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Aluminium Gettering in Silicon Wafers

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Abstract. — The effect of an evaporated thick aluminium layer on electrical properties of multicrystalline and gold contaminated FZ monocrystalline silicon wafers was investigated. By means of minority carrier diffusion length measurements and Deep Level Transient Spectroscopy, it was deduced that the material improvements observed after annealing at 900 °C are due to gettering of metallic impurities in the Al-Si alloyed layer.

1. Introduction

The electrical properties of semiconductor materials and devices are degraded by the presence of dissolved metallic impurities and of precipitates. Lifetime and diffusion length of minority carriers are specially affected.

Gettering techniques are used to remove the impurities from the active areas of the devices and to transport them in regions where they are not harmful, where they can be trapped or eliminated by a chemical etching. So, the gettering mechanism could be divided in three basic steps: extraction of impurities from active areas, fast transport and capture by gettering sites, as summarized in Figure 1.

When the gettering sites are located on external surfaces of the wafers, the gettering is called external. Conversely it is called internal when the gettering sites are located in the bulk.

For photovoltaic devices made with silicon, external gettering is required as the light absorption and diffusion of minority carriers occur in the entire volume, while for microelectronics devices internal gettering is generally used because the active area are close to the surface.

In the last few years, several papers reported that diffusion length and lifetime are improved when a thick aluminium layer is deposited on the surface of silicon wafers and after annealing at temperatures in the range between 450 and 950 °C [1–7].

Segregation of impurities by the aluminium layer or by the aluminium silicon interface was observed for metallic atoms like copper, silver and gold [1], and a recent publication of Apel *et al.* [8] has shown that similar results were obtained for cobalt in single crystalline and cast multicrystalline wafers.

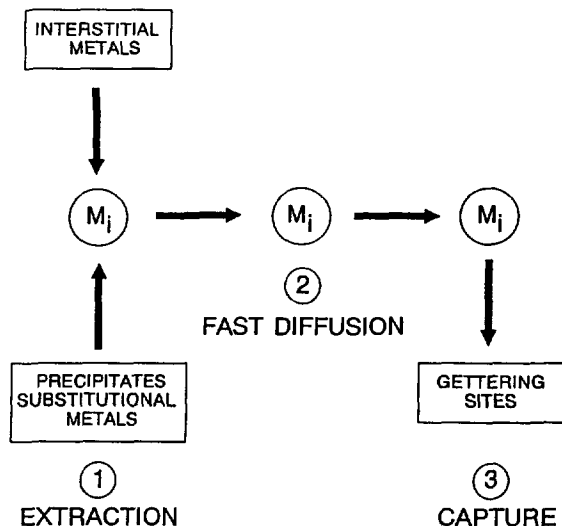


Fig. 1. — The three basic steps of gettering mechanism. The gettering techniques differ by the localization and by the nature of gettering sites.

A gettering effect was proposed to explain these improvements, because at temperatures higher than 600 °C a liquid Al-Si phase is formed in which the solubility of metallic impurities is higher than in the solid Si wafer, and because the silicon dissolution by aluminium damages the interface creating sinks for impurities.

However when *p*-type silicon wafers are used it is not precluded that the diffusion of aluminium from the back surface of a wafer forms a P^+ -*P* interface which developpes a Back Surface Field (BSF) [9] for minority carriers. When diffusion lengths (L) are determined by the so called surface photovoltage technique, the BSF can enhance the diffusion length value when the thickness of the sample is not sufficiently large compared to L (at least 3 times higher).

In addition the damaged back surface which results of the silicon dissolution by aluminium can act as a texturized surface which enhances the absorption of infrared light, increasing artificially the values of L .

A verification of the existence of a pure gettering effect is needed in these Al-Si structures, and this is the aim of the present paper.

We have used two types of *P* type silicon wafers: 1 mm thick multicrystalline wafers and gold contaminated FZ wafers which are characterized by a low oxygen concentration in order to avoid oxygen precipitation effects.

Thanks to diffusion length of minority carrier (L) measurements and to Deep Level Transient Spectroscopy (DLTS), we show that the material improvements by the aluminium treatment result from a gettering effect.

2. Experimental

P type large grained multicrystalline silicon wafers have been used to evaluate the effective minority carrier diffusion length before and after the aluminium treatment. They are boron doped ($N_A = 5 \times 10^{16} \text{ cm}^{-3}$), their thickness was 1 mm and their grain size are larger than few mm.

In this columnar growth materials the mean dislocation density and the interstitial oxygen concentration are about $5 \times 10^4 \text{ cm}^{-2}$ and $4 \times 10^{17} \text{ cm}^{-3}$, respectively. The dislocations are due to the crystal growth conditions and cross the entire wafer.

