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Detection of low-level copper contamination in p-type silicon by means of microwave photoconductive decay measurements

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Abstract

In order to achieve a better understanding of the behaviour of copper in p-type silicon, studies of the recombination of copper were carried out by the microwave photoconductive decay measurement method (μ PCD) using high-intensity bias light. It was observed that in the presence of small oxygen precipitates, high-intensity light could be used to activate precipitation of interstitial copper. It is suggested that high-intensity light changes the charge state of interstitial copper from positive to neutral, which enhances the precipitation. The precipitation follows Ham's kinetics and results in an increase in the recombination rate, which is detectable even with very low copper concentrations. This phenomenon can be used to detect low levels of copper contamination by the μ PCD method. In addition, it was observed that out-diffusion as well as in-diffusion of interstitial copper could be affected by an external corona charge. Thus, it is suggested that copper atoms do not form stable bonds at the Si–SiO₂ interface after out-diffusion from bulk silicon.

1. Introduction

The physical behaviour of copper in silicon is complex and interesting. The current knowledge of the topic has recently been reviewed by Istratov and Weber [1]. Copper, like most transition metals, has detrimental effects on the yield of integrated circuit devices [1]. Thus, there is a need in process control for reliable and sensitive measurement methods that can be used to detect low-level copper contamination. For detection of iron contamination, Zoth and Bergholz have developed a method in which surface photovoltage (SPV) is used to determine the iron concentration in silicon [2]. This method is routinely used in silicon production facilities [3].

The excess charge-carrier lifetime is limited by carrier recombination at oxygen- and metal-related defects and at the surfaces of silicon wafers. In n-type silicon the lifetime

correlates with the surface copper contamination, but it is difficult to detect a copper density below 10^{10} cm^{-2} [4, 5]. The difference in lifetime value between n-type and p-type silicon can be used to identify possible copper contamination [6].

Henley *et al* [7] and Ramappa [8] reported that optical and thermal activation degrade the charge-carrier diffusion length in copper-contaminated boron-doped silicon. They proposed that the activation procedure dissociates interstitial copper agglomerations and forms extended substitutional defects in silicon, which have much greater recombination activity.

It has been observed that oxygen precipitates are relatively inefficient as gettering sinks for copper [9]. This was tentatively explained by compressive strains generated by both oxide precipitates and copper precipitates and possibly by electrostatic effects. However, Bazzali *et al* [10] have demonstrated that wafers, which have small oxygen precipitates, could be used for detecting relatively low levels of copper contamination by the charge-carrier lifetime technique.

The microwave photoconductive decay measurement method (μ PCD) was selected for this study, as charge-carrier lifetime at high injection level is less sensitive to the oxygen precipitation compared to the charge-carrier lifetime at low injection level. Moreover, the high-injection-level lifetime is not sensitive to interstitial iron contamination, as formation of iron–boron pairs is prevented. Furthermore, the charge-carrier recombination rate at the wafer surface is lower at high injection than at low injection [11].

The aim of this experimental study is to demonstrate a method for detection of low-level copper contamination in p-type silicon. The method is based on our observations that interstitial copper atoms precipitate in the presence of small oxygen precipitates at room temperature only with optical activation and that surface corona charge can be used to prevent out-diffusion of interstitial copper.

2. Experimental details

2.1. Processing

The samples were single-side-polished 100 mm Czochralski grown silicon wafers, with thickness of $(525 \pm 20) \mu\text{m}$. The resistivity in boron-doped wafers was about $10 \Omega \text{ cm}$ and in phosphorus-doped wafers it was $3\text{--}3.9 \Omega \text{ cm}$. All wafers were oxidized at 1050°C for 15 min to grow a thermal oxide layer. This annealing also dissolves oxygen precipitate precursors that are present in as-grown silicon wafers to some extent. Small oxygen precipitates were grown in p-type silicon by two-step annealing. The wafers were annealed at 625°C for 4 h to nucleate oxygen precipitates. This was followed by the growth of precipitates at 800°C for 4 h.

The oxide-covered surfaces of the wafers were contaminated with copper by immersing the wafers into deionized water, which contained 1 ppba copper (II) sulfate pentahydrate. Copper was in-diffused into silicon at 800°C for 20 min in nitrogen atmosphere through the 17 nm silicon dioxide layer, which was used to diminish unintentional iron contamination.

