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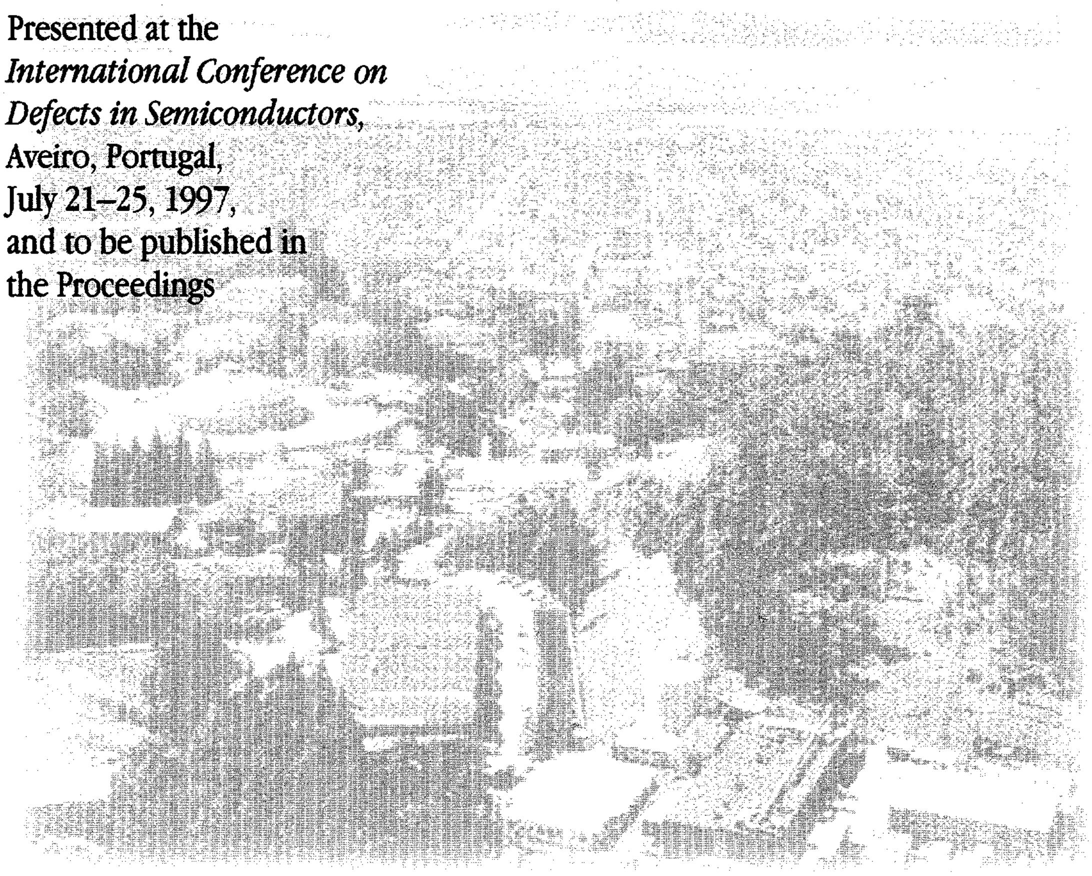

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RATE LIMITING MECHANISM OF TRANSITION METAL GETTERING IN MULTICRYSTALLINE SILICON

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keywords: multicrystalline silicon, dislocations, transition metals, x-ray fluorescence, gettering

Abstract

We have performed studies on multicrystalline silicon used for solar cells in the as-grown state and after a series of processing and gettering steps. The principal goal of this work is to determine the rate limiting step for metal impurity gettering from multicrystalline silicon with an emphasis on the release of impurities from structural defects. Synchrotron-based x-ray fluorescence mapping was used to monitor the release process. Copper and nickel impurities were found to reside primarily at dislocations in the as-grown state of the material. Short annealing treatments rapidly dissolved the impurity agglomerates. Based on these results and modeling of the dissolution process, copper and nickel is in the form of small agglomerates (<10nm) clustered together over micron-scale regions in the as-grown material. Aluminum gettering further disintegrated the agglomerates to below the sensitivity of the system, 2-5nm in radii. No significant barrier to release of copper or nickel from dislocations was observed.

