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Fifth Workshop on the Role of Impurities and Defects in Silicon Device Processing

Summary of Panel Discussions

B. Sopori, Chairman

Prepared by:
T. Tan, B. Sopori, S. Estreicher,
L. Jastrzebski

August 13-16, 1995
Copper Mountain, Colorado

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EXECUTIVE SUMMARY

Like previous workshops, the 5th Workshop was organized around a specific theme — Defect Engineering in Silicon Solar Cell Manufacture and Thin-Film Solar Cell Development that matched the current industry concerns. The workshop was very successful in achieving its objectives: (i) to provide a forum for discussing manufacturing and research issues that can help the silicon photovoltaic (PV) industry meet DOE cost objectives, and (ii) to identify how laboratory results of using defect/impurity engineering to make high-efficiency cells on low-cost substrates can be implemented into manufacturing processes. The title of the workshop was changed to "Role of Impurities and Defects in Silicon Device Processing" to reflect the appropriateness of the subject material to industry needs. In addition, the format of the program was somewhat different from previous workshops. The new format included oral presentations to review the subject matter of each session, followed by comprehensive panel discussions that focused on critical issues facing the industry. The workshop consisted of five sessions— (i) material issues, (ii) thin-film silicon solar cells, (iii) gettering and passivation, (iv) new processes, and (v) wrap-up discussion. The latest research and development (R&D) results were presented in two poster sessions involving 24 poster presentations. The workshop was attended by 78 participants representing the silicon PV industry, academia, and R&D facilities from the United States, Germany, Spain, Australia, and Italy.

The silicon PV industry has begun to incorporate several measures that will lower the silicon PV energy costs. These measures encompass cost-reduction strategies for substrate production, cell processing, and module fabrication. The substrate-related strategies include larger ingots, use of reusable crucibles, and wire sawing that reduces kerf loss and damage to the wafers. PV companies are also adding more capacity to meet increasing demands. Automated handling of wafers in cell fabrication and module assembly will reduce costs and allow use of thinner wafers.

The issues of primary concern in commercial bulk PV Si are related to (i) feedstock, (ii) wafer thickness, (iii) metallic impurities such as Fe and Cr, and (iv) defects such as dislocation clusters. There is a large demand by the semiconductor industry for off-grade substrates in integrated-circuit (IC) process development applications. This demand can partially deplete feedstock for solar cells. Going to thinner wafers certainly will help alleviate this problem and allow PV manufacturers to cope with any possible near-term feedstock shortage. Analyses of commercial silicon, performed under NREL's Silicon Materials Research Program, have clearly shown that the concentration of metallic impurities like Fe and Cr is greater than 10^{12}

atoms/cm^3. A high fraction of these impurities is gettered during solar-cell fabrication. Thus, although high concentrations of impurities may be present in the starting material, it is possible to getter many of these impurities by post-growth processing.

Gettering has become an essential process to remove impurities from the low-cost substrates. Gettering methods using Cl, Al, and P treatments can be very effective in improving the minority-carrier diffusion length in the substrates. Gettering can be achieved as a byproduct of P and Al treatments used for formation of front-junction and backsurface fields, respectively. Higher getting efficiencies can be attained by simultaneous P and Al treatments. A difficulty in gettering arises because heavily dislocated regions cannot be gettered well. Such regions contain impurities clustres and precipitates, which are immobile during gettering. Modeling of nonuniformities in solar cells has shown that low-performing regions have a disproportionately strong influence on the cell performance. Thus, an important area of future work is to develop techniques to improve the performance of highly dislocated regions. Much insight can be achieved by making a gettering simulator available to researchers.

