Influence of copper on the carrier lifetime of n-type and p-type silicon

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Abstract. Controlled contamination by ion implantation and careful surface passivation has been used to study the effect of copper on the recombination rate of charge carriers in silicon wafers. Our results confirm that copper strongly reduces the lifetime of n-type silicon, which approximately follows an $N_{Cu}^{-0.55}$ dependence on the copper dose. The effect of copper on p-type silicon, commonly used for solar cells, has been found to be as severe as on n-type silicon, when wafers having a similar dopant concentration are compared. The lifetime of copper contaminated silicon, both n-type and p-type is correlated to the phosphorus or boron concentration, respectively, with decreasing lifetimes corresponding to increasing doping levels. The fact that both the copper dose and the dopant concentration have a strong effect on the lifetime is an essential consideration for future studies of copper in silicon.

1. Introduction

Understanding the electronic consequences of copper contamination has become very important for integrated circuit technology and for silicon solar cells. Copper contamination is likely to occur during the wafering of photovoltaic silicon. A 1980 study of the effect of various impurities on the conversion efficiency of silicon solar cells [1] concluded that copper was the least damaging transition metal and indicated that concentrations of up to $10^{17}cm^{-3}$ could be tolerated. This presumed innocuity prompted the growth of silicon layers from copper solutions to develop thin film solar cells [2]. There is growing evidence, however, that copper has serious negative effects on carrier recombination. Experimental work by Naito et al. [3], cited in a recent review [4], found that copper contamination degraded the lifetime of n-type silicon by almost two orders of magnitude for a surface impurity concentration of $10^{13}cm^{-2}$. Surprisingly, the effect of copper on p-type silicon was found to be much weaker, with a factor of three reduction at a $10^{13}cm^{-2}$ dose and no degradation for lower contamination levels. Zhong et al. [5] did notice a factor of ten drop in the lifetime of p-type wafers having a $6x10^{13}cm^{-2}$ surface copper concentration. Rotondaro et al. [6] found that copper degraded the lifetime of n-type silicon drastically, from 700μs to 20μs, but did not practically affect p-type wafers. This was also the qualitative result of Henley et al. [7], who nevertheless observed that the lifetime of p-type silicon dropped, and drastically so, after optical or thermal activation. Thermal and optical activation were later found to be equivalent [8], with a total degradation of the lifetime of p-type silicon occurring after 15 min at 300°C. Tarasov et al. [9] further verified the irreversibility of the lifetime degradation after light activation, which is a distinctive feature that may be used to discern between copper and iron, since the latter permits a recovery of the lifetime after several hours in the dark. In addition, they measured an increasing degradation of the minority carrier diffusion length of p-type silicon with increasing copper dose. This recent evidence together with that presented in this paper, strongly suggests that the earlier preconception that p-type silicon was practically impervious to copper is wrong.

In this paper we investigate the following questions: how much copper is required to produce a noticeable degradation of the lifetime and how strong the effect is as the concentration of copper is augmented, whether p-type silicon is degraded by the presence of copper and what influence may wafer doping have.

2. Experimental techniques

CZ n-type, 5-10 Ωcm, 350 μm thick silicon wafers and FZ p-type and n-type wafers of various resistivities were used in the experiments. Copper doses of 10^{12}, 10^{13} and 10^{14} cm^{-2} were ion implanted at 80keV into the silicon wafers. Following Cu implantation, the

wafers were RCA cleaned, annealed at 850 ^{o}C for 1h in argon and pulled out of the furnace to room temperature without any particular quenching. This annealing step serves the dual purpose of healing the implantation damage and distributing the copper uniformly across the wafer. Approximately 10µm of silicon were subsequently etched off each side of the wafers in a nitric:HF solution. This helps to further eliminate residual implantation damage and possible copper pile-up at the surface [5]. Finally, SiN was deposited on both sides in a PECVD reactor at 400^{o}C (deposition time approximately 5 min per side) to provide good surface passivation. Lifetime measurements were then performed as a function of the excess carrier concentration using the quasi-steady-state photoconductance technique [8]. Control wafers were included in every experiment to verify that no unwanted contamination occurred during the annealing step and that the surface passivation was of sufficient quality.

