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SOLAR

LASER-ASSISTED SOLAR CELL METALLIZATION PROCESSING

Quarterly Report for the Period September 13—December 12, 1983

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By
S. Dutta

January 16, 1984

Work Performed Under Contract No. NAS-7-100-956615

Westinghouse R&D Center
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Jet Propulsion Laboratory
Contract No. 956615

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1. SUMMARY

The Westinghouse Electric Corporation has undertaken, in JPL Contract No. 956615, to investigate, develop, and characterize laser-assisted processing techniques utilized to produce the fine line, thin metal grid structures that are required to fabricate high-efficiency solar cells. Two basic techniques for metal deposition will be investigated, as follows: (1) photochemical decomposition of liquid or gas phase organometallic compounds utilizing either a focused, CW ultraviolet laser (System 1) or a mask and ultraviolet flood illumination, such as that provided by a repetitively pulsed, defocused excimer laser (System 2), for pattern definition, and (2) thermal deposition of metals from organometallic solutions or vapors utilizing a focused, CW laser beam as a local heat source to draw the metallization pattern.

The purpose of this contract is to investigate the various existing laser-assisted film deposition techniques in order to develop a new, cost-effective technology for solar cell metallization. The tasks that will be performed in the conduct of these investigations are detailed below and summarized in the milestone chart in Figure 1.

In the first three months of this contract, a comprehensive literature search has been carried out on the various state-of-the-art laser-assisted techniques for metal deposition, including laser chemical vapor deposition and laser photolysis of organometallics, as well as laser-enhanced electroplating. A compact system for the experiments involving laser-assisted photolysis of gas-phase compounds has been designed and constructed. Initial experiments on laser-enhanced electro-plating have yielded very promising results, with linewidths as fine as 25 μm and plating speeds as high as 12 μm/sec being achieved.

MILESTONE CHART
JPL CONTRACT 956615

Tasks/Milestones

1. Conduct literature search on current state-of-the-art laser metallization schemes.
2. Assemble and test each of the following systems:
   - 2.1 Photolytic metal deposition using a focused CW UV laser.
   - 2.2 Photolytic metal deposition using a mask and UV flood illumination.
   - 2.3 Pyrolytic metal deposition using a focused CW laser.
3. Fabricate fifty solar cells.
4. Characterize the cells and determine the effects of transient heat on solar cell junctions and on bulk lifetime.
5. Compare economics of laser-assisted processing with competing technologies

