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OPTIMIZATION OF TRANSPARENT ELECTRODE FOR SOLAR CELLS

Technical Progress Report

for Period

15 September, 1980 to 15 December, 1980

Work Performed Under Contract SERI-XS-Ø-9318-1

by

AC02-77CH00178

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OPTIMIZATION OF TRANSPARENT ELECTRODE FOR SOLAR CELLS

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Solar cells usually need a surface layer which simultaneously transmits almost all of the incident sunlight, and also conducts electricity very well. Such layers, called transparent electrodes, must also be strong, stable to weathering and sunlight, inexpensive, non-toxic, non-polluting, and composed of sufficiently abundant materials. This long list of requirements is best met by a film of fluorine-doped tin oxide made by a new process. The current research has as its goal further improvements in the properties of this transparent electrode material. The first phase of the work is seeking to find out what mechanisms now limit the transparency and electrical conductivity of this material. It is suspected that certain chemical impurities, and also mechanical imperfections at boundaries between small grains in the films, may have deleterious effects. The second phase of the work will attempt to minimize those deleterious factors which are identified in the first phase. Then all the other experimental factors will be varied systematically to obtain the most transparent and electrically conductive films possible. Finally, some samples of optimal films will be made, under the best conditions obtained.

During the first quarter, the test equipment and chemicals were acquired. The primary electrical measurement needed is the sheet resistance, and a Veeco 4-point instrument serves this purpose. For the determination of film thickness, an ellipsometer (Rudolph model El-2) was purchased. Both of these instruments have been delivered and tested on sample tin oxide films. For the optical transmission and absorption measurements, weighted according to a solar input spectrum and a solar cell detector, a commercial silicon solar cell was connected to a digital ammeter through a suitable load resistor. When placed in sunlight, readings taken with and without a tin oxide-coated glass plate, provide suitably weighted transmission measurements. This setup must be modified to provide reflection readings also, so that true absorption loss can be calculated.

Initial samples were prepared on glass and on single-crystal silicon substrates. Auger analysis shows the expected tin, oxygen and fluorine contents, and, in addition, sodium, in the samples prepared on glass substrates. The samples on silicon show significantly lower resistances, and no detectable sodium. This data suggests that sodium diffusion from the glass into the film, is contributing additional electron scattering, and increasing the resistance of the films on glass substrates. Increasing deposition temperature appears to increase crystallite size, and lower sheet resistance. This tendency might be due to reduced scattering at grain boundaries, or to increased crystallite perfection, or to a combination of these physical factors.

STATEMENT OF WORK

1. Prepare samples of tin oxide on substrates of low-cost glass, pyrex, quartz, single crystal silicon, and metals by chemical vapor deposition of the proposed reactant gas mixture. In particular, samples of tin oxide on low-cost soda lime glass will be emphasized.
2. Perform measurements on the material in order to determine what limits the optical transparency and electrical conductivity. Impurities in the starting materials, gas mixture and tin oxide film will be measured. The effects of polycrystalline grain boundaries will be examined. The electron mobility on dopant concentration will be measured. The question of impurity migration from the substrate to the tin oxide film will be evaluated.
3. Vary systemically the relevant experimental factors to optimize the deposition conditions for obtaining the most transparent and electrically conducting material. The effects of temperature of deposition on the performance of the material will be evaluated.

MILESTONES

1. Purchase equipment, gases and chemicals and install, test and calibrate equipment by end of first quarter - completed.
2. Prepare gas mixtures and initial samples and measure electrical and optical properties along with mobility on initial samples by end of second quarter - initial samples prepared, properties being measured.
3. The effects of impurities and polycrystalline grain boundaries on electrical and optical properties to be determined by end of third quarter.
4. By the end of the fourth quarter, samples of tin oxide to be prepared having a sheet resistance of less than one ohm per square along with a total solar absorption of less than four percent.

DELIVERABLES

Deliver to SERI/PVPO in a timely fashion the following:

- A. Four samples of at least 3 cm² area typical of the material being investigated by the end of the second quarter.
- B. Four samples of at least 3 cm² area, typical of the optimized material being investigated by the end of the 10th month.
- C. By the end of the fourth quarter, the Subcontractor shall deposit the best quality tin oxide on substrates and/or solar cells furnished by the technical monitor at SERI. Measurements on material and/or device properties will be for SERI internal use only. It will be previously determined as to the compatibility of the furnished substrates and/or cells with the appropriate fabrication approach. The number of such deposits shall be of a reasonable number determined by mutual agreement between the Subcontractor and the SERI technical monitor, but in no case shall it be less than six (6), 1 cm² samples.

