

N84 22000

D20

IRON-COPPER METALLIZATION FOR FLEXIBLE SOLAR CELL ARRAYS

by

HENRY W. LAVENDEL

Senior Staff Scientist

Lockheed Palo Alto Research Laboratory

Palo Alto, California

RESEARCH GOALS

The aim of the research discussed in this presentation is to explore feasibility of a copper-base metallization for shallow-junction cells applied in flexible solar arrays in space. This type of metallization will reduce usage of precious metals (such as silver), increase ease of bonding (by welding or by soldering) and eliminate heavy high Z interconnects (such as molybdenum). The main points of concern in the investigation are stability against thermally induced diffusion of copper into silicon which causes degradation of shallow cell junctions, and low series resistance of the contact with semiconductor which promotes cell efficiency.

CURRENT ART SILVER METALLIZATION

A major Flexible Solar Array Technology development program is currently in progress at Lockheed Missiles and Space Company, Sunnyvale, California, with a target design incorporating several hundred thousands of individual large area (5.9 by 5.9 cm) cells (Fig. 1), attached to a Kapton printed circuit substrate by contact welds between silver metallization and copper interconnects as shown in Fig. 2. Both N and P contacts are located on the cell back thanks to a dielectric wraparound for the N tabs (the assembly shown in Fig. 2 has a portion of the printed circuit removed to put in evidence the configuration of the wraparound N contact). Typical structure of the contact weld is shown in Fig. 3 in a cross section made at an angle of 6° to the sample surface in order to increase the thickness resolution by a factor of 10. The bond is a result of solid state diffusion between silver and copper and consists of the two terminal solid solutions (Fig. 4). Metallurgical quality and reliability of the attachment depend on controlling the welding reaction in a manner to avoid generating liquid phases and outgassing from the electroplated silver. An example of structural defects caused by the latter is shown in Fig. 5. Substituting copper metallization for the silver one will eliminate many weld problems since the bond will be made between two pieces of the same metal.

CANDIDATE COPPER-BASE METALLIZATION

The first order concern in considering copper metallization for solar cells is the tendency of the metal to diffuse into silicon and deteriorate the P/N junction. Consequently, an appropriate

diffusion barrier has to be found. Iron is a potential candidate because: (1) its alloying affinity towards copper is extremely limited below 700°C so that at temperatures prevailing in fabrication and service of the solar arrays copper is essentially insoluble in it (see Fig. 6); (2) it will not contaminate the P/N junction when a silicide contact is formed because the iron/silicon phases (Fig. 7) are formed by unilateral diffusion of silicon into iron. The most serious disadvantage is high resistivity of the iron silicides which poses problems of ohmic losses in an iron silicide contact. The data presented here are addressing only the ability of iron to inhibit diffusion of copper into silicon; dealing with the high ohmic resistivity of the contact is the subject of the next step of the investigation.

METALLURGICAL EVALUATION

Experimental solar cell substrates used in the research are single crystal P-silicon wafers with a 0.2 μm deep N^+ diffused layer ($\sim 10^{20} \text{ cm}^{-3}$ surface concentration of phosphorus). Initially the contact metallization was applied directly on the front (N) surface by vapor-depositing about 0.1 μm of iron followed by 0.5 μm of copper, and reacting the two layers between themselves and with the silicon at 600°C in vacuum for one hour. The reacted samples were cross sectioned and examined metallographically to determine the nature and extent of interaction. Fig. 8 shows a typical structure which discloses a non-uniform defective interface between the metallization and the silicon. Measurements of series resistance through the generated contact gave values in the order of 200 to 300 Ω . One probable reason for the high resistance is the defective metallurgical structure. However, the fact that the shallow P/N junction showed a rectifying diode behavior strongly suggests that diffusion of copper into it has been prevented.

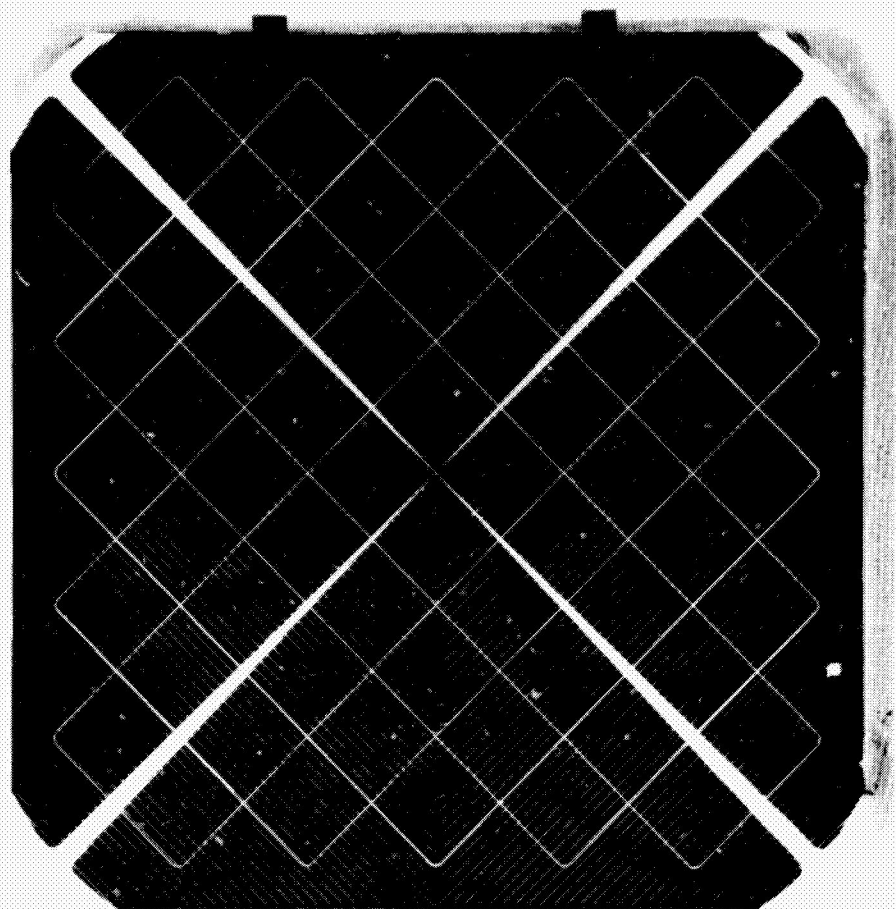
Improved uniform bonds were obtained interposing a vapor-deposited layer of amorphous silicon between the iron/copper metallization and the substrate silicon. Fig. 9 characterizes the resulting microstructure in a 6° angle cross section. Fig. 10 is an energy dispersive scan of it. The bond of the metallization to the silicon consists of an 0.5 μm thick Si/Fe/Cu alloy layer. Since the total thickness of combined as-deposited a-silicon and iron layers is of the same order of magnitude, the amorphous silicon acts as a sacrificial reactant in generating the interface while the solar cell material remains unaffected. A heat treatment for additional 2 hours at 500°C leaves this structure unchanged, as seen in Fig. 11. It is, therefore, evident that the ternary alloy generated by iron in the reaction with a-silicon and copper does indeed inhibit diffusion of copper into the cell substrate.

