Proc. 15th Int. Conference on Defects Recognition, Imaging and Physics in Semiconductors, Warsaw, Poland 2013

Development of a Storage Getter Test for Cu Contaminations in Silicon Wafers Based on ToF-SIMS Measurements

D. Kot[a,b,*], G. Kissinger[a,b], A. Sattler[c] and T. Müller[c]
[a]IHP, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany
[b]BTU Cottbus, Joint Lab IHP/BTU, Konrad-Wachsmann-Allee 1, D-03046 Cottbus, Germany
[c]Siltronic AG, Hanns-Seidel-Platz 4, 81737 München, Germany

This work presents development and results of a storage getter test based on the measurement of the metal concentration by time-of-flight secondary ion mass spectroscopy applied for a low Cu contamination level. It was found that Cu atoms introduced into the as-grown sample by a drive-in anneal at high temperature diffuse out from the bulk to the surface within 7 days of storage at room temperature. Annealing steps at low temperature should decrease the time which Cu needs for the outdiffusion to the surface. However, the Cu atoms in samples subjected to outdiffusion annealing at 250 °C or 400 °C precipitated in the bulk. The investigation of the getter efficiency by the storage test in silicon samples containing oxygen precipitates has shown that in order to achieve a getter efficiency above 90%, the density of bulk microdefects should be higher than 6×10^9 cm^{-3}.

DOI: 10.12693/APhysPolA.125.965
PACS:

1. Introduction

Cu atoms are one of the most harmful impurities for ultra-large scale integration devices. Due to the high solubility and diffusivity of Cu in silicon, Cu atoms can easily contaminate silicon wafers even at room temperature. One method which is used to remove Cu impurities from the device region is internal gettering (IG) which is based on oxygen precipitates generated in the bulk of silicon wafers. In order to determine the getter efficiency of oxygen precipitates, different getter tests can be used. The haze test is a fast and easy to perform method, and the equipment is of low cost [1]. Due to these advantages, this method is often used to determine the getter efficiency [2, 3]. However, the haze test uses a high level of contamination. Since the fabrication of microelectronic devices is a very pure process and the level of possible contamination is relatively low, the results of the haze test are rather inappropriate. It has been already demonstrated that the getter efficiency of oxygen precipitates for Cu strongly depends on the initial contamination level [4]. Therefore, many getter tests with low initial contamination level were developed. Most of them are based on contamination by spin coating. The concentration of metals is measured by ICP-MS or GF-AA after dissolution of the silicon layers containing metal atoms by chemical etching [5–7]. Although, the sensitivity of these getter tests is very high, they require whole wafers for the tests and just deliver an average getter efficiency for the whole wafer. In this work, a getter test based on the measurement of the surface concentration of Cu by time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was developed. The advantage of this test is the possibility to investigate several small samples of about 1 cm^2 from certain locations on a wafer simultaneously and the measurement time is very short.

So far, the SIMS method was mainly used for the investigation of the getter efficiency in implanted samples. The aim of such investigations was to measure the concentration depth profile and to observe the site of metal aggregation in the implanted projected range [8, 9]. The application of ToF-SIMS for the investigation of the metal concentration on the surface is much more difficult because of undesired surface effects which can influence the value of the measured concentration.

This work describes the development of a ToF-SIMS getter test, the problems which are associated with the measurement of the surface concentration and its limitations. Finally, the getter efficiency of oxygen precipitates is investigated by a 7 day storage getter test.

2. Experimental

The samples used for the investigations were mainly cut out from two types of wafers. One part of samples was cut out from B-doped (100) Czochralski (CZ) silicon wafers 200 mm in diameter with resistivity of about 10 Ωcm. The concentration of interstitial oxygen according to DIN 50438/1 was 6.5×10^{17} cm^{-3}. This type of samples will be named in the following “low Oi”. The second type of wafers used was B-doped (100) CZ-Si 150 mm in diameter with a resistivity of about 50 Ωcm. The concentration of interstitial oxygen according to DIN 50438/1 was 8.5×10^{17} cm^{-3}. This type of wafer will be called “high Oi”. Both wafer types were polished on the front side and etched on the back side. For the development of the ToF-SIMS 7 day storage getter test, four types of samples were used. The first sample was cut

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[*] corresponding author; e-mail: kot@ihp-microelectronics.com

out from a low Oi wafer. This sample was pre-treated by rapid thermal annealing (RTA) at 1250 °C for 30 s and annealed at 800 °C for 32 h in N_2. The second sample was cut out from a high Oi wafer. The third sample was cut out from a float zone (FZ) silicon wafer and the fourth from an n-type CZ silicon wafer.

