Investigation of Cu and Ni Diffusion Amounts for Silicon Substrates

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Abstract

An investigation regarding the Cu and Ni diffusion amounts for silicon substrates was conducted. A Cu and Ni reference solution was applied to a silicon substrate, heated to 350ºC for one or two hours, and then measured using TXRF. As a result, it was discovered that Cu diffused into the silicon substrate to such a level that it could be detected on the side opposite the Cu side, while Ni diffused only several hundred nm. It is assumed that preventative measures, such as gettering site forming for Cu, will be required. However, the effects of Ni used in electroformed dicing blades are considered minimal.

1. Introduction

In semiconductor device manufacturing, contamination caused by metal impurities has a large impact on decreases in device reliability. Use of heavy metals, such as Fe (iron) and Ni (nickel), and alkali metals, such as Na (sodium), is avoided, and in particular, Cu (copper), when a Si (silicon) substrate is being used (Fig. 1).

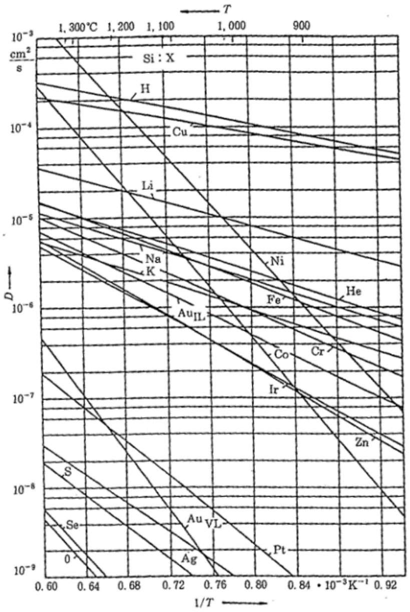

Fig. 1. Diffusion coefficient and temperature dependence on Si (1)

Cu, which has a high diffusion coefficient, requires control even on the sidewalls and backside of Si substrate memory devices especially, which are becoming thinner. Intentionally leaving processing damage as a gettering site on the backside of the Si substrate after thinning is used as a countermeasure for capturing Cu.

On the other hand, electroformed dicing blades are used in the dicing process, which singulates the Si substrates (Photo 1). These blades use Ni as the bond material. Essentially, the exposed section of the diamond grit is what contacts the Si (Photo 2). However, there are concerns of contamination from metal impurities due to the possibility of minute amounts of residual Ni in the Si substrate.

In this experiment, the amount of Cu and Ni diffusion in the Si substrate was investigated under temperature environment conditions harsher than those used in the back-end of the semiconductor device manufacturing process.

Photo 1. dicing blades

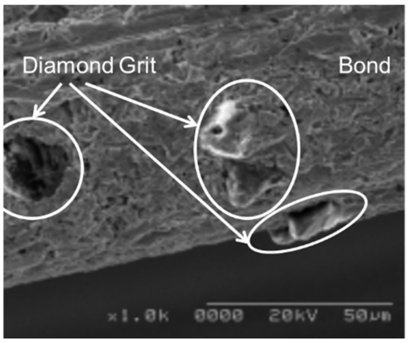

Photo 2. Bond and diamond abrasive grit

2. Method of Experiment

The method used to investigate the amount of diffusion in the Si substrate is shown below.

2-1. Method of Experiment

Cu standard solution and Ni standard solution reagents for optical absorption analysis (manufactured by Kanto Chemical Co., Ltd.) were each diluted and applied to the backside of 725 µm thick 8-inch diameter Si substrates so that the concentration was 1.00E13 atoms per square centimeter. After the substrates were natural-air dried, they were heated in an environment of 350°C using a clean oven for both one and two hours each and subjected to forced diffusion. The amount of Cu and Ni diffusion was then measured using a TREX6000 manufactured by Technos Corporation (TXRF: total reflection x-ray fluorescence).

2-2. Method of Measuring Cu Diffusion

Because Cu diffuses quickly on a Si substrate, the amount of Cu was measured on the side where the metal standard solution was applied and on the opposite side.

2-3. Method of Measuring Ni Diffusion

Because Ni diffuses slowly at low temperatures, the side with the metal standard solution applied was measured. After heating the substrate in a clean oven and measuring the amount of Ni on the outermost surface, the Ni was removed from the outermost surface using HCl + H_2O_2 + H_2O (hydrochloric acid perhydrate). Next, the naturally oxidized Si surface, or SiO_2 (silicon dioxide) layer, was removed using DHF (dilute hydrofluoric acid), a Standard Clean 1 was performed using NH_4OH (ammonium hydroxide) and H_2O_2 (hydrogen peroxide solution) mixed in deionized water, and a thin SiO_2 (silicon dioxide) layer was formed on the Si surface. Fine etching was performed repeatedly on the formed oxidization film and the amount of Ni was measured every several tens of nanometers.

3. Measurement Results

3-1. Amount of Cu Diffusion

In the Cu sample heated at 350°C for one hour, on the side opposite to where the Cu was applied, an average diffusion amount of 1.59E10 atoms per square centimeter and a maximum diffusion amount of 9.57E10 atoms per square centimeter were measured (Fig. 2).

