Physical mechanisms of *in situ* surface gettering of metals in ribbon silicon for solar cells

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The authors have employed synchrotron-based x-ray absorption near-edge spectroscopy and x-ray fluorescence microscopy to identify the chemical state and distribution of metals gettered to the surface of String Ribbon silicon grown with CO-ambient gas. Copper and nickel precipitates were observed in their equilibrium silicide phases, indicating a dominant relaxation gettering mechanism. In addition, microwave photoconductive decay measurements show a decrease in bulk iron concentration and a tenfold increase in minority carrier lifetime in CO-ambient grown material. Implications of the observed gettering mechanism on ribbon-type solar cells are discussed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2711523]

An increase in the price of semiconductor-grade silicon resulting from a recent shortage has strongly impacted the solar cell industry and motivated research on reducing material costs. Particularly promising are ribbon-type materials, which by avoiding ingot sawing significantly increase silicon utilization.[1] The use of dirtier, cheaper, solar-grade silicon holds the promise for further cost reductions and reduced supply constraints. Unfortunately, ribbon materials contain local regions of high dislocation density that, in combination with high concentrations of metallic impurities contained in so-called dirty silicon, reduce solar cell efficiencies and limit cost competitiveness.[2] Finding methods to increase minority carrier lifetime in ribbon Si grown from solar-grade silicon materials would be an ideal merger of both advantages.

Ribbon materials offer a unique opportunity to employ creative surface gettering methods to remove metals during growth, as the wafer bulk is never more than a few tens or hundreds of microns from a free surface. Previous studies have shown that the addition of carbon-rich gas into the ambient during growth getters metals to the surface and results in higher minority carrier lifetimes in the bulk.[3,4] Specifically, the gases create a carbon-rich surface layer with dendritic microdefects on the top surface and a SiC-rich layer up to $1-2$ μm below the surface.[4,5] It is believed that this SiC layer getters metals, although the exact mechanism is not well understood. Pivac *et al.*[3] have proposed a possible mechanism whereby SiC precipitates act as a sink for silicon self-interstitials (Si_I). It is argued that the high flux of Si_I towards the SiC-rich area aids the formation of chromium silicide precipitates, which also absorb Si_I and continue to stimulate the process.

Nevertheless, certain other impurities also found in silicon solar cell materials[6] do not absorb Si_I upon metal silicide formation. $NiSi_2$ is almost perfectly lattice matched with silicon, and the common copper silicide Cu_3Si ejects copious amounts of Si_I into the lattice, the opposite of $CrSi_2$. These common transition metals are therefore not subject to the mechanism described above and have not been previously investigated in surface gettering experiments. In general, lack of understanding of the chemical state and distribution of the gettered *metals* has precluded a solid understanding of the mechanisms for the observed gettering.

In this letter, we report on the surface gettering of Cu, Ni, and Fe in String Ribbon material. We elucidate the mechanism of surface gettering by measuring the chemical state and distribution of gettered and ungettered metals in ribbon Si. In addition, we quantify the magnitude of the beneficial effects of *in situ* surface gettering on String Ribbon grown from a heavily contaminated melt.

Samples of String Ribbon[1] silicon were grown at Evergreen Solar with approximately 840, 220, and 170 ppm weights of Cu, Ni, and Fe, respectively, in the melt. Samples were grown with and without CO gas added to the inert ambient. For each growth condition, a pair of samples was analyzed with and without a 10 μm silicon etch procedure, to distinguish between metals on the surface and in the bulk. All samples were cleaned in an ultrasonic acetone bath before measurement. The chemical phase and distribution of metals were identified by x-ray absorption near-edge spectroscopy (XANES) and x-ray fluorescence microscopy (μ-XRF), respectively,[7] at beamline 10.3.2 of the Advanced Light Source and beamline 20-ID-B of the Advanced Photon Source. XANES spectra were obtained with the sample held at grazing incidence to the beam to maximize fluorescence from metals on the surface.

Figures 1(a) and 1(b) show Cu and Ni XANES spectra from a nonetched sample grown with CO-ambient gas. These are compared with standard spectra of each metal silicide

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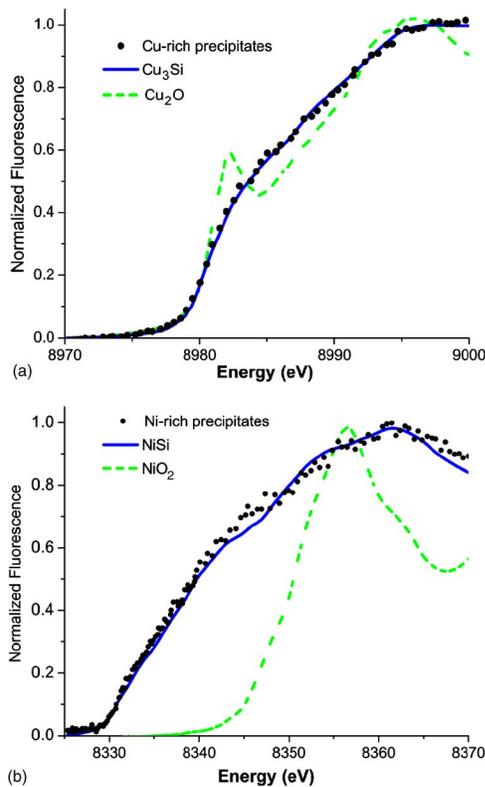c)Present address: Siltronic Corporation, 7200 NW Front Ave., M/S 10, Portland, OR 97210.

