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CUPROUS OXIDE PHOTOVOLTAIC CELLS

Third Quarterly Technical Progress Report, October 9, 1979—January 8, 1980

By
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CUPROUS OXIDE PHOTOVOLTAIC CELLS

Third Quarterly Technical Progress Report
for Period of October 9, 1979 to January 8, 1980

to the Department of Energy
SERI Photovoltaics Program Office
Emerging Materials Systems for Solar Cell Applications

Contract No. DE-AC04-79-ET23010

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I. INTRODUCTION

Previous work in this laboratory on cuprous oxide Schottky barrier photovoltaic cells showed that some potential improvements were limited by chemical degradations at the junction (1), e.g. in Al/Cu₂O cells, the aluminum reduced the surface of the Cu₂O to metallic Cu. The present project is being devoted to a study of methods to avoid this problem and also to the development of other methods of improving the efficiency of Cu₂O cells.

The first quarterly report was devoted to a study of thin oxide interlayers between the metal and the Cu₂O which gives MIS structures. The most stable interlayers were obtained with SiO₂. The second quarterly report covered some initial work on heterojunctions with other oxides on Cu₂O. The most stable heterojunctions were obtained with CdO on Cu₂O.

The present report presents some results on Auger studies of the oxide heterojunctions, the preparation of doped Cu₂O by introduction of impurities in the starting copper, the exploration of several methods for the study of diffusion length, and some initial attempts on the laser annealing of Cu₂O.

II. ANALYSIS OF HETEROJUNCTIONS BY AUGER METHODS

The previous work on heterojunctions on Cu₂O revealed the frequent presence of chemical reactions at the interface which lead to a deterioration of the photovoltaic properties of the cells. This occurred even with oxides that had been assumed to be relatively stable such as SnO₂, In₂O₃ and even Al₂O₃. However by varying the conditions of the deposition, it was found possible to diminish and even avoid the chemical reactions at the junction, e.g. in CdO/Cu₂O cells. The important criterion for detecting the presence

or absence of the chemical reactions in the detection of Cu(0) at the junction, and the technique which we have developed for this is high resolution Auger or ESCA spectroscopy.

Our earlier work in detecting the chemically formed Cu(0) in Schottky barriers, e.g. in Al/Cu₂O cells, was done with high resolution ESCA spectroscopy. This was a relatively slow procedure because the analysis had to be done point by point since it was necessary to pump down repeatedly in between each sputter etch and the ESCA scan. For the present work on heterojunctions some details of the Auger spectrum were explored since the Auger scans can be made continuously during the sputter etching.

Two Cu peaks were studied, one at low energies and one at high energies. These were done on Cu/Cu₂O junctions in order to calibrate the method. The samples were sputter etched with argon and the sputter depth was calibrated with a Ta₂O₅ standard. The profile of a Cu/Cu₂O junction used as a standard is shown in Fig. 1. The junction is located between 5 and 10 nm. This was used as a standard to measure two Cu peaks as a function of sputter depth. One peak is at low energies, the Cu MVV peak at ~57 eV, and the other is at high energies, the Cu LMM peak at ~909 eV. Several high resolution scans are shown in Figs. 2 and 3.

The low energy peak, Cu MVV, shown in Fig. 2 reveals a distinct change as sputter depth is varied. At low depths, 1.4 nm, where the surface is Cu(0) there is a characteristic deviation in the differential scan at ~58 eV. At greater depths, 16 nm, where the material becomes Cu₂O, the peak gives a smooth scan without the deviation observed in the Cu(0) region. Similar scans of the high energy peak, Cu LMM at ~909 eV, is shown for increasing sputter

Figure 1. Auger Composition Profile from a Cu/Cu₂O Junction

Figure 2. Differential Scans of a Cu MVV Auger Peak at Various Sputter Etch Depths on a Cu/Cu₂O Junction

Figure 3. Differential Scans of a Cu LMM Auger Peak at Various Sputter Etch Depths on a Cu/Cu₂O Junction

depths in Fig. 3. While there is some change in shape from 1.4 to 16 nm, the change is less pronounced than in the case of the low energy peak. Thus the low energy peak is more suitable for detecting the presence of Cu(0) at the junction.