Arrays of N^+P junctions (area 4 mm^2) were realized by phosphorus diffusion at $900 \text{ }^\circ\text{C}$ for 1h from a POCl_3 source. Then the back surface is chemically etched and covered by a thick aluminium layer ($\cong 1.2 \text{ }\mu\text{m}$) deposited by electron gun evaporation. The structures (labelled S_1) were annealed at $450 \text{ }^\circ\text{C}$ for 1 hour to obtain an ohmic contact on the backside. The initial value L_0 was evaluated from the spectral variations of the internal quantum efficiency and of the optical absorption coefficient when the junctions were illuminated by near infrared light.

Then the samples were annealed at $900 \text{ }^\circ\text{C}$ in argon for 1 hour and the new values of L were evaluated by means of the same diodes. Some samples (labelled S_2) were prepared after the removal of the two N^+ regions. In this case diodes were made after the aluminium treatment by the deposition of an evaporated 300 nm thick aluminium layer without subsequent annealing.

Other samples have been voluntary contaminated with gold. They were cut out of FZ (111) boron doped ($N_A = 5 \times 10^{15} \text{ cm}^{-3}$) monocrystalline wafers. A gold layer was deposited by electron gun evaporation on the two faces and gold diffusion was carried out at $1000 \text{ }^\circ\text{C}$ for 4h in a pure argon flow. Both surfaces were chemically etched (about $50 \text{ }\mu\text{m}$) to avoid the presence of the well known "U shape" profile and to get an uniform concentration of gold through the wafer. Then samples were covered on one face by a thick aluminium layer like the samples S_1 , and annealed at $900 \text{ }^\circ\text{C}$ for 4h. Samples not covered by aluminium were submitted to the same annealing and served as witness.

After these treatments, a thin aluminium layer (thickness $\cong 300 \text{ nm}$) is deposited on the free surfaces in order to realize an array of metal-semiconductor diodes of 1.5 mm in diameter. These diodes allowed the use of DLTS technique to reveal the presence of substitutional gold atoms thanks to the well known donor like level located at $E_v + 0.35 \text{ eV}$ in P type silicon. By means of successive chemical etchings and deposition of aluminium layers a gold profile was obtained.

Figure 2 displays the experimental sequences applied to the two type of samples.

3. Results

Figure 3 shows the variation of the minority carrier diffusion length L in samples S_1 as a function of the initial value L_0 .

The influence of the aluminium treatment is clear: $L \cong 2L_0$. This increase can be explained only by a gettering effect, as the values of L_0 are sufficiently small compared to the wafer thickness in order to preclude the influence of a back surface field. Similar improvements are observed for samples S_2 indicating that there is not a noticeable influence of the N^+ region due to phosphorus diffusion at $900 \text{ }^\circ\text{C}$ during the aluminium treatment.

When the thickness of the aluminium layer is less than $0.5 \text{ }\mu\text{m}$ or when the temperature is below $600 \text{ }^\circ\text{C}$, the effect of the treatment is drastically reduced [3].

A further indication of the gettering effect due to the aluminium treatment is given by DLTS measurements applied to gold contaminated FZ samples. As shown by Figure 4, the gold concentration, which is in the range between 2 and $4 \times 10^{14} \text{ cm}^{-3}$ in the contaminated

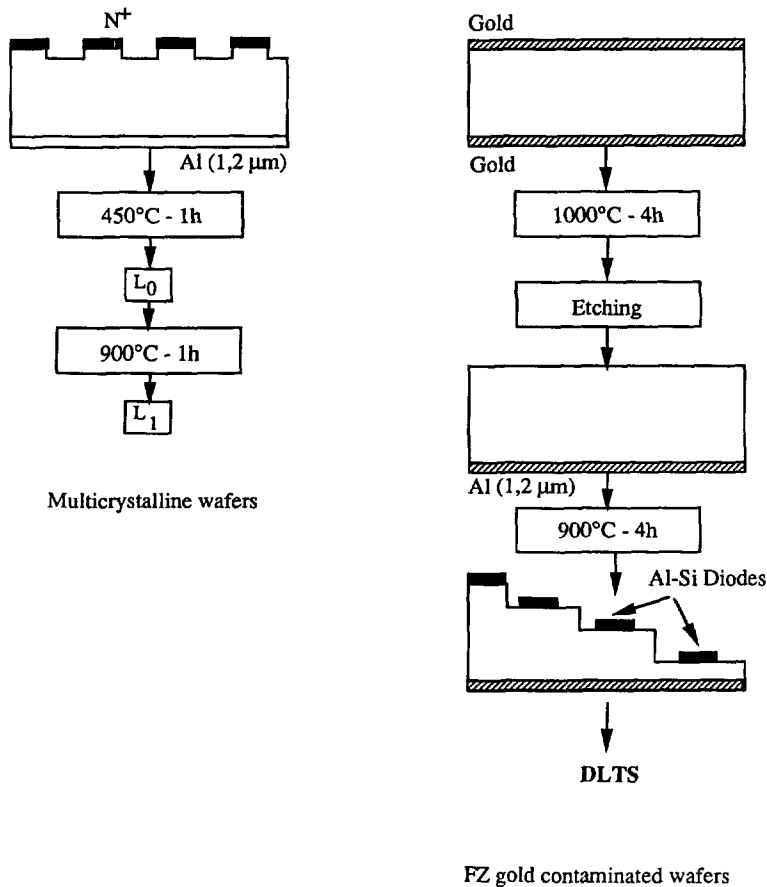


Fig. 2. — The experimental sequences applied to the two types of samples.

wafers, is decreased near the back surface by the aluminium treatment and becomes smaller than 10^{13} cm^{-3} at a distance less than $30 \mu\text{m}$ from the aluminium silicon interface.

