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## Quantitative copper measurement in oxidized p -type silicon wafers using microwave photoconductivity decay

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## Quantitative copper measurement in oxidized *p*-type silicon wafers using microwave photoconductivity decay

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We propose a method to measure trace copper contamination in *p*-type silicon using the microwave photoconductivity decay ( $\mu$ -PCD) technique. The method is based on the precipitation of interstitial copper, activated by high-intensity light, which results in enhanced minority carrier recombination activity. We show that there is a quantitative correlation between the enhanced recombination rate and the Cu concentration by comparing  $\mu$ -PCD measurements with transient ion drift and total reflection x-ray fluorescence measurements. The results indicate that the method is capable of measuring Cu concentrations down to  $10^{10} \text{ cm}^{-3}$ . There are no limitations to wafer storage time if corona charge is used on the oxidized wafer surfaces as the charge prevents copper outdiffusion. We briefly discuss the role of oxide precipitates both in the copper precipitation and in the charge carrier recombination processes. © 2005 American Institute of Physics. [DOI: 10.1063/1.1999008]

The recent introduction of copper interconnects in ultralarge scale integration technology has increased the need for sensitive and reliable detection tools for copper contamination in silicon wafers. In comparison to iron, copper detection is much more challenging, partly because copper does not form stable defects in the bulk but tends to outdiffuse to the wafer surfaces even at room temperature (RT). So far, only one electrical method, transient ion drift (TID),<sup>1,2</sup> has been introduced for the quantitative Cu measurement in *p* Si. However, high-temperature pretreatment and electrical contacts are required for the TID measurement. Vapor phase decomposition/total reflection x-ray fluorescence (VPD-TXRF) is a well-known analytical method to measure low Cu contamination but it is limited to measuring the surface concentration, although copper can be measured indirectly from the bulk by letting copper outdiffuse to the wafer surfaces.<sup>3</sup> Both TID and VPD-TXRF are destructive and somewhat time-consuming methods.

Contactless recombination lifetime methods offer an attractive alternative for detecting contamination in silicon. However, Cu contamination has only a weak impact on recombination lifetime compared to, for example, iron. In *n*-Si, the Cu concentration has to exceed  $10^{12} \text{ cm}^{-3}$  to affect the recombination lifetime, and in *p*-Si Cu concentration has to be even higher to have an impact on the lifetime.<sup>4</sup> The recombination lifetime method is, therefore, not suitable as such for the detection of trace Cu contamination. Nevertheless, Henley *et al.*<sup>5,6</sup> observed recently using surface photovoltage method that in copper contaminated samples optical or thermal activation decreases the diffusion length. They proposed that extended substitutional defects are formed as a result of the activation process. We have recently reported a similar method to detect trace Cu contamination in *p*-Si using the microwave photoconductivity decay ( $\mu$ -PCD) technique.<sup>7</sup> The method is based on light activation of interstitial Cu. We believe that the light illumination reduces the

electrostatic repulsion between positively charged interstitial Cu ions and Cu precipitates, enabling copper to precipitate in the wafer bulk even at a low contamination level. We showed qualitatively that such a formation of Cu precipitates increases the recombination activity, which can be easily measured by conventional lifetime methods. In this letter, we show how to measure Cu concentration quantitatively in silicon by a lifetime method. This is done by calibrating the measured lifetime with TID and VPD-TXRF.

The samples used in the experiments were Czochralski-grown *p*-type silicon wafers with a resistivity of  $22 \Omega \text{ cm}$ . The initial oxygen level was 14 ppma (ASTM F 121-83 standard). All wafers were first oxidized either at  $1050 \text{ }^\circ\text{C}$  or  $950 \text{ }^\circ\text{C}$  for 15 min to reduce the effect of the thermal history, and to form a protective surface oxide about 28 nm thick, or 5–8 nm, respectively. This anneal is often referred to as the homogenization. No differences in the measurement results could be observed later related to the oxide thickness. Therefore, we do not specify the thickness throughout this letter.

Wafers were sorted into three different groups by the oxide precipitate density. The first group remained homogenized and we can assume that the bulk microdefect (BMD) density is below  $10^6 \text{ cm}^{-3}$ . In the second and the third groups, small oxide precipitates were grown either by 4 h or 16 h nucleation anneal at  $625 \text{ }^\circ\text{C}$ , followed by 4 h growth anneal at  $800 \text{ }^\circ\text{C}$ . The radius of the oxide precipitates after the growth anneal can be estimated to be in the order of 3 nm.<sup>8</sup> The density of oxide precipitates after 4 h and 16 h nucleation is approximately  $5 \times 10^8$  and  $10^{10} \text{ cm}^{-3}$ , respectively.<sup>9</sup> In the remainder of the letter, we will refer to these wafer groups as “homogenized”, “low BMD”, and “high BMD” wafers.

