Impact of stress on the recombination at metal precipitates in silicon

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(Received 17 August 2010; accepted 6 October 2010; published online 18 November 2010)

Metals corrupt the performance of silicon solar cells severely. In this paper we investigate the recombination activity of metal precipitates and present a strong positive correlation between their recombination activity and the stress around them, independent of the type of metal forming the precipitate. This fundamental observation suggests that stress, together with the size of the precipitate, has a dominant effect on the recombination activity of metallic precipitates. We explain the recombination enhancing effect of stress near precipitates by the strong piezoresistance of silicon. © 2010 American Institute of Physics. [doi:10.1063/1.3511749]

I. INTRODUCTION

Transition metals are known to reduce the efficiency of Si solar cells by acting as recombination centers.1 Their recombination activity limits the carrier diffusion length and consequently the number of carriers that contribute to the charge separation in the solar cell. Transition metals are particularly detrimental when they are widely dispersed in the crystal.2 Thus the precipitation of transition metals at dislocations and grain boundaries can improve the solar cell performance by concentrating the impurities.3 On the other hand, the resulting metal precipitates can have a negative impact on solar cells. They increase the recombination activity at grain boundaries and dislocations4 and can cause shunts5 and electrical breakdown.6,7 Therefore, the understanding of the underlying mechanisms of the recombination activity of transition metal precipitates is a matter of fundamental scientific interest with direct impact on industrial applications.

The mechanism of recombination at metallic point defects can be well described by Shockley–Read–Hall theory8 based on capture cross sections and energy levels of the impurities. Theories9,10 existent for the recombination activity of transition metal precipitates explain the recombination activity either by an infinite surface recombination velocity at the precipitate surface or by a carrier lifetime of close to zero within the precipitate. However, there is comparatively little experimental evidence to validate these theories. The role of stress around transition metal precipitates in the recombination activity has been widely neglected. Stress is known to influence the carrier mobility markedly due to the strong piezoresistance of silicon (Si),11 an effect that could have a significant impact on the recombination activity. So far, the recombination activity of transition metal precipitates has been directly investigated by a combination of x-ray fluorescence spectroscopy (XRF) and electron beam induced current (EBIC) (Ref. 12) or x-ray beam induced current,13 respectively. These investigations found a linear correlation between the recombination activity and the transition metals concentration. Recent reports14,15 compared the diffusion length, which was measured by means of EBIC, to stress at grain boundaries. No correlation could be found, possibly due to the limited spatial resolution of EBIC and of scanning infrared polariscopy. So far, the detailed analysis of the recombination properties of typically nano-to-micrometer sized transition metal precipitates at grain boundaries as well as at dislocations has been limited by the low spatial resolution (>5 μm) of the available diffusion length measurement techniques. In addition, dislocations and the associated transition metal precipitates appear in multicrystalline (mc) Si in a wide variety of configurations. Likewise, the stress field built into the crystal around a single precipitate comprises of compressive as well as tensile components.16 Quantitative studies of the recombination activity of transition metal precipitates were thus only possible as averages over many different occurrences. As a consequence, previous reports failed to correlate the recombination activity to the geometric dimensions and the stress field around the transition metal precipitates. Furthermore, the investigation of Fe precipitates has not been feasible due to their typically small size and their relatively low recombination activity.12,13 In this approach, we use microphotoluminescence spectroscopy (μPLS) and micro-Raman spectroscopy (μRS) to investigate the recombination activity with high spatial resolution together with the quantitative analysis of the local stress field for well-defined individual types of transition metal precipitates at dislocation networks formed by wafer bonding.

II. EXPERIMENTAL

Recently we presented confocal μPLS with a spatial resolution of below 1 μm (Ref. 17) at high injection levels (up to 1019 cm−3), which allows investigating the recombination activity of single precipitate colonies. Within the same measurement, μPLS can quantitatively determine the stress using stress mapping by μPLS (SMAPS).18 This scans the stress induced band gap energy shift. Details on the setup have

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been published previously in refs. 17–20. μRS is possible with the same confocal microscope and allows measuring stress and recombination activity simultaneously by analyzing the Fano resonances with a spatial resolution of 500 nm. We utilize these techniques in combination with XRF at the nanoimaging station of the beamline ID22 at the European Synchrotron Radiation Facility with a spatial resolution of 150 nm, which allows investigating the correlation between the size of the transition metal precipitates, the induced stress and the recombination activity.