Introduction

Multicrystalline silicon (mc-silicon) is a very interesting material for terrestrial solar cells. Its low cost and respectable energy conversion efficiency (12-15%) makes it arguably the most cost competitive material for large-volume solar power generation. However, the efficiency of mc-silicon solar cells is severely degraded by regions of high minority carrier recombination which have been shown to largely possess dislocations and microdefects [1-3]. These structural defects are known to increase in recombination activity with transition metal decoration [4-9]. Therefore, frontside and/or backside segregation-type gettering of metal impurities from the mc-silicon bulk would be expected to greatly enhance solar cell performance as is observed in single crystal silicon [10-17]. Contrary to this rationale, experiments using these gettering treatments for mc-silicon have only improved regions of initially low recombination activity while little or no effect is observed on the initially high recombination regions and in turn only a slight improvement in overall cell performance is attained [2,3,14,18].

The gettering process can be described as a three step process of impurity release from its initial site, diffusion through the silicon matrix and capture into the gettering layer. Deep Level Transient Spectroscopy (DLTS) studies [3] have observed Fe in the highly dislocated regions of mc-silicon while still leaving the possibility of Cu, Ni and Co being present as well, due to the inability of DLTS to detect these impurities. All of these impurities diffuse rapidly in silicon [19], indicating the impurity diffusion from the initial site to the gettering layer occurs rapidly and would not limit the gettering process for a reasonably long gettering heat treatment. Measurements of metal impurity segregation coefficients for phosphorus and aluminum layers with respect to silicon [17,20], indicate one would expect a decrease of metal impurity concentration in the silicon on the order of 10^{-4} to 10^{-6}. This suggests the capture step is potent and does not limit the gettering process. The release of the impurities from their initial site is unstudied and may be responsible for the poor gettering of mc-silicon. Slow release may occur in mc-silicon but not in single crystal silicon due the presence of structural defects which stabilize the initial metal precipitates/agglomerates.

The goal of this research is to determine the mechanism by which gettering is ineffectual at improving high carrier recombination in mc-silicon. In the work presented here, we have analyzed metal impurity release from structural defects in mc-silicon after processing/gettering steps with the use of synchrotron-based x-ray fluorescence mapping and correlated structural defect analysis. Impurity release is compared to calculations of impurity diffusion from a precipitated state into the silicon matrix without any barrier to impurity release. We have been able to observe the dissolution process of Cu and Ni from dislocations as well as correlate the initial position of the impurities with specific structural defects.

Experimental Procedure

Boron doped mc-silicon with a resistivity of 1.0 ohm-cm and an oxygen concentration of $1\text{-}2\times10^{17}$ atoms/cm^3 was used. The 500μm thick wafers were formed by a casting method with subsequent cutting and etching to remove the damaged surface layer. Surface Photovoltage (SPV) apparatus was used to measure minority carrier diffusion length values over the as-grown mc-silicon wafer in order to locate high minority carrier recombination regions. These regions were rapid thermal annealed at 500°C for 30 seconds followed by a rapid quench to room temperature (≈1000K/s), to freeze in the kinetics of impurity release. This was followed by an Al gettering treatment at 800°C for 3 hours using a high purity 1μm Al layer on the sample backside. The frontside of the samples were analyzed using synchrotron-based x-ray fluorescence (XRF) mapping in order to determine metal impurity content and distribution at each step of the sample processing: in the as-grown state, following the RTA and lastly after the Al gettering treatment. Impurity mapping was performed on the same regions after each processing step by identifying fiducial marks on the sample surface. The XRF equipment generates 12.4 keV monochromatic radiation to excite elements in the sample with a spatial resolution of 1x1μm and a Si-Li detector to measure fluorescence x-rays from the sample, all in atmospheric conditions. System sensitivities are element specific but, for example, the system can detect a single Ni or Cu precipitate/agglomerate in silicon greater in radii than 2-5nm with a sampling depth on the order of 50μm. Impurity concentrations are quantified with the use of standard samples of known impurity concentrations. After Al gettering and XRF analysis, the diffusion length was measured with SPV and the samples were preferentially etched and analyzed with a scanning electron microscope to reveal structural defects.