The wafers were contaminated in copper-sulfate solutions with varying Cu concentrations (0.1–300 ppb). Copper indiffusion was carried out at  $800 \text{ }^\circ\text{C}$  for 20 min through the oxide-covered wafer surfaces to minimize unintentional iron contamination. After air cooling the wafers, a positive corona charge of  $1 \mu\text{C}/\text{cm}^2$  was deposited on both wafer surfaces to prevent copper from outdiffusing and/or precipitating.<sup>7</sup> VPD-

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TXRF measurements of the surface Cu concentration were carried out on some of the wafers both before and after indiffusion. The composition of the HF–H<sub>2</sub>O<sub>2</sub>–H<sub>2</sub>O collecting solution was 0.5% HF and 7% H<sub>2</sub>O<sub>2</sub> by weight.

High-intensity light (29 W/cm<sup>2</sup>, 973.5 nm) was used to activate the copper in a small area of the wafer (illumination area ~ 1 mm<sup>2</sup>), where the recombination lifetime was measured by  $\mu$ -PCD as a function of light illumination time using the WT-85X Lifetime Scanner by Semilab. The details of the  $\mu$ -PCD and VPD-TXRF measurements can be found elsewhere.<sup>7</sup> After  $\mu$ -PCD measurements, Cu concentration was measured by TID in the same wafers but far from the light illumination spot using a modified DLS-83D system by Semilab.

The wafers were air cooled, which creates a possibility that some amount of the copper is precipitated/out-diffused during the cooling, thereby escaping the detection of both TID and  $\mu$ -PCD. Therefore, a few wafers were annealed at rapid thermal processor at 600 °C and quenched to get all the copper in the interstitial state. Within the measurement accuracy no difference could be observed in the Cu concentrations measured by TID, after air-cooling compared to the quench. Thus, the results imply that the outdiffused amount of copper during air cooling in our wafers was insignificant.

We have observed earlier that, in copper contaminated wafers, the measured lifetime  $\tau(t)$  decreases exponentially under light illumination according to the following equation<sup>7</sup>

$$\tau^{-1}(t) = \tau_{\text{init}}^{-1} + \tau_{\text{Cu},t}^{-1}(t) = \tau_{\text{init}}^{-1} + \tau_{\text{Cu}}^{-1}[1 - \exp(-t/t_{\text{Cu}})], \quad (1)$$

where  $\tau_{\text{Cu}}^{-1} = (\tau_{\text{final}}^{-1} - \tau_{\text{init}}^{-1})$ . Here,  $t$  is the light activation time,  $\tau_{\text{init}}$  is the initial lifetime,  $\tau_{\text{final}}$  is the lifetime after complete light activation, and  $t_{\text{Cu}}$  is the time constant of copper-related excess recombination activity. We believe that the decrease in lifetime is a result of copper precipitation,<sup>7</sup> which agrees with previous observations that Cu precipitates are very effective recombination centers.<sup>4</sup> Notice that the measurement separates Cu clearly from Fe contamination as  $\mu$ -PCD operates at high injection level; the light illumination dissociates Fe–B pairs with a short time constant, which results in the increase of lifetime<sup>10</sup> at the beginning of the illumination while copper precipitates are formed with a longer time constant and the result is a decrease in the lifetime at the end of the illumination.

Figure 1 shows an example of experimentally measured lifetimes as a function of light illumination time in wafers with either [Fig. 1(a)] varying density of oxide precipitates or [Fig. 1(b)] varying Cu concentration, together with fitted results according to Eq. (1). The figure illustrates that both  $\tau_{\text{Cu}}$  and  $t_{\text{Cu}}$  depend on the Cu concentration and the oxide precipitate density.