TYPICAL DEPOSITION CONDITIONS

INPUT GAS MIXTURE: (IN MOLE PER CENT)

1% TETRAMETHYL TIN (CH_3)₄Sn

3% BROMOTRIFLUOROMETHANE CF_3Br

96% DRY AIR

SURFACE TEMPERATURE: 500 TO 600°C

REACTION TIME:

USUALLY LESS THAN ONE MINUTE;

INCREASES LINEARLY WITH DESIRED THICKNESS;

DECREASES WITH INCREASING TEMPERATURE

FLOW RATE: A FEW LITERS/MINUTE,

FOR A 10 cm x 10 cm SAMPLE;

INCREASES WITH INCREASING TEMPERATURE

COATED AREA: 10 cm BY 10 cm

UNIFORMITY: $\pm 10\%$ OVER CENTRAL

AREA OF ABOUT 8 cm x 8 cm

TYPICAL FILM PROPERTIES

SHEET RESISTANCE FOR A FILM 1 MICRON THICK:

- 1 $\Omega/\square$ ON SINGLE CRYSTAL SILICON
- 2 $\Omega/\square$ ON PYREX GLASS
- 4 $\Omega/\square$ ON SODA-LIME (WINDOW) GLASS

ELECTRON MOBILITY:

50 TO 70 $\text{cm}^2/\text{VOLT-SEC}$

ELECTRON CONCENTRATION:

ADJUSTABLE FROM 10^{20} TO 10^{21} cm^{-3}

INFRARED REFLECTIVITY AT 10 MICRON WAVELENGTH:

UP TO 90%

REFRACTIVE INDEX: 1.9 TO 2.0

VISIBLE ABSORPTION LOSS:

VARIABLES WITH THICKNESS AND DOPING LEVEL;

MORE MEASUREMENTS AND EQUIPMENT ARE NEEDED

**SUMMARY OF MECHANISMS WHICH COULD LIMIT
THE ELECTRON MOBILITY:**

- 1. ELECTRON-PHONON SCATTERING**
- 2. ELECTRON SCATTERING FROM THE FILM SURFACES**
- 3. SCATTERING BY DOPANT (FLUORINE)**
- 4. SCATTERING BY OTHER CHEMICAL IMPURITIES**
- 5. POINT OR LINE DEFECTS WITHIN CRYSTALLITES
(VACANCIES, INTERSTITIALS, DISLOCATIONS)**
- 6. CRYSTALLITE GRAIN BOUNDARIES**

1) Electron-phonon scattering is the only "intrinsic" mechanism remaining in a pure single-crystal of tin oxide. The best single-crystal mobility values reported for tin oxide are about four (4) times larger than those of the films. Thus, electron-phonon scattering might account for about one fourth of the observed scattering in the films. However, this comparison is of dubious significance, since the electron concentration of the films is so much higher than that of the single crystals..

2) Electron scattering from the film surfaces can reduce the effective mobility of electrons in thin films. We have estimated this surface effect using a theory developed originally for thin metal films. For tin oxide films of approximately 1 micron thickness, the surface scattering effect appears to be negligible.

3) Scattering by the fluorine dopant is expected to become important at higher doping levels. This may be the mechanism which causes the mobility to decrease when the doping level exceeds about 2%, as noted in the data shown in slide 6.

4) Scattering from other impurities, which may be introduced with the reactant gases, or which may diffuse from the substrate. The purest commercially available starting materials have analyses as follows:

From ALFA-Ventron:

tetramethyltin (high purity)		99.5%
organic solvents (ethers and hydrocarbons)		0.5%
germanium		5 ppm
boron		1 ppm
aluminum		1 ppm
other elements		not detected

From DuPont:

bromotrifluoromethane	CF_3Br	99.6%
chlorotrifluoromethane	CF_3Cl	0.25%
dibromodifluoromethane	CF_2Br_2	0.007%
bromodifluoromethane	CF_2BrH	0.004%

We estimate that impurities introduced from these reactants should have negligible effects on the mobility.

Impurities, such as sodium and other alkali metals, diffusing from the glass substrates, may have a more significant effect on the mobility. The observed tendency of film resistance to increase with alkali content of the substrate, tends to indicate an alkali impurity effect. Auger analysis of films on glass shows some sodium content, varying in the range of one per cent, also lending support to the alkali effect.

Electron scattering from 5) crystal defects or 6) grain boundaries. At present, we have little direct quantitative evidence for the effect of these physical imperfections on electron mobility. However, there appears to be a trend toward increased mobility at higher deposition temperatures, and this provides some indirect evidence for scattering from physical defects. It is known that higher deposition temperatures produce larger crystallites, and hence fewer grain boundaries. One can also expect that the crystallites have fewer internal defects when they are deposited at higher temperatures, since surface diffusion is faster, and fewer atoms are presumably trapped at inappropriate sites. With glass substrates, the available temperature range is limited by the softening of the glass to below about 600°C, but with silicon or sapphire substrates, a wider temperature range could be explored.

Crystallite size has been explored in a very preliminary way, by taking SEM pictures of the film surfaces, and of cross sections obtained by fracture. These show a typically polycrystalline upper surface, and a dense film structure with some evidence of columnar growth. Probably the crystallite size increases through the film thickness; such variation would complicate the quantitative determination of crystallite size by the SEM method.