FIG. 1. (Color online) XANES spectra of (a) Cu precipitates (black dots) and (b) Ni precipitates (black dots) on the surface of a CO-ambient non-etched sample compared with standards of their respective silicides (solid blue) and oxides (dashed green).

FIG. 3. (Color online) Histograms of minority carrier lifetime (μ-PCD) of etched samples grown in inert (black) and CO (red) ambients. (Inset) Fe point defect concentrations in etched inert and etched CO-ambient samples measured by dissociation of Fe_i-B_s pairs. Gray band marked "τ_{FeB}" indicates the maximum lifetime achievable with a given Fe_i-B_s point defect concentration, from Ref. 8.

spectroscopy data indicating gettering of Cr to within $1-2$ μm of the surface.[3] In contrast, comparison of Figs. 2(c) and 2(d) shows no difference in intensity or distribution of Cu for samples grown in an inert ambient, indicating that no surface gettering took place. Additionally, Fig. 2(a) shows that Cu precipitates on the surface in isolated locations rather than being distributed homogeneously. The μ-XRF maps of Ni fluorescence (not shown) are similar to Fig. 2, indicating that Ni is also gettered by the SiC surface layer and precipitates in isolated locations. No Fe-containing particles were observed above detection limits. This is not surprising, as the solubility of Fe is about two orders of magnitude lower than those of Cu and Ni, and such particles are traditionally more difficult to detect. Streaks of Fe oxide were observed in one nonetched sample grown in CO ambient, but it is unclear whether these were caused by surface contamination after cleaning or persisted through our cleaning procedure.

Minority carrier lifetimes were measured by microwave photoconductive decay (μ-PCD) and compared between an etched sample grown in the inert ambient versus an etched sample grown in a CO-rich ambient (Fig. 3). A significant increase of average minority carrier lifetime, on the order of ten times, is observed in samples grown in the CO-rich ambient. The interstitial Fe concentration was determined by measuring lifetime before and after Fe_i-B_s pair dissociation[8] and is correlated to the measured lifetimes as shown in the inset of Fig. 3. As the CO-ambient sample was etched before measurement, the decrease in Fe_i-B_s concentration suggests that Fe was gettered to the surface during growth.

The observation of Cu and Ni precipitation into their respective equilibrium silicides indicates that gettering occurs through relaxation, whereby supersaturated metal impurities precipitate when provided with energetically favorable nucleation sites. These sites can be structural defects (grain boundaries, dislocations, and voids), regions of favorable point defect concentration, or areas of favorable local strain (compressive or tensile). For example, previous studies have shown that Cu_3Si precipitation, which is associated with an atomic volume increase of 50% per metal atom,[9] is accompanied by a variety of strain relaxation phenomena such as elastic deformation and ejection of Si self-interstitials (Si_I).[10] SiC precipitation, on the other hand, *absorbs* Si_I, and therefore causes tensile strain. Hence, a possible explanation for

and a corresponding oxide. It is clear that both metals precipitated into equilibrium silicide phases: Cu_3Si and $NiSi_2$. One can deduce that these metals are precipitated at the sample surface by comparing plane-view μ-XRF maps of Cu for four samples: CO ambient before etching [Fig. 2(a)], CO ambient after etching [Fig. 2(b)], inert ambient before etching [Fig. 2(c)], and inert ambient after etching [Fig. 2(d)]. Comparison of Figs. 2(a) and 2(b) shows that in CO-ambient materials, Cu has been gettered to within at least 10 μm of the surface, consistent with previous secondary ion mass