   Preliminary Report

   Final Report
6. Support Meetings
7. Provide Documentation

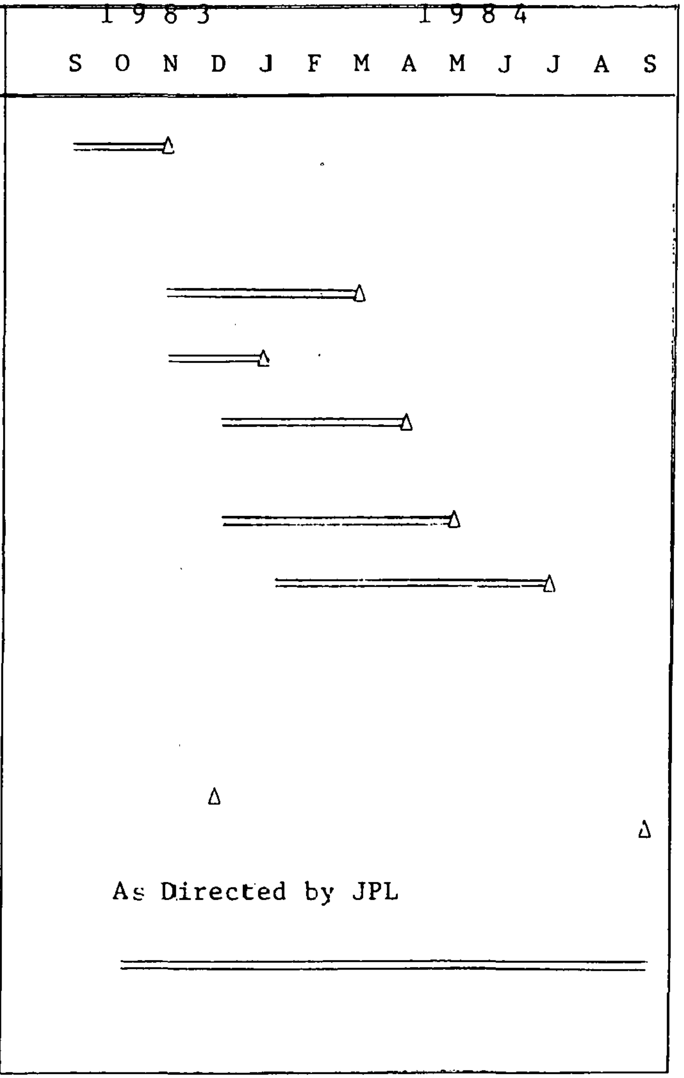

Figure 1

1.1 Literature Search

The results of the literature survey are briefly summarized in the following paragraphs.

1.1.1 Photodissociation Metal Deposition

Laser-induced photodecomposition of gas-phase organometallic compounds is fundamentally a nonthermal process, involving multiphoton absorption by the compound, which then dissociates, liberating metal atoms in the vicinity of a suitable substrate. These atoms then condense onto the illuminated regions of the substrate forming a metal film. Localization of the substrate illumination is achieved either by focusing the laser or by using flood illumination in conjunction with a mask.

Draper(1) has deposited both Cr and Mo using off-resonance laser-induced dielectric breakdown of metal-carbonyl vapors with a pulsed CO_2 laser. Solanki et al.(2) used a pulsed copper hollow cathode laser at 260 nm, utilizing the multiphoton absorption that occurs at this ultra-violet wavelength for carbonyl molecules, to deposit Cr, Mo, and W films. The laser was operated at 150 mW peak power with pulse widths of 120 μs. Ehrlich, Deutsch, and Osgood(3-6) have performed a variety of experiments using both pulsed (excimer lasers, 1-100 mJ, 10 ns) and CW (frequency-doubled Ar^+ laser, 10 μW-3) UV lasers. In one of their most interesting experiments,(4) a two-step process was used to deposit patterned Cd, Al, and Zn films from metal-alkyl vapors. In the first step, localized pre-nucleation was achieved by using a focused UV laser to irradiate the substrate in the requisite pattern, photodissociating a thin, adsorbed layer of metal-alkyl molecules. The laser was then defocused to illuminate the entire substrate, causing film growth to occur selectively in the pre-nucleated regions. These experiments also indicated that films of one metal, e.g., Al, could be grown on nucleation centers of a second, dissimilar metal, e.g., Zn. Table 1 lists the encapsulant gases Ehrlich et al. used in their experiments.

Table 1

Encapsulant Gases Used by M.I.T. Lincoln Laboratory for Photodissociation

$Cd(CH_3)_2$
$Zn(CH_3)_2$
$Sn(CH_3)_4$
$Ga(CH_3)_3$
$Bi(CH_3)_3$
$Si(CH_3)_4$
$Ge(CH_3)_4$
$Al_2(CH_3)_6$
$Fe(CO)_5$
$W(CO)_6$
$Cr(CO)_6$
CF_3I
$SnCl_4$

In another set of experiments, Coombe and Wodarczyk(7) used KrF (249 nm) and XeCl (308 nm) excimer lasers to induce the localized deposition of Zn and Mg films from the pure metal vapors. The laser pulses used in these experiments were typically 20 ns in duration and carried energies of up to 20 mJ (KrF) or 5 mJ (XeCl).

1.1.2 Pyrolytic Metal Deposition

Chemical vapor deposition (CVD) of metals is conventionally accomplished by resistively or inductively heating an appropriate substrate in a reactive atmosphere, with pyrolysis reactions at the substrate surface providing the basis for film growth. Laser chemical vapor deposition (LCVD) is achieved by using pulsed or CW lasers of suitable wavelengths to selectively heat localized areas of substrates which absorb at those wavelengths, areas adjacent to the illuminated regions remaining comparatively cool. Allen and Bass(8) have used a CO_2 laser to deposit nickel on quartz substrates from gaseous $Ni(CO)_4$. LCVD metal thicknesses tend to be self-limiting, with a maximum thickness of 550 Å being obtained for nickel.

