



Palladium contamination in silicon

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ABSTRACT

In this work palladium is characterized as a silicon contaminant by recombination lifetime, DLTS, C–V and C–t measurements of palladium-implanted wafers. Palladium introduced by ion implantation is found to remain in the solid solution in silicon after rapid thermal treatments, and to be a very effective recombination center. For this reason recombination lifetime measurements are the most sensitive method to detect palladium in silicon.

Two palladium-related levels were found by DLTS in p-type material. One of these levels corresponds to a level reported in the literature as the single donor level of substitutional palladium.

For what concerns MOS capacitors, palladium is responsible for negative oxide charge and for degradation of the generation lifetime.

In addition, palladium is confirmed to be a very fast diffuser, which segregates at the wafer surface even with low temperature treatments (250 °C). Microscopy inspections showed that palladium precipitates and surface defects were formed upon segregation.

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1. Introduction

It is very well known that palladium is a fast diffuser in silicon [1] and for this reason it is prone to surface segregation and haze formation at the silicon surface. Indeed intentional palladium contamination was used in the so-called “palladium test” to assess the efficiency of various gettering techniques by monitoring haze formation. Palladium is also reported to be responsible for the formation of deep levels in the silicon band gap [2,3].

Unintentional palladium contamination was considered an unlikely event, because palladium is not a common element. However, palladium was recently proposed [4–7] as a component of the final metallization, so palladium could be present in fabrication lines and contamination by palladium might be possible. It is therefore important to be able to reveal palladium contamination by the techniques commonly used to monitor metal contamination, for instance by measurements of recombination lifetime.

In this work we report the results of a set of experiments carried out to assess the ability of various techniques to detect palladium contamination in silicon. Samples intentionally contaminated with palladium were used to identify the most suitable techniques to reveal palladium contamination. Surface photovoltage (SPV) and Electrolytic metal tracer (Elymat) measurements were used to

obtain the recombination lifetime. The surface segregation of palladium was monitored by the reduction of the palladium recombination activity in the silicon volume measured by SPV. Finally, the palladium segregation at the wafer surface was checked by selective etching (Secco etching [8]) and by transmission electron microscopy (TEM) analyses. Deep level transient spectroscopy (DLTS) spectra were obtained for a comparison with the levels reported in the literature. Finally, capacitance vs. voltage (C–V) and capacitance vs. time (C–t) measurements were used to obtain the oxide charge and the generation lifetime in palladium-contaminated MOS capacitors.

2. Experimental details

2.1. Sample preparation

P-type, (100), 200 mm diameter, 725 μm thick 10 Ω cm resistivity Magnetic Czochralski (MCZ) wafers and n-type, 5 Ω cm resistivity CZ wafers were used in this study. MCZ material was chosen because of its low oxygen content ($<6 \times 10^{17} \text{ cm}^{-3}$, ASTM 1983 units) in order to prevent oxygen precipitation, which might confuse recombination lifetime data. No n-type MCZ material was available, so we used n-type CZ wafers with low oxygen content ($5.5\text{--}7.5 \times 10^{17} \text{ cm}^{-3}$). The samples were contaminated by ion implantation. The advantage of this method is that the contaminating dose and species are known. 200 mm wafers were implanted in

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a 175 mm diameter area, in order to discriminate between the effect of implanted metal and of random contamination. In addition, a few not implanted wafers were processed as a further reference. Low doses (10^{11} – 10^{12} cm $^{-2}$) were considered, in order to limit ourselves to realistic contamination levels in non-optimum process conditions. In previous experiments [9–11] it was shown that the implantation damage has no relevant impact on recombination lifetime data. Indeed, in all these experiments we found that the obtained results are specific of the contaminant, irrespective of the damage. The samples for palladium implantations were oxidized to 400 Å and implanted with 190 keV energy. The pre-implantation oxide has the purpose to prevent both a random contamination of the wafers and the out-diffusion of the implanted metal during further processing. Under these implantation conditions, according to SRIM simulations [12] more than 99% of the implanted dose is in silicon, and the expected projected range in silicon is about 600 Å. After the implantation, the wafers were thermally treated by RTP at 1100 °C for 3 min in an inert environment. This thermal treatment had the purpose to recover the implantation damage and to allow palladium diffusion in silicon.

In the samples for recombination lifetime and for DLTS measurements the oxide was etched off by immersion in a HF solution. The samples for recombination lifetime measurements required no further treatment.

To obtain Schottky diodes for DLTS measurements, 1000 Å titanium layer was deposited on the silicon surface, masked and etched to form 1 mm 2 area titanium dots.

In the samples for generation lifetime, a capacitor was created by depositing an aluminum layer on the oxide surface. The aluminum layer was then masked and etched by a reactive ion etching (RIE) process which selectively stops at the oxide surface. In these samples, the Si–SiO $_2$ interface state density should be as low as possible, otherwise such states would contribute to carrier generation and hence degrade the sensitivity of our measurements. For this reason, the wafers were annealed in a forming gas environment (30 min at 430 °C in N $_2$:H $_2$).

