BNL-67536

Lead-free Solder
Technology Transfer from ASE Americas

Report on a Workshop Organized by

Brookhaven National Laboratory (BNL)

October 19, 1999

Vail, Colorado

Hosted by

National Renewable Energy Laboratory (NREL)

PV Performance, Reliability and Standards Workshop

Vasilis Fthenakis, BNL

Ronald Gonsiorawski, ASE Americas, Inc.

Brookhaven National Laboratory
Environmental Sciences Department
Upton, New York 11973

Prepared for the U.S. Department of Energy
Contract No. DE-AC02-98-CH10886

Acknowledgment

We thank Dr. Charlie Gay for his gracious support of the workshop, and for his services to the PV industry as a whole. As president and CEO of ASE Americas Inc., he had the vision to offer the Pb-free solder technology, developed by Ron Gonsiorawski, to the rest of the PV community without charge: in his words, to "preserve the good, environmental image of PV globally". Thanks also are due to Edward Treglia, representing Steel Heddle Inc., a manufacturer of Sn/Ag ribbon solder, for offering to absorb the additional cost of this solder and thus help the industry go lead free.

This workshop was organized by the Brookhaven National Laboratory. It was supported by the US Department of Energy, Photovoltaic Energy Division, Conservation and Renewable Energy, James Rannels, Director, Alec Bulawka, Program Manager. We are grateful to the DOE administrators for their encouragement and support, and to National Renewable Energy Laboratory (NREL) for providing the space and facilities to hold this event during the PV Performance, Reliability and Standard workshop.

V.M. Fthenakis

"The general population has placed a mantle of expectations on our shoulders that requires us to actively, purposely and frequently reaffirm and advance our commitment to the environment. We can and must not only meet but exceed the expectations of our supporters!"

Charles F. Gay
(in "86400 Times a Day: The Role of Management in Photovoltaic Safety",
Solar Cells, 19, 203, 1986-1987)

CONTENTS

Acknowledgement

Objective 1

Background 1

Executive Summary 1

List of the Workshop Participants 4

1. Vasilis Fthenakis, The Case for Lead-free Solder in PV Modules 7

2. Ronald Gonsiorawski, Lead free Interconnected Photovoltaic Modules 22

3. Questions and Answers 38

Objective

The objective of the workshop "Lead-free Solder Technology Transfer" was to inform the photovoltaic (PV) industry about current trends to phase-out Pb in electronic devices, and to facilitate the transfer of the ASE Americas Inc.'s Sn/Ag solder to other PV manufacturers.

Background

The National Photovoltaic Environmental, Health and Safety (EH&S) Assistance Center

Brookhaven National Laboratory (BNL) operates the National Photovoltaic EH&S Assistance Center, under the auspices of the Department of Energy (DOE), to foster the safe and environmentally friendly operation of photovoltaic facilities and products, extending from R&D to manufacturing and use. The BNL Center undertakes the following activities: a) It directly supports DOE Headquarters, the National Renewable Energy Laboratory (NREL), and Sandia National Laboratory (SNL) to ensure that their facilities and those of their contractors are operated in an environmentally responsible manner. b) It conducts EH&S audits, safety reviews and incident investigations, as needed. c) It assists the photovoltaic industry to identify and examine potential EH&S barriers and hazard-control strategies for new photovoltaic materials, processes and applications before their large-scale commercialization.

The current workshop is guided by this proactive approach to EH&S. It was organized and chaired by Vasilis Fthenakis, BNL. The issue of lead-free solders was raised by the participants of a previous workshop "PV and the Environment" at Keystone, CO in July 1998.

Executive Summary

Fthenakis opened the session by welcoming the participants and emphasizing the need for open discussion and collaboration on EH&S issues among all members of the industry. The message he conveyed was that "working together means wining together".

To safeguard the environmental friendliness of photovoltaics, the PV industry follows a proactive, long-term environmental strategy involving a life-of-cycle approach to prevent

environmental damage by its processes and products from “cradle to grave.” Part of this strategy is to examine substituting lead-based solder on PV modules with other solder alloys. Lead is a toxic metal that, if ingested, can damage the brain, nervous system, liver and kidneys. Lead from solder in electronic products has been found to leach out from municipal waste landfills and municipal incinerator ash was found to be high in lead also because of disposed consumer electronics and batteries. Consequently, there is a movement in Europe and Japan to ban lead altogether from use in electronic products and to restrict the movement across geographical boundaries of waste containing lead.

Photovoltaic modules may contain small amounts of regulated materials, which vary from one technology to another. Environmental regulations impact the cost and complexity of dealing with end-of-life PV modules. If they were classified as “hazardous” according to Federal or State criteria, then special requirements for material handling, disposal, record-keeping and reporting would escalate the cost of decommissioning the modules. Fthenakis showed that several of today's x-Si modules failed the US-EPA Toxicity Characteristic Leaching Procedure (TCLP) for potential leaching of Pb in landfills and also California's standard on Total Threshold Limit Concentration (TTLC) for Pb. Consequently, such modules may be classified as "hazardous" waste. He highlighted potential legislation in Europe and Japan which could ban or restrict the use of lead and the efforts of the printed-circuit industries in developing Pb-free solder technologies in response to such expected legislation. Japanese firms already have introduced electronic products with Pb-free solder, and one PV manufacturer in the United States, ASE Americas has used a Pb-free solder exclusively in their modules since 1993. Finding a safe, reliable and cost-effective substitute for lead-containing solders is not easy. Tin/lead solder has been the standard solder technology for several decades and extensive knowledge has been gained on the practical and theoretical aspects of its use. The printed circuit and the electronics industries recently embarked on a multi-million-dollar R&D effort to develop such alternatives, focusing on material properties, manufacturing processes, cost of alloys and long-term availability and reliability. Fthenakis outlined such efforts and listed alternatives examined by the electronics industries. One of the most promising alternatives (for electronics) is the 96.5%Sn/3.5%Ag solder that ASE Americas developed and use. ASE Americas' research and independent field testing showed it is at least as reliable as the standard one. This solder is slightly more expensive than the regular Sn/Pb solder. However, to the audience gratification,

Steel Heddle, a solder manufacturer, announced that they will absorb the incremental cost and will supply 96.5%Sn/3.5%Ag at the same price as the conventional Sn/Pb solder ribbon. Another issue is the low TTLC for Ag in California (i.e., 0.5 g / kg of module), but Fthenakis showed that the Sn/Ag solder will add less than 10% of this quantity (i.e., 0.05 g of Ag / kg of module).

The major point made by Fthenakis was that alternatives exist that are both environmentally benign and cost-effective, and that the PV industry can only benefit by being proactive in switching to Pb-free materials, thereby exceeding the expectations of its supporters and averting potential future legislation.

Ronald Gonsiorawski, ASE Americas, gave the major contribution to this workshop. He first described the history of the Sn/Ag solder technology that he developed while at Mobil Solar. His incentive then was to find a better solder in response to failures of conventional Sn/Pb solder contacts at the interface of thick film silver to silicon. Gonsiorawski presented a series of results on thermal bond aging and solder bond strength which showed that the properties of the Sn/Ag solder were superior to those of conventional solder. He then discussed the use of the Sn/Ag solder and described how early problems in processing had been solved. He showed published results on the product's reliability obtained by field testing at the Arizona State University and the Florida Solar Energy Center. He concluded that there are no technical or reliability problems in adapting the 96.5%Sn/3.5%Ag to PV manufacturing, and that, in addition to the environmental advantage of a Pb-free solder, it improves the module's reliability.

After his slide presentation, Gonsiorawski answered questions for about 45 minutes on technical aspects of the Sn/Ag solder technology; the details he gave greatly interested the audience and gained their full appreciation for his expertise and the value of this Pb-free technology. The questions and answers section was recorded and is included in this report.