In an earlier work, dislocation networks built by direct wafer bonding were shown to be model systems to study transition metal precipitates due to their homogeneity and their strong activity as nucleation sites for transition metal precipitation. The results of the present paper are based on such bonded wafers, which were intentionally contaminated by Cu and Fe in-diffusion, respectively. The transition metals precipitated at the dislocation network during the slow cool-down after the high temperature step. Then the wafers were bevel polished with a shallow angle of about 2° in order to expose the dislocation network for PLS and XRF measurements. A 1.5 × 10^16 cm^{-3} B doped mc sample from the top of a block is used.

III. RESULTS

Our approach allows direct comparison (Fig. 1) between the intensity of the band-to-band (BB) photoluminescence (PL) (spectrally integrated between 1.09 μm and 1.13 μm), measured by μPLS and the density of the Cu and Fe, respectively, detected by μXRF. The metal concentrations were calculated using a calibration standard. The increased non-radiative recombination activity at the transition metal precipitates associated with reduced BB PL intensity is clearly detectable by μPLS.

A detailed quantitative analysis of the precipitate colony areas in comparison to the area affected by increased recombination in the μPLS measurements reveals a linear correlation between both quantities (Fig. 2). The 0.95 confidence bands of the fits for iron and copper, respectively, show that there is no significant element specific effect. The areas of the precipitate colonies were defined as the regions which have three times more XRF counts than the average background level in the μXRF measurement. The effective recombination active areas (parallel to the dislocation network) in the μPLS map are taken as the regions around the transition metal precipitates with number of counts below \((I_{BG} + I_{min}/2)\), with \(I_{BG}\) being the background intensity in an area.

FIG. 1. (Color online) Comparison of BB PL intensity (b) and (d) to Cu (a) and Fe (c) densities. The transition metal density was measured by μXRF. The increased recombination activity of the transition metal precipitates is visible as a reduced BB PL intensity (b) and (d).

FIG. 2. (Color online) The recombination active areas of the copper precipitates are proportional to their actual areas (a). The overlapping confidence bands around the linear fits for iron and copper show no significant dependence of the recombination active area on the element. (b) shows the excerpt of the iron precipitates from (a). While the scattered data cannot show a linear dependency for iron, at least a positive trend is visible from the linear fit. The recombination active area of a precipitate is defined on the upper left side of (a). The errors for the area estimation are defined by adding or removing one pixel layer around the precipitate.
around the precipitate colony that is unaffected by the precipitate, and $I_{\text{min}}$ being the minimum intensity at the precipitate (see the insert in Fig. 2). $I_{\text{BG}}$ is determined from the averaged intensity within a ring of 1 $\mu$m thickness. The ring radius is chosen in such a way that the investigated precipitate does not influence the intensity in this ring and that the influence of nearby transition metal precipitates is taken into account. We automated this evaluation procedure to guarantee an objective, reproducible determination of $I_{\text{BG}}$. The errors in the area determination were estimated by assuming, that around the precipitates one pixel layer is added or removed. The observed linearity for copper between precipitate size and recombination active area was expected, provided that within the transition metal precipitates the carrier lifetime was close to zero (Ref. 9) or that the precipitate surface had an infinite surface recombination velocity, leading to a carrier capture cross section linear to the surface area independent of the metal element. As theoretically expected there is no significant dependence on the precipitate element observed, but for a clarification of the influence of the element a measurements on larger iron precipitates would be required. The experimental data are also in good agreement with past investigations, where a linear correlation between uniaxial and hydrostatic stress. Since the stress level is below the detection limit of SMAPS. However it is very likely that also hydrostatic stress to be uniaxial in order to allow a quantitative analysis by SMAPS, both, $\mu$RS and SMAPS, might be affected by high injection effects; $\mu$RS by a lattice softening at high carrier concentrations, resulting in an underestimation, SMAPS by band gap narrowing, resulting in an overestimation of tensile stress at recombination active sites. Therefore the observed good agreement between both methods renders errors due to the high-injection conditions unlikely. FeSi$_2$ precipitates are expected to cause lower stress than Cu$_3$Si since the lattice mismatch between Si and FeSi$_2$ is only about 1% (Cu$_3$Si 5%). Figure 4, were the maximum stress at the precipitate is plotted against the maximum $C_{\text{PLS}}$, shows that

The precipitate volume was calculated following Ref. 23 assuming the transition metal precipitates consist of Cu$_3$Si and FeSi$_2$. Transition metal oxides are not likely to be present, because the bonded floatzone wafers contain only very small amounts of oxygen and the wafer bonding requires very clean, oxide free surfaces. Even though the thicknesses of the precipitate colonies can be assumed to be significantly larger than the calculated values, since the transition metal precipitates are not densely packed in the colonies, the calculated thickness is a valuable parameter specifying, the geometry of the precipitate colonies.