The main experimental difficulty in consistently reproducing this result lies in ensuring a defect-free barrier. Copper tends to shortcircuit the P/N junction by penetrating into the underlying silicon through structural imperfections such as pores or voids in the ternary layer. Fig. 12 shows this effect in a sample with relatively few open diffusion paths. Fig. 13, on the other hand, documents a sample with a heavy defect concentration; the depth of penetration is emphasized in this case by sectioning the sample at an angle of 6° to the surface. Within the single crystal silicon substrate the diffusion proceeds in the [100] direction along (100) planes of the lattice where the distance between atomic layers is the most favorable. The result are distinct geometric regions of a solid solution, or a compound, the composition of which is documented in Fig. 14. Fig. 15 shows the analysis of the Fe/Si/Cu interface layer where it is free of defects and is effective in stopping the copper diffusion.

The investigation summarized above indicates the metallurgical potential of developing a copper-base metallization for solar cells using iron as a diffusion inhibiting agent. Further research will determine whether this concept can also satisfy the requirements of photovoltaic performance.

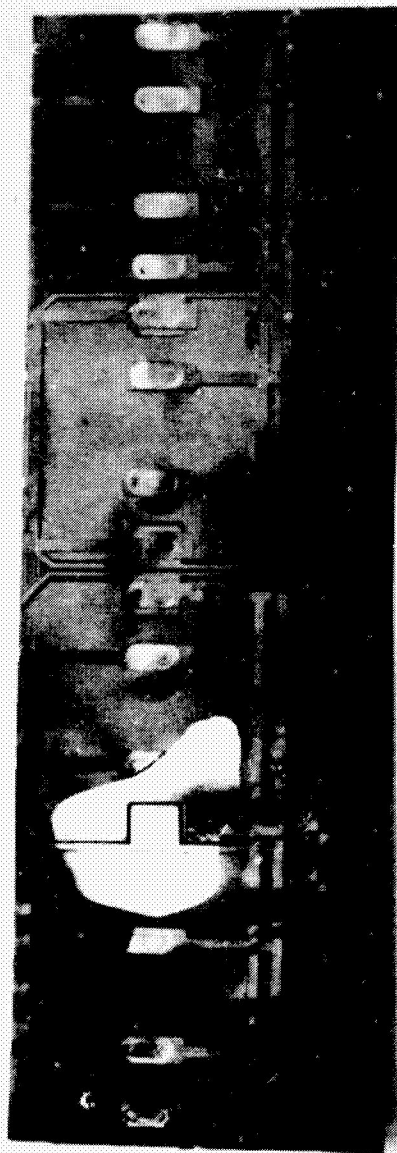
ORIGINAL PAGE IS
OF POOR QUALITY

Figure 1. Front Surface of the Flexible-Array Cell (2X)



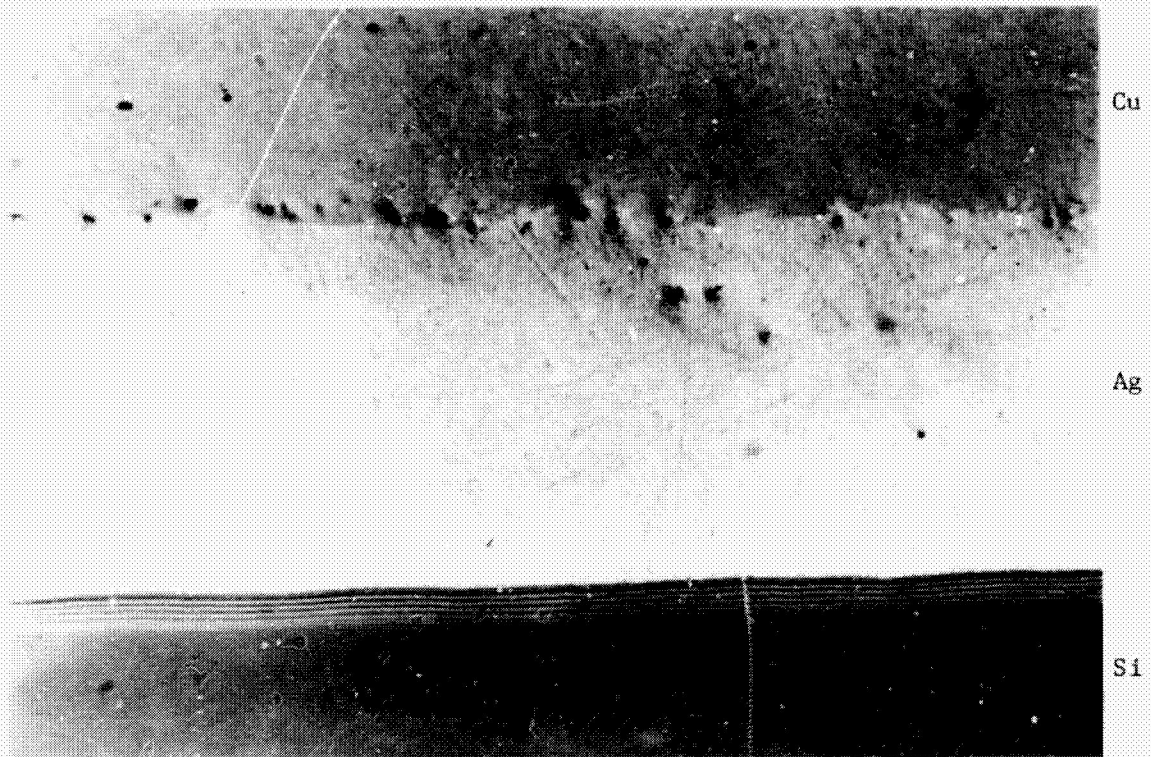
ORIGINAL PAGE 19
OF POOR QUALITY

Figure 2. Flexible Blanket Interconnect (0.67X)



