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Fourth Workshop on the Role of Point Defects/Defect Complexes in Silicon Device Processing

Summary Report

Workshop Chairman: B. Sopori

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

With Contributions from Session Chairmen: M. Stavola, D. Swanson, K. Kimmerling, B. Hall, S. Tsuo, R. Mertens, G. Rozgonyi, T. Ciszek, K. Mitchell

National Renewable Energy Laboratory
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Golden, Colorado 80401-3393
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EXECUTIVE SUMMARY

The 4th Point Defect Workshop was aimed at reviewing recent new-understanding of the defect engineering techniques that can improve the performance of solar cells fabricated on low-cost silicon substrates. The theme of the workshop was to identify approaches that can lead to 18% commercial silicon solar cells in the near future. These approaches also define the research tasks for the forthcoming new DOE/NREL silicon materials research program. The workshop was attended by 67 researchers, including representation from U.S. photovoltaics (PV) industry and universities, and researchers from Germany, the Netherlands, Israel, Belgium, and Spain. It was a consensus of workshop attendees that the goal of 18%-efficient multicrystalline silicon solar cells is right on target, and the pay-off for the investment by the U. S. Department of Energy (DOE) will manifest itself in the next few years as reduced costs for high-efficiency cell fabrication.

While the primary thrust of the workshop was on the post-growth quality ehnacement of the current thick (>200 μm) substrates, there were several papers and a discussion session to investigate growth and design of thin-film (< 50 μm) Si cells. The work in thin Si films is exciting in view of their potential to yield high efficiency, low-cost cells, and developments in the crosscutting areas of display, TFT and related microelectronics technologies.

Research performed under the current DOE/NREL Crystalline Silicon Materials Research Program has already led to a significant progress towards understanding and overcoming the performance limitations of low-cost commercial silicon solar cells. This understanding has resulted in fabrication processes that involve impurity gettering and impurity/defect passivation to yield high efficiency laboratory cells. These improved processes are now being assimilated into commercial cell fabrication lines, and promise a substantial reduction in the cell costs. This research has also identified a potential "showstopper" for further improvements in the performance of large-area cells. It has been determined that the localized regions of very high dislocation density, accompanied by low minority-carrier diffusion lengths, do not respond sufficiently to the traditional gettering/passivation methods used in solar cell processing. An effort devoted to understand their origins, and to mitigate their effects, has already begun. Two new processing approaches, optical processing and ultrasound treatments, have been developed and applied with some encouraging preliminary results. However, an understanding of the fundamental mechanisms of photon/phonon/defect/heavy-metal interactions involved in these processes is lacking. This knowledge is essential to further develop these technologies for high efficiency solar cell fabrication.

Recent results have also shown that the synergism of various gettering/passivation processes currently employed by the PV industry is not equally effective on different polysilicon materials. In fact the mechanisms involved in these interactions are not well understood, pointing out a continuing need for developing comprehensive basic models for gettering/passivation. This modeling effort is underway; preliminary results explain experimental observations of simultaneous Al and P gettering and H passivation.

The DOE/NREL program has been particularly successful in developing and applying a host of techniques for rapid characterization of large-area wafers and devices. These include laser microwave photoconductivity decay (LMPCD) and rf-PCD techniques for measurement of the surface and bulk minority-carrier lifetimes, SPV system for mapping minority-carrier diffusion length, and the Scanning Defect Mapping System for mapping dislocations and grain boundaries. These techniques can soon be adopted by the PV and microelectronics industries as QA tools to control the substrate material quality as well as to monitor cell fabrication processes, thus improving the yields and lowering the cell costs.

It is recognized that thin Si cells are capable of yielding high efficiencies on moderate quality material. Their development has been limited by lack of suitable growth and handling techniques. However, recent advances in the microelectronics technologies related to microcrystalline thin films for TFT's, display, and other surface devices, have opened up new avenues for controlling nucleation and grain growth of thin Si films. These new concepts include grain enhancement at low temperatures using point defect injection, zone melt recrystallization, and growth of separable films. These approaches can be applied to produce large-grain, thin Si films in configurations that are compatible with effective light trapping, offering potential for stable, high-efficiency, low-cost thin-film Si solar cells .

