The emergence of n-type silicon for solar cell manufacture

Daniel MACDONALD
The Australian National University, Canberra, ACT 0200, Australia.

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Abstract - The great majority of solar cells manufactured today are based on p-type silicon wafers. However, the most efficient modules are made with n-type silicon wafers. This is primarily due to the much greater tolerance of n-type silicon to the dominant defects in p-type material. In this paper we discuss some of the potential advantages and disadvantages of using p- or n-type silicon for industrial solar cell production, from the basic material properties, through to ingot growth and cell fabrication issues.

Introduction

P-type silicon has been the dominant base material for the photovoltaic industry for decades, both in the form of multicrystalline and monocrystalline (Czochralski-grown) ingots. Initially, p-type silicon was preferred over n-type due to its greater tolerance of radiation damage for space applications [1]. However, it also has other advantages, such as the lower temperatures required for the phosphorus diffusions for forming the p-n junction, compared to boron diffusions required for n-type cells, coupled with the fact that phosphorus diffusions provide effective removal of unwanted metallic impurities in multicrystalline silicon. P-type ingots also have a more uniform resistivity profile along their length, which is convenient for high yield cell fabrication. In addition, it has been thought that the higher minority carrier mobility for electrons in p-type silicon, which is typically three times that of holes in n-type silicon, would result in a longer minority carrier diffusion length, and therefore lead to improved solar cell currents. However, this last point has been shown in recent years to be incorrect, since the advantage in mobility is usually more than outweighed by the lower carrier lifetime in p-type silicon, as discussed in more detail below.

These real and perceived advantages of p-type silicon lead to early market dominance, and resulted in equipment suppliers and process development in industry being pre-disposed towards p-type cells. More recently, however, it has become quite clear that n-type silicon has some significant advantages over p-type silicon. The most important of these is the higher carrier lifetime of n-type silicon, primarily caused by the absence of the well-known boron-oxygen defect [2]. This is the fundamental reason behind the fact that the two highest efficiency modules available on the PV market today, manufactured by SunPower and Sanyo, are based on n-type silicon. Their market share remains small however, because these solar cells require more elaborate fabrication processes, and are therefore more expensive in terms of $\$/W_{peak}$, despite their higher efficiency. Many companies and institutes are now attempting to develop n-type solar cells that use standard low-cost screen-printing technology, whilst retaining efficiencies that are higher than can be achieved with p-type silicon.

In this paper we discuss some of the key technological advantages and disadvantages of n- and p-type silicon for solar cell manufacture, from basic electronic properties, through to ingot growth and cell fabrication issues.

Electronic properties of n- and p-type silicon

Most solar cells today are made either from p-type multicrystalline silicon (mc-Si) wafers, or p-type Czochralski-grown monocrystalline silicon (Cz-Si) wafers. The ultimate efficiency potential of each material is limited by the presence of particular defects and impurities, which reduce the minority carrier lifetime. In Cz-Si, the carrier lifetime is dominated by the well-known boron-oxygen defect [2], which is thought to be a complex involving both boron and oxygen. On the other hand, mc-Si is dominated by the presence of defects such as dislocations and grain boundaries, and metallic impurities, such as Fe, Cu and Ni, which are either dissolved in the silicon matrix, or precipitated at the crystal defects [3].

The boron-oxygen defect

Due to the dissolution of oxygen from the quartz crucible that contains the silicon melt during ingot growth, Cz-Si contains relatively high concentrations of dissolved oxygen – typically three times higher than mc-Si ingots. When present in boron-doped p-type silicon, this oxygen forms a recombination active centre under illumination, known as the boron-oxygen defect. This defect significantly reduces the efficiency of p-type solar cells made from Cz-Si [4]. The defect can be avoided by eliminating either the boron or the oxygen. Replacing boron with other p-type dopants such as Ga or In introduces other problems, such as large resistivity variations in the ingot. Therefore a practical solution to the problem is the use of phosphorus-doped n-type silicon wafers, which entirely eliminates the boron-oxygen defect, even if the oxygen concentration remains high. This is the fundamental reason for the very high efficiency in n-type modules made by Sanyo and SunPower.