1.1.3 Laser-Assisted Electroplating

Another new laser-processing technique that is of interest in this program is laser-assisted electroplating. Maskless plating was achieved by von Gutfield et al.,(9) utilizing a CW or pulsed laser focused onto an electroplating bath. Local plating enhancement rates as high as ~ 10^3 have been obtained by this technique. A CW multimode argon-ion (1.5 W output power) or a krypton-ion laser tuned to 647.1 nm (100 mW output power) was used, the argon-ion laser being particularly suitable for Ni and Cu plating solutions and the krypton-ion laser being better suited to Au plating solutions. The laser was focused to spot sizes of 100-300 μm onto a dielectric substrate predeposited with a thin, absorbing metallic film. The predeposited thin film consisting of W, Mo, or Ni ~ 1000 Å thick both absorbed the optical energy and served as the cathode of the electroplating cell.

1.2 Design and Construction of the Laser Photolysis System

Based on this literature search a set-up for conducting laser-assisted photolysis of gas-phase of organometallic compounds was designed and constructed. The system consists of a gas-fill and pumping station, as shown in Figures 2 and 3, which will be permanently installed in a chemical fume hood, and separate, portable sample chambers which will be evacuated, filled with the required organometallic compound, and carried to the laser for the photodecomposition experiments. A schematic of one of the sample chambers is shown in Figure 4. Separate sample chambers will be used for each different compound, thus reducing the risk of contamination. The gas-fill station is fitted with a heater assembly to enable it to be baked out and thoroughly degassed. The sample chamber will also have heating tape wrapped around it. Figure 5 shows a schematic of the experimental set-up for gas-phase photolysis. Over the next quarter extensive experiments will be carried out using this system to deposit some of the metals from the organometallic compounds listed in Table 2.

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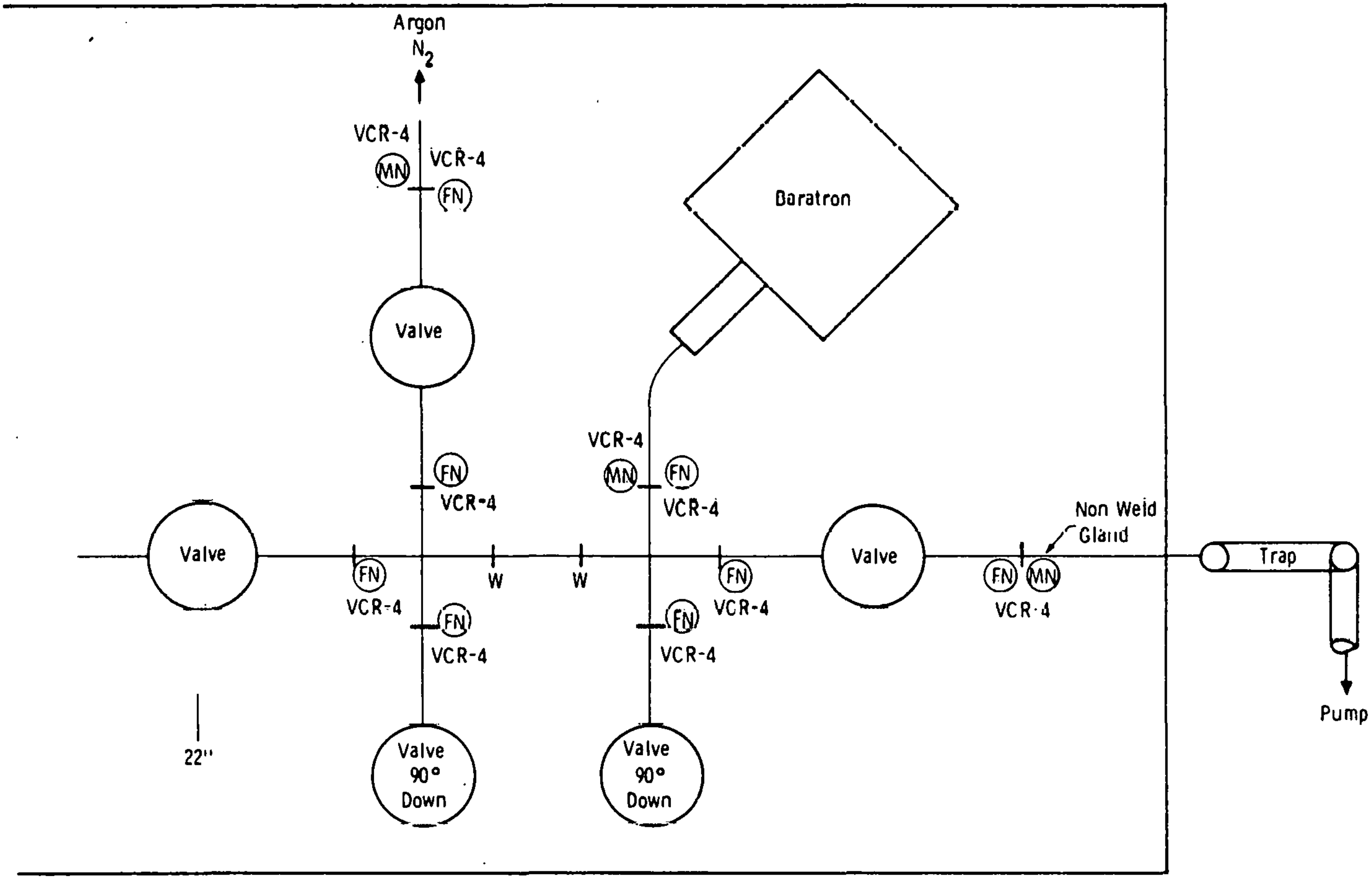