Therefore it is possible to sputter etch the various junctions and to monitor the peaks of interest continuously. The data can be stored in a computer and recalled for detailed examination and quantitative evaluation. Fig. 4 shows detailed scans of a CdO/Cu₂O junction and of a CdO·XSnO₂/Cu₂O junction. As judged by the characteristic deviation at ~58 eV, which indicates the presence of Cu(0), the CdO·XSnO₂/Cu₂O junction shows very distinctly the presence of Cu(0) while the CdO/Cu₂O junction is relatively free of Cu(0). The data can be tested by comparison with the reference curves from the Cu/Cu₂O junctions as in Fig. 2, to give the amounts of the various species. An example of the results is shown in Fig. 5. In the case of the CdO·XSnO₂/Cu₂O structure, a large amount of Cu(0) is present at the junction. This of course arises from the chemical reactions at the junction. As shown in Fig. 5, in the case of the CdO/Cu₂O, a small amount of Cu(0) may also be present. It is not certain yet whether this low amount is a real indication of the presence of Cu(0) or whether it may be an artifact due to limitations of the method at the present stage of development.

III. DOPING AND EFFECT OF IMPURITIES IN Cu₂O

A. Background

The purpose of this phase of the research is to study the effect of impurities in Cu₂O mainly to obtain an improvement in the properties by addition

Figure 4. Differential Scans of the Cu MVV Peak on a Cd/Cu₂O and a CdO·xSnO₂/Cu₂O junction

Figure 5. Composition Profiles for (A) a CdO/Cu₂O Junction and (B) a CdO·xSnO₂/Cu₂O Junction

of suitable dopants but also to identify harmful impurities which might degrade the properties of the cells. At present the bulk properties of Cu_2O , e.g. the conductivity, are primarily determined by a departure from stoichiometry which is adjusted by a properly chosen heat treatment, i.e. annealing at 500°C after oxidation at 1000°C . This is of limited value, since the lowest resistivities obtained by this procedure are $100 - 200 \Omega\cdot\text{cm}$. Also the character of the junction may very well be affected by the impurities that are left at the surface after the etching procedure.

In the normal procedures of making cells, we have experienced considerable variability in the photovoltaic properties of the cells. While this may be due to some variations in the processing, one plausible source of the problems could be the starting copper material. The earlier work was done with commercial OFE (oxygen-free electronic) grade Cu (99.95+% Cu), which gave good results. Recent lots of OFE grade material have not given as good results. Also higher purity grades of Cu such as ASARCO (99.999+% Cu), MARZ (99.999+% Cu) and Gallard-Schlesinger (99.9999+% Cu) do not give as good results as the earlier OFE lots but better than the recent OFE lots of Cu.

Still another reason for introducing impurities into the source Cu is that it might be possible to prepare thin films of Cu_2O on Cu by partial oxidation of Cu sheet in such a way as to make the back wall $\text{Cu}_2\text{O}/\text{Cu}$ junction ohmic. A suitable photovoltaic top contact would then be applied to prepare a front wall cell as we have already demonstrated. The advantage of the partial oxidation procedure with the ohmic back contact is that the processing time could be considerably shortened and the cell resistance could be reduced. The underlying copper then would be a relatively cheap supporting material as well as serving as a back contact.

In addition to the advantages mentioned above, the addition of beneficial dopants may allow a modification of the annealing procedures in order to reduce the concentration of defect species, which could result in improved properties such as increased lifetime and diffusion length of the minority carriers.

The method chosen for the current work is to add the impurities to the starting Cu rather than to dope the Cu_2O as previously investigated. This offers the advantages of simpler and more rapid processing, especially for the thin film configuration obtained by partial oxidation of the Cu. There are some potential disadvantages such as possible non-uniform distributions of the impurities in the Cu and in the Cu_2O , but these may not be serious problems for the concentration levels contemplated and in fact may be beneficial for certain purposes.

