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Role of copper in light induced minority-carrier lifetime degradation of silicon

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We investigate the impact of copper on the light induced minority-carrier lifetime degradation in various crystalline silicon materials. We demonstrate here that the presence of neither boron nor oxygen is necessary for the degradation effect. In addition, our experiments reveal that copper contamination alone can cause the light induced minority-carrier lifetime degradation. © *2009 American Institute of Physics*. [doi:10.1063/1.3250161]

Silicon solar cells with efficiencies higher than 15% are typically made of multicrystalline silicon (mc-Si) or single crystalline silicon, which can be either grown by Czochralski (CZ) or float-zone (FZ) technique. FZ silicon is used for high-efficiency applications while mc-Si is used when the costs need to be minimized. Solar cells made from CZ and FZ silicon are comparable in cost, but CZ solar cells suffer from an unstable efficiency, which tends to degrade under sunlight. This phenomenon is known as light induced degradation (LID) and it is currently a serious problem limiting the CZ cell efficiency.

LID has been studied extensively in recent years including both experimental[1–4] and theoretical[5,6] efforts. In the experimental studies, LID has been found to increase as a function of both boron and oxygen concentration.[2] Consequently, the phenomenon has been related to the so-called boron-oxygen complex, suggesting that the presence of both boron and oxygen is necessary for the observation of LID.[2] The possible effect of metal contamination has been ruled out simply by referring to the extremely pure starting material[7] or to some gettering treatment.[8] However, we have recently noticed that copper contaminated silicon tends to react to light similar to the boron-oxygen complex.[9,10] There are also other groups that have reported similar observations: Ramappa[11] noticed that copper causes degradation in the minority-carrier diffusion length during illumination. Belayachi *et al.* found out that during illumination copper either reacts in the wafer bulk or outdiffuses to the surfaces.[12]

In this paper we study the effect of copper, boron and oxygen on LID by means of minority-carrier lifetime, which is a key parameter for determining the efficiency of solar cells. Our results are somewhat surprising as we provide direct experimental evidence that the presence of neither boron nor oxygen is necessary for the observation of LID. In fact, our results show that the minority-carrier lifetime degradation has a clear dependency on copper concentration regardless of the silicon material, implying that LID can also occur solely due to copper.

It is well known that in *p*-type silicon, in contrast to *n*-type silicon, a low copper concentration does not affect the recombination lifetime.[13–15] However, if copper contaminated *p*-type silicon is exposed to light (e.g., sunlight or a halogen lamp), the lifetime decreases drastically in the areas of copper contamination even at low contamination

levels.[9,10] Figure 1(a) shows an example of such a phenomenon, i.e., the recombination lifetime map measured by microwave photoconductivity decay after light illumination of a *p*-type CZ silicon wafer (oxygen level 14.5 ppma, resistivity 17 Ω cm), contaminated with various levels of copper. Light illumination of the wafer was carried out by a halogen lamp with an intensity of 0.2 W/cm², which is comparable to the intensity of sunlight.

Copper contaminated areas are clearly visible as local lifetime degradation, for instance, under a 1.2×10^{14} cm^{-3} spot the lifetime value decreases from the initial value of about 372 μs to 16 μs due to illumination. The recombination lifetime in the same wafer as a function of illumination time [Fig. 1(b)] shows that the saturation value at the end depends on the copper concentration level. The recombination lifetime decreases also somewhat in the reference area, which was not intentionally copper contaminated, but it is likely that we have a small unintentional copper contamination in the reference area as the time dependency of the defect reaction is very similar to the copper contaminated areas. This experiment shows clearly that copper contamination induces or at least increases LID, but it does not rule out the possibility that boron and oxygen are also involved in the degradation effect.
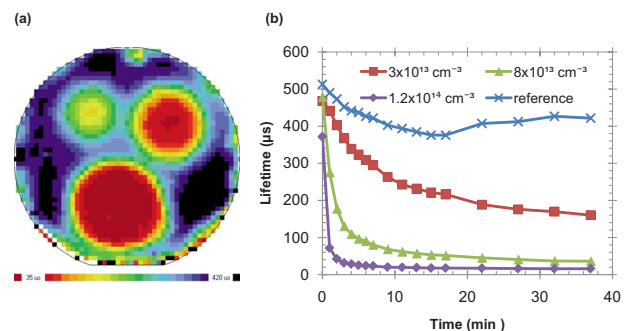