Results and Discussion

A minority carrier diffusion length (Ln) map of the mc-silicon wafer is shown in Figure 1. The material has a broad range of Ln values, from 10-80μm. These values are typical for a mc-silicon wafer and are not sufficient to make a high performance solar cell, further material improvement is required. A low diffusion length region with Ln=10μm was selected from the wafer and analyzed with XRF mapping. The XRF mapping revealed only Ni and Cu agglomerates. Maps of the impurity distributions are shown in Figures 2a&b. The Ni and Cu impurities are present at the same locations over regions spanning 2-5μm. Since the material was grown with a slow cooling rate and a concomitant low supersaturation of the impurities, the location of the Ni and

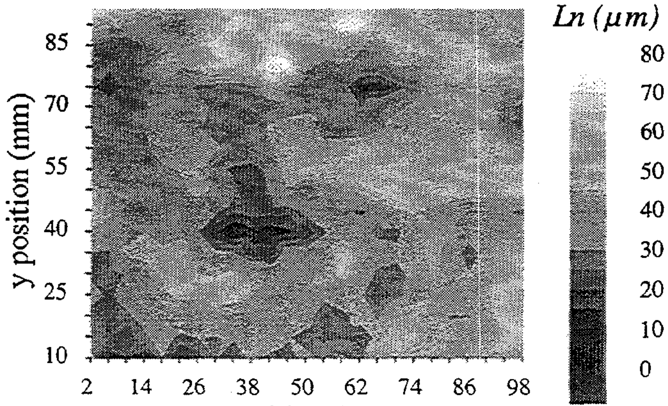
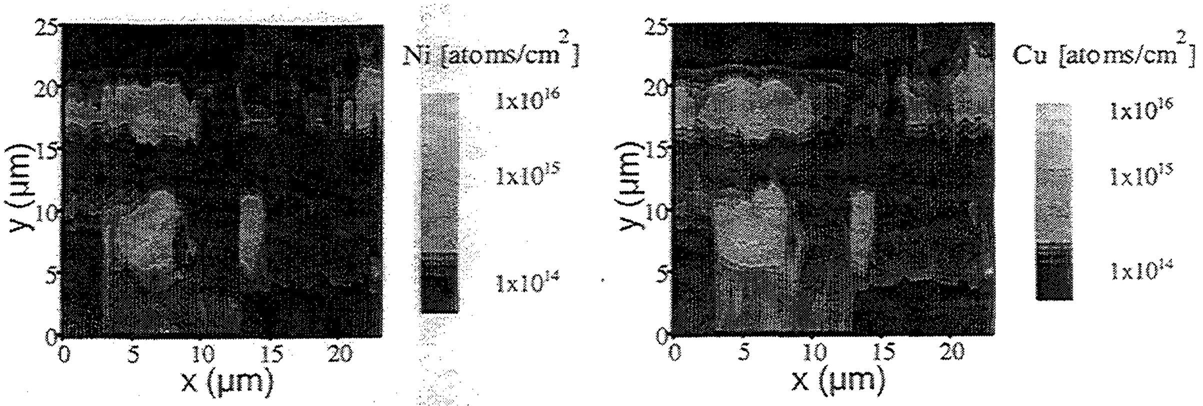


Figure 1: Minority carrier diffusion lengths (Ln) across a multicrystalline silicon wafer.



Figures 2a&b: Ni and Cu distributions in as-grown multicrystalline silicon as measured with x-ray fluorescence mapping. Deep black regions denote unscanned areas.

Cu are expected to be at the preferred precipitation sites. The sample was annealed at 500°C for 30 seconds with a rapid quench to room temperature in order to freeze in the kinetics of impurity dissolution. Based on diffusion data of Ni and Cu in silicon, [19], one would expect significant diffusion of both impurities for this anneal temperature and time. An XRF scan after the RTA treatment of the same region as in Figure 2, with some surrounding area, is shown in Figures 3a&b. Most impurity agglomerations have been dissolved. The few remaining positions with Ni and Cu at x,y (32,25-7)µm and to a lesser extent at (60,30)µm in Figures 3a&b correlate with peaks in Figures 2a&b at x,y (5,17)µm and (22,17.5)µm, respectively. It should be noted that the Ni and Cu agglomerates are no greater in size than the spatial resolution of the XRF system, 1 µm in diameter.