While work of this kind has not been attempted before for these purposes, there have been some related researches that can give some guide to the experiments. Recently Forman (2) has doped Cu_2O by diffusion into Cu_2O in a closed container and he has shown, of a variety of dopants tried, that Cd (as CdF_2) especially can lower the resistivity of Cu_2O . However we have found that Cd-doped Cu_2O does not give better cells.

There are some earlier reports on the effect of impurities in the starting Cu on the properties of Cu_2O rectifiers, especially by a Japanese group (3). Also Hassler, et al (4) found that Se and Te were especially harmful to the rectifier properties and that Sb was useful in increasing the reverse breakdown voltage.

Some useful information is available from the extensive literature on the oxidation of Cu (5). This work was done partly to test theories of oxidation

mechanisms and partly for the development of Cu alloys for corrosion resistance in air at high temperatures(6).

According to the Wagner mechanism of oxidation (7), the oxidation of copper at high temperatures takes place by movement of copper ions from the metal-Cu₂O interface through the Cu₂O by means of copper atom vacancies to the Cu₂O-oxygen interface where the Cu atoms join the oxygen to produce more Cu₂O. An equivalent view is that excess oxygen taken up at the Cu₂O-oxygen interface generates Cu atom vacancies at the surface and that the vacancies are driven by a concentration gradient of vacancies to the Cu-Cu₂O interface. The gradient and therefore the flux of vacancies and growth of the oxide film are inversely proportional to the thickness of the oxide so that $dW/dt = k_p/W$. This yields the parabolic growth law

$$W^2 = k_p t + C$$

At lower temperatures and for nucleation and thin film growth, other mechanisms and rate laws apply.

Simple extensions of the Wagner theory predict that doping with higher valent metals, e.g. Al³⁺ or Cr³⁺, should increase the vacancy concentration and increase the oxidation rate. This has been found in the case of the oxidation of nickel as well as a decrease in rate due to Li⁺ additions. However many complexities can occur.

Most of the Cu alloys that have been studied contained 1% or more of the other metal so that the formation of other oxide phases was frequently observed. In some cases, the foreign metal oxide was formed just at the surface and became protective against the oxidation of Cu. In other cases, the other oxide could exist as inclusions in the Cu₂O. Sometimes the other oxide was found

as a layer under the Cu_2O . Even under conditions such that the Cu was not oxidized, the alloy constituents could be oxidized within the Cu by internal oxidation (8), i.e. by diffusion of oxygen into the metal and selective reaction. It is likely that these complications which occur at higher alloy concentrations will be less likely to intrude at the concentrations suitable for doping levels. But it will be necessary to watch for the possibility of non-uniform distributions of the foreign metal.

Predictions of which elements could be effective dopants will be difficult since Cu_2O is a partly compensated semiconductor (9) in which both the acceptors and donors, which may be copper and oxygen vacancies, respectively, can vary in concentration depending upon the preparation conditions and the equilibria which are not yet well understood (10). The additions can be expected to compete and interact with these equilibria.

From the rectifier literature it is known that the quality of the Cu_2O rectifiers depended greatly on the source Cu. Cu from Chilean mines was considered necessary for good rectifiers (11), but testing was done on each batch of Cu by making sample rectifiers. Impurities that are commonly found in Cu are Ag, Si, Mg, Fe, Al, Ni, and S. Also Se and Te, which occur with S in copper sulfide ores, may not be completely removed in the electrorefining procedure. These are impurities that may have to be removed from the starting Cu. Possible beneficial additions may include Cd, Zn, Mg, Sb, Tl, the halogens, etc.

B. Experimental Methods

The general method adopted here for the preparation of Cu containing added impurities is to melt the Cu in the presence of the added material, allow the melt to run into a mold and solidify into a bar. The cast bar is subsequently rolled into a thin sheet.

Materials. The Cu used as a starting material in the first experiments is an ASARCO high purity grade Cu (99.999+% Cu) obtained from the ASARCO Metal Byproducts Division. The added impurities are usually reagent grade material or other best grade available.