$\mu$RS on mc Si including Fano resonance analysis give an indication that around large Ni precipitate colonies (detected by $\mu$XRF) the recombination activity (represented by $C_{\text{RS}}$) is correlated with stress (Fig. 3). At high tensile stresses (positive) the recombination activity tends to be increased, while at high compressive stresses (negative) the recombination activity tends to be decreased. Carrier lifetime measurements utilizing Fano resonances were shown to be in excellent agreement with $\mu$PLS measurements in Ref. 19 and provide an enhanced spatial resolution of about 500 nm. This gives an indication, that stress might play an important role in the recombination activity of transition metal precipitates.

In order to evaluate this correlation between recombination activity and stress, we focus on the maximum stress at each precipitate in the bonded samples and as above on $C_{\text{PLS}}$. The stress is evaluated by SMAPS (Ref. 18) and is assumed to be uniaxial in order to allow a quantitative analysis by SMAPS. However it is very likely that also hydrostatic stress components are present, but SMAPS cannot distinguish between uniaxial and hydrostatic stress. $\mu$RS following Refs. 18 and 24 confirmed the results for the Cu precipitates. For most Fe precipitates this analysis could not detect significant stress, since the stress level is below the detection limit of $\mu$RS. Both, $\mu$RS and SMAPS, might be affected by high injection effects; $\mu$RS by a lattice softening at high carrier concentrations, resulting in an underestimation, SMAPS by band gap narrowing, resulting in an overestimation of tensile stress at recombination active sites. Therefore the observed good agreement between both methods renders errors due to the high-injection conditions unlikely. FeSi$_2$ precipitates are expected to cause lower stress than Cu$_3$Si since the lattice mismatch between Si and FeSi$_2$ is only about 1% (Cu$_3$Si 5%). Figure 4, were the maximum stress at the precipitate is plotted against the maximum $C_{\text{PLS}}$, shows that

![Image of Figure 3](image-url)
FIG. 4. (Color online) Recombination activity, represented by the maximum $C_{\text{PLS}}$ at the precipitates, plotted against the maximum tensile stress at the precipitate. The graph shows a positive correlation, which is not significantly dependent on the type of the impurity element (Fe or Cu). Also the iron data points show a positive correlation between stress and $C_{\text{PLS}}$. The error bars indicate the uncertainty of SMAPS of about 8 MPa and an uncertainty in the contrast of about 10%. The fact, that the data points for iron are systematically on the right side of the simulation curve, could be due to the systematic overestimation of stress by SMAPS. The simulation (geometry on the right side, details in Sec. IV) shows a good agreement with the experimental data, considering the simplicity of the simulation model.

$C_{\text{PLS}}$ is positively correlated with the stress level with no measurable dependence on the type of the impurity element. Around the transition metal precipitates no compressive stress was measured, that would be expected around Cu$_3$Si due to its larger lattice constant. Our Raman measurements around Cu$_3$Si precipitates in mc Si and CBED measurements around SiO$_2$ precipitates$^{28,29}$ reveal that stress around transition metal precipitates depends on the crystal orientation and comprises of compressive and tensile components. Therefore our observation of only tensile stress is probably due to the specific geometry of the samples and we do not observe the typical “butterfly” formed stress patterns as in Fig. 3 and, e.g., Refs. 16 and 19.

IV. DISCUSSION

Our observations provide evidence for a direct correlation between stress and increased recombination activity. A direct causality is implied by the correlation in the bonded wafer as well as in the mc sample and the fact that no significant correlation to the transition metal type has been found. An explanation for such correlation is discussed in the following:

The carrier flux to the precipitate is proportional to the carrier mobility.$^{22}$ The mobility can be strongly increased/reduced by tensile/compressive stress due to the strong piezoresistance of Si.$^{11}$ This effect is widely used for the improvement of semiconductor devices (e.g., Ref. 29). Thus, increased tensile stress increases the recombination activity directly by increasing the carrier mobility and hence increasing the carrier flux to the transition metal precipitates, where the carriers recombine, while compressive stress reduces the recombination activity (Fig. 3). A simplified simulation of $C_{\text{PLS}}$, which assumes a homogeneous increased mobility around the precipitate (see Fig. 4 right side), shows a good agreement with the experimental data (Fig. 4). The only adjustable parameter in the model is the Shockley–Read–Hall lifetime in the bulk Si (5 $\mu$s for the calculation in the graph, which is a reasonable assumption for the given material). This confirms that stress can indeed have a significant influence on the recombination activity of transition metal precipitates. The shift in the Fe points compared to the simulation of 8 MPa is probably caused by the overestimation of stress by SMAPS particularly for low stress levels. The simulation is based on a two-dimensional (depth $z$ and radial distance $r$ from the excitation) continuity equation, taking the actual high injection conditions into account. A precipitate is assumed to have a practically infinite surface recombination velocity,$^{5,10}$ 0.2 $\mu$m thickness and 1.5 $\mu$m radius in a depth of 2 $\mu$m from the surface in the center of the laser excitation (cylindrical symmetry, Fig. 4 right side). Simulations indicate that precipitate thickness and radius have a minor effect on the BB PL intensity. The simulation takes all properties of the $\mu_{\text{PLS}}$ (excitation profile and level, spatial detection profile) explicitly into account. For the piezoresistance $\Pi_{11}$ the widely accepted value $-102.2 \times 10^{-11}$ Pa$^{-1}$ for electrons (holes)$^{11}$ in [1 0 0] direction (parallel to the laser beam) is used. Again the hydrostatic component of the stress is not taken into account, since SMAPS cannot measure the tensor properties. An important factor is the difference between actual spatial extent of the stress and the detection volume. From many TEM and CBED measurements around precipitates (e.g., Refs. 16, 28, and 30) a stress relaxation within 100 nm or less can be deduced. The extent of the stress volume is thus considerably smaller in comparison to the volume is thus considerably smaller in comparison to the extent of the stress.

The present model neglects that transition metal precipitates in Si may be surrounded by a space charge region due to electrical charge on the transition metal precipitates or a Schottky contact. This typically limits the flux of majority carriers and increases the flux of minority carriers to the precipitate and thus increases the recombination activity at...
the precipitate.\textsuperscript{22} At high injection levels, as in this paper, this is a minor effect. At low injection levels we expect the space charge region to increase the recombination activity of transition metal precipitates slightly. However the impact of the stress induced mobility enhancement on the recombination activity is not affected, since the carrier flux remains proportional to the mobility.\textsuperscript{22}

An alternative reason for the observed correlation is an indirect effect of stress on the recombination activity: Stress can be relieved by the formation of dislocations.\textsuperscript{32} These dislocations could increase the recombination activity. However this second explanation has to face some objections: the correlation to the recombination activity should be decreased by this stress relaxation due to dislocation formation. Furthermore, since the recombination activity of the dislocations would be largely determined by the impurity decoration, an element specific effect would be expected due to the different diffusion and precipitation parameters of Fe and Cu.\textsuperscript{33}

\textbf{V. CONCLUSION}

We combined two recent achievements: (i) the preparation of well defined transition metal precipitates at dislocations formed at a wafer-bonded interface and (ii) high resolution carrier lifetime, stress and precipitate size measurements using \( \mu RS \), \( \mu PLS \), and \( \mu XRF \). This allowed us to derive correlations between precipitate properties and recombination activity. Most importantly, we find a positive correlation between tensile stress and the recombination activity of transition metal precipitates in mc Si as well as in bonded samples. The correlation can be explained by the stress enhanced flux of carriers to the transition metal precipitates due to the strong piezo-resistance of Si. For the total recombination activity the precipitate surface area, as well as the surrounding stress field are important. A model which explains the recombination behavior by (i) transport to the precipitate dominated by a stress induced mobility increase and (ii) a highly recombinant precipitate surface allows recombination to be understood in good agreement with experimental evidence. This finding has the potential to open a new way for improving solar cells by optimizing the stress distribution during the block casting and the solar cell process, since compressive stress can reduce the recombination activity of transition metal precipitates significantly.

\textbf{ACKNOWLEDGMENTS}

We would like to thank H. Lautenschlager, M. Kwiatkowski, and M. Wolff for sample preparation, and J. Costello and W. Dopkins for proofreading. This work was funded by the German BMU in the SolarFocus project under Project No. 0327650H.