Organizer

Vasilis Fthenakis
Brookhaven National Laboratory
Bldg. 830
Upton, NY 11973
Tel. No. (631) 344-2830
Fax No. (631) 344-4486
Email: vmf@bnl.gov

Participants

The workshop had twenty nine participants; they are listed below with their affiliations:

Attendee List

Scot Albright
Global Solar Energy
12401 W. 49th Avenue
Wheat Ridge, Co 80033

Thomas S. Basso
National Renewable Energy Lab
1617 Cole Blvd., MS3411
Golden, CO 80401

William Bottenberg
Photovoltaics International, LLC
171 Commercial Street
Sunnyvale, CA 94086

Ward Bower
Sandia National Laboratories
PV Applications Department
MS 0753
Albuquerque, NM 87185-0753

Philip Capps
Siemens Solar
4650 Adohr Lane
PO Box 6032
Camarillo, CA 93011

Roger Clark
AstroPower, Inc.
461 Wyoming Road
Newark, DE 19716

Jerry Culik
AstroPower, Inc.
Solar Park
Newark, DE 19716-2000

Richard DeBlasio
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Neelkanth Dhere
UCF/Florida Solar Energy Center
1679 Clearlake Road
Cocoa, FL 32922-5703

Vasilis Fthenakis
Brookhaven National Laboratory
Bldg. 830
Upton, NY 11973
Tel. No. (631) 344-2830

Ronald Gonsiorawski
ASE Americas, Inc.
4 Suburban Park Drive
Billerica, MA 01821-3980

Line Grammond
BPSolar Inc.
2300 N. Watney Way
Fairfield, CA 94533

Stephen Hogan
Spire Corporation
One Patriots Park
Bedford, MA 01730

James P. Holihan
U. S. Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585

F. Michael Hosking
Sandia National Laboratories
PO Box 5800
MS 0367
Albuquerque, NM 87185-0367

Liang Ji
Arizona State University East
Photovoltaic Testing Laboratory
7349 E. Unity Avenue
Mesa, AZ 85212

Harjet Kapoor
SMUD
6201 "S" Street, A401
Sacramento, CA 95817-1899

Franz Kaufmann
ENLOG
155 West 68th Street, #620
New York, NY 10023

David King
Sandia National Laboratories
PO Box 5800
MS-0752
Albuquerque, NM 87185-0853

John Pern
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Michael Quintana
Sandia National Laboratories
PO Box 5800
Albuquerque, NM 87185-0752

Thomas Surek
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Jodi Sutherland
Spire Corporation
One Patriots Park
Bedford, MA 01730

Cathleen Thomas
AstroPower, Inc.
231 Lake Drive
Newark, DE 19702

Holly Thomas
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Y. Simon Tsuo
Motech Industries, Inc.
6 F, No. 59 Tsao-Dih Woei, Shen
Keng Hsiang, Taipei Hsien
Taiwan

Edward Witt
National Renewable Energy Laboratory
MS 3214
1617 Cole Blvd.
Golden, CO 80401

John Wohlgemuth
BP Solarex
630 Solarex Court
Frederick, MD 21703

Kenneth Zweibel
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

1. Vasilis Fthenakis

   The Case for Lead-free Solder in PV Modules

Lead-free Solder Technology Transfer from ASE Americas, Inc.

Vasilis Fthenakis

PV EH&S ASSISTANCE CENTER

Brookhaven National Laboratory

Oct. 19, 1999 -Vail, Co

BROOKHAVEN NATIONAL LABORATORY

BNL PV EH&S ASSISTANCE

- **Broad PV EH&S Issues**
  - Hazard Identification & Characterization of New Technologies, Materials & Processes
  - Energy-Environmental-Economic Analysis
  - Toxicology of New Materials
  - Waste Management/ Recycling

- **Facility Specific EH&S Issues**
  - Assistance on Start-up
  - Occupational Exposure Prevention
  - Pollution Control
  - Safety Audits/ Incident Analysis
  - Site Specific Risk Assessment / Safety Reviews

The Value of "Ultra-Green" PV

Brookhaven Science Associates
U.S. Department of Energy

BROOKHAVEN NATIONAL LABORATORY

The Case against Lead

- Even small quantities of Pb can damage the brain, nervous system, liver and kidneys if ingested
- It can leach into the soil (in municipal landfills) and pollute ground water
- Municipal incinerator ash was found high in Pb concentration due to disposed consumer electronics and batteries
- European countries proposed a complete ban on landfill disposal of electronic products containing Pb-solder and on the sale of such products
- Large Japanese electronics manufacturers announced voluntarily phasing out of Pb-solder from electronics, and launched Pb-free products in the market
- Lead in solder may cause "hazardous waste classification" for end-of-life PV modules

Waste Classification for "discarded" PV in the US

RCRA Waste Classification

Hazardous if:	End-of-Life PV Modules:
is a solid waste, and	are solid waste, unless recycled & excluded
is not explicitly excluded, and	are not excluded, unless household waste
is "listed" as inherently hazardous, or	are not listed
it exhibits hazardous "characteristics"	are subject to TCLP testing

California-HWCL Waste Classification

Hazardous if:	End-of-Life PV Modules:
Additional toxicity leaching requirements (STLC, TTLC)	hazardous waste according to TTLC

RCRA Leach Testing Results for x-Si, CdTe and CIS PV Modules

Constituent	Regulatory TC Limits (mg/l)	TCLP Results (mg/l)
x-Si		
Ag	5	0-0.1
Pb	**5**	3-**6.6**
CdTe		
Cd	**1**	0.7-**9.5**
Pb	5	0.04-0.4
Te	-	0.4-0.6
CIS		
Zn	-	2.8-18
Se	1	0.060-0.5
Cd	1	0.028-0.031

California TTLC Results for x-Si, CdTe and CIS PV Modules

Constituent	Regulatory Limits	Calculated Content
	TTLC Limit (g/kg)	(g/kg of module)
x-Si		
Ag	**0.5**	**0.65 (0.70); 0.8;1.25; 3.4**
Pb	**1**	**1**
Cu (ribbon)	**2.5**	**10**
CdTe		
Cd	**0.1**	**0.32**
Pb	1	0.05
Ni	2	0.02
CIS		
Zn	5	0.59
Se	**0.1**	**0.29**
Cd	0.1	0.02
Pb	1	0.17

PV Waste Classification in the US

Waste Classification per RCRA: Determinant is TCLP testing

- Some x-Si failed for Pb
- Some CdTe modules failed for Cd

Waste Classification per California EPA: Determinants are TCLP, TTLC and STLC

- x-Si likely to be hazardous based on TTLC & STLC for Ag, Pb & Cu
- CdTe likely to be hazardous based on TTLC for Cd & STLC for Cd & Pb
- CIS likely to be hazardous based on TTLC for Se & STLC for Se, Cd & Pb

Pb from solder and Cu from ribbon, problem for all cells

Europe- Towards Banning Lead from Electronics

DGXI Waste Unit–Draft of WEEE Directive proposes banning of landfill disposal and sale of electronics containing Pb, Hg, Cd, halogenated flame retardants and Cr(VI), by Jan. 2004

Regs on Tranboundary Movement of Electronic Assemblies and Scrap

- The Basel convention governs waste shipped for disposal or recovery/recycling across borders of 120 countries but not the US.
  New List of "hazardous waste" includes waste electronics containing Pb, Cd, Hg, PCBs, Be and ash from incineration of circuit boards.