The graphite used for the crucibles and the molds is Union Carbide UCAR brand graphite, grade ECL.

Apparatus. Each graphite crucible is machined from $1\frac{1}{4}$ " rod (32 mm diameter) which is cut to a 100 mm length, with a smaller diameter extension to fit into a hole in the pedestal. A hole 22 mm in diameter is drilled into most of the length of the rod. Into this is placed a close-fitting graphite insert, 64 mm long. A groove is machined into the insert, measuring $4.5 \times 15 \times 60 \text{ mm}^3$. This leaves a head room of 29 mm at the top of the crucible.

The crucible is placed on a graphite pedestal which is fastened to a water-cooled brass base. The crucible is surrounded by a 51 mm Vycor tube fitted with a flange that can be closed on the base with an O-ring seal. A tube at the top allows attachment to a vacuum system. A mechanical pump is used for evacuation and the pressure is measured with a thermocouple gauge. The heating is done by induction heating using a 10-turn water-cooled copper-tubing coil surrounding the Vycor tube and extending the length of the crucible. The power is provided by a 20 KW Thermonic 1070 induction heater controlled by custom made magnetic amplifier controller.

Procedure. The ASARCO 3/4" Cu rod (19 mm diameter) is cut into a 12 mm length. A small central hole is drilled half-way down into the rod. The machined slug is cleaned by etching in 4M HNO_3 and is washed with double-distilled water and dried. A weighed amount of the impurity addition is placed in the hole and the hole is closed with a plug made of the ASARCO Cu. The Cu slug weighs 35-40g and is calculated to fill the grooved cavity which serves as the mold.

The Cu slug is placed in the head space of the crucible. The system is sealed and is pumped down to the limit of the mechanical pump 60 mTorr. Power is applied from the induction heater at a rate predetermined to achieve melting of the copper. The graphite crucible begins to glow in about 3 min and the copper begins to melt after about 8 min. The melting proceeds rapidly and the molten Cu runs down into the cavity. The heating is continued for about another 2 minutes, and then the power is cut off completely.

The pumping is continued until the crucible is cool enough to handle, which requires about 15 minutes. The system is then opened, the crucible is removed and the insert is taken out. If this is done while the graphite is still somewhat warm, the cast Cu bar slips out easily. The Cu bar at this stage may be somewhat darkened by films from the added material or from some pickup of the graphite. A brief etch in 4M HNO_3 produces a bright Cu surface and often reveals very large crystals in the cast bar.

The bar is then rolled through hardened steel rolls by a series of gentle reductions to a final thickness of 0.6 mm, and this gives a strip ~ 40 cm long by ~ 17 mm wide.

C. Results

The initial experiments were done with additions of Se and Si in amounts of 0.01% to 0.05%. These were added usually to the ASARCO high purity (99.999%) Cu as described above. Usually a new crucible and insert were used for each run to avoid cross-contamination. Sometimes it was possible to re-use a crucible for a higher concentration of the same impurity.

1. ASARCO Cu with 0.01% Se: The Se was added as the element. Samples from the rolled sheet were oxidized at 1000°C and then were subjected to grain growth at 1100°C. The first samples were not further annealed. The resistivity values ranged from 8.7×10^3 to $3.7 \times 10^4 \Omega \cdot \text{cm}$. The best Cu/Cu₂O cell obtained from this material gave $V_{OC} = 0.20 \text{ V}$ and $J_{SC} = 0.68 \text{ mA/cm}^2$. Annealing of some of the grain growth samples at 500°C gave resistivities as low as $123 \Omega \cdot \text{cm}$, but gave no improvement in cell characteristics.

2. ASARCO Cu with 0.01% Si: The samples after oxidation were subjected to grain growth at 1100°C. The resistivity values were of the order of $3.0 \times 10^4 \Omega \cdot \text{cm}$. The best Cu/Cu₂O cell gave $V_{OC} = 0.23 \text{ V}$ and $J_{SC} = 0.75 \text{ mA/cm}^2$. Annealing at 500°C reduced the resistivity but did not improve the cell characteristics.