Figure 2. Top view of gas-fill and pumping station.

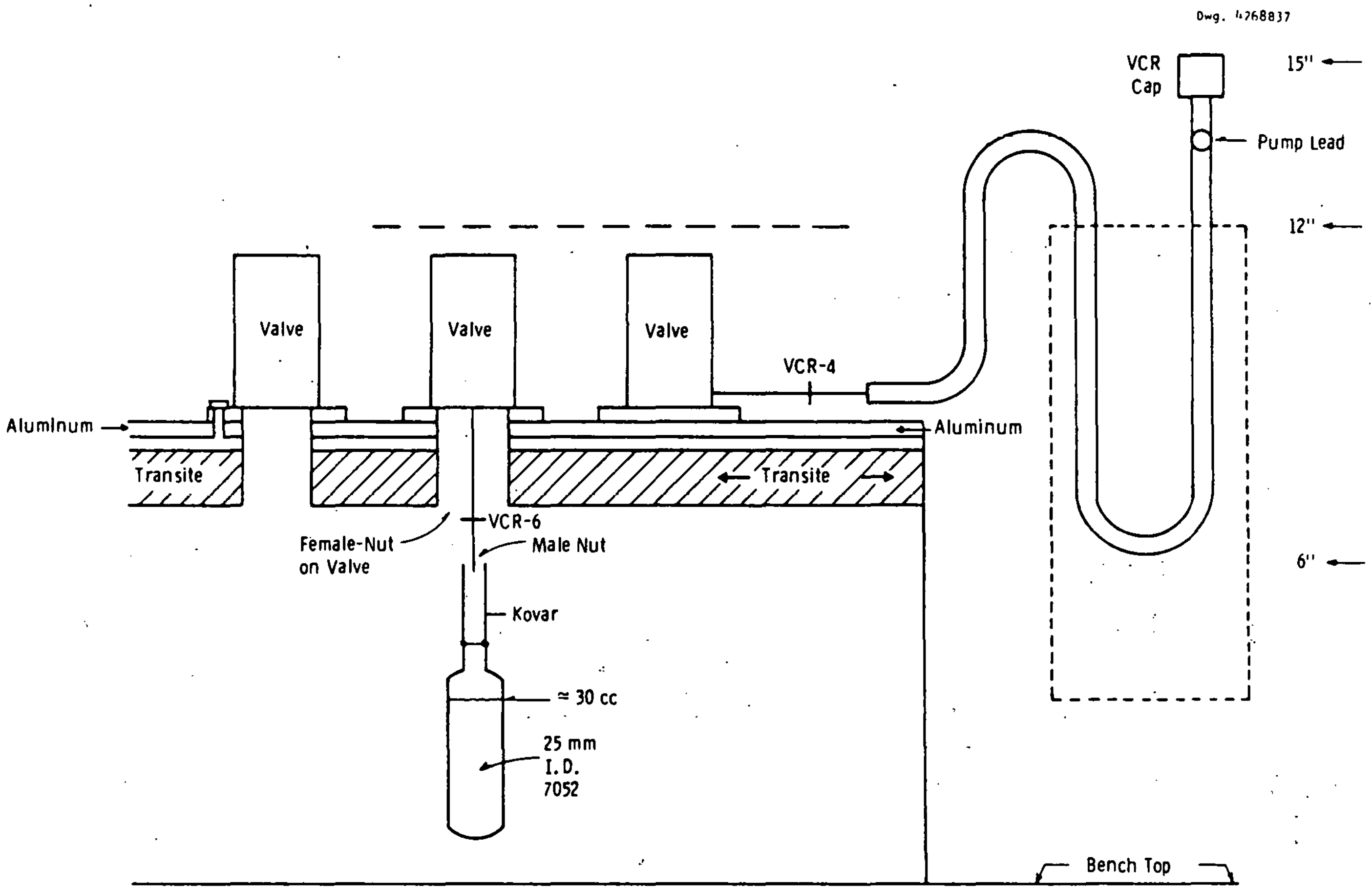

Figure 3. Cross section of gas-fill and pumping station.