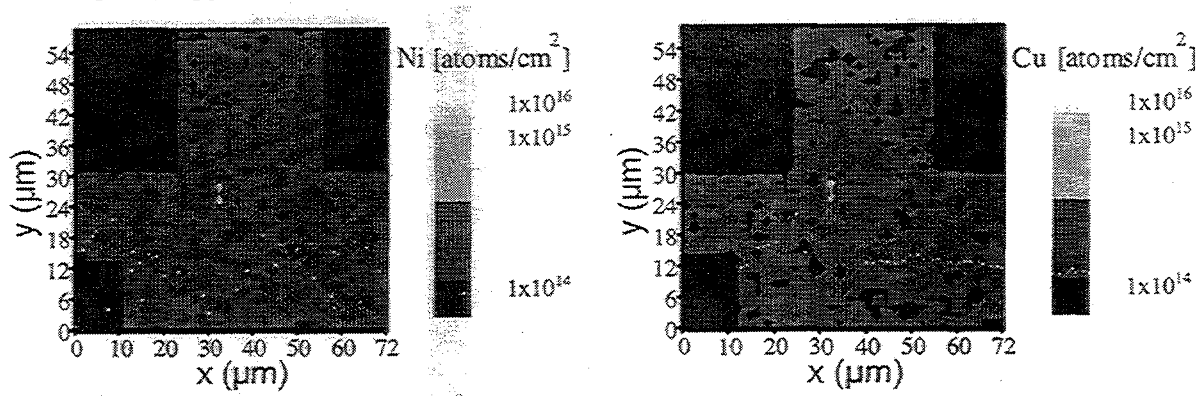


Figure 3a&b: Ni and Cu distributions in multicrystalline silicon after a 500°C-30 sec RTA quench. Only certain discrete agglomerations of impurities have remained from the as-grown state (Figure 2). Deep black regions denote unscanned areas.

The initial size and distribution of the Ni and Cu precipitates can be calculated by using the data in Figures 2&3 and the theoretical models of precipitate dissolution which consider the dissolution process to be limited only by impurity diffusion from the precipitate [21,22]. It is important to note that no consideration of the surface reaction rate is considered in this model. For Ni and Cu, the theory provides a relatively simple formula for the maximum precipitate radius, R_{max}, which will not completely shrink for an anneal of time, t,

$$R_{\max} = \sqrt{2Dt\left[\frac{C_i - C_m}{C_p - C_i}\right]} \tag{1}$$

where D is the impurity diffusivity in silicon, C_i is the impurity solubility in the silicon matrix at the dissolution temperature, C_m is the impurity concentration far from the precipitate and C_p is the metal concentration in the precipitate. Equation 2 is in this simple form because of the large difference of impurity solubility between the precipitate and the silicon matrix. R_{max} of $NiSi_2$ and Cu_3Si precipitates for a 500°C-30 sec anneal are calculated to be 3 and 11nm, respectively. Any precipitates greater in size than this will not dissolve completely, e.g. a 1μm diameter precipitate will be virtually unaffected by this anneal. Furthermore, this calculation taken in conjunction with the observed 2-5 μm size of the Ni and Cu rich regions in the as-grown material (Figure 2) and the rapid dissolution of these impurity rich regions (Figure 3), suggests most of the as-grown impurities are in the form of nm-scale precipitates which are clustered over micron-scale regions of the material. The few impurity rich points remaining after the 500°C dissolution treatment, in Figure 3, were initially greater in size than 3-11nm but now are at least ≤ 1μm, the XRF spatial resolution.

The same sample was aluminum gettered for 3 hours at 800°C and analyzed with XRF over an even larger area than Figures 2&3. No Cu or Ni agglomerates were detected over this region. Calculations based on equation 1 indicate that $NiSi_2$ and Cu_3Si precipitates with a diameter of <11.2μm and <23.2μm, respectively, should fully dissolve with the 800°C-3 hour treatment. Therefore, the precipitates in Figure 3, which are ≤ 1μm in diameter, are expected to completely dissolve after the gettering treatment, as was experimentally observed. Considering the sensitivity of the XRF system, these results provide evidence that no Ni or Cu exists in this region clustered or precipitated at a diameter >2-5nm. Moreover, the 800°C-3 hour aluminum gettering treatment should be more than sufficient to decrease the Ni and Cu concentration throughout the silicon by many orders of magnitude considering simple diffusion of the impurities from the silicon matrix into the aluminum layer which has a segregation coefficient of 10^{-4} to 10^{-6}. However, even with this rapid dissolution and sufficient diffusion/gettering times, the final minority carrier diffusion length was measured as 52μm, only slightly higher than its initial value of 10μm and significantly lower than required for a high performance solar cells. This low final diffusion length indicates a mechanism for minority carrier lifetime degradation remains in this region. Possible explanations for this residual degradation are discussed later.

