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Chemical etching to dissolve dislocation cores in multicrystalline silicon

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ABSTRACT

Multicrystalline silicon wafers are used for approximately half of all solar cells produced at present. These wafers typically have dislocation densities of up to $\sim 10^6\,cm^{-2}$. Dislocations and associated impurities act as strong recombination centres for electron–hole pairs and are one of the major limiting factors in multicrystalline silicon substrate performance. In this work we have explored the possibility of using chemical methods to etch out the cores of dislocations from mc-Si wafers. We aim to maximise the aspect ratio of the depth of the etched structure to its diameter. We first investigate the Secco etch ($1K_2Cr_2O_7$ (0.15 M): 2HF (49%)) as a function of time and temperature. This etch removes material from dislocation cores much faster than grain boundaries or the bulk, and produces tubular holes at dislocations. Aspect ratios of up to ~7:1 are achieved for ~15 μm deep tubes. The aspect ratio decreases with tube depth and for ~40 μm deep tubes is just ~2:1, which is not suitable for use in bulk multicrystalline silicon photovoltaics. We have also investigated a range of etches based on weaker oxidising agents. An etch comprising $1I_2$ (0.01 M): 2HF (49%) attacked dislocation cores, but its etching behaviour was extremely slow (<0.1 μm/h) and the pits produced had a low aspect ratio (<2:1).

1. Introduction

Half of all solar cells are produced from multicrystalline silicon (mc-Si) wafers. These substrates contain high concentrations of defects (grain boundaries, dislocations, precipitates, metallic impurities), which act as recombination centres and limit the efficiency of the final solar cell produced. Dislocations, which are typically present in concentrations up to $\sim 10^6\,cm^{-2}$ [1], are gettering centres for impurities and this decoration dramatically enhances their recombination activity [2]. This strong recombination activity makes it likely that dislocations and associated impurities are the most detrimental defects in mc-Si after gettering and passivation [3]. Finding a way to deal with dislocations is one of the most important problems in mc-Si substrate research.

One way to reduce dislocation densities in mc-Si is to alter casting processes [4,5]. Another approach is to remove the dislocations after growth. Annealing at 1366 °C has been shown to provide a significant reduction in dislocation density in string ribbon mc-Si [6]. However, at such high temperatures, processing is expensive and the high solubility of transition metals makes contamination likely. We are exploring another post-growth dislocation removal technique, which is to dissolve the dislocation cores away using chemical methods. This has the advantage of being a low temperature process, but the disadvantage of creating additional surfaces for which passivation will be required. To be a viable process in mc-Si photovoltaics the dislocation cores will need to be removed from at least the top ~20 μm of material, where ~80% of the solar spectrum is absorbed [8]. To minimise loss of useful silicon material we also require the aspect ratio (the depth of the dislocation tube relative to its width) to be as high as possible and we expect that an aspect ratio of ~10 is required for potential viability.

Defect-revealing etches are routinely used in laboratories to study extended defects such as dislocations, grain boundaries, and precipitates. These etches react preferentially with the defects and surrounding bulk to create features at the surface that can be seen under a microscope. One of the standard etches for revealing defects in silicon is the Secco etch [7]. In this paper we begin by investigating whether this etch can be used to dissolve dislocations deep into mc-Si wafers. We then explore possible etches based upon weaker oxidising agents.

2. Experimental methods

Experiments were performed on p-type mc-Si material with a resistivity of 1–10 Ω cm. Samples measuring 15 mm by 10 mm were diced from as-sawn wafers and these were polished to a colloidal silica finish. A small area of each sample was coated with Lacomit varnish, to protect it from subsequent etching. Specimens were then submerged in 30 ml of etchant per sample in a beaker held in a constant temperature water bath. The beaker was

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Table 1
Compositions of etchants investigated, together with a summary of their effects on dislocations and grain boundaries (GBs). All solutions are aqueous.

Oxidising agent	Composition	Effect on mc-Si
Potassium dichromate (Secco etch)	$1K_2Cr_2O_7$ (0.15 M): 2HF (49%)	GBs and dislocations revealed after <1 min
Iodine	$1I_2$ (0.01 M): 2HF (49%)	Little observable etching after 1 h. GBs and dislocations revealed after 16 h
Potassium iodide	1KI (0.15 M): 2HF (49%)	GBs revealed after 1 h. Dislocations not revealed after 16 h
Potassium permanganate	$1KMnO_4$ (0.15 M): 2HF (49%)	GBs revealed after 1 h. Dislocations not revealed after 16 h
Potassium iodate	$1KIO_3$ (0.15 M): 2HF (49%)	GBs revealed after 1 h, but bulk silicon also strongly attacked. Effect on dislocations unclear
Iron (III) chloride	$1FeCl_3$ (0.15 M or 1.5 M): 2HF (49%)	No GBs or dislocations revealed after 16 h

covered to ensure the etching was performed in dark conditions and with minimal evaporation of etchant. Compositions of the etchants investigated are given in Table 1. The etching behaviour of the Secco etch was investigated at a range of temperatures (from -15 °C to 45 °C). A chiller coil was used to reach low temperatures, for which antifreeze was added to the water bath. The temperature was measured from a plastic-coated thermocouple placed in the etching solution. The etching behaviour of the other etchants was investigated at room temperature (22 ± 2 °C).