More emphasis is sought on closer interactions among universities, industry, and government laboratories to improve and speed up technology transfer. Although dramatic progress has been made in fostering such interactions during recent years, there is still some room for improvement. Dissemination of the technologically important information and focusing on the issues relevant to the industry needs were identified as two most important areas.

Although a number of issues have remained unresolved, it was clear that there are some issues of immediate concern — homogeneity of the material, improved understanding of gettering and passivation, Optical Processing, and thin-film silicon cells. A large basic research effort is still required to address these issues and to facilitate technology implementation and transfer to the production environment.

Crystalline Si is clearly a matured technology responsible for the bulk of the current PV power. It is expected to continue to be in a strong position provided the new developments from PV laboratories and the microelectronics industry are incorporated into the production facilities. A continued strong DOE/NREL program is warranted to address further developments in gettering, defect passivation, low-cost cell fabrication and thin film growth techniques, and to ensure continuation of a mechanism for an effective transfer of theses developments to the PV industry.

Session 1: Material Growth Issues

Seven papers reported progress in the growth of multicrystalline silicon by HEM, dendritic web, LPE, CZ, FZ, casting, and sphere formation by droplet freezing. Substantial progress in defect reduction, material uniformity, and reproducibility of the material quality from ingot to ingot have been reported. Better understanding of defect-related issues has led to higher quality material yielding higher cell efficiencies.

Six papers were presented on characterization methods: DLTS, rf-PCD, light scattering for dislocation mapping, and measurements of factors limiting cell performances. Fe, Cr, Mo, and Ti were shown to limit diffusion length in certain material regions and cause cell performance degradation. One paper presented results of ultrasound treatment that resulted in improvement of localized low diffusion length region. One paper discussed the dependence of Fe diffusion on its charge state.

The scheduled informal discussions could not be conducted because the presentations over ran the allocated times.

Session 2: New Approaches To Cell Processing

Four papers were presented in this session. In the first paper, it was shown that a modified screen printing scheme together with Al gettering and antireflection (AR) coating can produce cells with >16% efficiency. In the second paper it was shown that a deposited emitter is suitable for cell fabrication using small-grain Si. The third paper addressed the industrial processing technology in Netherlands for yielding ~14.7%-efficiency cells, with optimization modeling work in progress. In the fourth paper, the Optical Processing (OP) technique is reported: it is a controlled temperature ramp rate RTP process, which yielded superior cell performances.

Discussions

The following points were made during the discussion:

- The selective emitter cell is believed to be cost-effective and suitable for manufacturing processes.
- During OP, the wafer temperature rises only to about 400°C. The mechanism of OP-induced enhancement of the Al-Si back contact is still under study.
- The poly emitter cells, formed by depositing fine-grain Si, exhibit a higher lifetime as compared to the diffused-emitter cells. A speculative explanation for this is that a poly emitter does not produce an increase in the grain boundary activity as is caused by phosphorus in-diffusion.
- ECN used a "factors-effect-response" approach for optimizing cell processing.

Session 3: Impurity Gettering In Silicon

There were five papers presented in this session, including both experimental and theoretical studies. In experimental studies, it has been shown that applications of the various gettering techniques, including polysilicon, Cl, P, Al, Al/RTA, can significantly improve the Si material lifetimes as well as cell efficiencies. In a theoretical study, it has been shown that the Al, the P, and the combined Al and P gettering processes can be modeled.

Discussion Session
Panel: Teh Tan, Ajeet Rohatgi, James Gee, Lubek Jastrzebski

The panel has listed the following items as discussion-focusing points:

- Basic issues

- Mechanisms of gettering
  Dissolution of metal precipitates
  Role of Si point defects (I_{Si} and V_{Si})
  Impurity stabilization: dislocations, and C and O
- Synergistic effect between gettering techniques, e.g., P & Al gettering
- Synergistic effect between gettering and passivation
- Will photonic effects (e.g., as in OP) help to dissolve metallic precipitates and induce impurity atom migration?
- Application issues
- Are different gettering techniques needed for different PV Si materials?
- Why is gettering not effective for 'bad' crystal regions? What can be done?
- Is the use of gettering in solar cell fabrication processes cost-effective?
- Is the statistical data of gettering in PV Si valid?