Hydrogen passivation of impurities and defects can be very effective in some materials such as edge-defined, film-fed growth ribbons (EFG) and AstroPower material. Variations in the degree of passivation due to hydrogen in different PV silicon substrates were determined to be related to concentrations of oxygen and carbon in the substrate. It has been proposed that these effects can be explained on the basis of hydrogen diffusion occurring via a vacancy-hydrogen pairing mechanism. Currently, an effective method for hydrogen passivation involves combining passivation and nitridation for antireflection (AR) coating using a plasma-enchanced chemical vapor deposition (PECVD) process. Further understanding hydrogen diffusion from a molecular ambient is needed to develop a cost-effective passivation process.

During the last few years many defect engineering concepts were successfully applied to fabricate higher-efficiency laboratory (small-area) silicon solar cells on low-cost substrates. Although application of these concepts have led to 17.8% small-area solar cells, there are several basic obstacles that must be overcome before such high-efficiency cells can be commercially manufactured by low-cost processes.

Thin-layer silicon solar cells offer a tremendous potential as low-cost energy sources. These thin-layer cells can use lower-quality silicon on low-cost substrates like glass to yield reasonably high efficiencies. Many approaches of cell design and material growth need to be evaluated. Some critical research areas are low-temperature deposition and processing of thin-layer silicon on a low-cost substrate, cell design that can invoke very effective light trapping, and methods to minimize interface recombination effects.

PA-1: Materials Issues in Commercial Bulk PV Si

Chairman: Chandra Khattak

Panelists: Kim Mitchell, Dan Meier, Steve Shea, Mike Kardauskas, Wolfgang Krumbe

Presently, the generic issues of concern in commercial bulk PV Si are primarily related to (i) feedstock, (ii) wafer thickness vs. mechanical strength, (iii) metallic impurities such as Fe and Cr, and (iv) defects such as dislocation clusters (also referred to as "bad regions" in this report) and grain boundaries (in multicrystalline material).

Up to now, PV Si feedstock consists primarily of scrap Si from IC rejects, at a cost of ~$10.00/kg. As the need for PV Si feedstock grows, it is expected that this cost will increase. In fact, Czochralski (CZ) solar Si feedstock has already exceeded $10.00/kg. It will be difficult for the PV industry to bear costs that may approach $30.00/kg. No consensus has been reached during the discussion on how to keep the feedstock Si at a reasonable cost, i.e., close to $10.00/kg.

As the trend in decreasing wafer thickness continues, the wafer mechanical strength becomes a serious concern. The new wafers will not be thick enough to stand small mechanical impact as may occur during normal wafer handling; yet, they will not be sufficiently thin to be elastic. No sufficient discussion was conducted on how to cope with the problem.

As is well known, the cell efficiencies are essentially limited by the defects in the as-grown materials, or formed during processing. CZ Si now has less dislocations and oxygen than previously attained, and 18% cells can be fabricated with appropriate but fairly usual processing schemes. In multicrystalline Si, the cell efficiencies range from 13%-15%, with metallic impurities and defects seemingly influencing/limiting the efficiency. The metallic impurities are primarily Fe and Cr, whereas the defects include dislocations, grain boundaries, and "“bad regions” consisting of high densities of grain boundaries, dislocations, and metal precipitates. These bad regions are seemingly related to stresses in the as-grown multicrystalline materials.

Relevant to the goal of achieving module costs of $1.00/W and 18% cell efficiency, it has been mentioned that both low cost and high efficiency are attainable now. This will require a careful consideration of process integration and some degree of equipment automation to increase throughput and reduce cycle time of each process step.

PA-2: R &D Requirements for Thin-Layer Cells

Chairman: Paul Basore

Panelists: Ted Ciszek, Harry Atwater, Bob Hall, Dieter Ast, Steve Fonash

Because of the newness of thin silicon cells, the following consensus on terminology was first established:

Active-layer thickness $<10\mu m$ ⇒ “Thin Film”
Active-layer thickness $> 10 - 100\mu m$ ⇒ “Thin Layer”

Grain size ≤ 1 mm ⇒ “Polycrystalline”
Grain size ≥ 1mm ⇒ “Multicrystalline”

It was generally agreed that the area throughput of any of the new approaches must compete with that of the ingot approaches (throughput defined as area per minute per machine, A/min./mach). Ingot growth has a typical throughput of 1000 cm^2/min/mach. The proposed techniques for thin-layer Si are generally low; but, within the range of uncertainty in other factors, throughput is feasible.