- The OECD system covers waste shipments destined for recovery within the 28 OECD countries. Electronic assemblies and scrap classified as "non-hazardous waste"

RECENT DEVELOPMENTS

- Proposed harmonization of the Basel and OECD Waste lists
- US Plans for Basel implementing legislation
- (EPA to propose legislation in 1999; new restrictions on exports of hazardous waste outside of North America expected)

Some Electronic Manufacturers' Proactive Approach

- But the drive towards Pb-free solder is not just a legislative issue. Some large companies see the marketing potential of having environmentally friendly products.
- Matsushita markets minidisc player with special label indicating that product is Pb-free. Matsushita's share of the market increased from 4% to 15% because of this product.
- On October 7, 1999, Sony, NEC, Hitachi and Matsushita announced plans to curtail use of Pb in their products

Status of Pb-free Solder Commercial Electronic Products

- The U. S. electronics industry has not selected a lead-free solder alloy yet. Lucent just proposed a 2-yr, $3,179 K project to develop commercially viable electrochemical processes to enable the use of Sn/Ag and Sn/Bi solders as drop-in replacements for Pb-based solders.
- Japanese companies have shipped product with Pb-free solders; they change alloys as they gain production and field reliability data.
- Europe leans toward Sn-Ag, Sn-Cu and Sn-Ag-Cu alloys for consumer, computer and telecommunications applications.
- Nortel used Sn/Cu for business telephones and Sn/Ag for DMS switches operating 24-hr/day in high temp environment

Solder Alloy Alternatives[1]

Alloy	Melting Range (°C)	Metal Cost[2] ($/cm^3)	Concerns
63 Sn/37 Pb (Standard)	**183**	**0.05**	**Pb content**
96.5Sn/3.5Ag	**221**	**0.10**	**-**
99.3Sn/0.7 Cu	227	0.06	-
98Sn/2Ag	221-226	0.09	-
95.5Sn/3.8Ag/0.7Cu	217	0.10	-
77.2Sn/20In/2.8Ag	179-189	0.38	In availability and cost-
95Sn/3.5Ag/1.5In	218	0.12	In availability
85Sn/10Bi/5Zn	168-190	0.06	Poor wetting from Zn
91Sn/9Zn	199	0.06	Poor wetting from Zn
96.7Sn/2Ag/0.8Cu/0.5Sb	216-222	0.09	Manufacturing difficulties
42Sn/58Bi	138	0.07	Bi availability Melting point too low?
91.7Sn/3.5Ag/4.8Bi	206-213	NA	Bi availability

[1] Source National Center for Manufacturing Sciences, Ann Arbor, Michigan, 1997

[2] Cost as of January 1997

Solder Alloy Alternatives[2]

Alloy	Relative Bar Cost ($/kg)	Relative Paste Cost ($/kg)
63Sn/37Pb (Standard)	**1**	**1.**
96.5Sn/3.5Ag	**2.29**	**1.07**
95Sn/3Ag/2Bi	2.17	1.06
96.1Sn/2.6Ag/0.8Cu/0.5 Sb	2.06	1.05
91.8Sn/3.4Ag/4.8Bi	2.26	1.06
95Sn/3.5Ag/0.5Cu/1.Zn	2.27	1.06
93.6Sn/4.7Ag/1.7Cu	2.56	1.08
96.1Sn/3.2Ag/0.7Cu	2.21	1.06
95.2Sn/3.5Ag/1.3Cu	2.28	1.06

Relative cost of selected metals: Pb=1, Zn=1.7, Cu=3, Sb=3.9, Bi=8.6, Sn=11, Ag=260, Au=15000

[2] Source: NEMI Lead Free Solder Meeting, Chicago, May 25, 1999

LEAD FREE SOLDER INTERCONNECTED

PHOTOVOLTAIC MODULES

by
Ronald Gonsiorawski
of
ASE Americas

Presented at:
The NREL sponsored:

PV Performance, Reliability and Standards Workshop
Vail, Colorado

Agenda

LEAD FREE SOLDER INTERCONNECTED
PHOTOVOLTAIC MODULES

1. **Objective(s)**

2. **A Pb Bearing Solder Alternative –Sn 96/Ag4**
3. **History**

4. **Thermal Bond Aging Resistance**

5. **Manufacturability**

6. **Product Reliability**

7. **Issues**

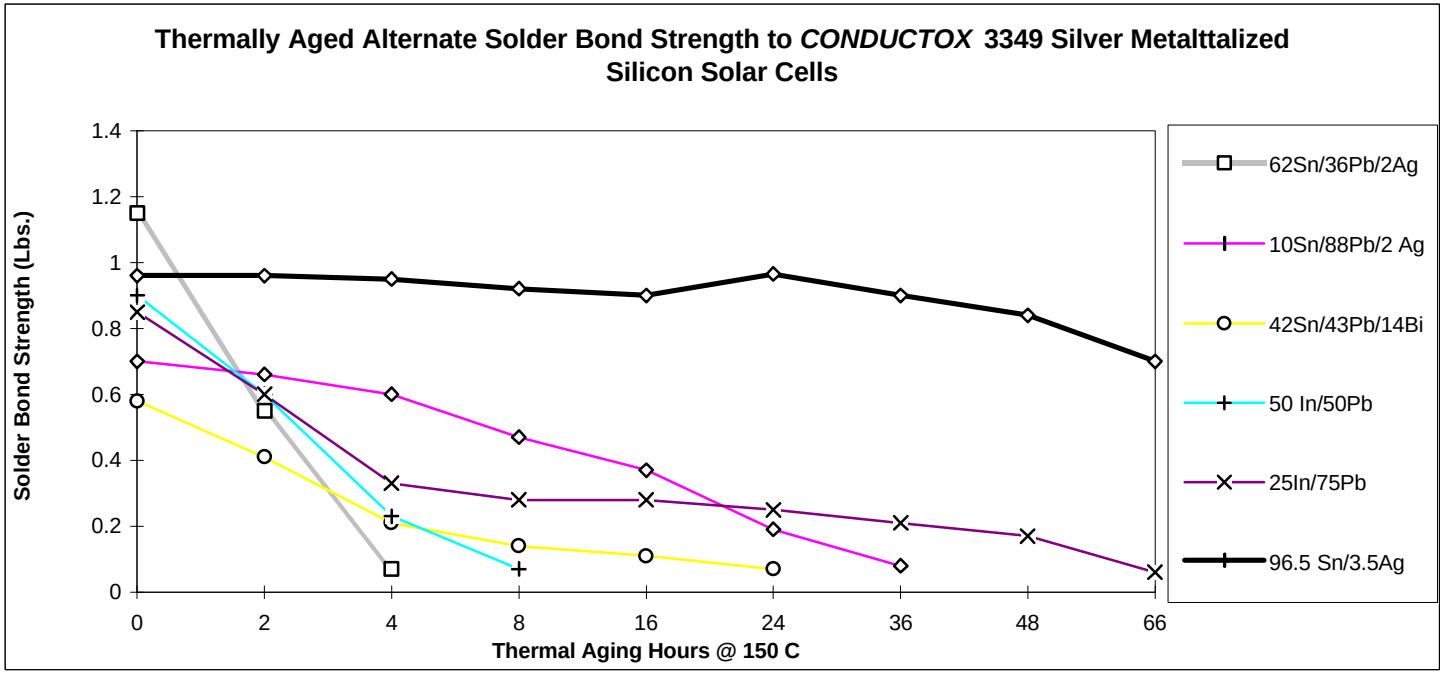
8. **Conclusion (s)**

1.0 OBJECTIVE(S):

1- **to radically improve the functional reliability of solder to thick film silver contacts**

2- **to avoid the classification of a “hazardous waste” product stigma**

3.0 A Pb Bearing Solder Alternative-Sn 96/Ag4



3.0 History

1989- identified failure mechanism of brittle fracture of solder contacts at Thick Film Silver to Silicon interface

1990- literature search identified phenomena effecting TFS ceramic circuits wherein solder bonds upon thermal storage weaken at the Ag/glass interface of the substrate. Ref- #1 Taylor,Felton,Larry ; Du Pont; IEEE 1980 #2Needs,Brown; DuPont; ISHAM Proceedings 1989