The general discussion brought out the following points:

- The efficiency of a gettering technique varies for different PV Si materials, e.g., OTC poly vs. EFG. This effect is also observed for H passivation with a better understanding of the mechanisms involved.
- The sink for metal atoms in TCE or TCA gettering is the chlorinated SiO_2.
- There are two mechanisms involved in stabilizing the impurity atoms gettered into the gettering sites: (i) relaxation by precipitation during cooling (but not at the gettering temperature)— the prime example is Fe gettered to internal gettering sites and used extensively in IC processing; and (ii) segregation of the gettered impurities at the gettering temperature, with the prime example being gettering by Al.
- Due to the presence of a misfit dislocation network produced by high concentration P diffusion, P gettering may involve both the segregation and relaxation gettering mechanisms: during high temperature P indiffusion, the segregation mechanism is operative, while during cooling the gettered impurities may precipitate out at the dislocation network.
- It might be possible to 'play' the gettering mechanisms so as to improve the PV Si 'bad' regions. In this context, the PV Si 'bad' regions is viewed as unintentionally introduced gettering regions, and it may be possible to apply (e.g.) Al gettering to compete with the 'bad' regions and improving the lifetime in this region.
- The European experience (opinion) is that (P+Al) gettering is the primary factor responsible for producing solar cells of respectable efficiencies on polysilicon materials.

- On OP vs. RTA: OP is RTA with controlled power input, and hence, controlled temperature ramp rate. Yet, OP yields improved lifetimes/cell-efficiencies not seen by RTA. One possibility is that, in OP, a temperature gradient exists throughout the Si wafer thickness for a sufficiently long time, leading to impurity 'thermal diffusion' (enhanced diffusion in the presence of a temperature gradient). Another possibility is that the smaller temperature rise rate in OP allowed more time for a photonic effect to take place via the 'radiation-induced migration' of impurities. In the latter case, a direct energy and momentum transfer from a photon to an impurity atom is involved.

- The wafer backside Al can improve the lifetimes/cell efficiencies in four different ways: (i) gettering; (ii) the production of a wafer backside p^+-p junction; (iii) the production of p^+-p junctions at dislocation core regions and/or grain boundaries; and (iv) serving as a catalyst for producing atomic H in forming gas annealing, leading to passivation of defects. However, for item (iii) the effect is not expected for exceeding a depth of ~20 μm from the wafer back surface, and there is no direct evidence for item (iv).

- Non-uniformity of PV Si, i.e., the existence of 'bad' or low lifetime regions, constitutes a key issue for large-area solar cells. Lifetime improvement in these regions seems to be difficult by using conventional gettering techniques, e.g., P diffusion gettering. Al, OP, and ultrasound techniques should be applied to gather data and establish application window.

- RTA/OP seem to be correct schemes for future processing. Its effect on wafer processing thermal budget, throughput, and materials properties needs to be assessed.

•Industry needs wafer specs, processing simplicity, etc.

Session 4: Impurity/Defect Passivation

In this session, eight papers were presented, including a presentation on German solar cell research program. Other papers ranging from detection of Si vacancy by positrons, to a hydrogenation system, to H passivation of Si defects. The last category includes both experimental and theoretical results. Experimental studies invariably showed the effectiveness of H passivation (including an instability associated with passivating small grain polysilicon). Theoretical results include H configurations in Si, with or without associated point defects, and their binding energies. In one experimental study, it is thought that the hydrogen-vacancy (H-V) pair diffusivity has been measured.

Discussions

Panel: Mike Stavola, Carl Seager, Noble Johnson, Stefan Estreicher

The discussion on H passivation was organized around the following topics:

Introductory

Is hydrogen passivation necessary?
Is the effect sufficiently stable?

I. Hydrogenation techniques

Implantation
Plasma
Forming Gas

What's best?

II. What is being passivated?

Dislocations?
Grain boundaries?
Bulk defects? (What bulk defects?)

III. How does H get there? Diffusion or enhanced diffusion?

In the discussion of these topics, it was agreed that H passivation is necessary and effective. However, because only small concentrations of H are involved in the passivation of dislocations and grain boundaries, it is difficult to identify chemically, and its presence must be inferred from its effect on defects and cell performance.

