

ENVIRONMENTALLY FRIENDLY CONDUCTOR MATERIALS FOR SILICON PHOTOVOLTAIC CELLS

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ABSTRACT: Solar energy generation offers an environmentally friendly way to provide power for human needs. Manufacture of solar cells often involves use of conductive pastes containing Cd, Pb and/or phthalates that are listed on the REACH Substances of Very High Concern. This work was undertaken to demonstrate that front silver, back silver and back aluminum pastes can be manufactured that are environmentally friendly and enable silicon solar cells of high efficiency to be made by volume production methods. A variety of Pb-, Cd- and phthalate-free pastes were formulated and tested as front Ag, back Ag and Al BSF metallization of solar cells. The electrical and morphological properties of the cells were characterized using IV analysis, contact resistance and SEM microscopy studies. While the performance of Pb-free Al pastes is known to be equivalent or better than leaded products for years, we also found that the electrical data of newly developed environmentally friendly Ag pastes is as good as leaded pastes. The paper also contains a comprehensive study of the effect of paste and emitter types on the performance of solar cells. Key words: Screen printed, metallization, lead-, cadmium- and phthalate-free pastes, RoHS and REACH.

1 INTRODUCTION

The Restriction of the use of Certain Hazardous Substances (RoHS) is an EU directive for electric and electronic devices, stipulating the maximum content of environmentally harmful substances allowed, including heavy metals. RoHS came into force on 1st July 2006 [1]. According to this restriction, a maximum content of 0.1 wt % lead (Pb) and 0.01 wt % cadmium (Cd) is allowed in homogeneous materials. Exceptions to these regulations exist only for hazardous substances for which either no substitutes exist or for which the substitutes are more dangerous than the substance itself. Besides heavy metals, flame retardants, such as polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) are also regulated. Although these exceptions are applicable to solar cells and modules, there is great industry wide effort to avoid Pb and Cd, since these would otherwise damage the “green” image of photovoltaics (PV).

The recently enacted Registration, Evaluation and Authorization of Chemicals (REACH) [2] is an EU restriction, which will regulate the trade with chemicals produced and imported in EU territory. Companies trading more than 1 ton in volume of chemicals per year have to register, to evaluate and to authorize their products. This restriction is applicable to PV industry, since the law also dwells on the dangers of products that can be in the food chain and be harmful to humans.

1.1 Heavy-metals in screen printed silicon solar cells

The presence of Cd and/or Pb is common in the glass component of solar pastes as glasses containing these elements become fluid at common solar cell processing temperatures and exhibit many technically desirable attributes related to compatibility and fired paste adhesion. Besides the firethrough of the silicon nitride antireflection coating, which is accomplished by the glass frit in the front side paste, the frit generally improves the contact formation between the silicon and the metal in the pastes [3, 4, 5]. Unfortunately, both Cd and Pb compounds are toxic materials and can represent a possible source of ground water contamination. For these reasons, elimination of these elements from solar pastes was undertaken. Pb- and Cd-free metallization pastes

have already been commercialized for the rear side metallization [6, 9]. In contrast, lead-free front side pastes are still in a laboratory stage and an industrial application is not known to the authors. But on a laboratory scale some results have been published [7,8,9] for new front side metallization pastes which are free of heavy-metal.

1.2 Phthalates

Phthalates are commonly used in screen printable pastes to provide necessary printing characteristics, including good paste flow during printing, leveling behavior without mesh marks and reasonable green strength for handling. The European Chemicals Agency, REACH regulations [2], have included commonly used phthalates, (Dibutyl phthalate and Benzyl butyl phthalate) on their list of Substances of Very High Concern, (SVHC). Development work at Ferro has resulted in solar paste products that meet all desired printing properties, provide excellent solar cell performance and do not contain substances on the REACH SVHC list. A variety of Pb-, Cd- and phthalate-free pastes were formulated and tested as front Ag, back Ag and Al BSF metallization of solar cells. The electrical and morphological properties of the cells were characterized using IV analysis and SEM microscopy studies. While the performance of Pb-free Al pastes is known to be equivalent or better than leaded products for years already, we also found that the electrical data of newly developed environmentally friendly Ag pastes is as good as leaded pastes (examples in Table II). The paper also contains comparison of adhesion and solderability data on lead free and leaded back Ag pastes and some bowing and electrical data on lead free and leaded back Al pastes. From this work we can conclude that solar cells can be manufactured with environmentally friendly paste materials at high volume and with very high performance. The promise of a truly environmentally friendly technology for producing electrical energy is further enabled by this work.