For the investigation of the getter efficiency in the samples contaminated with low concentration of Cu, both the low and the high Oi wafers were used. The samples were pre-treated by RTA at 1175 °C, 1200 °C, 1225 °C, or 1250 °C for 30 s and annealed at 800 °C for 1 h, 2 h, 4 h, 8 h, 16 h, or 32 h in N_2. After that, the samples of the low Oi and the high Oi wafers were contaminated with Cu in the range of 1.0×10^{13} cm^{-2} and 5.0×10^{12} cm^{-2}, respectively, and subjected to the ToF-SIMS 7 day storage getter test.

In order to investigate the influence of large oxygen precipitates on the bulk micro defects (BMD) density some samples were subjected to an additional growth anneal and then investigated by the ToF-SIMS 7 day storage getter test.

3. Results and discussion

3.1. Development of the ToF-SIMS getter test

3.1.1. Contamination procedure

The first step of the getter test is the contamination of the silicon samples with a well-defined concentration of Cu and the confirmation of this concentration by an analyzing technique like ToF-SIMS. In this getter test, pieces of Si wafers with an area of 1 cm × 1.3 cm were contaminated by dipping them in the contamination solution for 5 min. In order to contaminate the surface with 1×10^{13} cm^{-2} of Cu atoms, 70 μl of Cu standard solution (Cu 1000 ppm) were mixed with 1 l of H_2O. The pre-treatment of the sample surface plays a very important role for the measurement of the Cu concentration by ToF-SIMS. The measurement of the Cu concentration on the silicon surface is very sensitive to a native oxide therefore it is important to dip the sample in an HF solution before contamination. The relative sensitivity factor (RSF) of Cu which is used to calibrate the concentration measured is different for different materials [10]. This means that the amount of ejected ions can be different for silicon surfaces with oxide and without oxide layer.

Figure 1 shows the results of three samples contaminated with Cu by dipping the samples in the same Cu contamination solution. The first sample was annealed in oxygen atmosphere at 1000 °C to generate an oxide layer. The second sample was first dipped in an HF (5%) solution for 10 min and then subjected to a hydrophilization treatment in a $NH_4OH : H_2O_2 : H_2O$ (1:1:5) solution for 5 min. The third sample was hydrophobized in an HF (50%) solution for 10 min. The concentrations determined by ToF-SIMS differ by orders of magnitude as demonstrated in Fig. 1. In the sample with an oxide, the very low concentration of Cu is caused by the matrix effect. This means that the RSF factor of Cu in silicon is no more valid in this kind of sample. In the sample subjected to a hydrophilization, some matrix effect can also take place therefore the concentration is smaller than in the third hydrophobized sample where the concentration measurement is reliable.

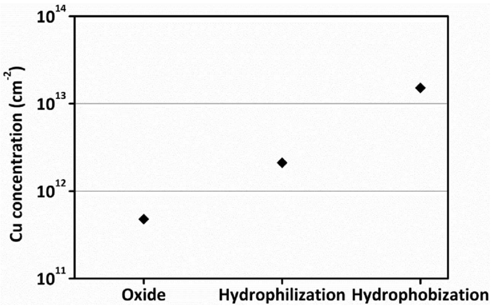


Fig. 1. Cu concentration measured on three differently pre-treated samples contaminated with 1×10^{13} cm^{-2} of Cu atoms.

In many getter tests, the contamination is based on hydrophilization solutions which can be helpful in the homogeneous distribution of metals on the silicon surface especially for spin-on contamination [4]. However, as it was just demonstrated the hydrophilization pre-treatment can be of negative influence on the concentration measurement by ToF-SIMS.

An initial Cu concentration of 1×10^{12} cm^{-2} can be obtained if 35 μl of Cu standard solution mixed with 1 l of H_2O is twice diluted in H_2O with a ratio of 0.1 : 0.9. The detection limit of the measurement of the Cu concentration on the silicon surface by this detection technique was about 1×10^{10} cm^{-2}.

3.1.2. Drive-in anneal and storage

After contamination, the samples were annealed at 1000 °C for 10 min in N_2 in order to in-diffuse the Cu into the Si bulk. As the result of this drive-in anneal, the concentration of Cu on the surface of the sample decreases and the Cu getter efficiency was found to be above 90% in any kind of sample. It is impossible to measure a useful getter efficiency at this point in time, because after 7 days of storage at RT most of the ungettered Cu diffuses out of the bulk and returns to the surface of the sample. A similar effect was observed by [5]. If most of the Cu is gettered by defects the getter efficiency remains above 90% even after 1 month. In this case Cu is permanently trapped at getter sites. The process flow of the final ToF-SIMS 7 day storage getter test respecting all the results mentioned above is schematically shown in Fig. 2.