Let us first study the excess recombination rate caused by light activated copper defects in more detail. It is instructive to plot the inverse of  $\tau_{\text{Cu}}$ , as the effective density of recombination centers is proportional to the inverse of carrier lifetime if there is only one predominant type of lifetime limiting defects in the wafer. Figure 2 shows  $1/\tau_{\text{Cu}}$  as a function of Cu concentration quantified by either VPD-TXRF or TID. We can see that there is a clear correlation between  $1/\tau_{\text{Cu}}$  and the Cu concentration in all wafer groups. Some of the wafers were remeasured by TID and  $\mu$ -PCD a year after copper contamination, resulting in the same values, which confirms that there are no limits for the wafer

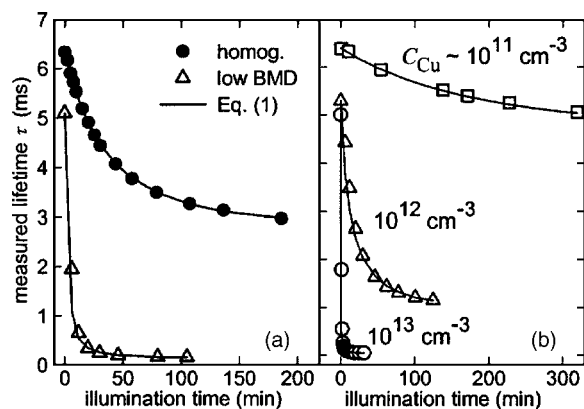


FIG. 1. Measured lifetime as a function of light illumination time and the fitted curves [Eq. (1)]. (a) The wafers have same amount of copper ( $5 \times 10^{12} \text{ cm}^{-3}$ ) but different density of oxide precipitates (circles  $< 10^6 \text{ cm}^{-3}$ , triangles  $5 \times 10^8 \text{ cm}^{-3}$ ). (b) The wafers have the same density of oxide precipitates ( $5 \times 10^8 \text{ cm}^{-3}$ ) but different amount of copper (circles  $1.3 \times 10^{13} \text{ cm}^{-3}$ , triangles  $1.7 \times 10^{12} \text{ cm}^{-3}$ , squares  $3.0 \times 10^{11} \text{ cm}^{-3}$ ).

storage time. Figure 2 also demonstrates well how the detection limit of  $\mu$ -PCD can be improved by increasing the density of oxide precipitates.

It seems that  $\mu$ -PCD is more sensitive for detecting low Cu concentrations than TID, especially in wafers with a high density of oxide precipitates. As an example of this, we had a wafer with no intentional copper contamination but which had a low level of copper due to unintentional contamination, probably from the oxidation furnace or wafer polishing. In this wafer, the lifetime decreased from the initial value of 1.4 ms to 0.7 ms after light illumination. However, we did not observe any capacitance transient in the TID measurement. We confirmed that the measured lifetime decrease was due to copper by letting copper outdiffuse to the surfaces using negative corona charge<sup>7</sup> and by verifying that the outdiffusion kinetics corresponded to the reported RT copper diffusivity.<sup>11</sup>

The above results enable us to make a quantitative correlation between the measured lifetime decrease and Cu concentration. Power fit results in the following equation in the case of wafers without oxide precipitates

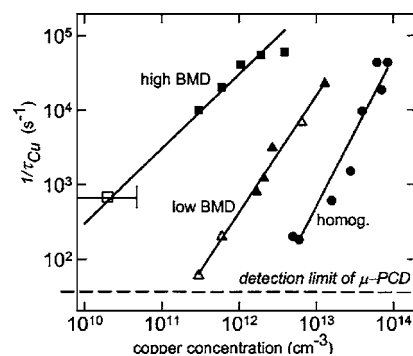


FIG. 2. Correlation between copper concentration and light activated lifetime in three different groups of wafers, with varying density of oxide precipitates: Homogenized (circles), low BMD (triangles), and high BMD (squares). Open triangles represent the wafers measured by VPD-TXRF. Also shown are the fitted curves Eqs. (2a)–(2c). The wafer with lowest level of copper could not be accurately positioned to the x axis as it is below the detection limit of TID and VPD-TXRF after indiffusion.

$$\tau_{\text{Cu}}^{-1} = (4.0 \pm 0.5) \times 10^{-24} C_{\text{Cu}}^2, \quad (2a)$$

where  $\tau_{\text{Cu}}$  is given in seconds and Cu concentration  $C_{\text{Cu}}$  is given in  $\text{cm}^{-3}$ . In the presence of oxide precipitates the equations become

$$\tau_{\text{Cu}}^{-1} = (2.5 \pm 0.5) \times 10^{-17} C_{\text{Cu}}^{1.6} \quad (\text{low BMD}), \quad (2b)$$

$$\tau_{\text{Cu}}^{-1} = (3.0 \pm 0.2) \times 10^{-8} C_{\text{Cu}} \quad (\text{high BMD}). \quad (2c)$$