Most discussion revolved around the use of an α-Si precursor layer that is crystallized by solid-state crystallization using RTA. This approach appears to be compatible with the use of a glass substrate; other approaches are not as clearly compatible with glass.

We recognized that for thin-layer polycrystalline Si, the dominant recombination site would be the grain boundaries rather than intragrain defects. However, there are concerns if grain boundary "debris" can cause intra-grain degradation in fine-grain poly-Si. It is also likely that junction or surface recombination accelerated by defect interactions may become dominant. Hence, hydrogen passivation is likely to assume a more important role in thin-layer cells to passivate grain boundaries in small grain layers. It is not clear whether silicon layers (either a-Si or poly Si) grown as hydrogen-rich layers offer any advantage over introducing hydrogen during or after cell fabrication.

PA-3: Scope and Limits of Gettering and Passivation

Chairman: George Rozgonyi

Panelists: John Poate, Eicke Weber, Antonio Luque,
Klaus Graff, Wolfgang Schroeter, Teh Tan

Because of the use of P and Al in solar cell device structures, the effects of gettering due to P and Al naturally exist in most solar-cell processing schemes. The real issue in cost minimization is the optimization of gettering benefits using the conventional device fabrication processes. For some commercial solar-cell processes (which use extra gettering steps), the cost may be so high that the use of float-zone (FZ) substrates and very clean lines might just be equally competitive.

It has been demonstrated that the driving force for gettering of Fe by B derives from Fe-B pairing, which depends on the charge state of the interstitial Fe. This is a Fermi-level effect with its effectiveness exhibit B concentration and temperature dependencies. Thus, for a given B concentration, the gettering process is less effective or less stable at higher temperatures.

It is extremely difficult to getter Ti, because of its low diffusivity. So far, Ti has only been only gettered from Si surface regions in high-temperature HCl oxidation runs.

Charge states of the metal atoms determine its solubility as well as diffusivity. Thus, it is expected that optical processing can enhance the metal atom diffusivity.

The dissolution of metal silicide precipitates can depend on the Si point defect concentrations. Thus, a Si self-interstitial (I) supersaturation may enhance the dissolution of silicide precipitates of some metal species while retarding that of other metal species; the effect may be complementary for Si vacancies (V). Similarly, the presence of an I supersaturation may enhance the diffusion of some metal atoms while retarding that of others, with a complementary effect for V.

Modeling/simulation of the gettering of some impurities by P, by Al, and by P and Al simultaneously, has been accomplished. Based on this advancement, it is judged that a gettering simulator can be developed. However, this will require substantial time, effort, and support.

PA-4: Implementation of Advanced Processing in Commercial Silicon Solar-Cell Fabrication

Chairman: Ajeet Rohatgi

Panelists: Mohan Narayanan, Richard King, Jim Rand, James Gee, Martin Green, Juris Kalejs

A variety of processes were evaluated with the objective of determining:

- barriers to low-cost PV manufacturing
- are the current processing approaches impeding cost reduction?
- schemes that have very low potential of becoming manufacturable processes

These process steps were considered according to the following criteria for being acceptable as a solar-cell manufacturing process:

- throughput
- capability for producing an efficiency > 18%
- requirement for capital equipment
- process yield.

Diffusion was considered to be an appropriate process for junction formation. However, there were some concerns about the safe use of PH_3 as a diffusion source and in the possibility of contamination associated with belt furnaces in making 15% cells. No significant concerns were raised in other diffusion techniques such as use of $POCl_3$ and conventional furnaces, and no new diffusion technique was suggested.