2.2. Measurement

The high-injection-level excess charge-carrier lifetime was determined by the microwave photoconductive decay technique using the WT-85 XL system of Semilab Inc. The bias light power was adjusted in order to maintain 10^{16} cm^{-3} excess charge-carrier concentration during the measurement. The optical activation was performed with 973.5 nm light, whose intensity was $40 \pm 10 \text{ W cm}^{-2}$. Carrier lifetime measurements were not feasible during the

optical activation because of a too-high excess charge-carrier concentration. The measured excess charge-carrier lifetime values were converted to optically activated excess charge-carrier recombination rate values $R(t)$ using the equation

$$R(t) = \Delta n \left[\frac{1}{\tau(t)} - \frac{1}{\tau(t=0)} \right] \quad (1)$$

where $\tau(t)$ is the measured high-injection-level lifetime value as a function of optical activation time t . We used a value of 10^{16} cm^{-3} for the excess charge-carrier concentration Δn . A surface charge density of $+1$ or $-1 \mu\text{C cm}^{-2}$ was deposited on the wafer surfaces with a corona charge generator. We used high surface charge density to eliminate the possibility of the optical activation significantly changing the surface potential of the wafer.

3. Results and discussion

3.1. Impact of copper and oxygen on charge-carrier lifetime

The intentional copper contamination decreased the value of the lifetime in n-type silicon from 3.2 to 1.1 ms, which corresponds to a copper surface contamination value of less than 10^{12} cm^{-2} [4, 5]. This low copper content estimate was supported by the observation of a small increase in the lifetime of p-type wafers after copper contamination. This passivation effect of copper has been observed earlier with low copper concentrations [1]. It was also verified that the grown-in oxygen precipitates do not have an impact on the charge-carrier lifetime.

3.2. Precipitation of copper

The wafer surfaces were positively charged within half an hour after the last furnace process in order to keep interstitial copper in the bulk. Optical activation decreased the charge-carrier lifetime from 1.5 to 0.154 ms in a p-type silicon sample that had small oxygen precipitates and a low level of copper contamination. Without optical activation, no decrease in lifetime was observed. Figure 1 shows the optically activated excess charge-carrier recombination rate as a function of optical activation time. The recombination rate values were calculated with equation (1).

Ham's law [12, 13] was applied to explain the measurement results of figure 1. By assuming that (i) the solubility of interstitial copper is zero during optical activation, i.e. at room temperature, (ii) the optically activated recombination rate is proportional to the precipitation rate of copper and (iii) the precipitation radius is fixed, we get the equation

$$R(t) = R_{\text{final}}(1 - \exp(-t/\tau_0)). \quad (2)$$

In equation (2), R_{final} is the optically activated excess charge-carrier recombination rate when the optical activation time is much larger than the time constant of Ham's law τ_0 :

$$\tau_0 = 1/(4\pi nr_0 D) \quad (3)$$

where n is the precipitation site density, r_0 is the fixed precipitate radius and D is the diffusion constant of the precipitating metal.

The value $1650 \pm 50 \text{ s}$ for the time constant τ_0 was obtained by fitting measurement points to equation (2). The fitted curve is shown in figure 1. The diffusion coefficient of interstitial copper is $9.68 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for 10^{15} cm^{-3} boron-doped silicon at temperature 297 K [14]. Therefore, the measured time constant gives $nr_0 = 500 \text{ cm}^{-2}$. The nucleation step for oxygen precipitates produced about 10^9 cm^{-3} density of oxygen precipitates [15]. By assuming that the oxygen precipitate density corresponds to the precipitate site density, we get the value 5 nm for the effective radius of the precipitates, which is a reasonable value.