3. Dependence of the lifetime on copper dose

To study the effect of copper contamination level, we initially used 7.5 Ωcm, 350 µm thick CZ n-type, silicon wafers. Although the out diffusion of copper from the wafers cannot be completely excluded, earlier neutron activation analysis of Cu implanted and annealed wafers indicated that this effect is very small in our experimental conditions [9]. A dose of 10^{13}cm^{-2} can therefore be expected to produce a total copper concentration in the range of $3x10^{14}$cm^{-3} in these wafers, which is relatively high, by comparison to the dopant density of approximately $6x10^{14}$cm^{-3}. Such a copper concentration produced a ten fold reduction of the minority carrier lifetime, from about 1ms of the non-contaminated wafer to approximately 100µs. A lower dose of 10^{12}cm^{-2} resulted in less degradation, while for a dose of 10^{14}cm^{-2} the lifetime dropped to approximately 10µs. Fig.1 gives the low injection lifetime measured for wafers implanted with copper doses of 10^{12}, 10^{13} and 10^{14} cm^{-2}. The line fit corresponds to a $N_{Cu}^{-0.55}$ lifetime dependence, where N_{Cu} is the copper dose. Considering the the SRH lifetime should, in principle, follow an inverse dependence on the trap concentration, the observed dependence suggests that there probably is a varying degree of copper precipitation with increasing dose. Compared to the control wafer, shown as the left-most point in Fig.1, this strong dependence of the lifetime on copper dose is a clear evidence of the detrimental effects of copper contamination.

Some experiments where repeated up to three times, and the lifetime of samples implanted with the same copper dose was not perfectly repeatable. This variability, which is represented by the error bars in Fig.1, is attributed to slightly different cooling rates between the three experiments. Copper precipitates rapidly [7] and slight changes in the cooling rate are likely to affect the number of recombination centres that form in the bulk of the wafer. Variations in the implanted dose or unintended contamination are not believed to be responsible, since both where carefully controlled. The variability observed for the non-implanted control samples is attributed to a slightly different surface passivation quality; this is, nonetheless, relatively unimportant in these experiments.

A similar degradation of the lifetime with increasing copper concentration can be expected for p-type silicon. Tarasov et al. [9] indeed observed such behaviour through minority carrier diffusion length measurements of lowly doped 27Ωcm p-type silicon, particularly when the wafers were furnace annealed at 1000^{o}C and quenched into liquid nitrogen. Compared to a control sample, degradation factors of 2.5, 4-12 and 37 times were found for surface copper concentrations of 10^{12}cm^{-2}, 10^{13}cm^{-2} and 10^{14}cm^{-2}, respectively.

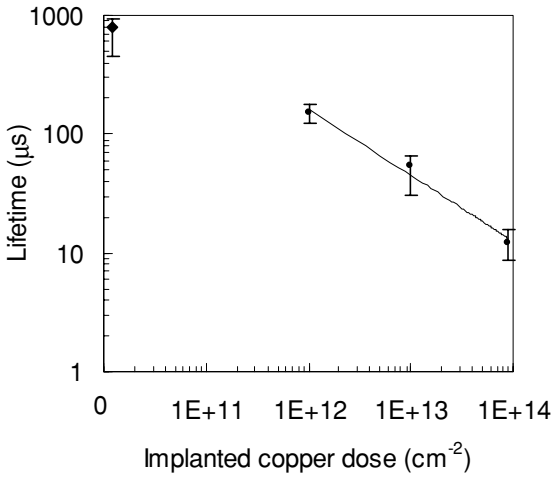

Figure 1. Minority carrier lifetime measured for copper contaminated *n-type* 7.5 Ωcm CZ silicon wafers. The left-most data point corresponds to the non-implanted control wafers.