3.1.3. Drive-out

In order to accelerate the outdiffusion of ungettered Cu from the Si bulk and to make the getter test faster, an annealing step at temperatures higher than RT can be applied as reported by [5]. Oxide layers at the samples, exceeding 3 nm must be removed before outdiffusion because otherwise Cu will not diffuse out [5, 11]. One

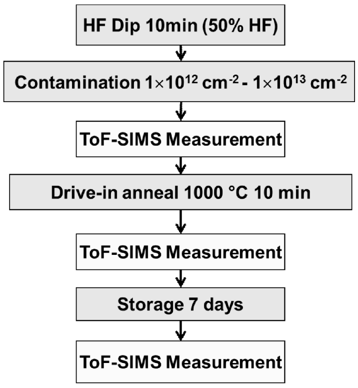


Fig. 2. Process flow of the ToF-SIMS 7 day storage getter test.

hour of annealing at 400 °C should be long enough to remove more than 90% of the Cu from p-type wafers [5]. However, the results obtained in this work are opposite as shown in Fig. 3. The getter efficiencies of as-grown samples (p-type CZ, FZ, and n-type CZ) subjected to a 7 day storage test are much lower than in the similar samples subjected to a drive-out anneal at 400 °C and 250 °C for 1 h. Even after 7 days, Cu atoms did not diffuse out of the samples subjected to the drive-out step. This means that the Cu remains in the bulk of the samples subjected to a drive-out anneal while in the samples subjected to a 7 seven day storage test a large part of the Cu diffuses out of the bulk. The sample indicated by R is a referential sample which contains oxygen precipitates and therefore exhibits a high getter efficiency.

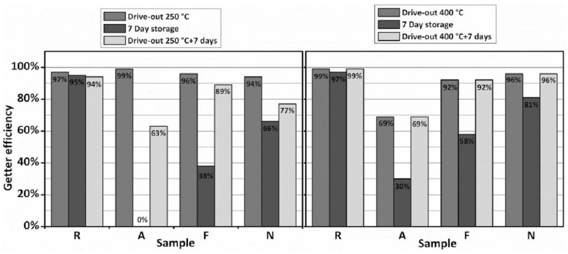
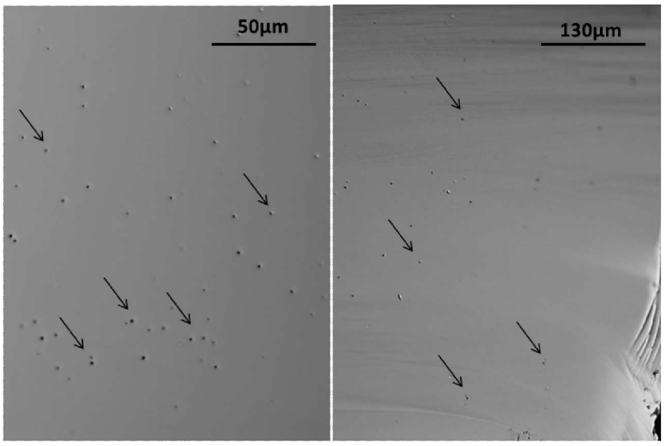


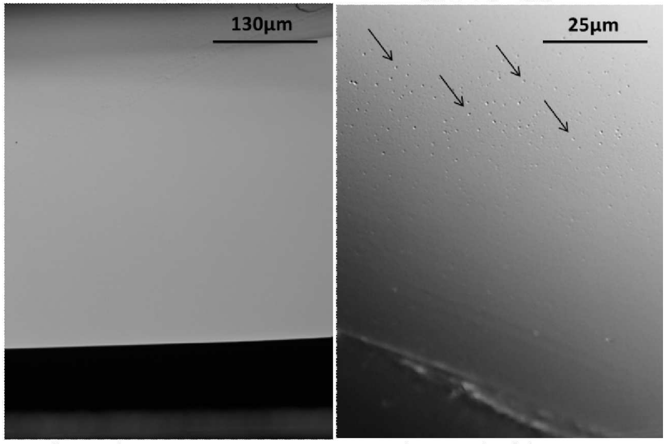
Fig. 3. Comparison of the results from a 250 °C or 400 °C drive-out tests and from a 7 day storage test. The initial Cu concentration was $\approx 1\times10^{12}$ cm^{-2}. R — CZ samples with high BMD density, A — CZ as-grown p-type, F — FZ p-type, N — CZ as-grown n-type.