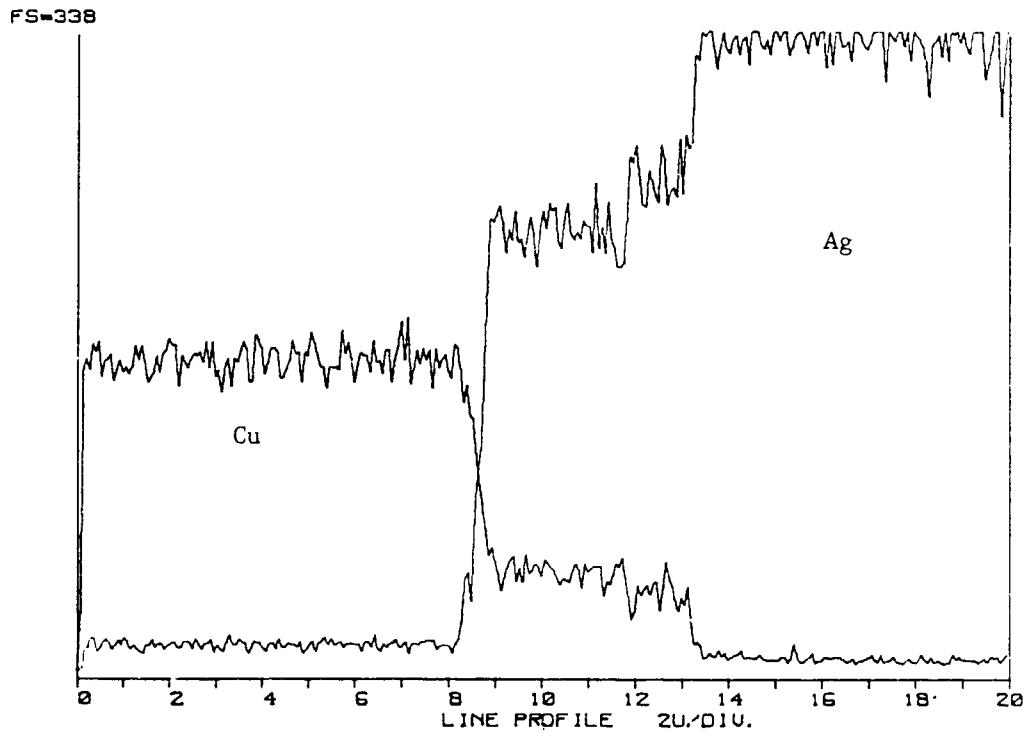
ORIGINAL PAGE IS
OF POOR QUALITY

Figure 3. Structure of Ag-Cu Weld (500X)



ORIGINAL PAGE IS
OF POOR QUALITY

Figure 4. Energy-Dispersive SEM Analysis of Ag-Cu Contact Weld



ORIGINAL PAGE 19
OF POOR QUALITY

Figure 5. Defects in Ag-Cu Contact Weld (200X)