After etching, samples were characterised by optical microscopy and scanning electron microscopy (SEM) using a JEOL JSM-840F. For etches that reveal dislocations, an angle-lapping technique was then used to measure the depth to which the dislocations were etched out. Samples were mounted at a shallow angle ($\sim1°$) on a stub and this was then arranged so that polishing occurred with the stub surface parallel to the polishing wheel. The depth of the etched dislocations could therefore be seen under an optical microscope by scrolling down this angled surface until a position was reached at which the full length of the etched structures had been polished away such that no etch features were visible. A Dektak surface profiler was used to correlate this position with depth of the material removed. The surface profiler was also used to determine the bulk etch rate by measuring the step between the masked-off unetched region and the etched material.

3. Results and discussion

3.1. Secco etching

As expected from a standard defect-revealing etch [7], the Secco etch rapidly revealed dislocations and grain boundaries in mc-Si. An optical micrograph of a typical etched microstructure is shown in Fig. 1(a). The etched structures produced at dislocations were imaged by SEM and typical micrographs are shown in Fig. 2. The micrographs show deep tubular structures are produced along dislocation cores. Fig. 2(a) also shows that some dislocation cores do not run normal to the wafer surface. The micrograph in Fig. 2(b) shows a dislocation in mc-Si etched for 30 min at 25 °C. Whilst the tubular structure produced is deep, as desired, it is clear that its aspect ratio is not sufficient for the application intended. It should be noted that although the etch features produced by the Secco etch are generally referred to in the literature as etch "pits" [7] in many instances they are better described as etch "tubes", as they often penetrate deeply into the material compared to their diameter at the surface.

The aspect ratio of the etch tube produced is controlled by the relative etching rates of the dislocation core and the bulk material surrounding the tube created. Silicon atoms at the core of dislocations have a higher energy than those in the bulk, so the change in their energy on dissolution will depend on their location relative to the dislocation. In turn, since the dissolution process is thermally activated, different dissolution energies may lead to the ratio of the etch rate at dislocations and at the bulk surface varying with temperature. It might therefore be possible to improve the etch tube aspect ratio by changing the etching temperature. Parameters of the Secco etch as a function of time at different temperatures, from -15 to 45 °C, are shown in Fig. 3. Plotted are the depth of the etch tube relative to the final flat sample surface, the average diameter of the etch tubes at the surface, and the thickness of bulk material removed by the etch.

The average tube diameter and the bulk etch rate varied approximately linearly with time at all temperatures investigated. The rate of material removal from the bulk surface varies according to the following Arrhenius relationship:

$$\frac{d(z_{\text{bulk}})}{\text{dt}} = 10.2\exp\left(-\frac{0.30\,\text{eV}}{kT}\right)\mu m/\text{min} \tag{1}$$

The depth of the dislocation etch tubes varies non-linearly with etching time. For short times the etch tube length increases at a faster rate than for longer times. The aspect ratio of the tubes therefore decreases with etching time. At the highest temperature studied (45 °C) the aspect ratio of tube depth relative to final surface position to tube diameter is $\sim$3:1 for a 3 min etch, falling to <1:1 for a 40 min etch. The situation is slightly improved at the lowest temperature studied (-15 °C), at which aspect ratios achieved are $\sim$6:1 for 20 min of etching and $\sim$2:1 for 120 min of etching. However, this highest aspect ratio is achieved only for $\sim$6 μm deep tubes. The most promising aspect ratio measured was for samples etched at 25 °C for 5 min, which gave an aspect ratio of 7:1 for a tube depth of $\sim$15 μm.

In a silicon solar cell $\sim$80% of light is absorbed in the top $\sim$20 μm of material [8]. In order to be a useful technology for mc-Si solar cells, dislocation removal etching must remove dislocations to this depth or beyond with a good aspect ratio. The results presented in Fig. 3 show aspect ratios for 20 μm deep tubes of $\sim$2–3:1 at -15 °C, $\sim$2:1 at 3 °C, 3–4:1 at 25 °C, and $\sim$2.5:1 at 45 °C. It is therefore clear that whilst Secco etching can dissolve dislocation cores to the required depth, it is unable to do so with a sufficiently large aspect ratio to be useful for the removal of dislocations from bulk mc-Si solar cells. In addition, it is clear that the process is, unfortunately, rather slow and is thus incompatible with commercial processing.

3.2. Other etching

The data in Fig. 3 show that the aspect ratio decreases with etching time. This suggests that transport of the potassium dichromate oxidising agent to the tip of the tube (or reaction products away from the tip) is limiting the reaction rate as the tube becomes deeper. To improve the aspect ratio of the tubes it is therefore necessary to slow the intrinsic etching reaction so that dislocation dissolution is not transport limited. This should allow the better aspect ratios achieved for short tubes to be maintained as the tubes get longer.