

Platinum Diffusion at Low Temperatures

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Abstract

In a series of experiments, the diffusion of platinum in silicon was investigated at low temperatures in the range from 700 °C to 800 °C. Depth profiles measured in as-grown float zone (FZ) silicon were found to differ strongly from those in as-grown Czochralski (CZ) silicon. These differences as well as different profiles measured in various FZ wafers after identical processing can be attributed to different initial concentrations of intrinsic point defects. In general, platinum depth profiles were found to agree qualitatively with the predictions of standard diffusion theories, but not quantitatively. Therefore, parameters for platinum and point defect diffusion reported in the literature were modified to describe consistently the diffusion in both kinds of material.

1. Introduction

Platinum forms deep electronic levels in silicon which act as recombination centers for carriers. Because of this feature platinum is used to adjust lifetime in fast switching diodes or thyristors. Another application of platinum in silicon technology is the formation of ohmic and Schottky contacts with platinum or platinum silicide, but the unintended diffusion of the transition metal may affect device performance. For both cases, quantitative knowledge of the diffusion of platinum in silicon is required. On the one hand, if platinum is used to adjust lifetime it is necessary to determine the most adequate diffusion conditions like diffusion time and temperature, and on the other hand, for the use of platinum as contact material one has to prevent unintended contamination of the silicon substrate.

It is generally assumed that platinum diffuses in silicon predominantly as interstitial atoms. In equilibrium, however, platinum atoms occupy mainly substitutional sites where they are assumed to be immobile. The change of an impurity from an interstitial position to a substitutional site can take place by two different reactions: Either, an interstitial platinum atom recombines with a lattice vacancy (Frank-Turnbull mechanism [1]), or, it generates a self-interstitial when occupying a substitutional site (kick-out mechanism [2]). Based on these considerations, a system of partial differential equations for the substitutional platinum atoms, the interstitial platinum atoms,

the silicon self-interstitials, and the vacancies can be derived [3] describing the redistribution of the platinum atoms and the intrinsic point defects.

Prabhakar et al. [4] investigated the diffusion of platinum into silicon from PtSi/Si interfaces at temperatures between 300 °C and 800 °C. Mantovani et al. [5] performed similar experiments with epitaxially grown silicon substrates at temperatures between 700 °C and 850 °C. In both cases, the observed concentrations of substitutional platinum after diffusions at 700 °C and 750 °C for half an hour in depths up to a few microns were around 10^{12} cm^{-3} . The depth profiles in the region close to the surface were interpreted using the kick-out mechanism. On the contrary, Zimmermann et al. [3] found much higher concentrations on the order of 10^{14} cm^{-3} after diffusions at 700 °C and 770 °C. They concluded that for temperatures below approximately 850 °C, the Frank-Turnbull or dissociative mechanism governs platinum diffusion. Our goal was to investigate the diffusion of platinum at low temperatures and for short times in different kinds of silicon substrates, namely in FZ and CZ silicon.

2. Experimental

The experiments were performed on as-grown, dislocation-free, (100)-oriented p-type silicon substrates. Both, FZ wafers with diameters of 100 mm, thicknesses of 535 μm , and resistivities of 4-6 Ωcm , and CZ wafers with diameters of 150 mm, thicknesses of 675 μm , and resistivities of 60 Ωcm were used. One- and double-sided diffusion was investigated. The back-sides of the wafers for investigation of one-sided diffusion were covered by low-temperature oxide. After a short dip in fluoric acid and water rinsing, platinum was deposited at the oxide-free surfaces with a thickness of the order of one atomic layer to prevent point-defect generation by silicidation. Drive-in diffusions were performed in a horizontal furnace in nitrogen ambient. Furnace and sample holder were preheated to guarantee that the wafers reach the nominal process temperature as fast as possible. Already four minutes after loading, the sample temperature was only 4 °C below the final value. Depth profiles of substitutional platinum were obtained from DLTS measurements on bevelled specimens.

3. Results

In general, in as-grown, commercially available FZ wafers, platinum concentrations around 10^{14} cm^{-3} were measured after short time and low temperature diffusion.