Concerns exist regarding the cost-effectiveness of having too many steps associated with the buried contact process (compared to the screen printing process). It was thought that the extra cost involved in using of the buried contact process must be offset by an increase in the cell efficiency by 7.5%. Counter arguments suggested that the buried contact yielded a 25% increase in the cell efficiency compared to screen printing. It was proposed that improvements in the screen printing process are needed to reduce the contact resistance and improve the short-wavelength response. It was suggested that evaporated metals through a shadow mask may become cost-effective.

Rapid thermal processing, as used today, was thought to have throughput limitations. Modifications on the conventional system are needed to meet the requirement of 1000 wafers per hour. Possibilities include use of low-temperature processing such as optical processing.

Three techniques are currently used for hydrogenation: (i) ion implantation, (ii) forming gas (FG) anneal, and (iii) PECVD nitridation. ASE Americas is using the PECVD nitride process in their manufacturing. However, there appears to be a need for increasing the throughput. The EFG cells with PECVD and FG hydrogenation exhibit different light-intensity dependencies. It was recognized that hydrogen passivation is material sensitive. It was pointed out that hydrogen passivation improves CZ wafers and intragrain regions of multicrystalline wafers/cells.

It was thought that chemical texturing of multicrystalline silicon was not very effective. Other forms of texturing that are being investigated are mechanical texturing and textured AR coating consisting of CVD ZnO. Both of these were favorably received by industry representatives.

It was pointed out that backsurface field due to Al may not be adequate to lower the surface recombination velocity (SRV) to <1000 cm/s required for thin cells (thickness 175 µm or less). Although boron diffusions can produce low SRV, it requires higher-temperature diffusions, which degrade the cell performance. A technique that involves boron-doped Al-paste seems to be promising.

PA-5: WRAP-UP

Lubek Jastrzebski, John Benner, Richard Swanson

The crystalline-Si technology has been called "mature," with some uncertainty whether it can reach its long-term goal of 1$/watt or 18% cell efficiency or both. Continued funding at or near the 1995 level is to be expected, with some emphasis on research.

However, considerable progress has been achieved not only in improving the average efficiency of the cells (now around 15%), but also in the more precise identification of the key limiting-factors. Highlights of the 5th PV Workshop are as follows:

1. Bad regions

Bad regions of the cells are "sinks" for charge carriers and limit the efficiency of the entire device. These regions are defect-related and involve dislocations, heavy metal and other impurities, and perhaps grain boundaries as well. There seem to be "good" dislocations, those that get easily passivated by hydrogen, and "bad" dislocations, which resist passivation. The precipitation of transition metals or other impurities may render a good dislocation bad, but little is known about this. It may be noted that the issue of bad regions is related to many processes, including crystal growth, contamination (feedstock or processing), diffusion, gettering, and hydrogen passivation.

2. Gettering

Much progress has been made in the understanding of the key ingredients of gettering — the basic understanding of the thermodynamics is there. However, much less microscopic information is available on charge and spin states of transition metals, diffusion mechanisms and energies involved, and the role of vacancies or self-interstitials etc.

New gettering centers, such as voids and platelets, were briefly discussed.

3. New approaches and ideas

a) Ultra-sound-enhanced passivation, vacancy-enhanced diffusion of hydrogen, hydrogenation of thin films, and the apparent role played by nitrogen in hydrogenation have all been mentioned. The details are either not understood or are poorly understood.

b) Low-temperature optical processing, ultrasonic treatment, and rapid thermal processing appear very promising. However, it is not clear how to apply those processes to large-scale production. Many details still need to be investigated.

c) Several issues related to device design have been discussed, notably the use of buried contacts, texturing, and thin multi-layer cells.

The following areas of emphasis have been identified for future research:

1. Bad areas

Minimize their occurrence in crystal growth and determine post-growth techniques that can mitigate their effects. Also, perform research to study dislocations, precipitation at dislocations, and passivation.

2. Gettering

Develop a commercial software package to simulate gettering, and gain a better microscopic understanding of transition metal impurities.