The reason why Cu does not diffuse out of the Si bulk is illustrated in Fig. 4 where the images of preferentially etched as-grown samples are shown after dive-out annealing. On all the samples subjected to a drive-out anneal, characteristic etch pits of Cu precipitates were detected no matter if the initial concentration of Cu was 1×10^{12} cm^{-2} or 1×10^{13} cm^{-2}. In case of the sample subjected to 7 day storage test, no etch pits were found. These results mean that the drive-out anneals cannot be used to accelerate the outdiffusion of Cu because the Cu precipitates during the drive-out anneal. However, if the sample is stored at RT the Cu atoms can easily diffuse out. Therefore only the 7 day storage test can be used for the determination of the getter efficiency.



after 400°C drive-out
Cu 1×10^{13} cm^{-2}

after 400°C drive-out
Cu 1×10^{12} cm^{-2}



after 7 day storage test
Cu 1×10^{12} cm^{-2}

after 250°C drive-out
Cu 1×10^{12} cm^{-2}

Fig. 4. CZ as-grown sample subjected to a drive-out anneal or a 7 day storage test etched by the Secco etchant. Arrows indicate some of the etch pits of Cu precipitates.

3.2. Cu getter efficiency

Now, the 7 day storage test was used for the determination of the getter efficiency. The getter efficiency was calculated according to equation

$$\eta_{7\mathrm{day}} = \left(1 - \frac{\mathrm{Cu}_{\mathrm{In}}}{\mathrm{Cu}_{\mathrm{Ref}}}\right) 100\%, \tag{1}$$

where $\mathrm{Cu}_{\mathrm{In}}$ is the concentration of Cu measured on the surface of the sample after 7 day storage at RT and $\mathrm{Cu}_{\mathrm{Ref}}$ is the concentration of Cu measured on the surface of the sample after the contamination.

Figure 5 shows the Cu getter efficiency as a function of the BMD density for samples subjected to a growth anneal at 1000 °C for 16 h. Such samples are characterized by large oxygen precipitates with comparable size

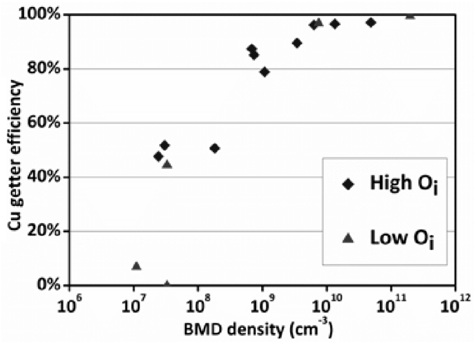


Fig. 5. Cu getter efficiency as a function of the BMD density for oxygen precipitates of nearly equal size. The initial concentration of Cu was $\approx 1 \times 10^{13}$ cm^{-2}.

accompanied by secondary defects like punched-out dislocations and stacking faults. The different density of the defects was achieved by an RTA pre-treatment of the samples at various temperatures which were subsequently annealed at various nucleation temperatures. The getter efficiency increases with an increasing density of defects and saturates for a BMD density of 6×10^9 cm^{-3}. This value is in a good agreement with the values obtained in Ref. [12] and about one order of magnitude higher than the value obtained by Isomae et al. [4]. The reason why Isomae et al. observed efficient Cu gettering by a BMD density of 5×10^8 cm^{-3} could be that it was a different type of getter test. They contaminated the back surface of the samples and after an in-diffusion step at 1000 °C for 5 min by using RTA, they measured the Cu concentration on the front surface. By comparing the concentration of Cu on the surface with the referential concentration they determined getter efficiency. The high getter efficiency achieved for a low BMD density could be the results of the Cu measurement carried out directly after in-diffusion step. As it was observed in this work Cu needs much more time to diffuse out from the Si bulk. A high getter efficiency of about 90% in the samples directly after the drive-in step was always observed but after 7 day storage it decreased far below 90%.

4. Conclusions

In this work the development of a 7 day storage getter test was presented. By means of the 7 day getter test, the getter efficiency in the samples contaminated with low concentration of Cu was determined. The results were compared to the results of other authors. The development of the getter test and the results of the getter test carried out on the samples contaminated with low concentration of Cu have shown that:

1. The contamination step requires pre-treatment in HF (50%) solution for reliable Cu concentration measurements by ToF-SIMS.
2. The detection limit of the Cu concentration measurement by ToF-SIMS on Si substrates equals 1×10^{10} cm^{-2}.
3. Directly after the drive-in step, most of the Cu remains in the Si bulk.
4. After 7 day storage at RT most of the ungettered Cu atoms diffuse out of the bulk. After this step it is possible to distinguish the samples with sufficient gettering from samples with insufficient gettering.
5. Cu out-diffusion could not be accelerated by out-diffusion anneals at 250 °C or 400 °C for Cu contamination levels of 1×10^{12} cm^{-2} and 1×10^{13} cm^{-2} because Cu precipitates during these anneals.

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