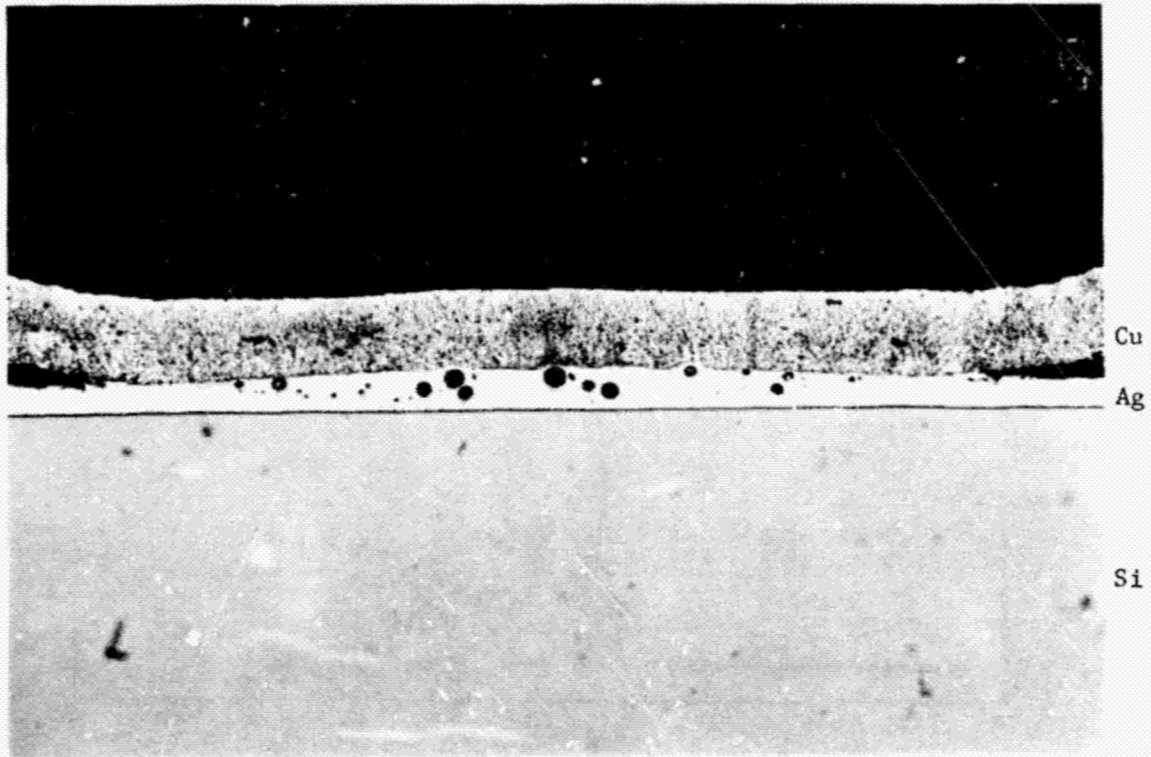


Figure 6. Copper-Iron Phase Diagram

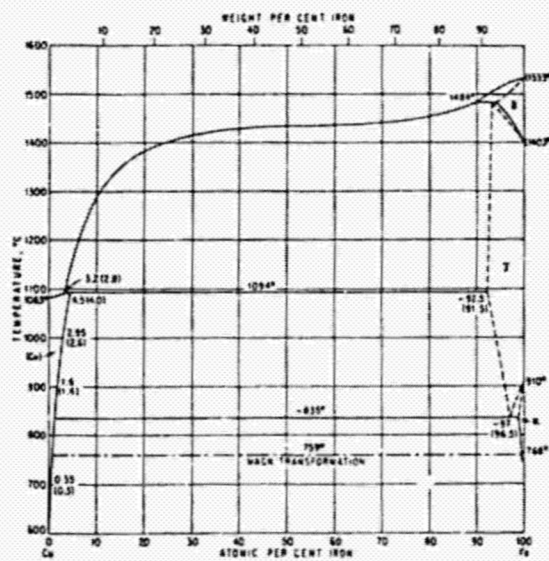
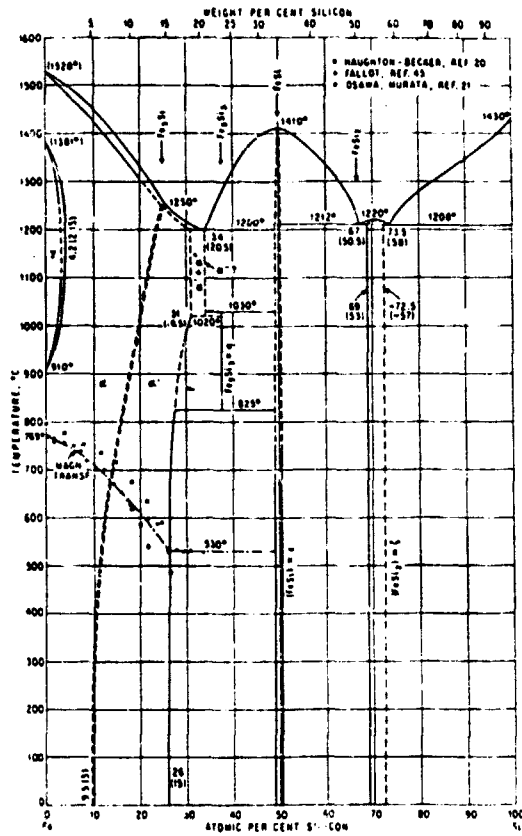


Figure 7. Iron-Silicon Phase Diagram



ORIGINAL PAGE IS
OF POOR QUALITY

ORIGINAL PAGE IS
OF POOR QUALITY

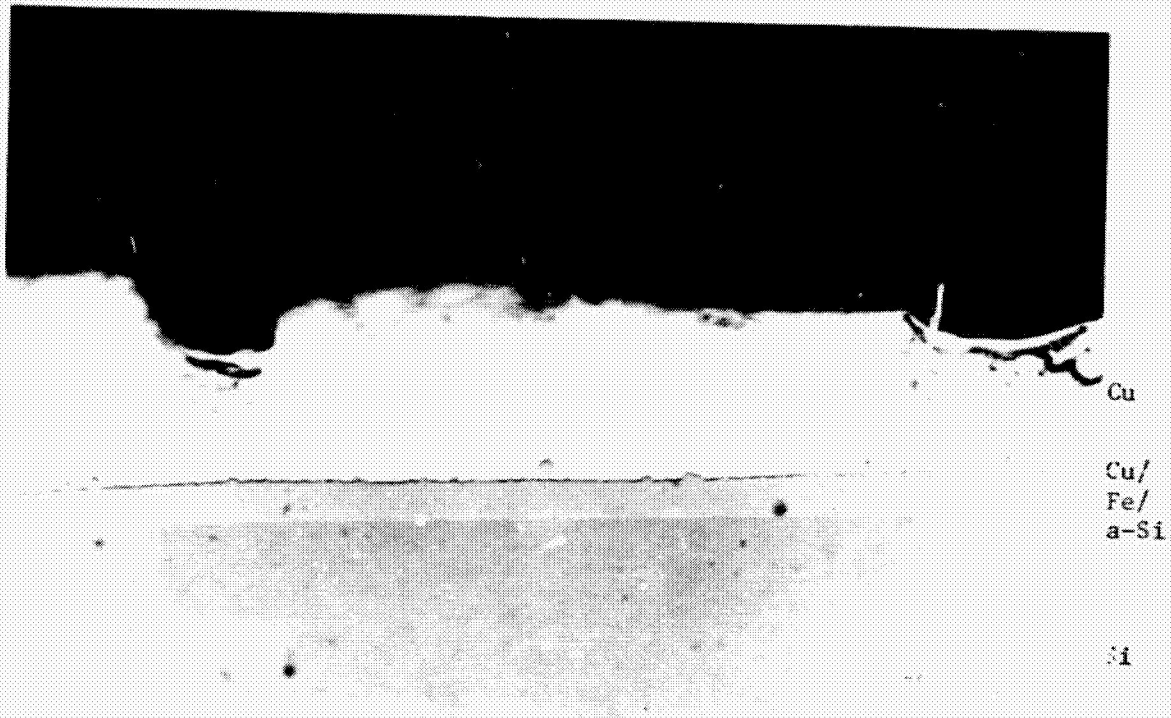
Figure 8. Cu-Fe Bond to Single-Crystal Silicon (200X)



