurement of the mean values (36 measurements in each wafer) of electron lifetime (τ_n) and diffusion length (L_n), and also by light-beam-induced current (LBIC) contrast, τ_n and L_n scan maps.

Notice that LBIC contrast is defined by the ratio

$$C = (I_0 - I_{\text{def}})/I_0,$$

where I_{def} is the current collected at a defect and I_0 the background current, as it is the case for electron-beam-induced-current scan maps. However, in the following LBIC pictures, the reverse of C is displayed (in grey levels or in false colours) because it is directly related to the local lifetime or diffusion length values [8]. Companion wafers were also subjected to a phosphorus diffusion from POCl₃ at 850 °C for 30 min to create a collecting structure for LBIC and L_n scan maps and to a gettering treatment by phosphorus diffusion at 900 °C for 2 h. Mean values of L_n in raw wafers were measured using of Al–Si metal–insulator–semiconductor diodes obtained by the deposition of a 9 nm thick metal layer on chemically polished surfaces by electron gun evaporation. In phosphorus diffused and

phosphorus gettered wafers, mean values of L_n were measured thanks to the n⁺p junctions. Mean values of the electron lifetime (τ_n) were determined by means of microwave contact-less quasi-steady-state photoconductance when the surfaces were passivated by an iodine ethanol solution [5]. L_n was deduced from the spectral variations of the photocurrent and of the optical absorption coefficient in the near-infra-red spectrum. Scan maps of LBIC contrast, of L_n and τ_n , were also obtained, the τ_n ones were carried out by means of the contact-less phase shift (μ WPS) technique when the samples were excited by a laser diode emitting at 940 nm. All these measurement techniques, as well as the scanning techniques, have been already described elsewhere [6–8]. Interstitial iron concentration was determined from the variation of τ_n before and after the dissociation of iron–boron pairs by illumination [9,10]. Hall mobilities of majority carriers were measured at room temperature by means of a BioRad system.

3. Results and discussion

Fig. 1 gives the variation of L_n in raw wafers along the block as a function of the distance from the bottom. As expected, and in agreement with published results [1,2], the values of L_n (which are in good concordance with those of τ_n , taking into account a diffusion coefficient of 20 cm²/s for electrons) are the lowest at the block extremities and more specially at the top, where $L_n \sim 30$ μ m and $\tau_n = 0.8$ μ s, while $L_n \sim 75$ μ m and $\tau_n \sim 2.9$ μ s in “MB”. In the central part of the ingot, the decrease in L_n with the distance is due to a progressive increase in impurity concentration in the solid itself, due to an increase in the impurity concentration in the liquid, the impurities being partly transferred to the solid. The marked decreases in L_n in “T” and “B” are

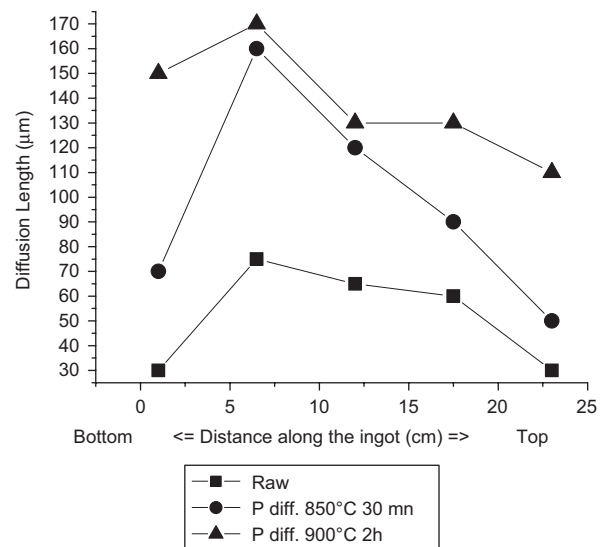


Fig. 1. Variation of the mean values of minority carrier diffusion length along a block of the investigated ingot. R: raw wafers; P: phosphorus diffused wafers at 850 °C for 30 min; G: gettered wafers by phosphorus diffusion at 900 °C for 2 h.

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