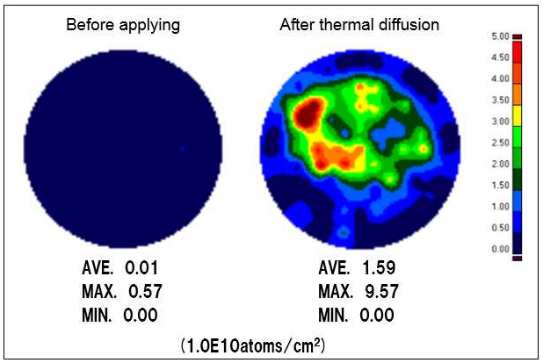

Fig. 2. Amount of Cu diffusion in 1 hour at 350°C (TXRF)

In the Cu sample heated at 350°C for two hours, the average diffusion amount was 2.52E10 atoms per square centimeter and the maximum diffusion amount was 19.52E10 atoms per square centimeter (Fig. 3).

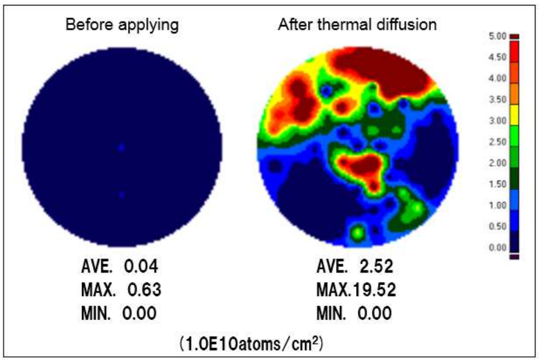

Fig. 3. Amount of Cu diffusion in 2 hours at 350°C (TXRF)

3-2. Amount of Ni Diffusion

Because the diffusion speed was slow in the Ni diffusion measurements, the amount of Ni was measured while performing fine etching on a surface with metal standard solution applied.As is shown in the graphs in Fig. 4, Ni (Y-axis) was present in each process step (X-axis). However, for the sample subjected to thermal diffusion at 350°C for one hour, almost all of the Ni had been removed in the cleaning of the outermost surface where it had been applied. Fine etching was performed repeatedly and the amount of Ni was measured every 10 nanometers.

In the Y-log graph, even though it was a small amount, it is clear that the Ni diffused and was present inside the Si substrate. Taking the average Ni diffusion amount into consideration, the amount of Ni below a depth of 60 nm was less than 0.50E10 atoms per square centimeter.

It is also clear that the Ni diffused further into the substrate in the sample that was subjected to thermal distribution for two hours at a temperature of 350°C than the sample that was subjected to thermal diffusion for one hour at a temperature of 350°C (Fig.5). Taking the average Ni diffusion amount into consideration, the amount of Ni below a depth of 250 nm was less than 0.50E10 atoms per square centimeter.