2 EXPERIMENTAL

To conduct the study of lead free front silver, back silver and back Al pastes, we selected two types of emitters ,

emitter 1 and emitter 2 of sheet rho 65 ohm/square poly crystalline wafers of dimensions 156x156 mm and 180 micron thickness from commercial sources. The back silver paste used in this study was PS 33-610 (lead free) and back Al paste used was AL 53-112 (lead free). We screen printed 10 wafers each for the lead free front contact pastes A1 and A2 along with leaded front contact reference paste A. A 325 mesh or 280 mesh screen was used for front silver with deposit weight < 0.2 grams. For back silver printing, 200 mesh screen was used with deposit weight < 0.20 grams. For back Al pastes, we used 200 mesh screen with deposit weight >1.3 grams and < 1.7 grams. All cells were dried on a belt furnace at 200° C and then fired in a Despatch furnace using profile 400-400-500-700-800-920 (or 940) ° C (see Figure 1) at belt speed of 200 ipm.

All cells were characterized using NPC IV tester. For back silver lead free paste, we prepared 6 samples each with lead free paste PS 33-610 and reference leaded paste B on the same poly crystalline wafers and fired using the same profile as front silver. We used a pull tester for measuring pull strength of both leaded and lead free pastes.

For Al pastes, we used 200 micron poly silicon wafers and printed 6 wafers each with lead free paste 53-112 and leaded paste 53-038. We used leaded reference paste for front and back silver paste. Cells were fired in a Despatch furnace using the same profile as front silver. IV testing was done on all cells along with bowing measurements for each cell. All lead free pastes were sent to UL for ROHS certification.

3. RESULTS

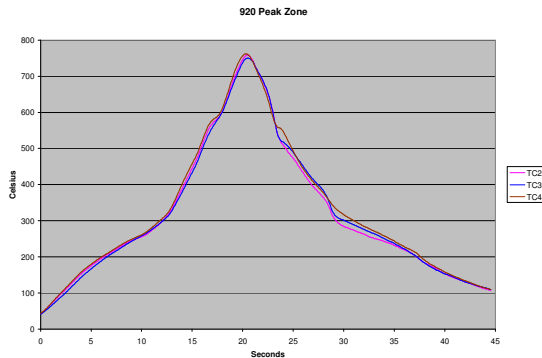


Figure 1: Typical temperature profile of a co-firing cycle used. The measurement was performed using a SunKIC datalogger from KIC.

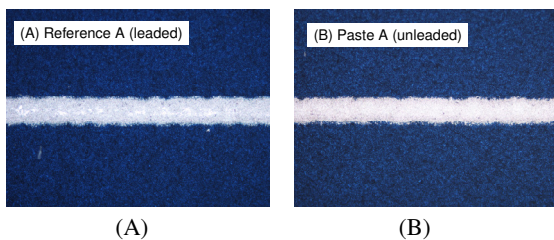


Figure 2: Optical microscope images showing slightly narrower and smoother fired finger line from lead-free paste A compared to leaded reference paste A

Figure 1 shows actual wafer temperature profile for the furnace setting 400-400-500-700-800-920 C at belt speed of 200 ipm.

Figure 2 shows optical micrographs of front silver finger of fired cells with lead-, cadmium- and phthalate-free and leaded silver paste. It can be seen that we get slightly narrower lines with lead-, cadmium- and phthalate-free pastes compared to leaded paste.

Table I: RoHS Test Results

Sample	Concentration (ppm or mg/kg)					
	Pb	Cd	Hg	Cr ⁶⁺	PBB	PBDE
ROHS MCVs	1000	100	100	1000	1000	1000
Paste A (Front Ag)	30	<10	<10	<1	<40	<40
PS33-610 (Back Ag)	10	<10	<10	<1	<10	<10
Al53-112 (Back Al)	<10	<5	<5	<2	<20	<10

Table I shows summary of RoHS results for all three lead free pastes, clearly showing that all three pastes are compliant with respect to ROHS requirements.

Table II: Typical performance of lead-free front Ag paste compared to leaded paste.

Front Ag Paste	EFF	FF	Rs	Voc	Isc
Reference A (leaded)	1.00	1.00	1.00	1.00	1.00
Paste A1 (Pb-free)/Emitter 1	1.04	1.02	0.89	1.00	1.01
Paste A1 (Pb-free)/Emitter 2	0.86	0.85	2.28	1.01	1.01
Paste A2 (Pb-free)/Emitter 2	0.98	0.94	1.45	1.01	1.03

Table II shows normalized data on performance of lead-free front pastes A1 and A2 along with leaded front paste A on emitter 1 and emitter 2. From the table it is clear that lead-free paste A1 performs better than leaded paste A on emitter 1. However, the performance of the same paste A1 is lower than leaded paste A on emitter 2. Work to make the lead free front silver paste robust with respect to emitter type is currently underway.