3. Thin cells and related issues

New designs need to be investigated that can combine material and cell issues. New understanding may come from bonding thin wafers on glass (growth, binding, thermal effects). Recent developments in ribbon technology are important as well because they reflect the possibility of growing thinner substrates.

4. Feedstock

The issue of attaining large amounts of PV grade Si feedstock was raised, although it does not appear to be an immediate problem. It was estimated that the manufacture at about $20/kg would require a yearly demand of 2000 metric tons. This raised the question of what "PV-grade" Si is and the issue of establishing standards for the PV community.

Finally, a few comments about the format of the workshop:

1. The new format with fewer, but longer, talks and sufficient time for debate and discussion worked very well.

2. Some fine-tuning was suggested:

   - Expand the workshop to 4 days, to include a significant amount of foreign contributions

   - Add more free time (e.g., after lunch) for private discussions.

   This would move the workshop format closer to the Gordon Conference format.

3. Be more active in inviting foreign participation.

(Abstract submitted by L. C. Kimerling at the Workshop)

Electronic Properties of Defects and Impurities in Si

L. C. Kimerling

The most important electronic property of defects and impurities in PV applications is that they constitute carrier recombination centers, which limits the efficiencies of the fabricated solar cells. The electronic properties of the impurity atoms also affect the solubility and diffusivity of the species. For these reasons, control of defects and impurities in Si is an important part of PV engineering. In this talk, the electronic properties of point defects, dislocations, grain boundaries, transition metals, and oxygen are reviewed.

Isolated Si self-interstitials have been observed. Associates with B, C, O, and P have been studied extensively as B_i, C_i, O_i, B_iO_i, and C_iP_s. These impurities have bonded configurations [bond-centered (111) or split (100)]. Other interstitial impurities, e.g., Li_i and Fe_i, occupying tetrahedral sites, are unbonded. The outer-shell electronic structure of the impurity atom(s) determine its bonding states in Si by the following rule: those with p orbitals occupied by electrons require bonded structures whereas those with only s orbitals occupied by electrons prefer the unbonded structure. Charge-state changes that modify orbital occupancy by electrons can lead to structure instability. This instability provides the coupling between charge recombination and atomic motion, to promote recombination-enhanced defect reaction (REDR). Static multi-stable structures yield different energy levels for the same defect under different conditions. For interstitial defects, REDR and multi-stability are common properties.

Iron-acceptor pairs form by electrostatic attraction of mobile iron donors (Fe^+) to boron acceptors (B^-). This interaction directly modifies the iron recombination center properties. The negative acceptor proximity pushes donor states toward the conduction band. Pair configurations of first- and second-neighbor Fe yield two unique energy levels. Iron stability is controlled by boron doping through the electron-hole equilibrium. When extrinsic at process temperatures, the Fe solubility increases linearly with B doping. A defect engineering analysis showed that minority carrier lifetimes greater than 100 μs are achieved for process temperatures below 700°C due to reduced Fe solubility. Transition metals act as surface recombination centers. We have calculated Cr on Si (100), with RFPCD lifetime and TXRF concentration measurements, to determine the value of the hole-capturing cross-section $\sigma_p=2\text{x}10^{-17}$ cm^2.

Dislocations constitute the dominant recombination centers in high-quality PV Si. Kink sites, which control the dislocation motion, are the active recombination sites on the dislocation line. A state at E_c-0.4 eV is the recombination center. Doping increases the kink-site density and hence also the dislocation mobility as well as recombination-site density.

Oxygen precipitates are ubiquitous in CZ Si. The nucleation gateway for precipitation is the "thermal donor" centers. It is a double donor with levels at E_c-0.07 eV and E_c-0.15 eV. The electron-hole equilibria make donor formation, and hence precipitation, easier in p-material than in n-material.

In summary, the electronic states of defects and impurities limit minority-carrier lifetimes. These states also allow the solubility and kinetic processes to be controlled for defect engineering.