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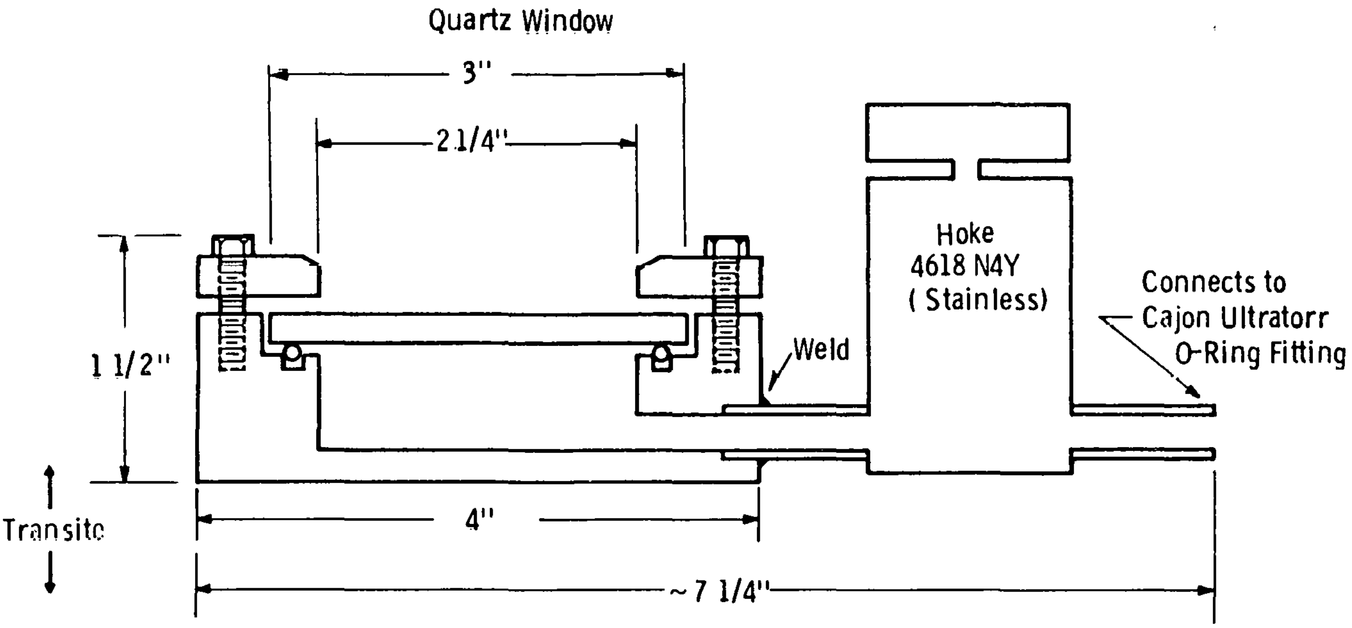

Figure 4. Schematic of sample chamber.