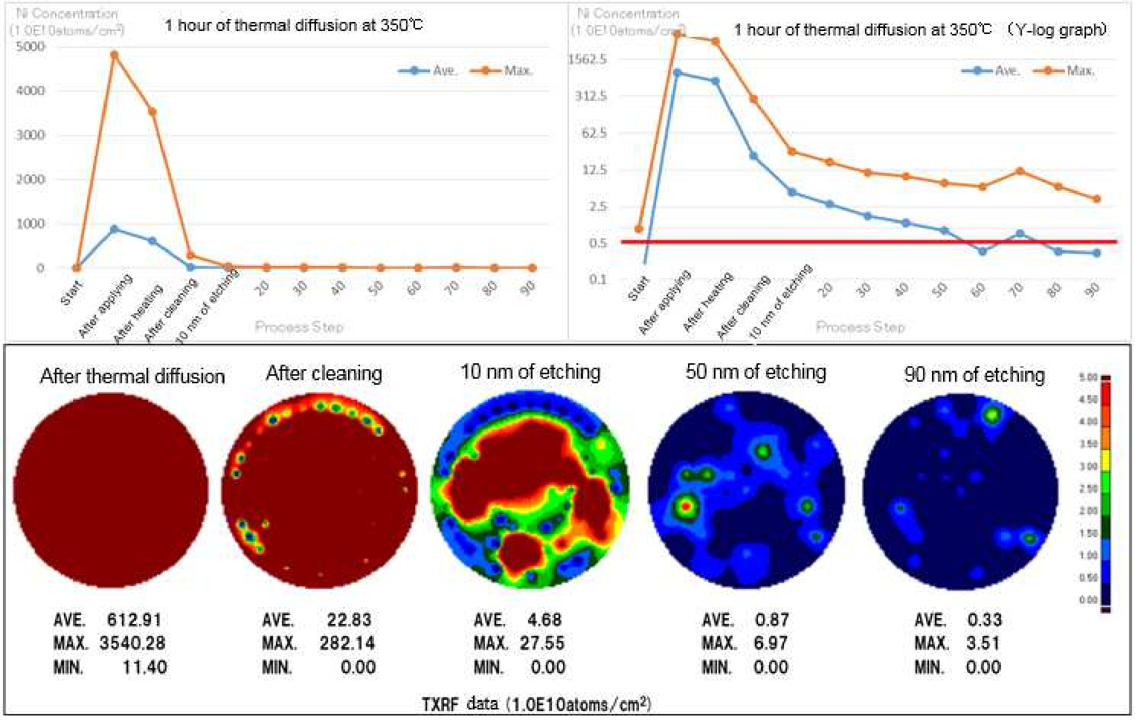

Fig. 4. Amount of Ni diffusion in 1 hour at 350°C

4. Discussion

In the accelerated experiment of one hour in a 350°C environment (which is a harsher temperature environment than what is used in the back-end of the semiconductor device manufacturing process), we observed that the Cu diffused through to the reverse side of the 725 µm thick Si substrate. Even though this experiment was performed under a harsher temperature environment than that which is used in the actual manufacturing process, because of the high diffusivity, it is thought that preventative measures for Cu contamination from the backside of the Si substrate, such as gettering, are required.

In contrast, it was evident that Ni only diffuses several hundred nanometers even in an accelerated experiment. Ni is already known as a stable compound that is easy to use when reacting with Si and is used on circuits on the front side of devices, such as in the NiSi (nickel solinoid) adjacent to gate electrodes(2)(3).

Thus, based on the information above, we can deduce that the Ni in the electroformed dicing blades used in the dicing process has very little impact on Si die, even when it adheres to the sidewall of the die.

5. Conclusion

By forcibly contaminating Si substrates with Cu and Ni and investigating the amount of diffusion in temperature environment conditions even harsher than those used in the back-end of the semiconductor device manufacturing process, we verified that Cu has a high diffusivity and Ni has a low diffusivity.

It was confirmed that Cu, which has a high diffusivity, can be captured in a gettering site, which causes processing damage to remain on the

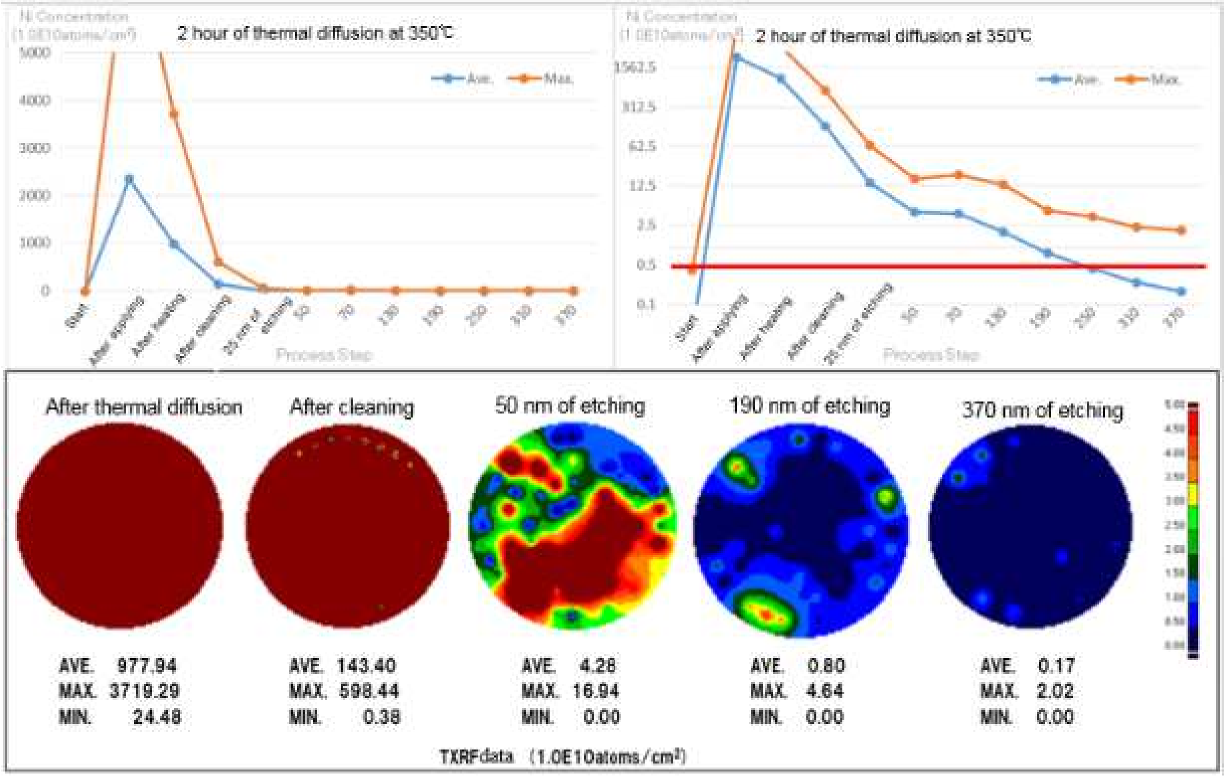

Fig. 5. Amount of Ni diffusion in 2 hours at 350°C

substrate. However, it is not clear yet whether this is also possible for Ni. We will continue our investigation and determine whether Ni can be captured in a gettering site by processing damage.

References

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