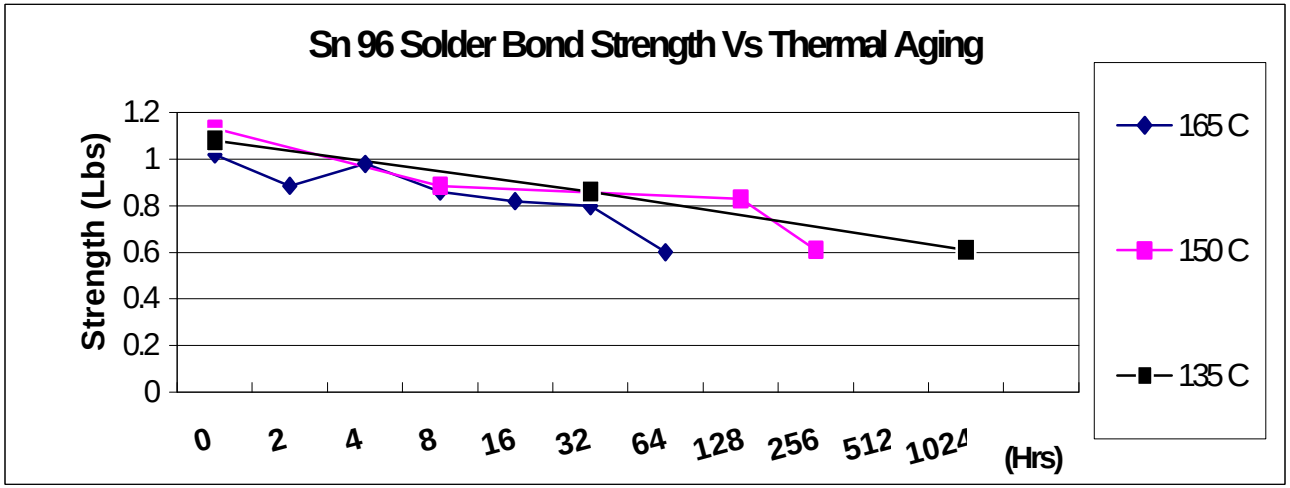
1991- commenced manufacturing (PVUSA) with Sn 96 solder paste using preheated stage and hot tip methodology

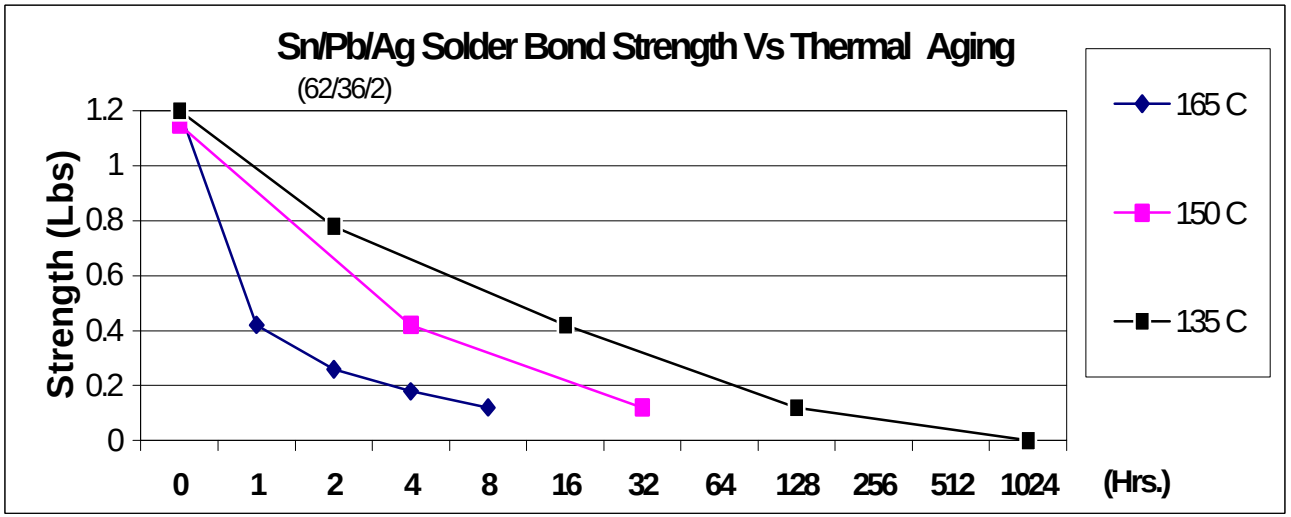
1993-presentation @ NREL's PV Workshop of Thermal Bond Aging of Thick Film Metallized Solar Cells

1993 commenced Hot Air heating method at 16 simultaneous bond sites using paste source of Sn 96/4 Ag solder

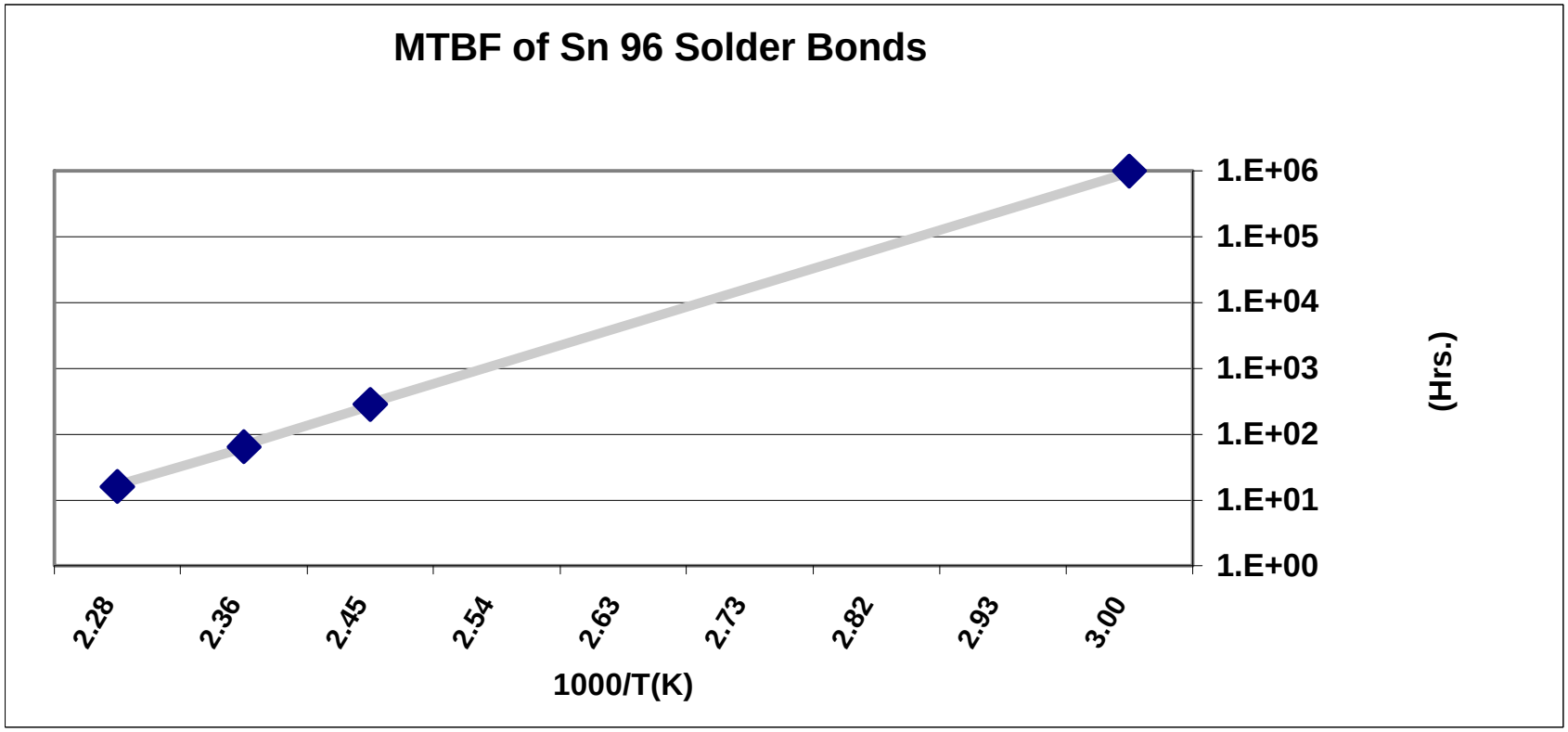
1996- commenced IR solder reflow with Spire Assembler and Steel Heddle supplied Sn96 hot dip coated copper tabbing

4.01 THERMAL BOND AGING





4.02 THERMAL BOND AGING



4.02 THERMAL BOND AGING

5.01 Manufacturability

The Sn 96/Ag4 system can directly replace Sn/Pb systems for solar cell tabbing/interconnection given adequate thermal power delivery.