An interesting case is the use of compensated n-type Cz-Si, in which significant quantities of boron are still present, although at lower concentrations than the phosphorus. This situation might occur if low-cost solar-grade silicon feedstocks were used for Cz ingot growth. Unfortunately, it has been demonstrated very recently that the presence of boron in n-type Cz-Si does lead to significant lifetime degradation [5], presumably due to the boron-oxygen defect. This is despite earlier results on compensated p-type Cz-Si, which showed that in p-type silicon, the defect concentration is in fact determined by the net doping, rather than the boron concentration [6], which had led to hopes that the defect might be absent in compensated n-type Cz-Si. These observations have proven difficult to explain with existing models for the defect, and reveal that it remains poorly understood, despite is great significance for silicon solar cell technology.

Metallic impurities

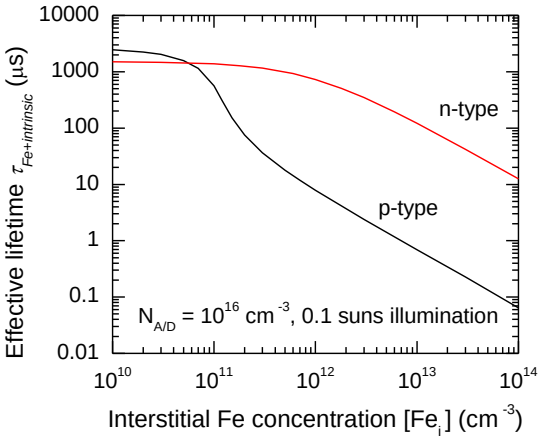

Fig 1. Effective lifetimes in n- and p-type Si as a function of the interstitial Fe concentration [Fe_i].

It has been shown relatively recently that some of the most common metal impurities that remain dissolved in the silicon matrix, are significantly less detrimental in n-type silicon that p-type. The most important example is interstitial Fe [7], which, courtesy of its positive charge state, is much more effective at capturing electrons than holes. Since electrons are the minority carriers in p-type silicon, and since the capture of minority carriers controls the carrier lifetime in low or mid injection (which are the operating conditions for silicon solar cells), the presence of interstitial Fe in p-type silicon causes a lower lifetime than in n-type silicon. This is illustrated in Figure 1, which shows the calculated effective lifetime for n- and p-type silicon as a function of the interstitial Fe concentration [Fe_i]. Here a doping concentration of 10^{16} cm^{-3} is assumed, and a generation rate of 0.1 suns is used, which approximates the injection level at maximum power point. The QSS-Model software was used for these simulations [8]. Auger recombination [9] is also included in the calculation, which causes the saturation at lower Fe concentrations.

Clearly there is a large difference in the lifetimes caused by Fe_i in n- and p-type silicon, courtesy of the charge state of dissolved Fe. The same is true for a number of other interstitial metals in Si, such as Ti, V, W and Mo [7]. On the other hand, some dissolved metals are thought to be more detrimental in n-type Si, such as Au and Zn . Fast-diffusing metals such as Ni, Cu and Co are rarely present in the dissolved state, and their behaviour when present as precipitates is not well understood at present. On balance though, silicon wafers that contain a relatively large amount of metal contamination are likely to yield better lifetimes if they are n-type. Indeed, significantly higher lifetimes have been observed in n-type mc-Si than for p-type mc-Si [10].

Growth of n- and p-type ingots

Directionally-solidified silicon ingots, such as mc-Si and Cz-Si, suffer from resistivity variations due to segregation of dopants into the liquid phase during crystal growth. The dominant p-type dopant, boron, has a segregation coefficient of around 0.7, and so only causes mild resistivity variations – typically a factor of 3 from bottom to top. This is tolerable for typical industrial solar cell processes. On the other hand, the standard n-type dopant, phosphorus, has a segregation coefficient of around 0.35, leading to a factor of 10 variation in resistivity. For some cell designs this means that only certain sections of an ingot are suitable for cell fabrication, significantly reducing ingot yield. This is potentially a disadvantage for n-type silicon solar cells. Possible solutions include developing cell designs that are tolerant

of large resistivity variations, and using methods such as melt-replenishment and dopant engineering [11] to reduce the resistivity variation in the ingot.