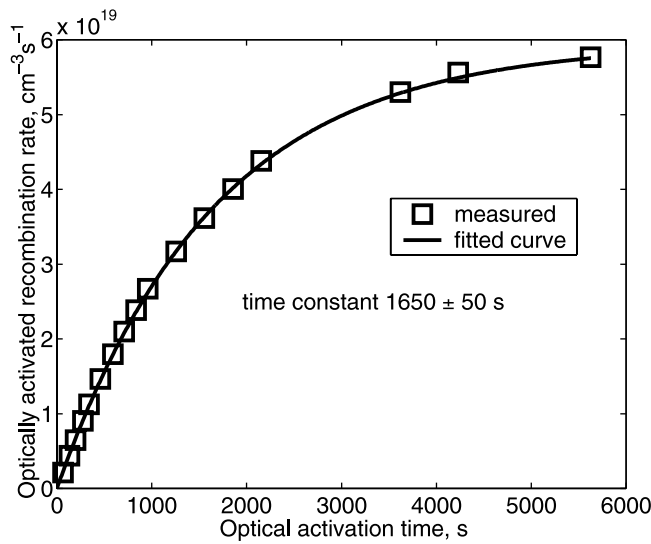


Figure 1. Optically activated excess charge-carrier recombination rate as a function of optical activation time. The squares are the measurement points and the solid curve is the curve fitted to the measurement points.

The results indicate that in the case of low copper concentrations the interstitial copper atoms do not precipitate in the presence of small oxygen precipitates at room temperature without high-intensity light. It has been reported that both interstitial copper atoms [1] and small oxygen precipitates have positive charge states [16, 17]. A possible physical reason for the observation of high-intensity light enhancing the precipitation of copper in the presence of small oxygen precipitates is that the charge state of some of the interstitial copper atoms changes from positive to neutral. The electronic Fermi-level position during the optical activation was about $E_c - 0.15$ eV, which is the same as the energy level of interstitial copper [18]. Another possible explanation for the precipitation of copper is that the high-intensity light generates a large excess charge-carrier density, which screens the positive charge of the oxygen precipitates. Thus high-intensity light may decrease the precipitation barrier which exists around the oxygen precipitates. In addition, the electron Fermi-level changes at the surfaces of the oxygen precipitates could change the charge state of the interface states at the silicon–oxygen precipitate interface, as occurs at the silicon surface.

The results confirm that electrostatic effects between interstitial copper atoms and small oxide precipitates slow down the precipitation of copper at small oxide precipitates. That could explain the recently reported result that oxide precipitates are relatively inefficient as gettering sinks for copper [9].

3.3. Out-diffusion of copper

It has been reported [19] that the band bending at the wafer surface affects the out-diffusion of copper. Therefore, we deposited positive corona charge on the wafer surfaces, which results in band bending of about 0.8 V. After deposition of the positive surface charge, the optically activated recombination rate was measured to be about the same after one hour and after two days. This demonstrates that high positive corona charge can be used to prevent out-diffusion of interstitial copper.

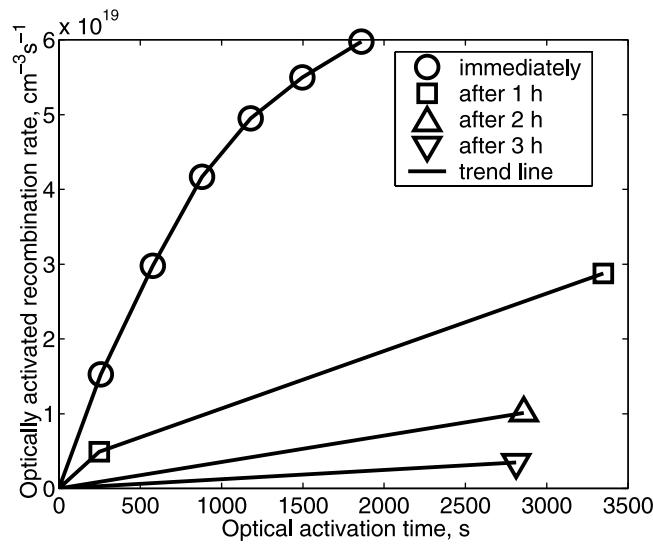


Figure 2. Optically activated excess charge-carrier recombination rate as a function of optical activation time. The optical activation was started immediately and after 1, 2 and 3 h after the surface charge was changed from positive to negative polarity.

In our study, the wafer surfaces were first positively charged within 40 min after the last furnace process. After two days, the wafer surfaces were negatively charged in order to study the time constant of copper out-diffusion. Figure 2 shows the optically induced charge-carrier recombination rate as a function of optical activation time after the deposition of the negative corona charge for different time periods after the deposition. From figure 2 it can be seen that the recombination rate value saturated to a significantly lower value after 1 h when compared to the value measured immediately after the polarity change of the surface charge. The time constant obtained for the recombination rate change was 3600 ± 200 s from 1, 2 and 3 h results.