Table III: Typical lead free back Ag paste properties.

Back Ag Paste	Adhesion	Resistivity	Solderability
Reference B (leaded)	1.00	1.00	Excellent
PS33-610 (Pb-free)	1.15	1.00	Excellent

Table III shows normalized performance of lead free back silver paste PS 33-610 compared to leaded reference paste B. From the table, it is evident that lead-free back silver paste performs better than leaded back silver paste with respect to adhesion strength and has the same performance as leaded paste with respect to resistivity and solderability.

Table IV: Typical back Al paste performance compared to leaded paste.

Back Al Paste	Voc	Efficiency	Bow
Al53-038 (leaded)	1.00	1.00	1.00
Al53-112 (unleaded)	1.00	1.04	0.64

Table IV shows normalized comparison between lead-free Al paste AL 53-112 and leaded paste AL 53-038. From the table it is clear that lead-free Al paste performs as good as leaded paste electrically and shows 40% lower bowing than leaded paste.

Cell Efficiency with Emitter 1

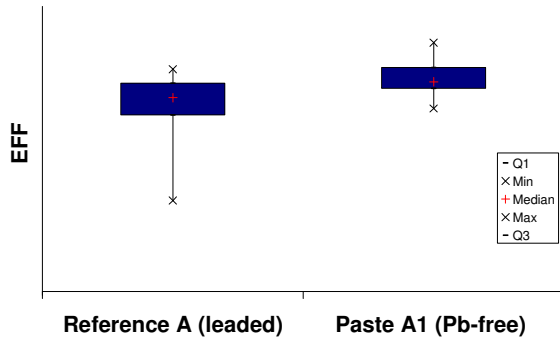


Figure 3: Lead-Lead free paste A1 showing higher efficiency than leaded paste reference A

Figure 3 is a box plot of efficiency for lead-free front paste A1 and reference leaded front silver paste on emitter 1. The lead-free paste shows higher efficiency as well as lower spread compared to leaded front silver paste.

Cell Rs with Emitter 1

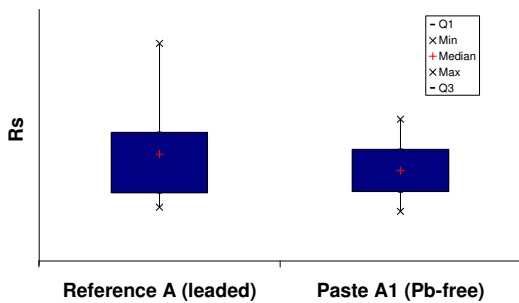


Figure 4: Lead-free paste A1 showing similar or slightly lower Rs than leaded paste.

Figure 4 is a box plot for Rs values obtained for lead-free front and leaded front silver pastes. The lead-free paste shows lower Rs and lower spread in Rs compared to reference leaded paste. Figure 5 is a similar box plot of Voc for lead-free and leaded paste. The Voc is higher for lead-free front paste and the spread is smaller compared to that of leaded paste.

Cell Voc with Emitter 1

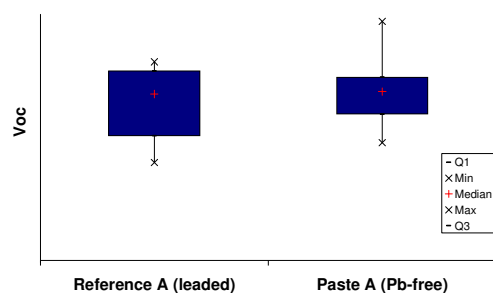


Figure 5: Lead-free paste A1 showing similar or slightly

higher Voc than leaded paste.

Front Ag Adhesion Comparison

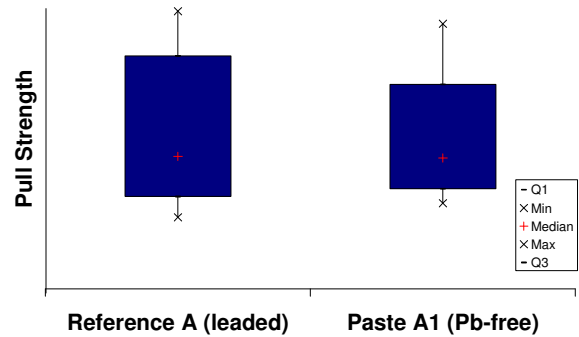


Figure 6: Lead-free front Ag paste showing comparable pull strength to the leaded paste.