As noted above, the potential use of low-cost solar-grade silicon feedstocks in solar cell production has to contend with higher concentrations of both n- and p-type dopants. In general, boron is more easily removed from such feedstocks than phosphorus. This may provide an advantage for producing n-type solar-grade ingots, notwithstanding the need for controlled resistivity profiles, and the impact of the boron-oxygen defect on carrier lifetime in compensated n-type Cz-Si.

Cell fabrication for n- and p-type silicon

Cells made with p-type wafers typically have a phosphorus diffusion on the front surface to form the p-n junction. This phosphorus diffusion is also effective at removing mobile metal impurities such as Fe and Cr, a process known as 'gettering', which helps to improve cell efficiency in mc-Si wafers [12]. This has been viewed as an advantage for p-type silicon cells. In n-type cells, this phosphorus diffusion is replaced with a boron diffusion. It has recently been found that boron diffusions can also provide excellent gettering, in fact even better than phosphorus, but only under certain conditions [12]. During boron diffusion, a Boron-Rich Layer (BRL) forms on the wafer surface. This BRL is an excellent gettering site. However, if the BRL is oxidised out after the diffusion is complete, as is often done to facilitate subsequent removal of the borosilicate glass, the gettering effect is reversed, and the impurities are injected back into the wafer. In addition, the presence of the BRL makes it very difficult to achieve high quality surface passivation, a requirement for high efficiency solar cells. Very recently, chemical methods for removing the BRL at low temperature, and thereby avoiding the re-injection of the gettered impurities, have been developed [13,14], which could be an important step in allowing high efficiency n-type mc-Si solar cells to be fabricated. Boron diffusions have also been associated with reduced bulk lifetimes due to the generation of dislocations. However, this can also be avoided under the right conditions [14].

Another important historical impediment to the development of industrial n-type solar cells has been the absence, until recently, of a suitable surface passivating film for boron diffusions. In the laboratory, passivation of boron diffused surfaces has generally been performed by thermal oxidation. However, this has not been considered suitable for low-cost production, in which deposited films are preferred (a notable exception is the n-type Panda technology developed by Yingli/ECN, which uses a low temperature acid-grown oxide to passivate the boron diffused surface). For standard p-type cells, plasma-deposited silicon nitride films provide very good passivation of the phosphorus diffused surface, courtesy of their high fixed positive charge, and are ubiquitous in industry. However, the recent advent of negatively-charged aluminium oxide films [15], which can be deposited by various low temperature methods, has opened the way to low-cost passivation of boron diffusions.

Metallisation is another aspect of cell fabrication that presents challenges when considering a move to n-type substrates. A potential advantage is related to the fact that typical p-type cells

use an alloyed aluminium doped p-type region on the rear side to allow good contact and to partly reduce rear surface recombination. However, the surface passivation provided by this p+ region is not of high quality, due to the relatively low doping achieved in aluminium alloyed regions. Moving to n-type wafers allows the rear aluminium doped region to be replaced with a phosphorus diffusion, which is much more heavily doped, and when coated with SiN, provides considerably better surface passivation, and also permits good electrical contact. This comes with a potential down-side though. The need for a second high temperature diffusion means that a suitable diffusion mask may be required to block the phosphorus diffusion from over-doping the boron diffusion. This potentially adds to cell complexity.

Conclusions

There are some compelling reasons based on material properties to prefer n-type silicon over p-type for solar cell fabrication, mainly related to the absence of the boron-oxygen defect in Cz-Si, and the greater tolerance to key metal impurities in mc-Si. Nevertheless, there remain potential impediments related to ingot growth, primarily the larger resistivity variation, and in cell fabrication, principally metallisation, which need to be resolved before n-type silicon solar cells can compete with p-type substrates when producing low-cost, screen-printed, front junction devices. Numerous institutes and companies are currently working to develop such low-cost n-type cell technologies, the most advanced being the Panda technology developed by ECN and Yingli [ref]. At ANU we are currently working with Trina Solar, via a project supported by Trina and the Australian Solar Institute, to develop an industrial process for 20% n-type silicon solar cells.

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