Si

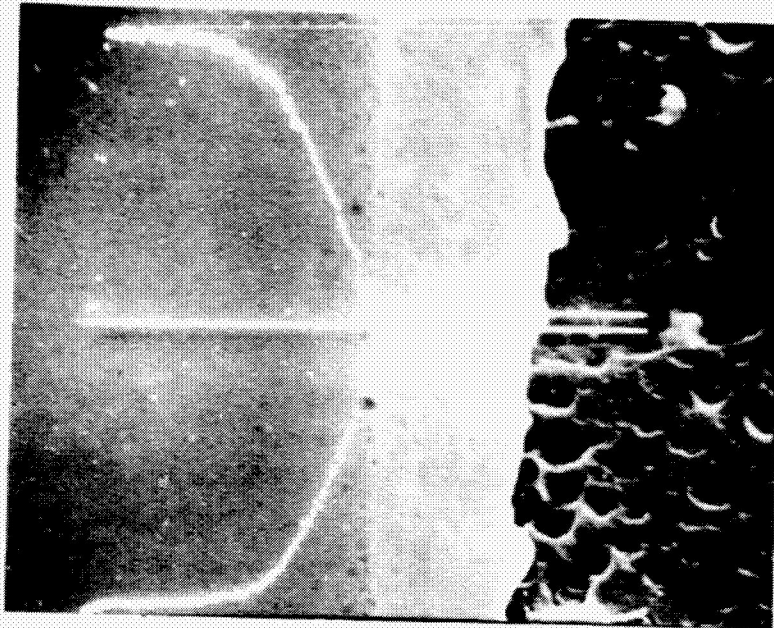
ORIGINAL PAGE IS
OF POOR QUALITY

Figure 9. Cu-Fe-Si to Silicon Bond (1000X)

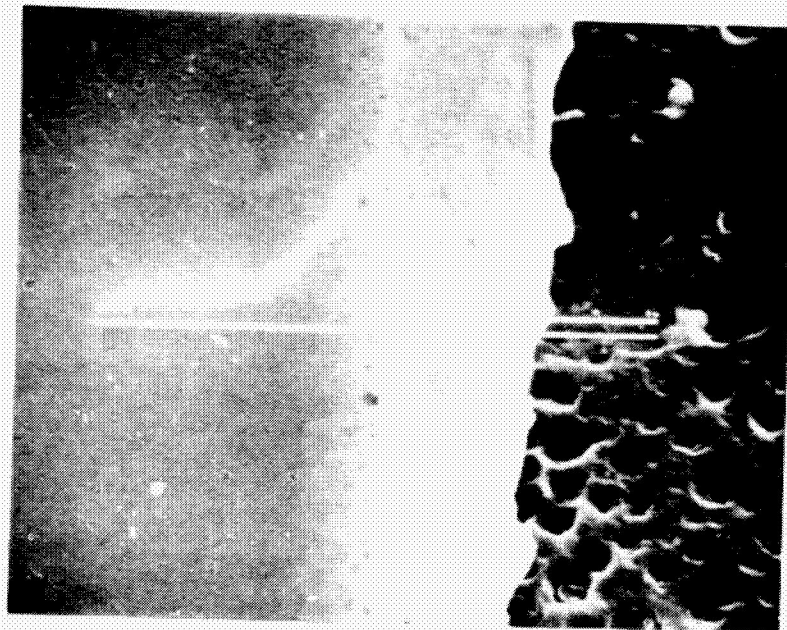


ORIGINAL IMAGE IS
OF POOR QUALITY

Figure 10. SEM Analysis of Typical Cu-Fe-a-Si Bond (1050X)