In one of these experiments, platinum was diffused from the front side into three different FZ wafers at 730 °C for 20 min (Fig. 1). Remarkable is that the profiles do not correspond although the processing conditions were identical. This indicates a non-negligible influence of the initial concentrations of the intrinsic point defects. Also, it was not possible to reproduce the shape of the platinum distributions by numerical simulations with the parameters for point defect and platinum diffusion given by Zimmermann and Ryssel [3].

Simulations revealed that platinum diffusion in FZ wafers at the low temperatures of this investigation is dominated by the Frank-Turnbull mechanism. One of the main reasons for the major discrepancy between measured profiles and simulations is that Zimmermann and Ryssel underestimated drastically the Frank-Turnbull reaction constant because this parameter was not as important for their investigations. Besides this reaction constant, simulations were found to be sensitive predominantly to the initial concentration of vacancies, the product of interstitial platinum diffusion

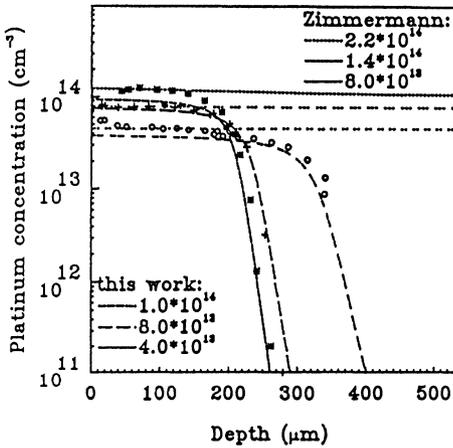


Fig. 1 One-sided diffusion in three different FZ wafers at 730 °C for 20 min

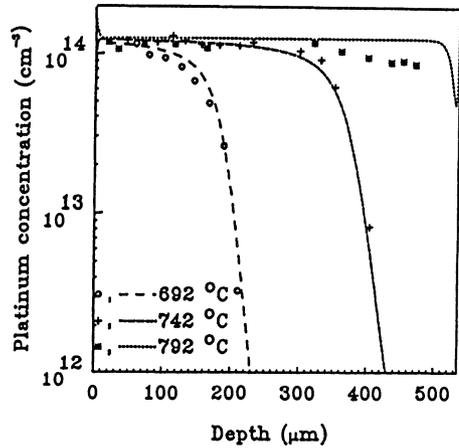


Fig. 2 One-sided diffusion for 1 h in FZ silicon

coefficient and interstitial platinum equilibrium concentration, and to the quotient of vacancy equilibrium concentration and substitutional platinum equilibrium concentration. The latter two parameters were determined from various experiments whereas the initial concentration of vacancies was assumed to vary from wafer to wafer. The Frank-Turnbull forward reaction was found to be diffusion limited with a reaction radius of 1 nm. The simulated results were obtained with the following parameters:

$$k_{FT} = 1.89 \cdot 10^{-8} \exp(-0.604 \text{ eV}/kT) \text{ s}^{-1}$$

$$D_i \cdot C_i^{eq} = 6.62 \cdot 10^{19} \exp(-2.52 \text{ eV}/kT) \text{ cm}^{-1} \text{ s}^{-1}$$

$$C_V^{eq}/C_s^{eq} = 3.28 \cdot 10^{-7} \exp(1.05 \text{ eV}/kT)$$

Here and below, the symbols D and C^{eq} denote diffusion coefficients and equilibrium concentrations, k_{FT} stands for the Frank-Turnbull reaction constant, and the subscripts i , s , and V refer to interstitial and substitutional platinum and vacancies. From the profiles in Fig. 1, the initial concentrations of vacancies in the three investigated samples were estimated as $1 \cdot 10^{14} \text{ cm}^{-3}$, $8 \cdot 10^{13} \text{ cm}^{-3}$, and $4 \cdot 10^{13} \text{ cm}^{-3}$. Such different initial concentrations of vacancies can be explained easily by different thermal histories of the wafers during cooling after zone melting.