2.2. Experimental techniques

2.2.1. Surface photovoltage (SPV)

The carrier diffusion length is obtained from SPV measurements by illuminating the sample with light of various wavelengths. The generated minority carriers are collected in the depletion region at the wafer surface and produce a variation in surface potential, which is recorded as a function of light wavelength. SPV measurements of carrier diffusion length are always obtained under very low injection conditions. In the standard SPV technique [13], the diffusion length L_{diff} is extracted from these data by assuming that sample thickness is much larger than diffusion length. If this hypothesis holds, the SPV signal is a linear function of the light penetration depth, and the carrier diffusion length is obtained as the negative intercept at zero of a linear best-fit of the SPV signal as a function of the light penetration depth. The standard SPV assumption often fails in present wafers, and the actual wafer thickness must be taken into account. An “enhanced SPV” [14] technique is available for this purpose. In this approach, the real wafer thickness is taken into account by imposing the correct boundary condition at the wafer backside, i.e. by taking into account the surface recombination at wafer backside. It was also shown [14] that the exact value of the surface recombination velocity s_b is not relevant provided it is high enough ($\geq 10^4$ cm/s), as it is usually when the surface is not oxidized. We assumed $s_b = 10^5$ cm/s to extract our diffusion length data in the enhanced mode. Standard or enhanced SPV was used for palladium-implanted regions, according to needs, and enhanced SPV for reference regions.

Both standard and enhanced SPV are only sensitive to bulk recombination, so SPV cannot detect surface-segregated contaminants. In SPV measurements, the probed region is of the order of light penetration depth $1/\alpha$ (where α is the absorption coefficient of the incident light) plus carrier diffusion length, so this region can be shorter than the wafer thickness, and can to some extent be varied by selecting suitable wavelengths.

SPV measurements can also be associated with optical activation to identify some contaminants. The optical activation is based on the evidence that some contaminants increase their electrical activity upon illumination with light of sufficient intensity. Examples of this sort are iron [15] and cobalt [16], and for these contaminants the optical activation is due to the dissociation of the metal–boron pair. We investigated whether a similar activation occurs in palladium-contaminated silicon.

In this work the SPV tool in the FAaST SDI system was used. This instrument is equipped with a set of filters producing monochromatic light at seven different wavelengths, ranging from 800 nm to 1 μ m. These wavelengths correspond to light penetration depths ranging from 11 μ m to 160 μ m. A halogen lamp is used for optical activation.

2.2.2. Electrolytic metal tracer (Elymat)

In this technique excess carriers are generated by a laser beam, and the diffusion length is extracted from photocurrent measurements [17]. The results can be also reported in terms of the carrier recombination lifetime τ , which is related in a straightforward way to the carrier diffusion length by $L_{\text{diff}} = \sqrt{D\tau}$, where D is the minority carrier diffusivity. The contribution of surface recombination is suppressed by immersion in a HF solution [18] which also provides Schottky contacts for carrier collection. Carrier diffusion length (or carrier recombination lifetime) data are obtained by injecting carriers at wafers frontside and measuring the photocurrent at wafer backside (backside photocurrent, BPC) or at wafer frontside (frontside photocurrent, FPC). BPC measurements have a practical limitation in that no current can be collected at wafer backside if the carrier diffusion length is too short. Under our experimental conditions, this fact limits BPC measurements to $L_{\text{diff}} > 100$ μ m. For lower values of the carrier diffusion length, FPC measurements must be used. It was previously shown [19] that reliable lifetime data can be obtained from FPC measurements provided $L_{\text{diff}} < 1/\alpha$. On the other hand, diffusion length data are extracted from BPC measurements under the hypothesis $L_{\text{diff}} \gg 1/\alpha$, so a laser with 830 nm wavelength ($1/\alpha = 14$ μ m) was used for BPC measurements and a laser with 980 nm wavelength ($1/\alpha = 105$ μ m) for FPC measurements. BPC and FPC measurements also differ for the thickness of the probed region. In backside photocurrent measurements, in principle the whole wafer thickness is probed. FPC measurements are similar to SPV measurements from this point of view, in that the probed region is of the order of light penetration depth plus carrier diffusion length.

The Elymat technique allows the injection level to be varied by varying the intensity of the laser beam, so that measurements of lifetime as a function of the injection level are possible. In p-type silicon, the injection level is defined as $\delta n/p_0$, where δn is the minority carrier excess and p_0 is the equilibrium majority carrier concentration. In a previous work [10] it was shown that data of lifetime vs. injection level can be used for the identification of contaminants. Indeed, according to the Shockley–Read–Hall theory, the dependence of recombination lifetime on the injection level is uniquely determined by the properties (energy levels and capture cross sections) of dominant recombination centers. If one impurity dominates recombination in a sample, the function $\tau(\delta n/p_0)$ is a feature of the corresponding recombination centers, and this helps us to identify this impurity and to give a quantitative

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