FIG. 1. (Color online) LID in a *p*-type CZ silicon wafer with various copper contamination levels. (a) Cu contamination (left upper spot 3×10^{13} cm^{-3}, right upper spot 8×10^{13} cm^{-3}, and lower spot 1.2×10^{14} cm^{-3}) appears in the measured recombination lifetime map as local lifetime degradation spots after 37 min of light illumination. Cu concentration values have been evaluated from the change in the measured lifetime using the equation given in Ref. 9. (b) LID as a function of illumination time in the same wafer. Different symbols refer to different copper concentrations, as shown in the legend. Reference measurement is carried out outside the intentional Cu contamination spots.
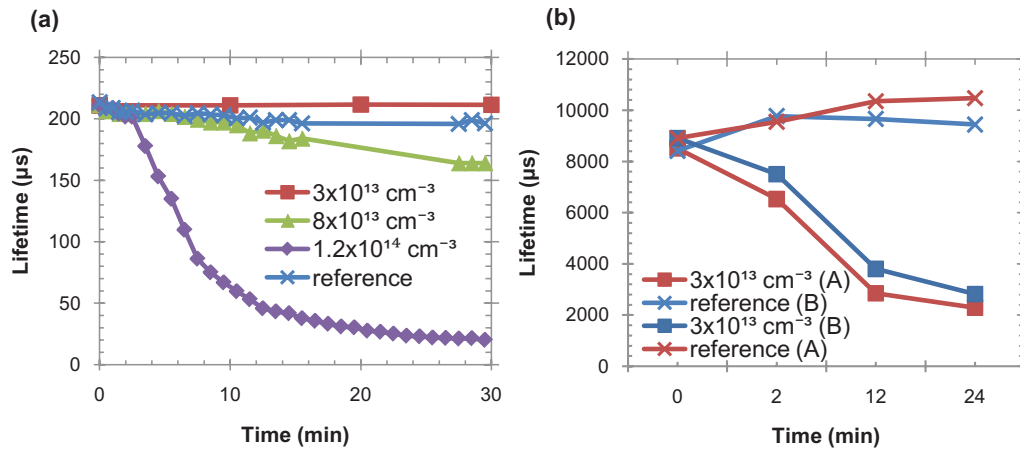
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FIG. 2. (Color online) LID in FZ silicon wafers as a function of illumination time. (a) *p*-type FZ (0.5 Ω cm) and (b) *n*-type FZ (>5 kΩ cm). Different symbols refer to different copper concentrations, as shown in the legend. A and B refer to different but identical wafers.

CZ silicon contains always some amount of oxygen, which is incorporated into the crystal already during ingot growth. FZ silicon, on the other hand, is usually considered to be free of oxygen due to the different growth technique. Consequently, LID is not expected in FZ.[1] However, in order to study closer the role of oxygen in LID, we decided to contaminate *p*-type FZ silicon wafers (resistivity 0.5 Ω cm) with copper similar to the above CZ wafers. Quite surprisingly we observed LID also in those wafers. Analogous to CZ wafer, LID increases as a function of copper concentration in *p*-type FZ silicon [Fig. 2(a)]. However, light illumination does not affect the lifetime under the 3×10^{13} cm^{-3} spot or the reference location in FZ silicon, in contrast to CZ silicon, indicating that the threshold copper concentration for LID is much higher in FZ than in CZ. Measurement data given in Ref. 16 further supports this result. In addition, in FZ the same copper concentration results in a slower defect reaction than in CZ. These results imply that oxygen has a role in the defect formation but most importantly, oxygen is not necessary for the defect formation as we see LID also in oxygen-free FZ when contaminated with a sufficient amount of copper.