In Fig. 2, the influence of diffusion temperature on one-sided platinum diffusion is shown for processes of 1 h duration. All three samples were quarters from the same FZ wafer. The initial concentration of vacancies was estimated to be $1.3 \cdot 10^{14} \text{ cm}^{-3}$ consistently. Due to the low temperature, the vacancies are nearly immobile. For steady state, because of the expected constant initial concentration of vacancies, a constant platinum concentration is expected which depends predominantly on the initial concentration of vacancies and only slightly on temperature. At the highest temperature, local equilibrium is nearly reached after 1 h.

In contrast to FZ wafers, platinum diffusion experiments at 730 °C and 780 °C with as-grown CZ silicon wafers resulted in much lower platinum concentrations with U-shaped depth profiles (Fig. 3, Fig. 4). Such profiles are typical for a dominance of the kick-out mechanism. The platinum concentration in the middle of the wafer was found to increase proportionally to the square root of diffusion time. Simulations at

730 °C shown in Fig. 3 used the product $C_s^{eq} \cdot D_I \cdot C_I^{eq} = 5.9 \cdot 10^{14} \text{ cm}^{-4}\text{s}^{-1}$, whereas at 780 °C, a value of $C_s^{eq} \cdot D_I \cdot C_I^{eq} = 5.6 \cdot 10^{16} \text{ cm}^{-4}\text{s}^{-1}$ was used. The symbol I refers to self-interstitials. The dominance of the kick-out mechanism indicates that the initial concentration of vacancies did not influence the platinum diffusion in the investigated CZ wafers. A value of $C_V(t = 0) = 3 \cdot 10^{10} \text{ cm}^{-3}$ was used for the presented simulations. Therefore, the concentration of vacancies in these as-grown CZ silicon wafers was at least three orders of magnitude lower than in as-grown FZ silicon. Simulations with various values for the initial self-interstitial concentration showed a slight influence on the resulting platinum concentration in the bulk. The best fit was obtained by $C_I(t = 0) = 3 \cdot 10^{10} \text{ cm}^{-3}$, but this value can only be interpreted as a rough estimation.

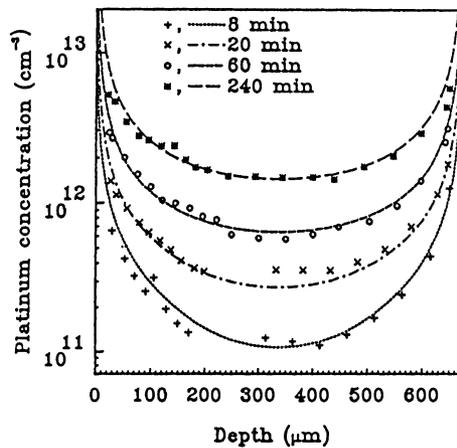
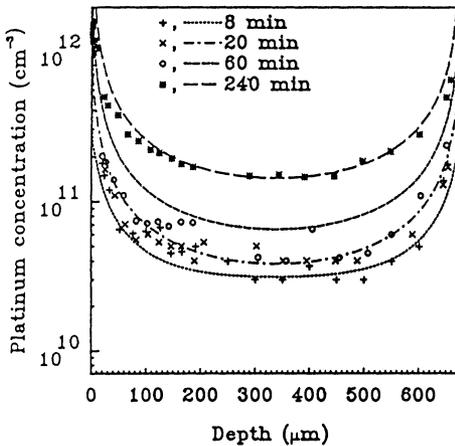


Fig. 3 Diffusion in CZ silicon at 730 °C Fig. 4 Diffusion in CZ silicon at 780 °C

4. Conclusions

Platinum diffusion in as-grown FZ and CZ silicon was investigated in the low temperature range from 700 °C to 800 °C. In FZ silicon it was found that the Frank-Turnbull mechanism dominates the platinum diffusion because of high initial vacancy concentrations in the range from $4 \cdot 10^{13} \text{ cm}^{-3}$ to $2 \cdot 10^{14} \text{ cm}^{-3}$. In contrast, in CZ silicon wafers the vacancy concentrations were so low that the kick-out mechanism dominates the platinum diffusion. We conclude that the initial vacancy concentration is the key to understand the different diffusion behavior in FZ and CZ silicon.

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