A. Silicon (upper scan) and Copper (lower scan)

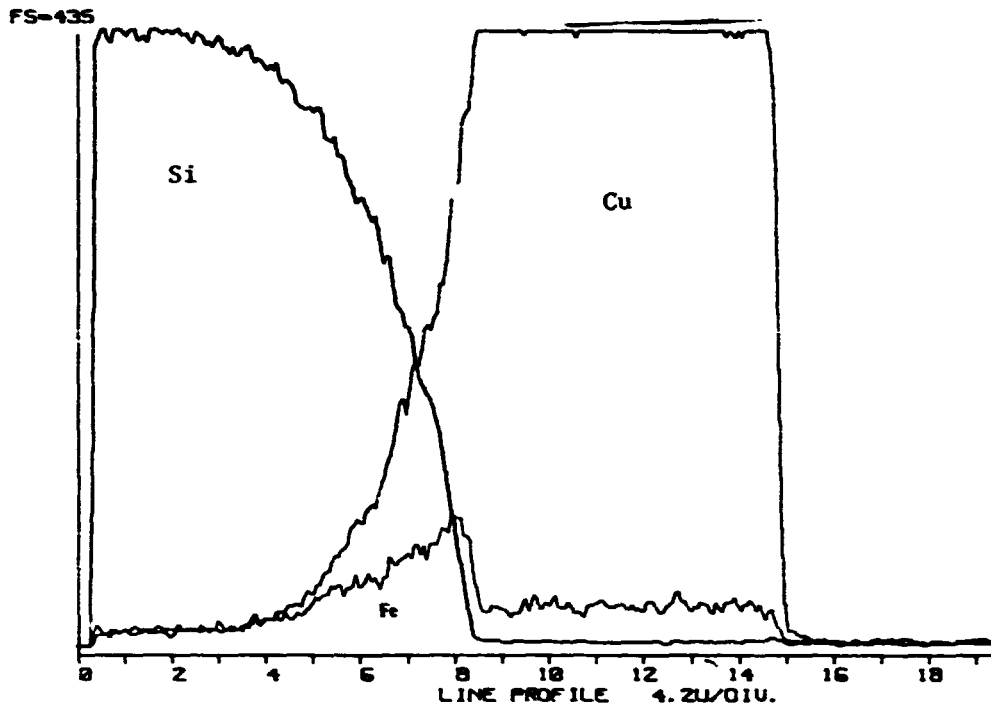


B. Iron scan

ORIGINAL PAGE IS
OF POOR QUALITY

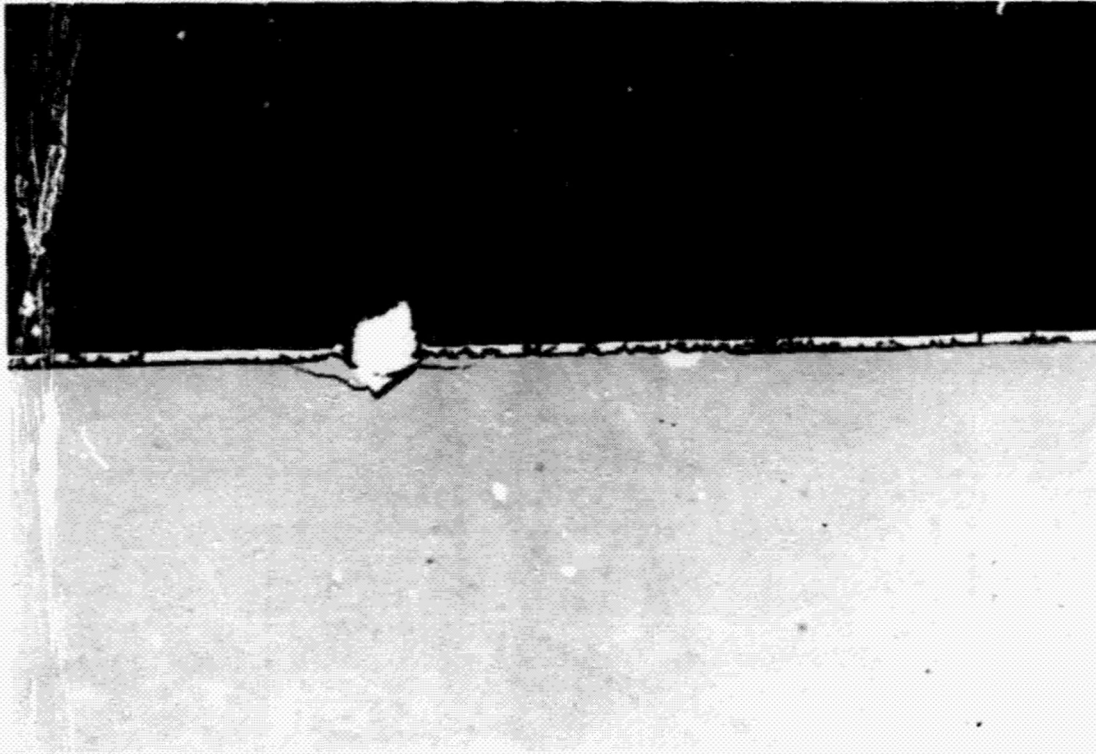
Figure 11. Energy-Dispersive SEM Analysis of
Heat-Treated Cu-Fe-a-Si Bond

FE/CU METALLIZATION



ORIGINAL PAGE IS
OF POOR QUALITY

Figure 12. Cross Section of Defective Cu-Fe-a-Si Bond (500X)



ORIGINAL PAGE IS
OF POOR QUALITY

Figure 13. 6-deg-Angle Cross Section of Defective
Cu-Fe-a-Si Bond (500X)

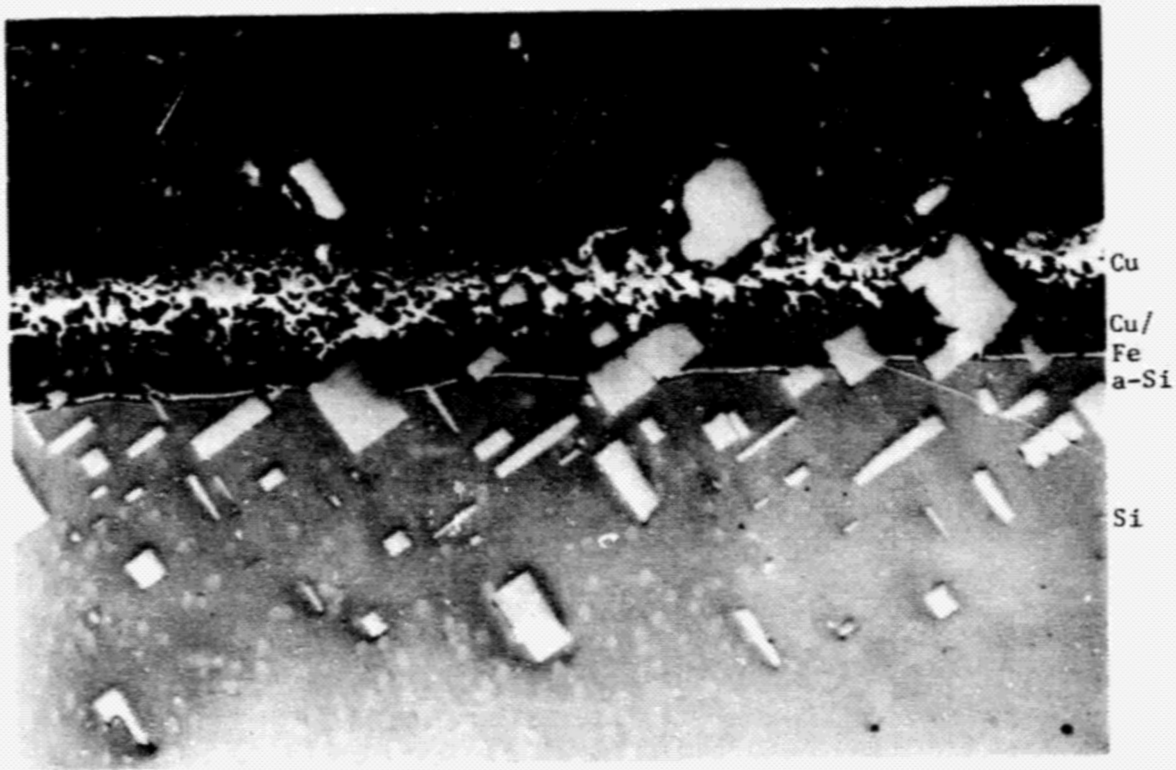
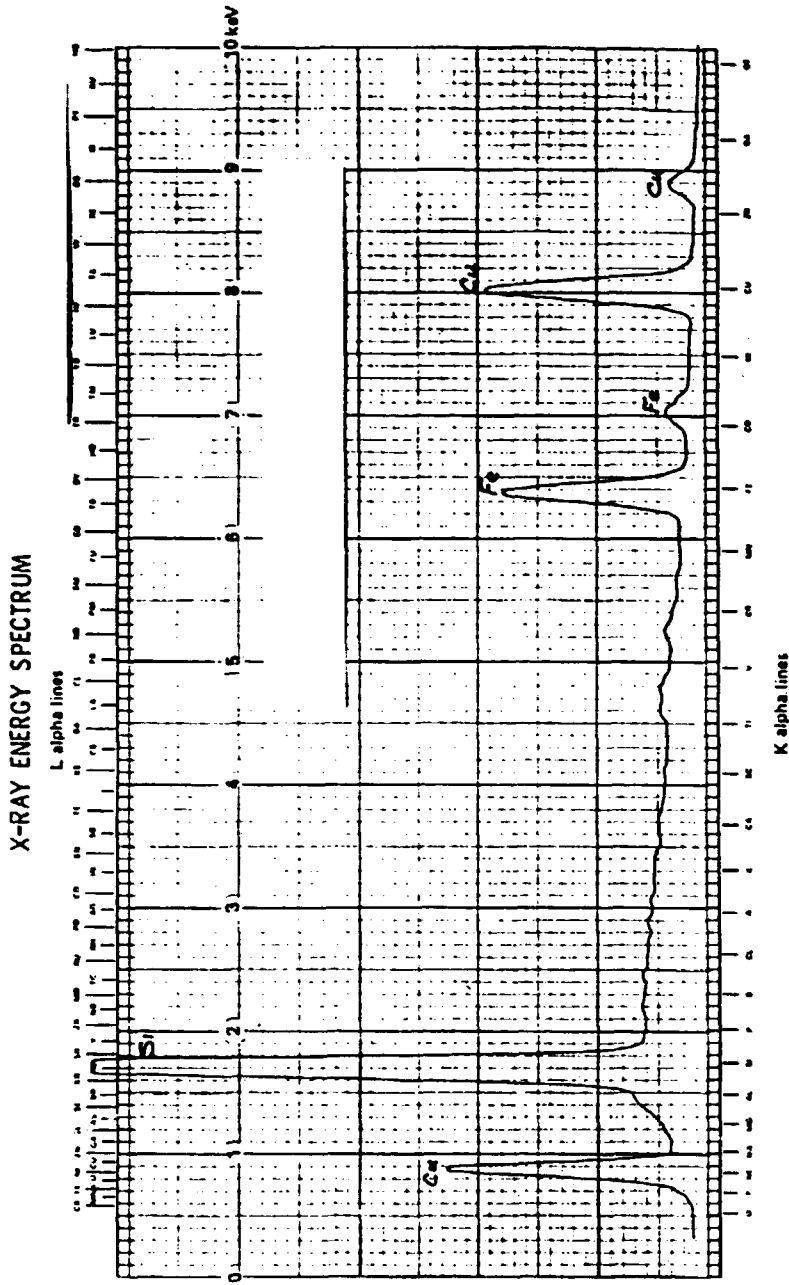