Notice that in the witness samples (gold contaminated and annealed without the aluminium layer) gold concentration is found to be approximately constant.

4. Discussion

The results obtained with multicrystalline and monocrystalline wafers contribute both to ascribe the aluminium effects to a gettering of metallic impurities by the aluminium silicon alloyed layers. The Al-Si interface plays a secondary role only, because poor effects are obtained when the thickness of the aluminium film deposited by thermal evaporation is less than $0.3 \mu\text{m}$ or when the annealing temperature is below the eutectic point (577°C). Consequently the gettering mechanism should result from a segregation induced trapping.

However a difference appears between the multicrystalline and the monocrystalline samples: the thickness of the "cleaned" region is neatly larger in the multicrystalline wafers because

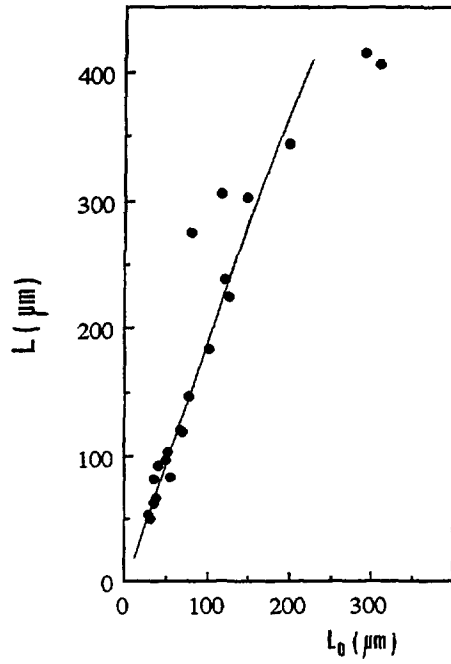


Fig. 3. — Variation of the effective minority carrier diffusion length L after the aluminium treatment as a function of the initial value L_0 , in 1 mm thick multicrystalline samples.

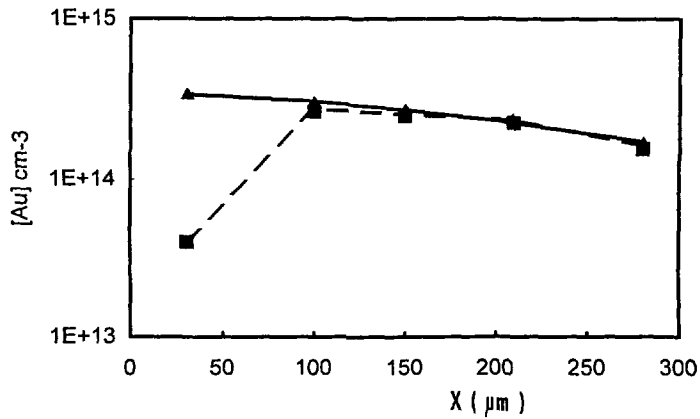


Fig. 4. — Substitutional gold profile in contaminated FZ monocrystalline samples with (—■—) and without (—▲—) aluminium treatment (900 °C - 4 h).

their thickness is close to 1 mm. This could be explained by the influence of dislocations which cross the multicrystalline wafers and which can act as diffusion pipes for impurities, enhancing their trapping by the alloyed layer. Such an influence has been already observed at low [3] and high [7] annealing temperatures.

An additional explanation could be that in the multicrystalline wafer the main metallic impurity atoms are iron. As these atoms are typically interstitials, they diffuse more easily than gold substitutional atoms, although gold atoms can exchange their position in the silicon lattice due to their interaction with point defects [10].

The in-diffusion of aluminium cannot be neglected, but even in grain boundaries and in dislocation containing materials [11] the diffusion coefficient is too small at temperatures close to 900 °C (and below) in order that these atoms can migrate in silicon at distances larger than 10 μm .

5. Conclusion

Thanks to diffusion lengths of minority carriers and DLTS measurements applied to multicrystalline and FZ monocrystalline silicon wafers, we have demonstrated that aluminium treatments which improve silicon wafers are due to a gettering of metallic impurities, like gold, by the aluminium-silicon alloy. The mechanism should be segregation enhanced in nature. Thanks to dislocations, the aluminium treatment has a long range action in columnar growth multicrystalline materials.

Acknowledgments

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