4. Injection level dependence of the lifetime

Fig.2 presents the lifetime as a function of injection level for copper contaminated wafers from a single, simultaneous experiment. A strong lifetime dependency with excess carrier concentration is present for the 10^{12}cm^{-2} and, to a lesser extent, for the 10^{13}cm^{-2} Cu dose. The lifetime increases with increasing excess carrier concentration, reaches a maximum at approximately 5×10^{15}cm^{-3} (note that the dopant density is $6\text{x}10^{14}$cm^{-3}) and drops thereafter due to Auger recombination. This behaviour is typical of Shockley Read Hall recombination when the capture cross sections of electrons and holes are strongly asymmetric and the energy level is within a broad range around the middle of the band gap (that is, excluding shallow levels). Previous research [4,6] has identified two main trap energy levels for copper in n-type material, one at E_c–0.16 eV, believed to be due to free interstitial copper with an electron capture cross section of 3.3×10^{-17}cm^2 and a second level at E_c–0.4 eV due to copper precipitate related defects, with a electron capture cross section of 2×10^{-10}cm^2. There is little information on the hole capture coefficients and this makes it difficult to accurately model the measured injection level dependence of the lifetime. Nevertheless, preliminary theoretical analysis suggests that copper related centres with deep or intermediate energy levels dominate carrier recombination in these wafers. A second, shallower level, seems to be present in the high resistivity samples, but is not the dominant centre at injection levels of practical interest.

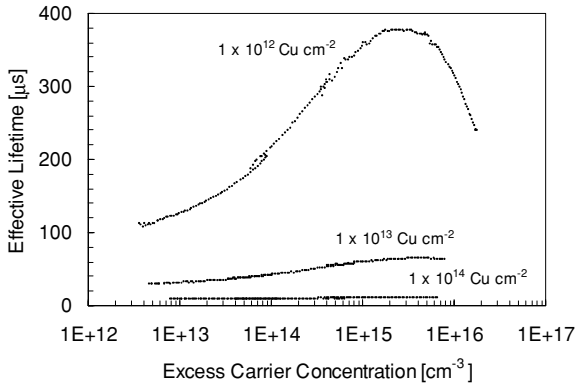

Figure 2. Effective lifetime of n-type 7.5 Ωcm silicon as a function of excess carrier concentration for implanted copper doses of 10^{12}, 10^{13} and 10^{14} Cu cm^{-2}.

As the copper dose is increased, the dependence on excess carrier concentration is less marked. This may indicate a change in the dominant recombination centres (different capture cross-sections, different energy level, or both). It can be expected that the proportion of precipitated copper increases with its concentration.

5. Doping dependence of the lifetime of copper contaminated wafers

Given that copper reduces the lifetime to quite low values, it may be expected that the lifetime of equally contaminated wafers would be dominated by the Cu-related centres and be practically independent of the original, pre-contamination lifetime of the wafers. To investigate this we used phosphorus doped wafers with resistivities between 0.75Ωcm and 75Ωcm and corresponding initial lifetimes between 330µs and more than 1ms. Companion wafers were contaminated with a copper dose of 10^{13} cm^{-2}. A similar experiment was conducted with float zone p-type wafers with resistivities from 0.3Ωcm to 70Ωcm. The p-type control wafers presented lower lifetimes than what is customary for this type of material and may be affected by a non-optimal SiN surface passivation. Nevertheless, the passivation quality is sufficient to reveal the effect of copper contamination.

Both the n-type and p-type wafers showed a strong reduction of the lifetime due to copper contamination, but the higher resistivity wafers were able to better maintain a reasonable lifetime than the lower resistivity ones. As Fig. 3 shows, there is a correlation between the low injection effective lifetime and the density of dopant atoms (either phosphorus or boron) in the wafer. Such correlation can be expected for SRH centres that are not too deep, but are in the transitional region between deep and shallow. The recombination strength of such intermediate centres increases considerably with doping concentration. Note that the observed dependence is not wholly attributable to the effect of copper, since the control wafers also show a trend to lower lifetimes with increasing doping. The results indicate, nevertheless, that there is a synergistic effect between copper contamination and wafer doping.