The consensus of the group was that H passivation effects are sufficiently stable in the presently used Si materials. There has been no degradation of modules that have been lifetime tested for several years. A report was made on light-induced metastabilities associated with passivating small-grain polysilicon films. A similar effect has not been observed in solar cells fabricated using large grain polysilicon materials. It was suggested that the number of grain boundary states that can show light-induced metastability constitute only a small fraction of the total number and hence would not affect performance in materials of current interest. However, this metastability could be an important concern for solar cells built using small-grain thin-film polysilicon.

There were varied opinions on which passivation techniques are best. Two points were noted. First, the H passivation that occurs during silicon-nitride deposition was absent from the list of techniques and that this may be a preferred method. Second, the passivation technique that is best depends strongly on what material is being considered and that these cannot be separated.

In the discussion, it was noted that passivation techniques that do not require vacuum would be best for processing. Plasma passivation appears to be highly effective. Forming gas anneals would be attractive if further study shows that this is an effective passivation method for materials that are of interest.

As to what is being passivated, it is thought that dislocation passivation is of primary importance. In EFG material, for example, grains are sufficiently large that recombination at grain boundaries does not limit performance. With regard to bulk defects, evidence was presented that H passivation of transition-metal impurities appears not to be effective. If metals are present, carrier lifetime will be degraded, irrespective of H passivation. On the other hand, results from previous workshops showed that decorated dislocation or defects generated by dislocation motion are effectively passivated.

There was some discussion on what H passivation actually means. It was noted in many cases that the gap is not swept clean of states. This is the case for dislocations and transition metals: levels are shifted but are still present. Shifting of deep states away from mid-gap position is sufficient to increase the recombination lifetime and that removing all states from the gap is not necessary.

Finally, how H gets into materials was discussed. "Enhanced" diffusion may not be required to explain the passivation depths that are observed. What the "effective diffusion constant" for H will be and how the hydrogen diffusion constant is affected by defects in solar-grade materials during processing is controversial. The mechanism for the introduction of H during forming gas annealing at 400°C was also discussed. Results suggest that Al deposited on the Si surfaces has a catalytic effect on the dissociation of H_2 and that catalysis at the surface or at defects may be required for H introduction at relatively low temperatures (~400°C).

Session 5: New Concepts in Silicon Growth/ Improved Initial Quality and Thin Films

The session included presentations involving new concepts for growing thin Si films on low-cost substrates, and on the design of thin-film Si cells. The growth techniques included solid phase diffusion for grain size enhancement, zone melt recrystallization, use of LPE on single and metallurgical grade polycrystalline silicon substrates, and reusable substrates consisting of CaF_2 layer on Si substrates. Other presentations included a review of University of New South Whales thin-film approach, and an analysis of effective light trapping for thin-film cells.

Discussions
Panel: Bob Hall, Kim Mitchell

The panel has put forth four major issues for discussion:

- Polysilicon feed stock
- Substrate type
- Cell design processing
- Module assembly

In CZ growth, it has been found that the origin of the polysilicon feedstock, specifically Si 'rejects' vs. virgin polysilicon, does not influence the crystal quality. Silicon 'reject' means the rejected Si crystals from the IC industry. One reason for this outcome is probably that the metal segregation coefficient is on the order of 10^{-5} (only ~10^{-5} parts of metal in Si melt will be incorporated into the Si crystal). It is evident that Si rejects do not contain much more metal than semiconductor-grade polysilicon. It remains to be seen whether metallurgical grade polysilicon can be used as CZ feedstock (probably not). In other crystal techniques, contamination from the crystal growth apparatus must be controlled, e.g., Ti in the graphite die used in EFG growth. This is because of the faster crystal growth rate, which may not allow an equilibrium segregation of impurities between the liquid and solid Si to be established, and/or because of the incorporation of the apparatus materials in the solidifying Si as inclusions on a large scale.

There are currently mainly two types of substrates: ribbon (as grown) vs. wafers cut from bulk CZ or cast or HEM Si. With recent progress in CZ crystal growth speed and wire sawing for making wafers, it is not necessary that CZ wafers will be more expensive than ribbon materials in the near future. For the ribbon material EFG Si, the inhomogeneity problem must be addressed for producing better than 15% efficiency cells.