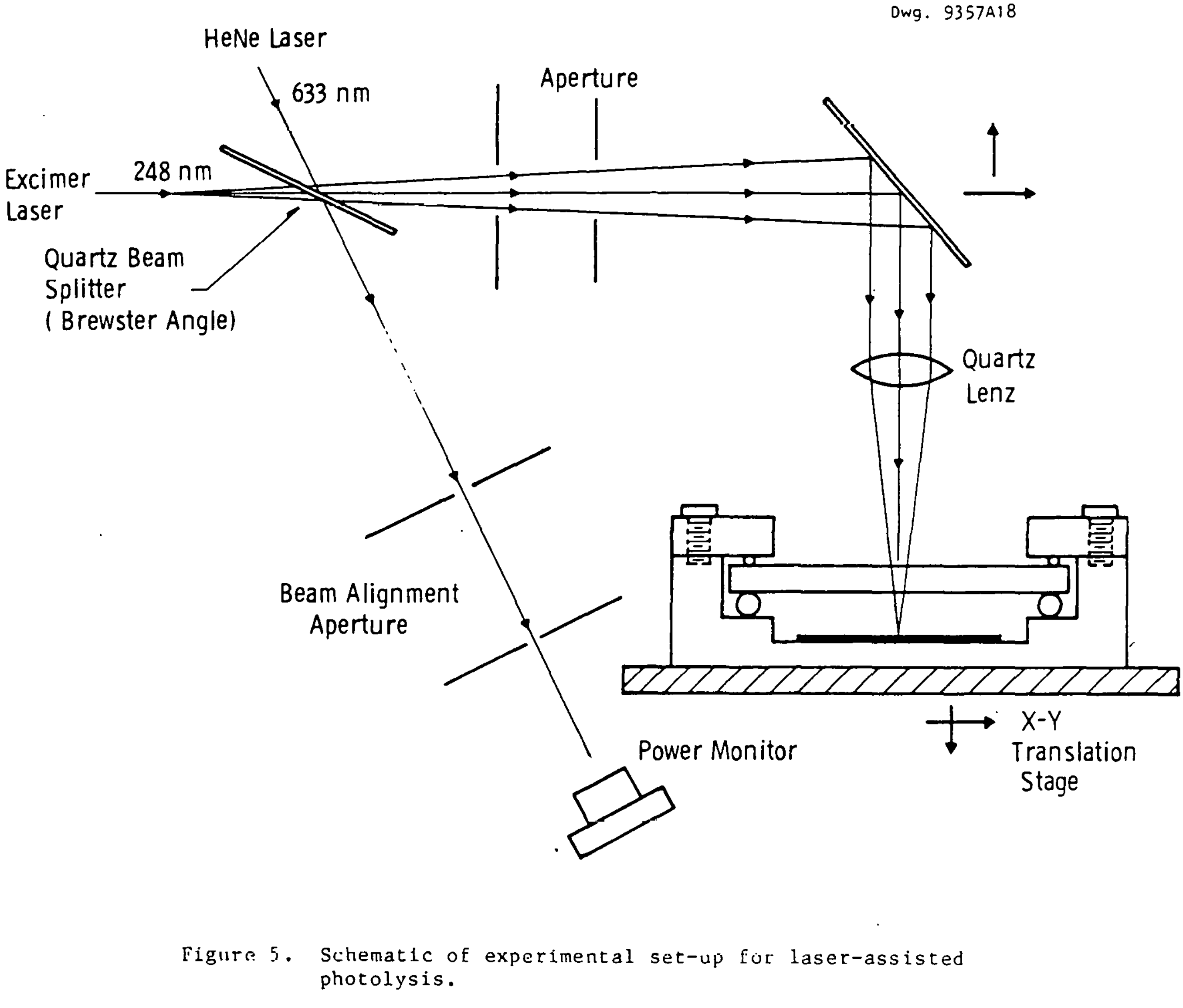

Figure 5. Schematic of experimental set-up for laser-assisted photolysis.