To determine the detection limit for the  $\mu$ -PCD, we require that the lifetime after light illumination must decrease at least 10% from the initial value. Then, by considering the initial lifetime of 3 ms, the detection limit in homogenized wafers becomes  $3 \times 10^{12} \text{ cm}^{-3}$ , in low BMD wafers  $3 \times 10^{11} \text{ cm}^{-3}$ , and in high BMD wafers  $1 \times 10^9 \text{ cm}^{-3}$ . Notice that here, the high BMD density does not decrease the initial lifetime significantly as the defect size is relatively small and therefore the detection limit is not reduced. The high value of the initial lifetime (over milliseconds) is a combination of clean wafers, a high injection level and a corona charge.

The results show that with the same contamination level, copper has the strongest effect on the measured lifetime in the high BMD wafer group. It is likely that oxide precipitates or related defects provide heterogeneous nucleation sites for copper enhancing the nucleation of copper precipitates, like reported by Sachdeva *et al.*<sup>12</sup> Similar observations were made by Veve *et al.*,<sup>13</sup> who noticed that when oxide precipitates are present, copper atoms precipitate in their vicinity but the size of the copper precipitates is smaller than in as-grown wafers since copper is precipitated to a larger number of nucleation sites. Thus, the larger surface area together with the high density of centers could explain the strong recombination activity. Falster *et al.*<sup>14</sup> reported that a maximum density of about  $5 \times 10^7 \text{ cm}^{-3}$  BMD sites take part in the precipitation of copper, which suggests that not all of the oxide precipitates in our wafers are active precipitation sites. In those studies,<sup>12–14</sup> however, the Cu concentration was rather high and the precipitation took place during cooling. It is possible that copper behavior is different when it is present in smaller quantities and the precipitation is activated by light. In homogenized wafers, the density of existing heterogeneous nucleation sites is extremely low and copper may need to precipitate homogeneously, which results in the low density of copper defects. The superlinear recombination activity within the two of the wafer groups (homogenized and low BMD) suggests that the increase of copper atoms results in the strong nucleation of centers at high density rather than the growth of large precipitates at low density.

Next, we can more closely study the second parameter—the time constant of the copper defect formation  $t_{\text{Cu}}$ —which is obtained from the measurements by fitting Eq. (1) to the measured data. Figure 3 shows that the time constant is also dependent on the Cu concentration and the density of oxide precipitates. The higher the BMD in the wafer, the smaller the time constant. The larger time constant of copper precipitation in homogenized and low BMD wafers could be explained by the low density of the precipitation sites for copper. A main trend within the wafer groups is that increasing Cu concentration decreases the time constant, which is quite natural as there are more copper atoms to react.

Without any further studies, it is impossible to make final conclusions about the quantitative density and the size of the precipitates formed during light illumination. Further

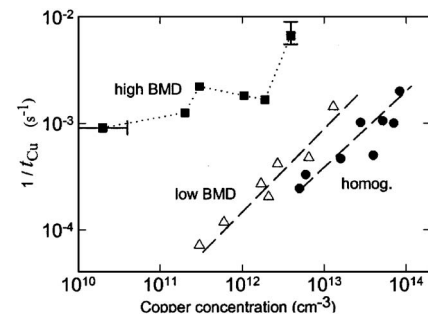


FIG. 3. Time constant of the defect formation as a function of copper concentration in three different groups of wafers, with varying density of oxide precipitates: Homogenized (circles), low BMD (triangles), and high BMD (squares). Also shown are the trend lines.

studies are in progress to obtain more accurate information about the density, morphology, and size of the copper defects.

Even though the quantitative measurement of low Cu concentration using  $\mu$ -PCD requires that the density of oxide precipitates is known, it can also have a beneficial effect; if the Cu concentration of the wafer is known, the method can be used for measuring the density of small oxide precipitates.

In conclusion, we have shown how to measure copper in  $p$ -type silicon using the photoconductive decay method. The results show that an ideal monitor wafer for copper contamination is an oxidized  $p$ -type wafer with high BMD density. The Cu concentration can be measured quantitatively if the BMD density is known as shown in Fig. 2. The method is also suitable for wafers that do not have oxide precipitates although the sensitivity of the measurement is then reduced. The only requirement is that the wafers have at least a 5 nm oxide layer, but there are no limits for the storage time after processing of the wafers. The major benefits of the method include the possibility to measure both Fe and Cu at the same point with only one measurement.

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