The degradation of p-type silicon is even stronger than for n-type material with a similar dopant concentration. This contradicts most previous reports [3,5,6] that copper contamination had little effect on p-

type silicon wafers. Although qualitatively in agreement with our results, the lifetimes in [9] are quantitatively lower. For a copper dose of 10^{13} cm^{-2} (measurement technique not specified) the latter researchers measured lifetimes of 0.7µs and 9.3µs for a doping density of $5x10^{14}$ cm^{-3}, while our measurement for a similar wafers is in the vicinity of 100µs.

It is important to note that, in the light of the evidence in [7,8] that the lifetime of p-type silicon is considerably reduced after thermal or optical activation, our lifetime values should be considered characteristic of the activated state of the copper-related recombination centres, due to the deposition of a surface passivating SiN layer at 400°C. Such annealing temperatures are also common in device processing, as a forming gas anneal to reduce interface states or a sintering of the metal contacts. For the typical resistivity used for silicon solar cells, p-type 1 Ωcm, copper can produce a very serious degradation of the minority carrier lifetime, from more than 120µs to slightly less than 10µs. The degraded lifetime is, of course, relevant to solar cell operation.

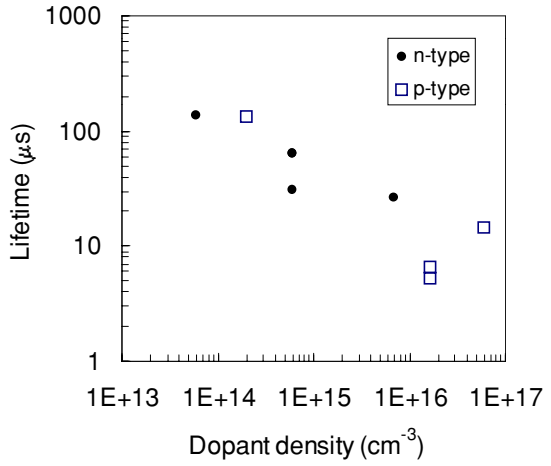

Figure 3. Dependence of the lifetime on the dopant concentration of n-type and p-type silicon wafers contaminated with a $10^{13}cm^{-2}$ copper dose.

6. Conclusions

Our experiments clearly show that copper contamination strongly degrades the minority carrier lifetime of both n-type and p-type silicon. This is contrary to previous findings that p-type silicon was almost insensitive to copper contamination and stresses the importance of avoiding copper contamination in commonly used photovoltaic silicon materials. The reason for early researchers not having observed a strong degradation may be the recent evidence that the copper-related recombination centres dominant in p-type material are activated by light or temperature. Compared to other metals like iron, the levels of copper required to produce a drastic reduction of the lifetime are relatively high and relatively acceptable lifetimes are still found for heavily contaminated silicon. For example, the lifetime of 1Ωcm p-type silicon is nearly 10µs for a copper concentration of approximately $3x10^{14}cm^{-3}$, which is consistent with a diffusion length of 160µm. Higher copper doses degrade the lifetime even further, and a saturation of this trend was not yet found for a concentration of $3x10^{15}cm^{-3}$. It is also important to note that the lifetimes that can be achieved for a particular copper concentration are very different depending on the resistivity of the wafer, with lower lifetimes corresponding to lower resistivities. This is an important fact that has been generally overlooked. The fact that both the copper dose and the dopant concentration have a strong effect on the lifetime is important for future studies of copper in silicon. A multi-factorial study complemented with a detailed analysis of the injection level dependence of the lifetime could increase the limited present knowledge of this important metal impurity.

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