Figure 14. Electron Microprobe Analysis of Cu-Fe-a-Si Bond



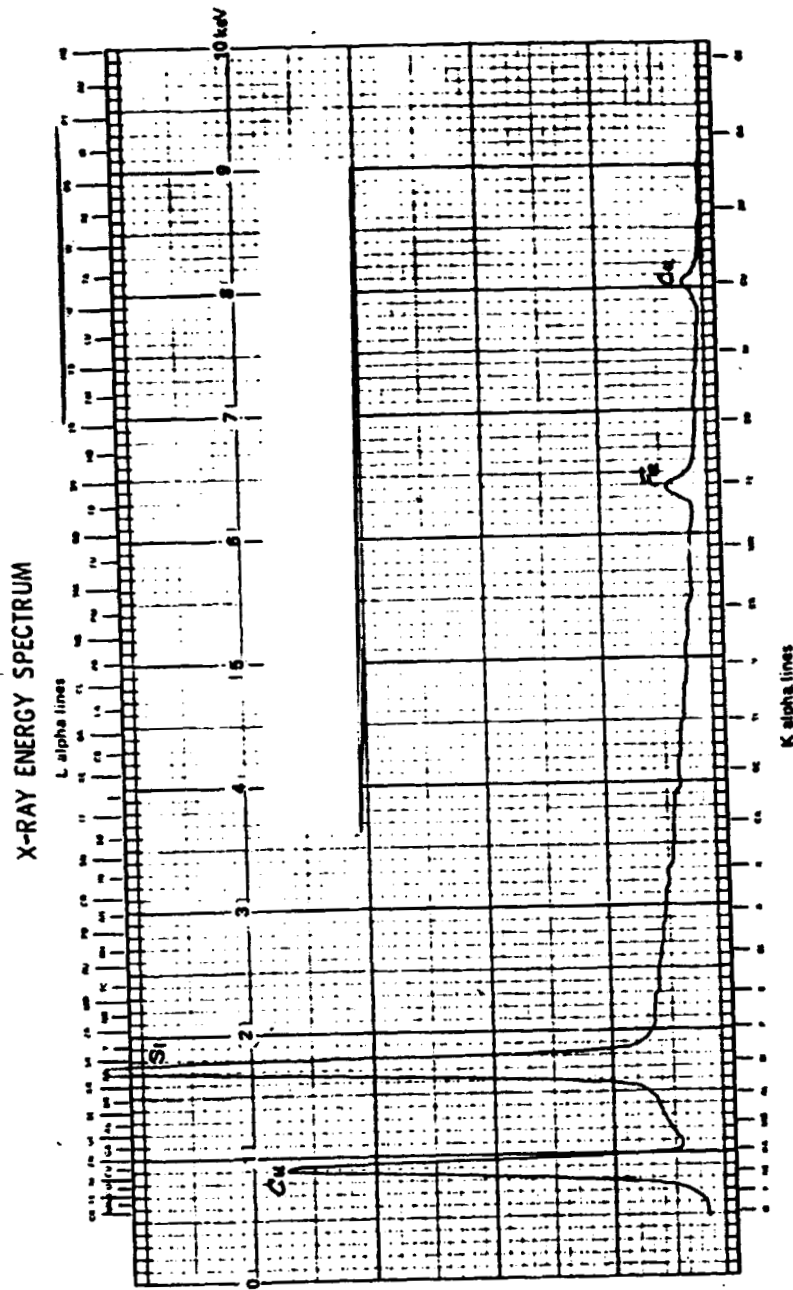
ORIGINAL PAGE IS
OF POOR QUALITY

SAMPLE IDENTIFICATION NUMBER *Rdm 164 coating #73*

DATE *1 Mar 1983* KeV *1.5* Full scale *2048*
 Data #3 Bank *HLM4B* Max *30* Ct. Time *100* Sec's

NOTES: All lines may be due to thin conductive coating added.
 Elements not detectable by EDS are C, N, O, B, I, Be, Bi.
 Spectral line interferences: Mo-Sr, Pb, Te-Sr, He-Zn, etc.