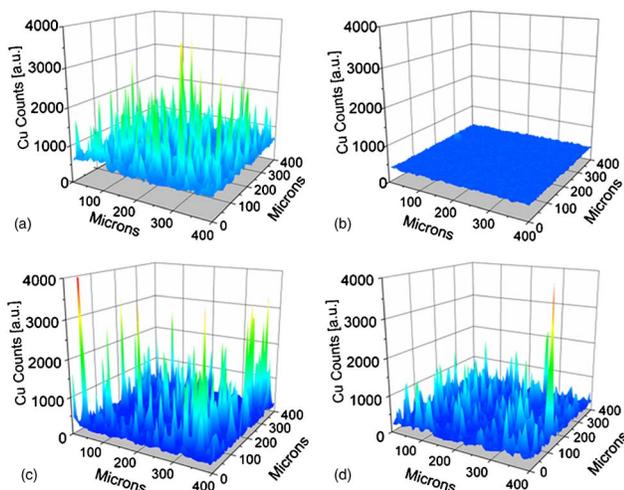FIG. 2. (Color online) 400×400 μm^2 μ-XRF maps of copper distribution in (a) nonetched String Ribbon sample grown in CO ambient, (b) silicon-etched sample grown in CO ambient, (c) nonetched sample grown in inert ambient, and (d) etched sample grown in inert ambient.
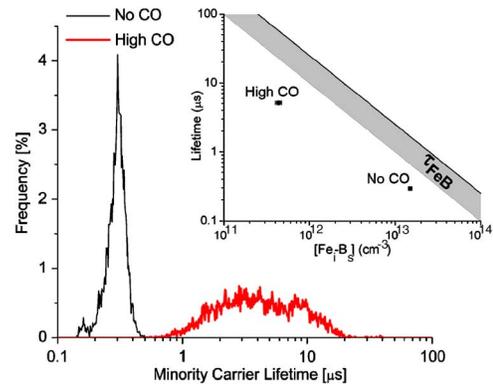
the gettering of Cu is that regions of the material with high SiC content provide the energetically favorable nucleation sites necessary for Cu$_3$Si precipitation via strain compensation through point defects. The spatial inhomogeneity of the gettered Cu observed in Fig. 2(a) provides further evidence for heterogeneous Cu precipitation after supersaturation.

NiSi$_2$, unlike Cu$_3$Si, causes only a 2% (Ref. 9) decrease in atomic volume per metal atom. It can therefore precipitate readily without causing much lattice strain and should not be significantly affected by point defect gradients. However, we do observe the gettering of Ni in XRF maps similar to Fig. 2, while Fig. 1 shows that Ni precipitates as NiSi$_2$. Additionally, the decreased bulk Fe concentration in CO-ambient grown material shown in Fig. 3 indicates that Fe, whose common silicide FeSi$_2$ is associated with a decrease in atomic volume per metal atom of 11%,[9] is also gettered, despite the fact that point defect concentration gradients caused by SiC (Si$_I$ absorbing) would be expected to suppress Fe precipitation in a relaxation mechanism, assuming Fe also precipitates as a silicide and therefore also absorbs Si$_I$. Heterogeneous nucleation, however, can be a result of a variety of effects, not limited to favorable point defect concentrations. The surface of CO-ambient grown material has general lattice damage[5] which can create favorable nucleation sites for a species with varying lattice mismatch. In this way the gettering of many different metals in ribbon-type material can be explained. In addition, we have previously observed that the precipitation of one metal species can aid the precipitation of another. Specifically, in ingot cast material we have observed the coprecipitation of Cu and Ni at structural defects[11] and the coprecipitation of Cu and Fe at SiC microdefects.[12] The precipitation of multiple metals at the surface observed in this study therefore suggests that metal-metal interactions may also play a role in reducing the energy barrier to nucleation.

We note that the relaxation mechanism outlined here is distinct from the kinetic process proposed by Pivac *et al.*[3] and outlined in the introduction, which would limit gettering to species such as Cr and Fe (which precipitate as silicides with smaller lattice constants than Si). Our observations of gettering of a variety of metals indicate that metal gettering by a SiC surface layer is more pervasive. Our data also support previous suspicions that oxide formation is not the necessary cause of gettering.[3]

The identification of this *in situ* gettering process as a relaxation mechanism has implications for solar cell processing. First, relaxation gettering implies that there is a minimum metal concentration remaining in the bulk equal to the metal solubility at the lowest temperature that still allows sufficient mobility to reach the sink on the surface. This provides an ultimate limit for reductions in bulk metal concentration. Second, the low dissolution temperatures of metal silicide precipitates demand that the surface layer be etched off before any processing anneals which often take place at temperatures around 800–900 °C, more than sufficient for the reintroduction of metals into the bulk.[13]

In summary, a combination of μ-XRF and XANES on String Ribbon silicon grown with CO added to the ambient has elucidated the distribution and chemical state of metals gettered to the surface. We observe silicide precipitate formation of both Cu and Ni, which suggests a dominant relaxation gettering mechanism. The precipitation of metal silicides with different lattice constants relative to Si suggests that the formation of a SiC surface layer creates a variety of energetically favorable nucleation sites for precipitation allowing for the gettering of many different metals. More generally, the observation of a strong influence of ambient gases on metal precipitation and gettering is important and warrants further studies on the effects of other gases on impurities in silicon. Additional understanding of ambient gas effects on silicon defects at high temperatures could provide more options for the successful use of dirty silicon in solar cell manufacturing.

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