Table 2

Sources of Useful Metals for Photovoltaic Applications

Metal	Source	Properties
Chromium	$Cr\ (CO)_6$	Crystalline; m.p. 110° decomposes; density 1.77
Molybdenum	$Mo\ (CO)_6$	Crystalline; m.p. 150° decomposes; b.p. 156.4/766 mm; density 1.96
Nickel	$Ni\ (CO)_4$	liquid; air-sensitive; m.p. - 25°; b.p. 43°; density 1.32
Tin	$(CH_3)_4\ Sn$	liquid; m.p. - 54.8°; b.p. 78°; density 1.3149
Titanium	$Ti\ [N(CH_3)_2]_4$	liquid; moisture-sensitive; b.p. 50°/0.05 nm; vap. press. 8 mm/80°C
Tungsten	$W\ (CO)_6$	crystalline; m.p. approx. 150° decomposes; b.p. 175/766 mm; density 2.65

1.3 Summary of Laser-Enhanced Electroplating Results

Experiments on laser-enhanced electroplating were carried out using a focused argon-ion laser, x-y scanning mirrors, a copper plating solution, and silicon wafers coated with evaporated titanium-palladium layers. Details of the experiment are presented in Section 1.3.1. The laser power, focussed spot size, plating current, and volume of electrolyte were all varied to determine the finest line that could be plated. The plated spots and lines were characterized by Nomarski microscopy and Talystep profiling. A 1 cm-long, dense, uniform line, 25 μm wide and 6000 Å thick, was plated using a mirror scan rate of 25 cm/sec, a total exposure time of 25 sec, a laser power of 4 W, and a negative plating current of 1 mA. A dramatically high plating rate of 12 μm/sec was achieved using this technique.

1.3.1 Experimental Details

Details of the experiments on laser-enhanced electroplating and a summary of the data obtained are presented in this section.

The electrolyte used was a copper plating solution of the following composition: 37.4 g. $CuSO_4 \cdot 5H_2O$ and 4.2 ml. H_2SO_4 in 200 ml. de-ionized water. Electroplating was carried out on 2-inch silicon wafers coated with thin films of evaporated metal -- 1000 Å titanium, 1000 Å palladium, and a two-layer system of palladium on titanium, each 1000 Å thick. Plating was observed to occur only on the two-metal system -- the titanium alone could not be plated upon, and the palladium alone did not adhere to the silicon surface. An insulated wire was attached to each wafer surface with silver epoxy, allowing the wafer to be used as the cathode of the electrolytic cell. A copper strip was used as the anode. The wafer was placed flat in a shallow dish containing the electrolyte. A multimode argon-ion laser was focussed to a 30 μm spot onto the wafer surface. The laser spot could be scanned across the wafer by x-y mirrors.

Careful experiments were carried out to determine the factors affecting the size of the plated region. Plating current, laser power, focal distance, and level of electrolyte were all varied to determine the effect of each on the plated spot size. Using ac bias caused the plated spots to deplate with time, so negative bias was used. At higher laser powers, the electrolyte would start boiling, thus broadening the plated spot. The size of the spot was also found to be proportional to the plating current and the volume of electrolyte. The dependence on focal distance was weak at higher laser powers and plating currents, but became much sharper when the laser power and plating current were reduced to minimal values.

The smallest spot plated with a total laser exposure time of 5 sec was 80 μm, as shown in Figure 6. The laser power used was 4 W and the plating current applied was 1 mA.

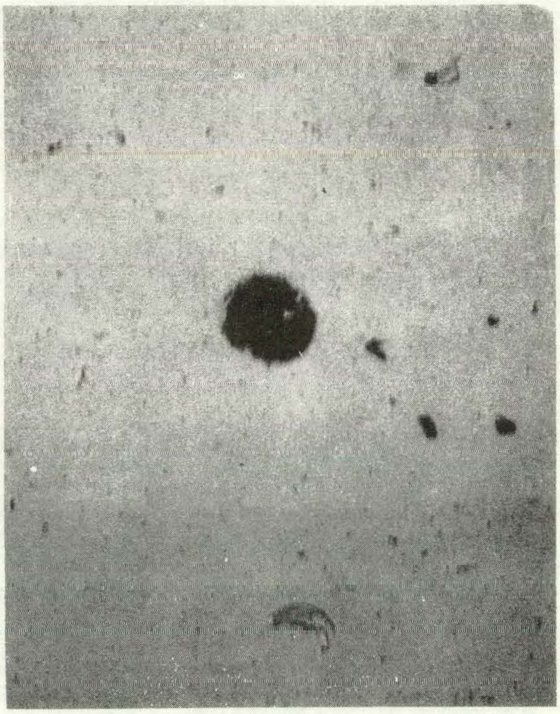

Figure 6. 150X Nomarski micrograph of line plated using single slow scan.