Examples of which include:

Parallel Gap (Unitek)	Hot Bar (Unitek,Ascor)
Hot Air (Leister)	IR (Spire ,NPC)

The higher liquidus temperature of 221°C is no problem in the above equipment

The Sn 96 solder source can be as pastes/cream , preforms and solder coated tabbing either plated or hot dipped

5.02 MANUFACTURABILITY

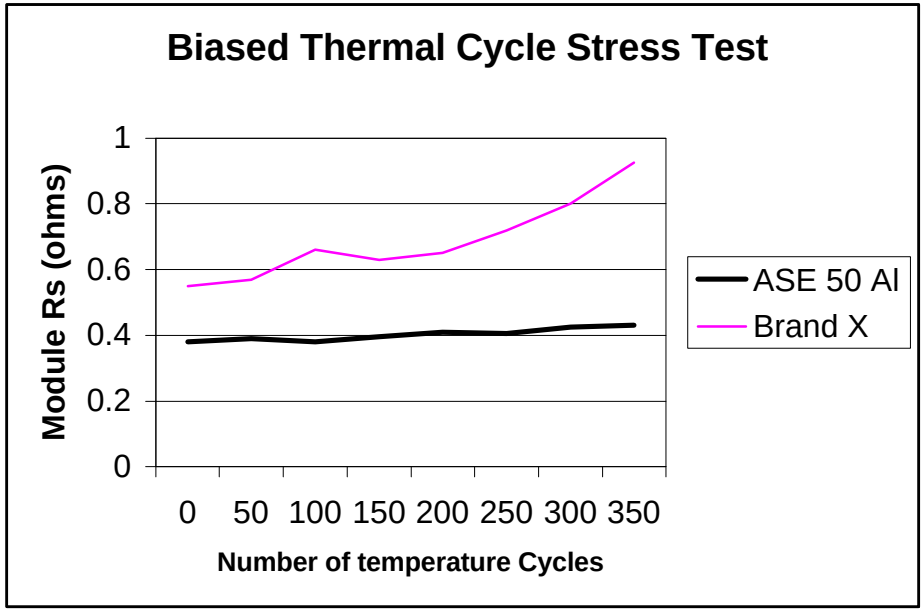
A wide choice of fluxing systems exist that are extremely compatible including :

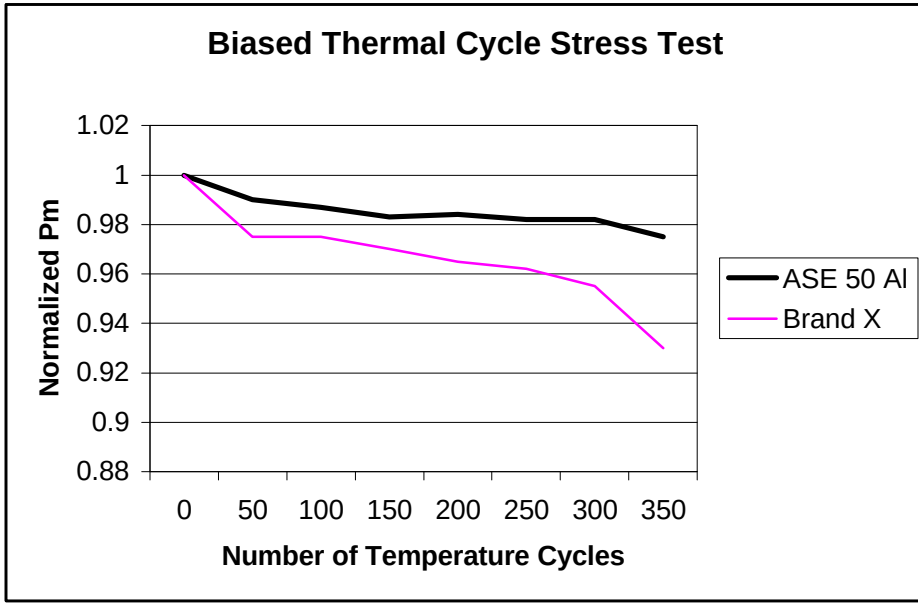
RMA- Halide free- No clean and Low solid carboxylates (water of IPA based)

Fast cycle time of 4 seconds per cell (preheat+bond +cooling) are routine by either ASE's Hot Air Equipment or a Spire Assembler using 10 [illegible] thick Sn96 coated tabbing

Cell pretreatment of cleaning or silver burnishing is not required although the latter accommodates thinner solder coated tab sources