It is suggested that cell and module integration issues and costs must be addressed.

Session 6: Silicon Solar Cell Design Opportunities

Two papers were presented in this session. The first addressed the PV industry in which cost-effectiveness had been emphasized for all steps leading to the final module. The second paper reported on an European effort of processing 18%-efficient solar cells. It is emphasized that such an efficiency is only obtained via (P+Al) gettering.

Session 7

Panel Discussion: What Will it Take to Make 18% Cells/What Research Issues Need to be Addressed?

Panel: Richard Swanson, Antonio Luque, Robert Mertens, Ajeet Rohatgi, Rob Steeman

In view of the significant progress already made in the last few years towards improving quality of the substrates, and fabricating ~18%-efficient laboratory cells on low-cost CZ and poly, the discussion focussed on the issues that are necessary to meet the challenge of reaching 18% or better commercial solar cells at a low cost. The group reviewed the technologies that are needed to achieve such a goal. The results are grouped in three main categories, each containing a number of issues, in tabulated form. Each item is designated as either a long-term (L) or/and an immediate (I) issue, and ranked (R) from 1 (lowest) through 5 (highest) in terms of its priority of needing attention. These are summarized as follows:

Wafer

	L	I	R
1. Larger wafer	√	_	2
2. Improved homogeneity	√	√	5
3. Lower lost feedstock	_	√	2
4. Reduced cost CZ	_	√	2
5. New slicing method	_	√	3
6. High τ CZ	√	_	3–4
7. Non-sliced substrates	√	_	3–4
8. New growth method (e.g., FZ, EMC)	√	_	4
9. Thin film Si	√	_	5

Cell Processing

	L	I	R
1. New structures	√	_	4
2. Process simplification	_	_	3
3. Improved screen printing	_	√	1
4. Alternatives to screen printing	√	_	2
5. New barriers (α-Si, SIPOS, etc.)	√	_	2
6. Gettering	√	√	5
7. Surface/Defect passivation	√	√	5
8. Hydrogenation	√	√	5
9. Handling thin wafers	=	√	1
10. Optical processing/RTP	√	√	5
11. Reduced chemical usage	_	√	1

Lamination

	L	I	R
1. New encapsulants	_	√	3
2. New interconnect schemes	√	_	4
3. Assembly automation	_	√	5
4. Monolithic module	√	_	2

Session 8
Wrap-Up/Future Directions

The Workshop concluded with a Wrap-Up Session chaired by John Benner. Items discussed were

1. The general conclusions from various presentations and discussions are

- Different materials respond differently to the same processing steps, such as gettering and passivation.
- Material non-uniformities are thought to be the performance-limiting factor for many commercial cells. There continues to be a major concern because it is not clear how the low-performance regions can be improved by post-growth processing.
- Effective gettering appears to be a "must" for cell processing. There is a general feeling that gettering is a panacea to clean up all the "junk" from the material. However, primary emphasis should be on minimizing impurity contamination/defects during the growth.
- How can the technology developed in the research laboratories be transferred to the industry? Is the technology cost-effective?
- Although interactions between the industry and the research laboratories have already been established, a still closer cooperation is deemed to be necessary.

2. Accomplishments of the last few years include

- The quality of the starting materials has been significantly improved.
- The average cell performance has improved.
- A significantly higher level of understanding of the mechanisms related to gettering and passivation has been acquired.
- Techniques for material and cell characterization have been greatly improved. In particular, mapping techniques that can rapidly measure material/device parameters have been developed.

3. Workshop format

Workshop should reduce the number of talks in favor of discussions. This could be accomplished by (i) having review presentations, (ii) having a formal program committee that can select presentations that emphasize new material, (iii) reducing the oral part of the presentation to 10 min. followed by a 5-10 min. discussion, (iv) include some poster presentations for material that involves lot of details, and (v) provide a copy of VU-graphs or a book of extended abstracts to the attendees at the registration.

There was a discussion as to whether the Workshop should be extended to include manufacturing details. This was not thought to be appropriate for the workshop. Another suggestion of alternating workshop theme among material, point defects, processing physics, and cell manufacturing issues, was discussed. It was an overwhelming opinion that extending the workshop scope further from the present focus could undermine the effectiveness of the workshop.

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