The theoretical time constant for the out-diffusion of particles is

$$\tau_{od} = \frac{d^2}{\pi^2 D} \quad (4)$$

where d is the thickness of wafer and D is the diffusion coefficient. Equation (4) was used to calculate the diffusion coefficient of out-diffusing particles. The diffusion coefficient determined, $(8 \pm 1) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, is in excellent agreement with the reported copper diffusivity value, which is $9.68 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ in 10^{15} cm^{-3} boron-doped silicon at temperature 297 K [14]. We can thus conclude that the decrease in the recombination rate in figure 2 after several hours of change in surface charge polarity is due to the out-diffusion of interstitial copper.

It is worth mentioning that three hours after the change in the surface charge polarity the interstitial copper concentration has been considerably decreased due to out-diffusion compared to the situation immediately after the change in surface charge polarity. Even with such low concentrations, the change in recombination rate is still detectable. This result indicates that low copper concentrations can be detected in silicon by the μ PCD method.

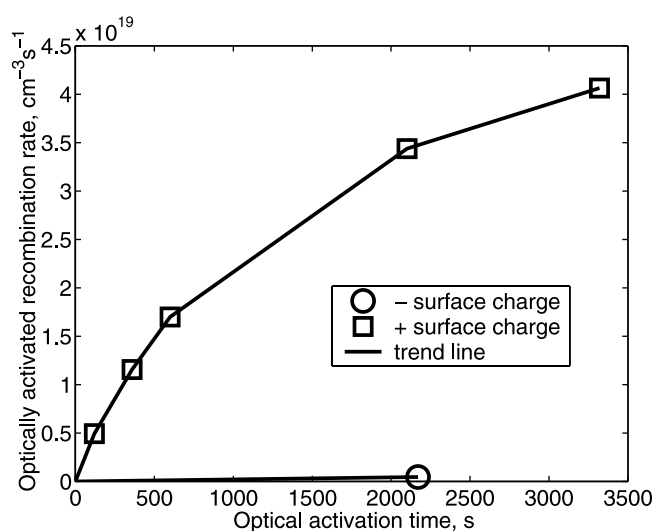


Figure 3. Optically activated charge-carrier recombination rate as a function of optical activation time. The key shows the polarity of the surface charge during the optical activation.

3.4. In-diffusion of copper

The wafer surfaces were negatively charged within 20 min after the last furnace process to enhance the out-diffusion of interstitial copper. The first optical activation measurement was done after five days, during which period copper had enough time to out-diffuse almost completely from bulk silicon. Then the surface charge was changed from negative to positive and the optical activation measurement was repeated. Figure 3 shows the optically activated charge-carrier recombination rate as a function of optical activation time before and after the surface charge change from negative to positive polarity. Figure 3 shows that the optical activation increases the charge-carrier recombination rate again after the change of surface charge polarity. The result can be interpreted in the following way. Copper atoms that out-diffused to the wafer surface during the period of negative surface charge can diffuse back into the bulk of silicon when the surface potential of the wafer with respect to the bulk is increased with positive corona charge.

As a result, we suggest that copper does not form stable bonds at the silicon–silicon dioxide interface at room temperature, because copper atoms can diffuse back into bulk silicon from wafer surfaces due to a band bending of about 0.8 V. We assume that optical activation does not dissociate copper bonds at the wafer surface.

4. Conclusions

It was observed that at room temperature the interstitial copper atoms do not precipitate in the presence of small oxygen precipitates without excitation. A high-intensity optical activation enhances the precipitation, which follows Ham's kinetics during the optical activation. This optically activated precipitation increases the recombination rate—which can be detected by means of μPCD even in the case of very low levels of copper contamination. Our results show that out-diffusion of copper atoms in p-type wafers can be prevented with a high-density positive corona charge. This positive charge can also be used to in-diffuse copper atoms into bulk silicon from the silicon–silicon dioxide interface, i.e. release the copper atoms from the

surface of a wafer. Further study is needed to obtain a full understanding of these phenomena and to use them for quantitative measurements of copper contamination.

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