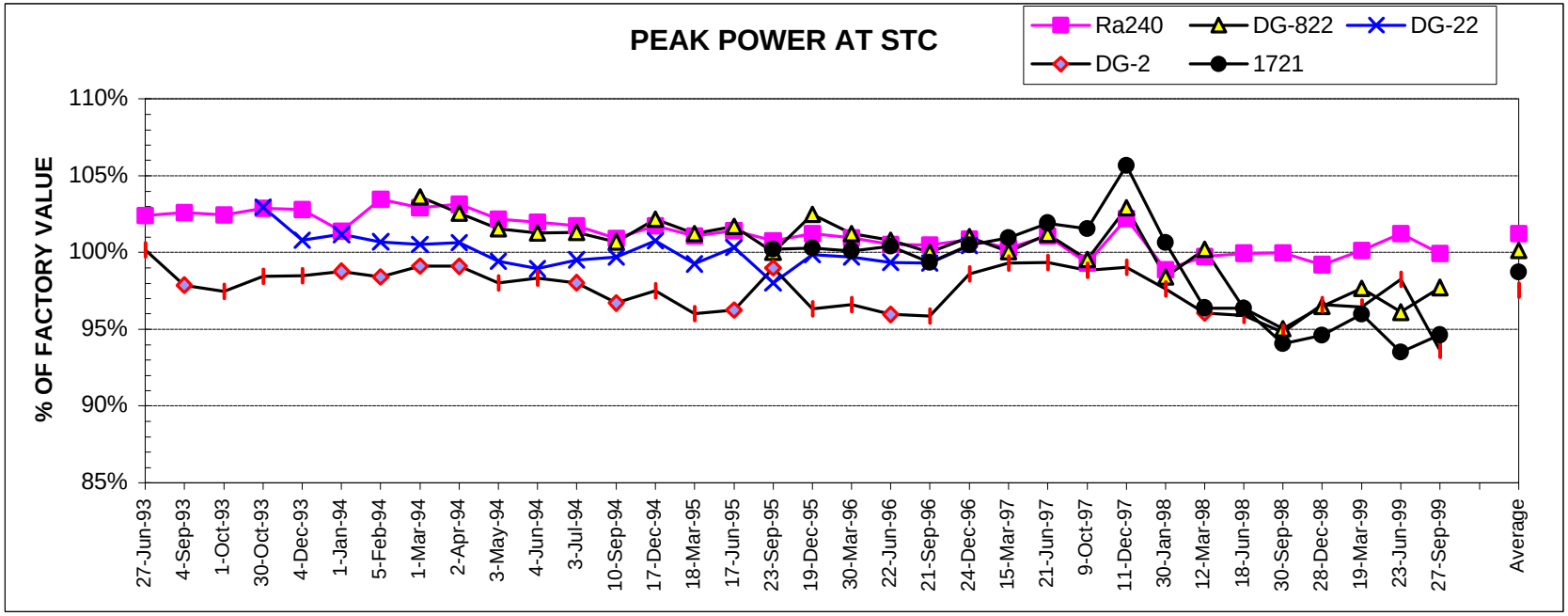
6.01 PRODUCT RELIABILITY



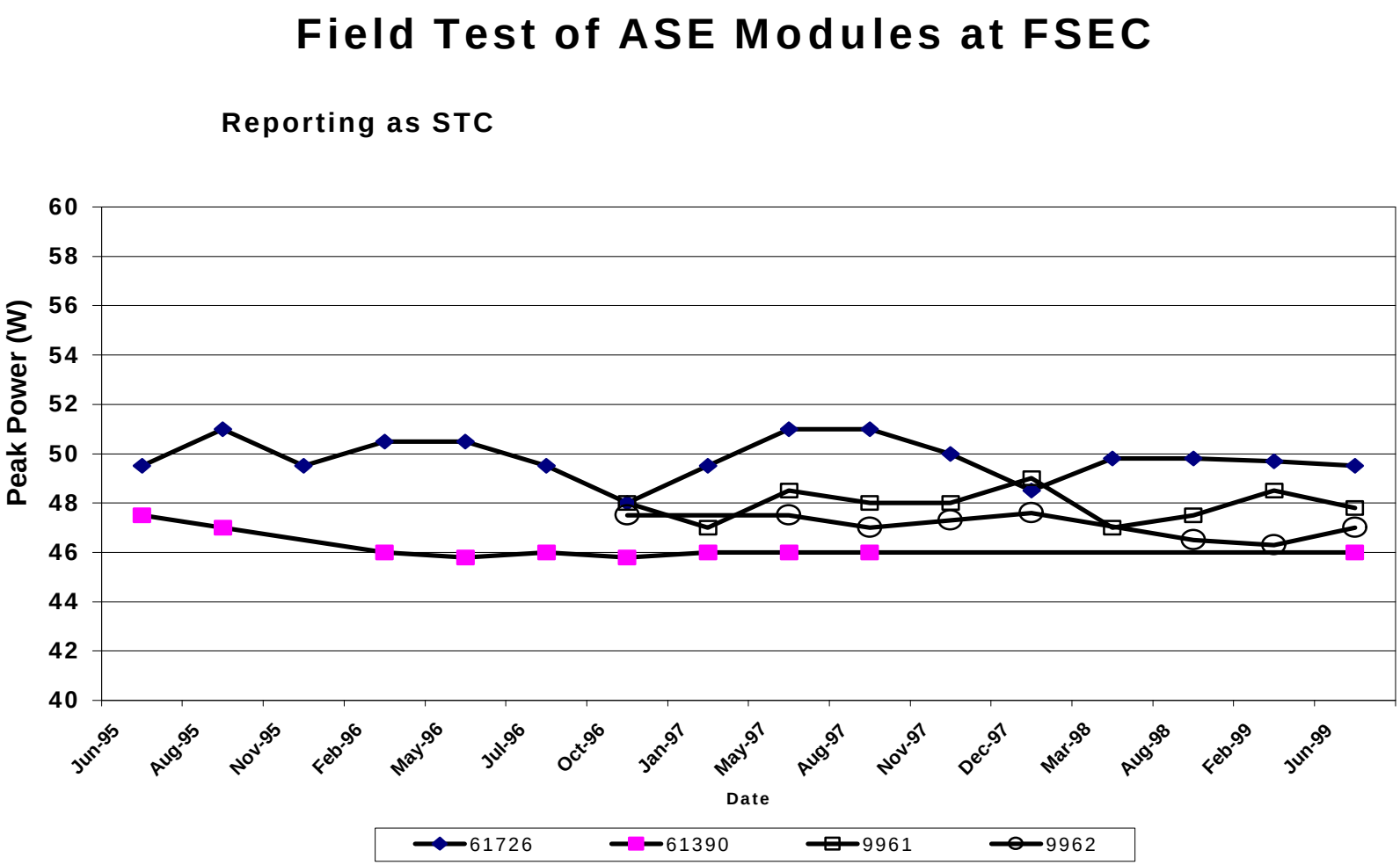


6.02 PRODUCT RELIABILITY

Field Performance of ASE Modules at ASU



6.03 PRODUCT RELIABILITY



7.0 ISSUES

Silver scavenging or leaching:

This is a manageable problem of silver dissolution that is common to all moderately high tin bearing solder systems.

Limiting the time and temperature of the soldering process will avoid this problem given reasonable silver thickness (> 5 [illegible])

Manual soldering iron methods: (hardly a real manufacturing situation)

Inadequate thermal ramp rates limits solder reflow mechanisms reducing solder bond area and bond strength. This is not an issue using solder pastes due to high mass action effects.

Use solder irons of high power(≥ 60W) with large and clean tips set to =/< 750 F. An additional aid for improved solder Sn 96 manual bonds is to elevating the cell temperature on a silicone heating mat to 75 C.

8.0 CONCLUSIONS:

There are no real barriers to adapting to a lead (Pb) free soldering system for conventional crystalline /semicrystalline solar cells employing solderable metallization that includes the common thick film silver system.

Utilizing the Tin 96.5%/Silver 3.5% eutectic solder system is readily adaptable to PV manufacturing equipment, material quality knowledge abounds in the commercial sector and improved solar module reliability is a bonus.

Questions and Answers

(Vasilis Fthenakis was the moderator of this discussion. Ron Gonsiorawski gave all the answers unless stated differently).

Q. Ron one of your plots shows the stress of bias temperature cycling. Can you tell me what the temperature was?

A. It was -40 to +90 degrees. That work was actually done by Carl Osterwald of NRL and if I understood that work, the bias was not applied at the low temperature regime otherwise the module wouldn't reach minus -40 degrees.

Q. Without exposing the grand scheme, could you give us an identifier?

A. The module went directly through Carl and I believe the recent module was manufactured within the past 18 months.

Q. I didn't see any curve on the graph representing a tin/lead cell stringing

A. Yes, it is the top one here with the open square and it is the plot point here (pointing on the graph).

Q. That's tin/lead/silver. Did you do straight tin/lead ?

A. Just plain tin/lead? No. It is sort of an oxymoron in a silver system because you will dissolve silver into it very rapidly. We did all this illustrated work using solder paste, I have done work with thick tin/lead solder coated tabbing? I have samples of them with me. You might find them interesting to look at……..…..compare their strengths to the tin silver system. Because these cells have been thermally aged for five hours at 150 degrees you may find it

interesting ,that you can clearly see the interface of failure, which I like to point out, as my belief, that it is probably the prime mechanism for solder bond failure.

Q. So, in all those cases, even the best case there is still a silicone silver interface?

A. Right.

Q. Do you see any effects of the age of the foil? Do you have to store it in any specialty ways?

A. No, not at all.

Q. Which do you apply the flux to? The silver or the foil?

A. We apply the flux to the foil. At the beginning, I thought that it would be helpful to apply it to the silver but experimentally I determined that it isn't any help at all. And it turns out to be far more affective to manage the flux residue if you apply it to the tabbing because it will wick along the tabbing as opposed to wicking along the silver/cell surface where it could cause encapsulant delamination problems or whatever.. …So it is very affective on the tabbing

Q. Was all this work done on the thick-film silver ?

A. Yes, in all of this work.

Q. Have you done other work on other silvers?

A. We did work on other solar cell structures including plated contacts. They were very forgiving. They don't suffer from this fault mechanism. This Thermal Bond aging effects which is brittle fracture I believe only exists with thick-film solar silver structures. We did look at the structure of the silver and found that if you

have a very compact silver structure, such as, you might get from a spherical silver particles you can slow down these effects and improve reliability. But, it then posses a difficulty on the manufacturer because if he has to provide you with very specific sized spherical particles. It is not workable on particles that are too fine because it packs so tightly that when you dry the system , it ruptures and cracks apart. So there were manufacturing issues with trying to adjust silver structure. Working with other people like DuPont, if they change the base of the glass frit , they can mitigate these effects but not without adverse effects on the cell efficiency. So we have been using Ferro Corporation's 3349 through all of this work and it is only now that viable alternatives are being identified.

Q. Did you have to control the pressure on the tabs? I mean there are a variety of methods.

A. It is not terribly critical. In the case where you saw a phase there is such a thick liquid layer that the tabbing can get? Held in capillary action and there is almost no pressure at all. But it is helpful to apply pressure when the source is not so liquidous as it would be in the case of thick solder coated tabbing and the judicious application of pressure is helpful but we don't want to apply so much that we break cells. Our experience with EFG sheet silicon is that it is pretty brittle. If you have a lot of temperature and a lot of local pressure that is what will break solar cells. So, we have to be judicious in how we do that but the commercial Spire Assembler is quite effective.