As a final step we wanted to study LID in a wafer that does not contain boron or oxygen. Typically in *n*-type silicon, copper degrades lifetime already after indiffusion without illumination.[14] This is because the Fermi-level is located close to the charge neutrality level of the copper precipitate, which enables positively charged copper to precipitate already at low concentration levels.[15] Therefore, it is quite natural that copper related LID cannot be detected in such cases. In our experiments, however, we used copper contaminated *n*-type FZ silicon wafers with high-resistivity (>5 kΩ cm), where the Fermi-level is located close to the midgap. In these wafers we were able to observe very similar LID behavior to that in *p*-type silicon as demonstrated in Fig. 2(b). In clean reference areas we do not see any lifetime degradation, but under the 3×10^{13} cm^{-3} copper spot LID clearly takes place. If we add more copper than 3×10^{13} cm^{-3}, the initial lifetime decreases too much as copper already precipitates without illumination similar to high resistivity *p*-type silicon, where copper itself changes the material to *n*-type triggering the precipitation.[15] Notice that the reference points are measured from the same wafer outside the copper contamination spots, so that the measure-

ment and processing conditions were identical to those of the copper spots. The main point in this experiment was to demonstrate that LID in Fig. 2(b) is solely due to copper as the wafer contains no oxygen nor boron, so they cannot play any role in the observed LID.

To explain LID by means of copper, we can use the same electrostatic precipitation model that is proposed in Ref. 15, which was used to explain the difference in copper precipitation behavior between *n*-type and *p*-type silicon. Analogously to the proposed model, the light activation reduces the electrostatic repulsion between positively charged interstitial copper ions and copper precipitates. The reduction in electrostatic repulsion enables copper to precipitate in the wafer bulk even at a low concentration level. Consequently, such formation of copper precipitates increases the recombination activity and reduces the lifetime in silicon.

It is also relatively easy to explain the differences between CZ and FZ experiments, namely the role of oxygen in the copper related LID. CZ silicon contains oxygen, both interstitial and small oxide precipitates and related defects. The latter ones provide nucleation sites for copper precipitates so that the threshold copper concentration for LID is much smaller in CZ than in FZ. Therefore, also the density of the copper precipitates is likely to be higher in CZ than in FZ resulting in a smaller precipitation time constant with the same copper contamination level. It is actually possible to control the magnitude of LID by controlling the density of oxide precipitates in CZ silicon, as shown in Ref. 9, where LID was maximized using a high density of small oxide precipitates for optimal copper detection in CZ silicon.

Now that we have shown that copper is able to induce severe LID in silicon, the question remains: How small concentrations are detrimental for the device operation? Based on Ref. 9 in a typical CZ material for solar cells,[17] the required amount of copper that induces LID is extremely small (about 10^9 cm^{-3}). Based on the same Ref. 9, on the other hand, in "defect-free" silicon the critical copper concentration for LID is much higher (about 10^{12} cm^{-3}), which explains the insensitivity of FZ to copper induced LID. Overall, it may be an extremely challenging task to minimize the copper concentration to the level where it does not cause LID, especially in CZ silicon.

All results presented here suggest that cell manufacturers should concentrate on getting rid of copper from their manu-

facturing lines or deactivate the copper defect by other means to minimize copper related LID. The latter one can be realized by (i) reducing the density of as-grown oxide precipitates in (solar) CZ silicon, which can be realized by decreasing the initial oxygen concentration or by using high temperature preannealing for dissolution/coarsening of as-grown oxide precipitates, (ii) optimizing the gettering of copper, or (iii) using rather high concentration of copper ($>10^{14}$ cm^{-3}) by engineering large copper precipitates with low density.[18] While the last approach might not be practical in high efficiency solar cells, it can explain why in mc-silicon, which typically has high unintentional metal contamination, copper related LID is not observed that often. In fact, we have noticed LID also in low-oxygen mc-silicon with a background copper concentration of 10^{14} cm^{-3} in the cast material[16] after dissolution of copper from the precipitates at high temperatures. Nonetheless, the copper problem does not only concern the industry using CZ silicon, but also those who use mc-Si.

In conclusion, we have shown that the LID of minority-carrier lifetime has a clear dependency on copper concentration regardless of the silicon material. In addition, we have demonstrated that the presence of boron and oxygen are not necessary for the observation of LID in silicon as the effect is also seen in *n*-type FZ silicon with no oxygen or boron present. Moreover, our results imply that oxygen plays a role in copper related LID; however not in the form of interstitial oxygen, but more likely in the form of oxide precipitates and related defects. In summary, copper can strongly decrease the stable efficiency of CZ, FZ, and mc-Si solar cells if it is not well controlled.

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