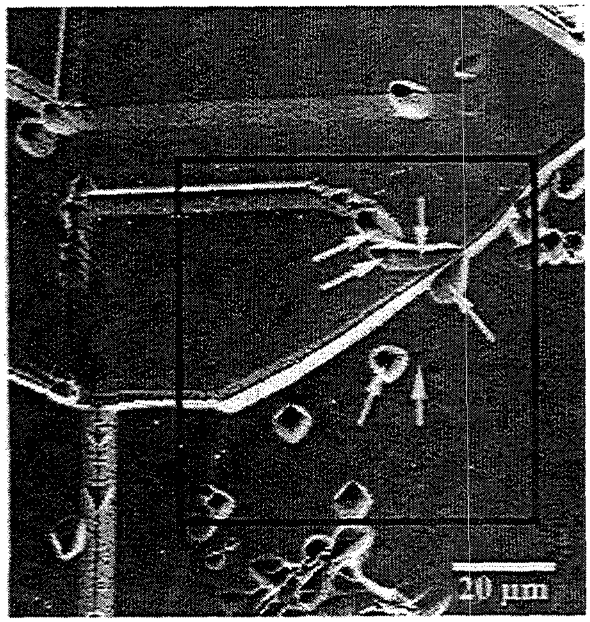


Figure 4: SEM image of the XRF mapped regions (Figures 2&3) after etching. The white arrows locate Ni and Cu regions in the as-grown material. The black box indicates the area scanned with XRF after Al gettering.

A correlation between the Ni and Cu agglomerates of Figure 2 and the structural defects in the material was established with preferential etching and imaging with a scanning electron microscope. The results are shown in Figure 4 where the white arrows denote where the Ni and Cu was located in the as-grown material (Figure 2). The etch grooves are etched grain boundaries and the deep, black pits are etched dislocations. A strong correlation is seen between the Ni and Cu rich regions and dislocations, with a single grain boundary possessing a small amount of Ni and Cu. The arrow farthest down and to the right points to a very shallow etch pit which is characteristic of a microdefect, e.g. a swirl defect or an oxygen precipitate. Considering the high concentration of impurities at this defect in the material's initial state, identification and investigation of this microdefect is desirable. Recent work has been carried out to identify microdefects in mc-silicon [23] with initial identifications showing predominantly single and multiple plate-like precipitates and a significantly lower concentration of spherical-like precipitates.

Since the material was cooled very slowly during growth, such that impurities were only slightly supersaturated during the cooling, the results of initial impurity distributions indicate dislocations are the preferred precipitation site in mc-silicon. In turn the dislocations would be expected to be the most thermodynamically-stable site for the impurity during dissolution. Even in this most stable configuration, the impurities quickly release from the dislocations and are fully removed with an Al gettering treatment, however, the minority carrier diffusion length of the material is not greatly enhanced. Considering the Al gettering treatment has more than sufficient thermal load for complete impurity diffusion from the dislocations to the Al layer and the segregation coefficient of the Al layer with respect to the silicon matrix is $\approx 10^5$, one would expect all released impurities to be completely gettered to the Al layer and, consequently, the minority carrier diffusion length would greatly increase. This is not observed, however, metal impurities may still be the dominant mechanism for this residual poor diffusion length. Two possible mechanisms are presented here: 1) the strain field of the structural defect may stabilize extremely small Ni and Cu clusters, <2-5nm, and 2) if one considers the structural defect as a completely different phase than the surrounding silicon matrix, this defect phase may possess a higher impurity solubility than the surrounding silicon. In the latter case the segregation-type gettering action of the Al backside layer will be severely retarded since the defect phase acts as a segregation-type gettering mechanism as well. Furthermore, both proposed mechanisms suggest once metal impurities interact with structural defects in silicon, complete impurity removal from the defect is an arduous task.

Conclusions

Dislocations were found to be the preferred precipitation site for Ni and Cu impurities in multicrystalline silicon. Rapid thermal treatments rapidly released impurities from their initial state without any observable limitation other than simple diffusion in the silicon matrix. Gettering treatments dissolved the metal impurity precipitates below the sensitivity of these experiments (<2-5nm), however, the gettering treatment does not greatly enhance minority carrier diffusion length values. This indicates metal impurities may remain either as very small precipitates/clusters or in a dissolved state within the phase of the dislocation.

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