Q. Do you minimize the time that it is heating? Is that the way you optimize the joint?

A. Right. If I get a brand new system, what I try to do while I am at the equipment is to lower the heat input and in the and the case of the SPIRE system, that would be the line voltage and take it down to a point where there is a marginal level of heat flux to either melt the solder to the undersurface. At that point find the very thickest blanks in the work place and make a modest increase in the heat flux (Lamp voltage). If that adjustment made successful initial solder bonds you are reasonably well assured that you are operating in the best window for solder bond reliability. And then you do the statistical test. All of this can be done in a matter of three or four hours.

Q. You mentioned residue from the flux. Can you share with us any experiences you have with the SPIRE machine managing that residence?

A. I can speak to the SPIRE assembler and the provided fluxing system. That system did not dry the flux at elevated temperature and it left a virtually invisible residue that had a negative interaction with the ASE encapsulant system.. We do not use EVA, we use something else and that flux system, left a very thin residue that absorbed moisture which interacted with our encapsulant in the lamination process to cause numerous small delamination sites. So what we thought we needed to do is thoroughly dry this flux system on the tabbing so that we would minimize vapors and what would get trapped at the under side or front cell surface. Because in the SPIRE system, this is how we presented the cells which presented a problem because there isn't the greatest ventilation of the flux system. So we added additional ventilation via extra holes adjacent the tabbing to the transport belt system. We apply a flux coating off –line that is three microns thick,

and dry it very very thoroughly and we see virtually no residue. You really can not see it. But if we are not very thorough in the lamination process, and for example compromised the lamination pressure, we could have of the encapsaulant to the cell surface where there were low levels of residual flux. Those are tough issues. There are other flux systems based on our experience, that may leave more visible residue but which do not have any casual impact of delamination, however but they tend to limit the solder's reflow from our tabs to the cell's silver electrodes. I can't speak for what the flux residue do for the EVA encapsulating system but I think they are generally manageable.

Q. Ronald, when you did the pull test, how long did you wait for the cell/tab system samples to cool down?

A. We put them on the bench and when they were cold to the touch we could start pulling the solder bonds. We didn't find any dependence on how long they cool. Never found any dependence on the atmospheric conditions of the thermal soaking either. We did this work in nitrogen, did it in vacuum, did it in air. The atmosphere didn't seem to have any affect.

Q. What pull test equipment did you use?

A. We were basically using Chatillon strain gauges although at the outset we were using Instron equipment

Q. How many degrees ?

A. We are effecting a 90-degree stress that applies a tension force. The equipment records the peak tension force to destroy the individual solder bond sites.

Q. How thick are the tabs and the plating?

A. In our case we use 4 mils copper …….we specify the OFHC alloy. We found that a good process window for the solder thickness resides in the range of 450 micro inches to 850 micro inches. There is a strange reason for that upper limit and that is that in the SPIRE system we have a network of vacuum holes in the transport belt and when the solder gets too thick there are a network of solder icicles that form and cause the cell to get stuck.

Q. You've gotten lead out of the tab. Do you think we will be getting lead out of the silver thick film material ?

A. No. We had a nice system from DuPont that gave us real good cell efficiency with good low contact resistance but the lead free system had other environmental nasty stuff.

Q. I guess that if we collaborate and pressure the suppliers as an industry we could make progress on that front. We are ultimately going to require a lead free system. We will have to do that.

Q. I was wondering if all this work applies to the interconnects, as well because you talk about tabbing all the time.

A. Well, obviously it affects interconnects in some ways. We use Sn 96.5% solder for the bond attachment to a cell and for bonding cross ties or interconnect busses to these tabs, and so within a laminated module all that solder is always tin-silver lead free solder. The only place we have lead bearing /solder is in a purchased

diode card in the J-box. That item can be removed for recycling before trashing the module to a landfill at the end of its useful life.

Q. Solder bond strength tests that you've showed on this chart here, where they for the discrete joints or the continuous joints?

A. These were based on all discrete joints. In this case we were reporting four solder dots along a length of 4 inches of tabbing therefore with two lengths of continuous tabs per cell we have 8 discrete joints to the rear and an equal number to the front cell surface.

Q. Was the strength the same for the front and the back?

A. Nearly the same. The wide back pad electrodes provide a larger bond are but because of infiltrating impurities like aluminum their strength only slightly exceed that of the front bus bonds. The back pad bonds maybe 1 – 1 ½ pounds initially but after thermally aging for 5 hours at 165 degrees centigrade they degrade to ~0 .8 lbs. The front bus bonds with Sn/Ag solder never go down; they almost always go up slightly.

Q. Are you saying that you have all these tests in operation?

A. Yes. We've adopted something called Precontrol which says that you turn this over to the manufacturer operating staff on the floor and they will test the bonds at a frequency which represents a 7% AQL. So we are doing this twice a week once on the first shift and once on the third shift.

Q. How many contacts ?

A. Well, they'll take an 18-cell string, take nine of those 18 cells and establish the initial bonds for the front and back surface. Then they will take the balance of those cells and will measure the bond strengths after thermally aging. That full test routine would involve a total of 128 solder bonds from 16 cells. An abbreviated and standard routine only tests the thermally aged case for Statistical Process Control (SPC) documentation.

Q. I would like to talk about burnishing if I could?

A. Surely.

Q. Is this so called burnishing the removal of an antireflection (AR) coating on the front cell surface ?

A. Not in our case. We're all familiar with that. But if one takes a number 2-pencil eraser and rubs the silver structure pretty hard, you'll develop a nice polished surface. What you will find if you do that is if you had tabbing where the solder layer was thin you could get a good joint. But if you were to use that thin solder on an unburnished region, you would get a weak joint because there is not enough liquid to go down in to the textured surface.

Q. Have you had any experience or do you know of anyone who has had experience with using cells that have had their AR coating burnished off?

A. No, I do not have any direct experience with that. I believe that is the case with Solarex cells but I do not have direct contact.

Q. The composition of the solder paste system ?

A. If I understand, the question was the structure of the metal/solder component to the solder paste.

A. They make spherical metal particles much like they would make fluidized bed silicon. That product is then sorted for size and shape because you don't want needle like particles because they will get stuck in the dispenser. So they remove those. In our case I think we would work in a range of 50-75 micron diameter spheres. The organic additives are for adjustment of thixotropic properties plus fluxing agents. In one case of Multicore Corporation they have a non-formaldehyde producing flux. A more competitive company, ESL in Rhode Island, uses a conventional RMA flux. The Multicore system was a little more expensive, at about 60 cents a gram; ESP is 25 cents per gram. These are dispensing systems where you can dispense all day without getting clogged.

Q. The operation is silver and some lead. Is there any steel?

A. No. you can get any composition you want. All the soft solder alloys are available. There is a long laundry list of soder base. Vasilis showed that list.

Q. The silver metallization?

A. Are you speaking of the silver structure on the solar cell?

Q. Right. _____?

A. Yes, Ferro's 3349.

Q. What is that?

A Very high purity silver with primarily a spherical shape but there is a high silver flake content. And then there is a glass frit which composes five weight percent of the total composition .The lead oxide content of the glass frit is approximately 45% so it is a high lead content as John points out. The basic idea of that system is that leaded glass melts at low temperatures, like at 450 degrees, it is an aggressive liquid, it flows down through the silver structure after the organic content has been burnt off. The glass frit resides at the silicon- silver interface, it holds it all together as well as bonding the system to the silicon cell surface. By some magic, it makes contact!

Q. I was just going to ask you how it works?

A. Well, we found that if we go to real high magnification like at 3000 X on an SEM with high electrical/optical resolution, you can actually find microalloy pits? These triangle pits suggest a true alloy. And if we have those in high population, we get low contact resistance. When they are there in low population with get high contact resistance. It is a very interactive system, but you have to do a lot of optimization to get the most out of it.

Moderator.

Just to give a break to Ronald I will ask Michael Quintona of Sandia to inform us of the performance of ASE Americas modules tested in the PV USA site. Ron I think you would need to give them ASE's consent to disclose this type of information.

A. I asked this question of Dave King but he was rushing off. May be Michael can speak to us but if Michael didn't bring materials with him, I don't want to put Michael on the spot if it is not an area he is familiar with.