Using the x and y scanning mirrors, plated lines were written. In one experiment, one of the mirrors was scanned a single time over 1 cm, the scan period being 25 sec. The laser power and plating current were 4 W and 1 mA, respectively. The plated line was somewhat uneven, varying in width from 40-60 μm, as shown in Figure 7, with a thickness of approximately 3000 Å, as determined by Talystep profiling.

The finest and densest line was plated using a rapid scan rate of 25 cm/sec over a total exposure time of 20 sec. A laser power of 4 W and a plating current of 2 mA were used. The 1 cm-long plated line was 25 μm wide, 6000 Å thick, and very even along its entire length, as shown in Figure 8. A plating rate as high as 12 μm/sec was achieved with this line.

The laser-enhanced electroplating experiments have yielded exciting results. If time permits, it would be interesting to pursue further experiments along these lines using a silver plating solution.

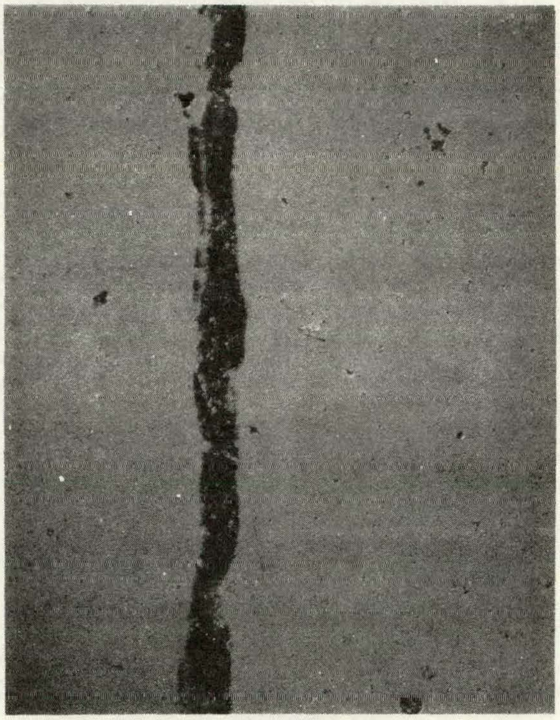

Figure 7. 100X Nomarski micrograph of line plated using single slow scan.

Figure 8. 200X Nomarski micrograph of line plated using multiple rapid scans.

2. CONCLUSIONS AND RECOMMENDATIONS

The literature survey of the current state-of-the-art laser metallization schemes indicates that the excellent surface adhesion, the quality of the metal deposited, the cleanliness of the system, the ability to direct-write a metal pattern, and the fine-line resolution obtained make such systems particularly attractive for solar cell metallization. Another advantage of laser-assisted metallization for photovoltaic applications is the in-situ, localized sintering that takes place, shallow junction degradation being avoided because of the very short laser wavelengths used. The major drawback to laser-assisted pyrolytic and photolytic metal deposition from gas-phase compounds may be the relatively slow deposition rates. A detailed evaluation of the economics of the direct-write versus the mask/flood illumination techniques will be made, and the experiments on gas-phase photolysis carried out in the next quarter will be used to refine the preliminary evaluation. In the meantime, it appears that laser-assisted deposition from the liquid phase may be particularly promising because of the much higher deposition rates expected. Experiments using a laser to thermally decompose spin-on metal-bearing polymer films and metallo-organic inks are planned for the next quarter.

The promising results of the laser-enhanced electroplating experiments have opened up yet another possibility. The initial diffusion barrier layers may be deposited over the entire wafer by flood illumination-enhanced photolysis, with subsequent laser-assisted electroplating being used for pattern definition. This technique would have the advantage of having the entire silicon surface protected by the diffusion barrier during electro-plating, the unplated regions being etched away later.

3. PROJECTION OF ACTIVITIES FOR SECOND QUARTER

A preliminary evaluation of the economics of the laser metallization schemes under study will be made. Extensive experiments on metal deposition by excimer laser-assisted photolysis of gas-phase organometallic compounds will be carried out using the system described in Section 1.2. The direct-write and mask/flood illumination techniques for patterning will be compared. Laser-assisted pyrolytic decomposition of liquids will be studied. Metallo-organic silver inks and spin-on metal-bearing polymer films will be used for these experiments. If time permits, the laser-enhanced electroplating experiments may be continued using silver plating solutions.

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