Back Ag Adhesion Comparison

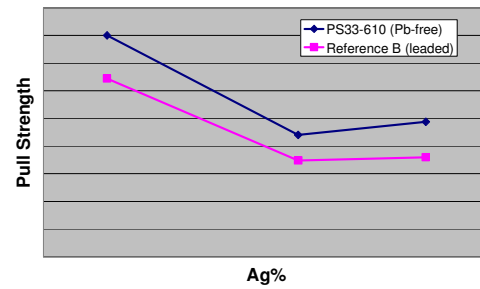


Figure 7: Lead-free back Ag paste B showed higher pull strength than leaded back Ag paste reference B.

Figure 6 is a box plot for lead-free front silver paste with respect to pull strength. It is evident from Figure 6 that lead-free front silver paste gives equally good pull strength as leaded front silver paste with a tighter spread.

Figure 7 shows plots of pull strength of back silver paste as function of percent silver present in the paste. The pull strength is a function of silver content and goes down with increasing silver content for both lead-free and leaded silver paste. The pull strength of lead-free silver paste is higher than that of leaded silver paste for all levels of silver content that were tested.

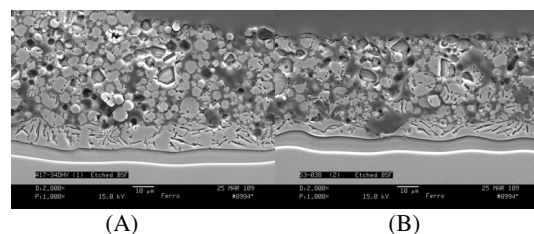


Figure 8: SEM Cross Section Images: wafers fired at 920° C peak temperature, (a) Lead-free paste 53-112 and (b) Leaded paste 53-038 showing good BSF with both pastes.

Figure 8 shows cross section SEM micrographs of lead-free Al paste AL53-112 and leaded Al paste AL53-038. Both micrographs show good BSF formation in lead free as well as leaded back Al pastes. In addition, the bowing obtained on 200 micron thick poly wafers was found to 40% lower in lead-free Al paste AL 53-112 compared to leaded Al paste 53-038.

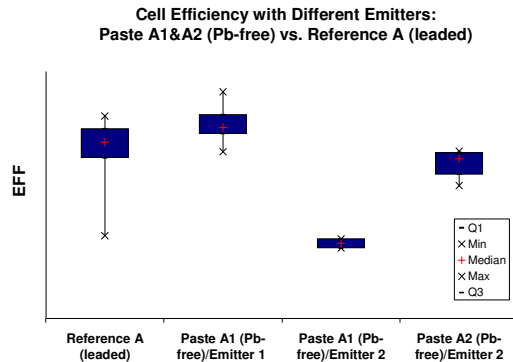


Figure 9 Box plot showing efficiency with different pastes A1 and A2 (lead free) along with reference leaded paste A on two types of emitters.

Figure 9 shows box plot of efficiency as function of paste chemistry and emitter types. From the plot we can observe that lead free paste A performs better than reference leaded paste A on emitter 1 but no as good on emitter 2. However improved lead free paste A2 does show better performance on emitter. This is a work in progress and we continue our development efforts towards robust lead free paste with excellent performance on all types of emitters.

4. SUMMARY

In this paper, we have investigated the performance of lead-, cadmium- and phthalate-free front silver, back silver and back aluminum pastes for silicon solar applications. We have demonstrated that lead-free front silver paste that are compliant with RoHS and REACH regulations give similar or better electrical performance than their leaded counter parts. We have also shown that lead-free back silver paste PS 33-610 has been developed that gives superior adhesion properties, with no compromise on resistivity or solderability of the pastes.

We have also demonstrated that our recently developed lead free back Al paste AL 53-112, compliant with RoHS regulations, gives comparable electrical performance to our first generation lead Al paste AL 53-038, with 40% reduced bowing on 200 micron wafers. This development now enables solar cell manufacturers to use wafers as low as 160 micron in thickness and still get bowing within acceptable limits. The microstructure studies on cross section reveals a good BSF formation with lead-free paste chemistry similar to that obtained with leaded chemistry.

We continue our effort to further improve performance of all our lead free pastes that are consistent with the changing solar industry requirements both from productivity and regulatory point of view.

5 REFERENCES

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