Figure 15. Electron Microprobe Analysis of Cu-Si Phase in Silicon



SAMPLE IDENTIFICATION NUMBER Run 164 Particle # 3

Data #3 DATE 1/28/83 KeV / e Full Scale 2048
 Bank: HLK17 No. 112 Ct. Time 100 Sec's

*NOTES: All lines may be due to thin conductive coating added.
 Elements not detectable by EDS are C, H, O, S, F, Be, Bi.
 Spectral line interference: Mo-S, Pb, Te-Si, Na-Zn, etc.

ORIGINAL PAGE IS OF POOR QUALITY

DISCUSSION

WONG: Those solid solutions or compounds, do you think they are formed during cooling due to precipitation?

LAVENDEL: That is a good question. Well, undoubtedly copper penetrates into silicon when you are heating it. Probably the distribution of the copper atoms within the single-crystal silicon might change when you cool down from your 600° or 500°. The time involved is rather short, by which I mean your cooling is probably half an hour or something. It might be that you mostly quench the situation that arises at high temperature so by some kind of gross approximation you might say that what you see actually happens at time of fusion.

WONG: Did you happen to microprobe other areas in the vicinity of the defect?

LAVENDEL: No, not in the immediate vicinity. It is the pattern that I get from the ternary layer -- I wouldn't say in the immediate vicinity of that defect, but where it does not seem have been penetrated by copper.

WONG: It might be an interesting point to probe in the vicinity to see whether there is a copper gradient.

LAVENDEL: Let me go back. If I correctly understand you, you would like to see what happens right here.

WONG: Yes.

LAVENDEL: No. I didn't look at this area, I either looked at areas like this or smack right in the middle of these compounds or alloys. Whether there is anything peculiar here at the interface between this and the layer here I don't know.

WONG: Would you go to the following one, please? What I mean is, if you probe from the copper perpendicularly up.

LAVENDEL: Don't be fooled by the fact that this is a very shallow section, so actually what you are really looking at here is a section that is done this way.

SCHWUTTKE: Do I understand that you have a bevel?

LAVENDEL: That is right. That is why you see this, you see on this picture, this copper-silicon alloy, both apparently in copper and in silicon, but actually what you see here is the cross section of a thing like that that protrudes up and it seems to be about in the copper, and both in the copper and the silicon. If you cross section it at a low angle like that you will see it on both sides of the internal barrier.

PRYOR: On the samples where you had minimal copper penetration or pinholes, did you succeed in getting a low series resistance?

LAVENDEL: I don't know, I didn't measure it yet. This series of samples is relatively recent, and I really did not have time to get that measurement reliably. I certainly hope to get it within a month or so. If I don't get low series resistance, then we have an additional problem, which means that I will accept the fact that the iron is really effective in stopping the diffusion, but I will have to worry about interposing something between that iron layer and the cell itself at the normal contact.

BLAKE: You use a layer of amorphous silicon as a sacrificial layer; between the silicon and the iron how thick was this, and how was it applied?

LAVENDEL: It was applied by the decomposition of silane. The thickness of that layer was about half a micron.

AMICK: Henry, if you put copper, now, in contact with that top surface and you wait, with time the chemical potential with the copper in the silicon will be governed by the chemical potential of the copper in the copper, will it not? Won't you always have the risk of copper precipitating in the silicon?

LAVENDEL: Yes, you are undoubtedly right. However, our heat treatment of one hour at 600°, and 2 hours at 500° additional to that, did not produce penetration when the barrier was good -- did not produce any measurable penetration of copper into silicon. I would say that if you operate your cells at temperatures of 150°C, 200°C, it will take centuries to get there by diffusion. I don't think that we can ever hope to achieve an ideal, completely impenetratable barrier; the diffusion will always go on. As Marc Nicolet said, you have defects in your structures always, vacancies, grain boundaries. I, as a matter of fact, am amazed that that half a micron of the ternary stops the diffusion to that extent.

AMICK: Do I understand then from the pictures that you consume all the copper that was originally on top?

LAVENDEL: Oh, no, no, no. Let me go back to the pictures, this is pure copper. The whole layer is pure copper. This is the interface. This is silicon, this is chemical potential of pure copper.

WONG: I have another question, if you don't mind. The picture you showed, the silicide at the interface -- the silicide forms cracks perpendicular to the interface; do you think this crack was formed due to the lattice mismatch or due to the thermal cycling?

LAVENDEL: Thermal cycling, I believe.

WONG: OK, it is not formed during formation, in other words?

LAVENDEL: I don't think so. I cannot tell you really that it isn't, I just don't think so, it might be. There might be a contribution of that too.

WONG: Amorphous silicon at the interface, how do you know it is amorphous?

LAVENDEL: By X-ray.

AMICK: Henry, in this picture, is that still free copper on the top surface?

LAVENDEL: Yes, this is free copper, and actually the interface is somewhere here.

STEIN: Could you please describe your welding technique?

LAVENDEL: I'm sorry, it is proprietary. I can only tell you one thing, that it is done by parallel gap welding and it is very, very closely monitored by the system -- by the temperature itself, the cycle itself (the temperature-time cycle). It is very very closely monitored by a set-up that LSMC developed. I, myself, know very little about it. The weld that I have shown you before is a typical result of that operation, so formation of the eutectic there happens very, very seldom and it happens only if their equipment malfunctions.