Moderator

I can tell that David King said to me that there are no problems at all with all ASE Americas modules tested since 1993. I regret that he is not here to give you more quantitative information and I hoped that Michael could.

Ron let me ask you a simple question. Is there anything special with the flux that one has to use with tin/silver solder?

A. No, I do not think that there is anything special that one has to do. And I say that because we have two systems, one uses hot air and it uses a solder base and here that flux system is fairly old. It is called Rosin Mildly Activated (RMA). It is free of halides so you wouldn't get corrosion. But there can be quite a bit of organic residue left behind on that system. It doesn't cause us any problems because for reasons I can't explain they are innocuous to our module system. And then we have on the other hand the SPIRE system. Here we needed a more aggressive flux to get good reflow for a system where the liquid thickness is an order of magnitude less than with the solder paste. In fact, as we first started out in doing this I was using burnishing to get good results. So I worked on the flux system and I struck a lot of success with the newer fluxes offered by Kester, Alpha and Multicore. Almost all of these were designed for the PCB industry where they are not going to clean it. They are called no clean systems and the solid content is in the range of 2-5%. I do get excellent soldering results with nearly all of them.

They were amazing in their effectiveness for good reflow. The only problem I had was that some of them left very thin film residue, which interfered with my lamination process. I am not sure if they would not interfere with EVA. Our encapsulate is not quite as forgiving.

Moderator

If the industry is interested to see the qualitative results of the outdoor testing we could facilitate it and include it in the minutes of this workshop. But you the industry have to tell us that you want to see these data.

Mike Quintona.

I just want to make a clarification. I know what Vasilis is talking about and I will say that we recently tested a 93-manufactured modular that was ASE's and that is right on. It is the same vintage as the modulars that were installed at the PV USA. But I would also like to say that by the same token we have a control module from Solarex that is probably a 1991 that has been right on for 8 or 9 years also. So I don't think that you can just walk off and say that performance-wise you got on that is right on and maybe on that isn't right on. And I really want to address one of the slides that are on hand which is the bias- thermal cycle stress test that had the normalized power dropping off in that modular. The reason I asked what vintage that module was is because I am a little concerned with that because I have been looking at modules for about three years now and I have seen

especially in one manufacturer some really big strides at making better solder joints and I am a little bit concerned by the relative loss in power in that particular module because it is probably much higher than one of the recent slides that was presented at our AOP meeting and our colleagues could probably recall that but we had a slide that David made that showed degradation rate as 1, 2, and 3% per year and this is a little alarming to me because effectively a year's worth of cycling. So I am curious about that one because I got the opposite example in the Solarex module. I think that is really the data that we can present right now. Obviously we have other data that do take larger compilation. I will say that we have this long term exposure test going at (name of site) _____ our colleagues down there and I think that we need to continue to support that test because that test itself will definitely tell us where we are headed and I guess I would be real curious about looking at the next set of series resistance measurement that we make on those modulars which we will bring to San Diego I guess in the near future.

Moderator

I know that is difficult to compare one type of module with another and I don't ask for it. What the community needs to know is if the modules that have the tin/silver solder perform well in outdoors tests. The question is on everybody's mind because tin silver is a new alloy and we don’t have experience with it. So if Sandia can shed some light on this, I think it would be vital to the whole community.

Q. Are there any plans to look at continuous joints?

A. In the SPIRE system there is a system of springs to hold the tabbing at discrete sites to the back of our cell. To the front of the cell however, there could be pressure all along the tab to put the tab into contact with the silver bus. Because our blanks? are not flat, we don't always get a continuous bond but I would feel comfortable in saying that 70% of the bonds are virtually continuous from that SPIRE equipment. I have some, you can pull them and you can see for yourself. I don't find the continuous bond to be any worse in performance in reliability then the spot bond.

Q. So you have done some thermal aging?

A. We haven't done simple thermal aging of modules but a lot of accelerating temperature stress tests. It is not unusual for us to do thermal cycling up to about 1000 cycles and I get very upset if I see anything more than 3% degradation.

Q. I have another suggestion and maybe I can talk you into it. I could probably get a competitor to give you some tin lead solder coated tabbing but would you consider making up modules that has the tin lead coated ribbon and then going through this particular bias thermal cycle?

A. Yes, if it fits our equipment, I will be glad to do it.

Q. I think it would be a very valid test because then we take out all the other variables including your encapsulant and some of the other things that may be on with other manufacturers.

A. Yes, I really did that same thing before we bought the SPIRE equipment. A number of my colleagues went to SPIRE to qualify the equipment and they were having difficulty getting good bonds. I went there and what I thought I saw was that the temperatures were too hot and the failure interface was between the silver and the silicon as opposed to the solder /silver interface. They needed to reduce the IR temperature. They reduced temperature as much as possible, made up a lot of strings using pure tin coated tabbing and others using tin lead coated tabbing .They made a lot of strings which were exposed to Temperature Cycle stress testing The contrasting result was a real shock. Our tin lead system was not that good. You might ask well maybe the tin lead problems of ASE is because of the ASE Americas (Mobil Solar) EFG solar cell.. We recently were in a situation where we could not meet our opportunities for selling modulars. We were running out of solar cell stocks. We bought solar cells from Siemens and I tried those with tin lead and they were horrific and I have some samples of them with me tonight. They were really horrible. Tweaking those with tin/silver made them far more reliable. I don’t think this problem is unique to the ASE Americas modules.

Q. Technical comment on what Michael is proposing. If you do that, what you need to do is test the tin silver and the tin lead or any of the other solders using the

same acceleration temperature. When you test all of them at 150 degrees C, you have different melting points so you would expect something like tin silver to perform better. If you select a more moderate temperature, tin silver will probably still perform better but it will bring the data a little bit closer together.

A. One of the alloys I tested has a very high lead content and a very high melting point and it didn't do well either. However, I understand your point of view.

Q. I'm not criticizing your data. What I am saying is if you do that there would be no questions that tin silver is really high power above every other alloy. It would be the alloy to work with.

A. Right I think you might find it interesting to read those articles that I referred to. I have a colleague who works in the hybrid microcircuit industry and he tells me that for the most reliable hybrid circuits, still use gold. Because silver can not satisfy all high level requirements. I don't work in that area but I take him at his word.

Q. Do the other manufacturers who are here think there is an issue in thermal stress on their cells with a higher temperature? The reason I ask that is that I was involved in kind of a qualification process if you wish with another manufacturer and the temperature got away just like you mentioned and we did the filed test and low and behold the failure was at the same place and they were using the tin

lead. I think that it occurs, it happens. I would be curious as to whether or not your cell reacts a little bit different than Siemens and Astro Powers and Solarex

A. I understand but I would rater not comment.

Moderator

Any comments from any of the other manufacturers?

A. (Astropower) We are certainly going to test it. Our cells are a little bit thicker than everybody else's so we think we have a problem getting enough thermal heat into it quickly enough. When we do that we have a tendency to fracture them. We are investigating this as an option and will see how that affects our cells.

Moderator

Any other comment?

A. (Siemens Solar) We are planning on trying it. I already bought the tabbing ribbon. In my case it is a matter of getting out of production quickly which is never trivial, we'll give it a try. I firmly believe that a year from now we could probably have a lead free system.

A. (Franz Kaufman, independant sales representative) As a matter of fact, I would probably say it did better then our standard tin lead ribbon. We were evaluating the machine and one of the reels was tin lead and the other was tin silver and he

was elated to have the opportunity to have a side by side comparison. It was an interesting ploy on words, but it was an opportunity.

A. I am glad to hear that you had a good result.

Q. We intend to pursue it in the near future.

A. Great. You have my e-mail address and I will be glad to help any and all of you. I know Dr. Gay will support you, because he wants to support the industry. So I will assist you in any way. There is no reason for you to feel inhibited. Please give me a call. I'll be glad to help you with suppliers, operational guidelines and you can come to our facility. This is something that I think the industry can move forward on.

Thank you very much for the opportunity.

STRONG APLLAUSE

Moderator

Ron we are all grateful for sharing with us your expertise …