3. ASARCO Cu with 0.05% Si: The samples after oxidation and grain growth gave resistivities of 1.5×10^4 to $3.9 \times 10^4 \Omega \cdot \text{cm}$. The best cell had $V_{OC} = 0.20 \text{ V}$ and $J_{SC} = 0.55 \text{ mA/cm}^2$.

However, if similar samples were simply oxidized at 1000°C and if the samples were not subjected to the grain growth at 1100°C and also were not annealed at 500°C, much lower resistivities were obtained and better photovoltaic characteristics were also observed. The results are compared in Tables IA and IB.

While these results are preliminary, it appears that Si at the 0.05% level may be useful as an addition to Cu before oxidation. However, the results depend strongly on the treatment procedures. While one could speculate on the meaning of these results, it probably would be advisable to withhold judgement

until further studies are made, e.g. microprobe analyses of the distribution of the impurity.

Table IA

Solar Cells Made from Copper Doped with 0.05% Si

Samples were Oxidized at 1000°C and Subjected to Grain Growth at 1100°C

Sample	$\rho(\Omega \cdot \text{cm})$	$J_{SC}(\text{mA}/\text{cm}^2)$	$V_{OC}(\text{Volt})$
1	1.52×10^4	0.35	0.09
2	2.08×10^4	0.55	0.20
3	3.9×10^4	0.20	0.125

Table IB

Solar Cells Made from Copper Doped with 0.05% Si

Samples Were Oxidized at 1000°C and Were Not Subjected to Grain Growth

Sample	$\rho(\Omega \cdot \text{cm})$	$J_{SC}(\text{mA}/\text{cm}^2)$	$V_{OC}(\text{Volt})$
1	220	3.0	0.175
2	1142	2.0	0.275
3	202	3.0	0.175

IV DIFFUSION LENGTH MEASUREMENTS

Because of the importance of diffusion length in determining the quality of solar cells, a reliable method determining diffusion lengths in Cu_2O is required so that the effect of various processing procedures can be properly evaluated. Some measurements have been made using the Surface Photovoltage Method (SPV) and values up to $2\text{-}4\text{ }\mu\text{m}$ have been obtained. Our collaborators in Strasbourg have obtained similar values.

However the SPV method depends on having accurate values of the absorption coefficient since the diffusion length is obtained by extrapolation of a linear plot of light intensity vs. the reciprocal of the absorption coefficient. The results are in doubt because of uncertainties in the existing absorption data. We have relied principally on the measurements of Pastrnak (12) which give a maximum value of $\alpha \sim 1.4 \times 10^4\text{ cm}^{-1}$. Preliminary measurements by us appear to confirm Pastrnak's results in the region of low absorption coefficients near the absorption edge. However other measurements by Brahms et al. (13) and by Olsen (14) give values for α which are higher by an order of magnitude or greater. This discrepancy will need to be resolved before valid values for the diffusion length can be obtained by the SPV method. We expect to undertake more extended measurements of the absorption spectrum of Cu_2O .

Other methods for measuring diffusion length are being considered as alternatives to the SPV method and as confirmative methods for the SPV results. The Morton-Haynes and the floating light spot methods are unlikely to be useful because the relatively short diffusion lengths, of the order of a few micrometers, would require too small a light spot. However electron beam excitation in a scanning electron microscope could be useful. The Strasbourg group has obtained some preliminary results with the method. We expect to try the method also.

The beveled junction method (15) was also considered. However there may be a problem of preparing suitable samples for measurement since the thickness of the sample should be in the range of a few microns to perhaps 15 μm . This may be attainable in the back-wall structure or by sputtered films on a metal substrate but the Cu_2O in these structures may not be representative of the material used in photovoltaic cells.

The method that has been selected for initial exploration is one that involves measurement of the photocurrent in a Schottky barrier as a function of applied voltage in order to vary the width of the depletion layer.

Under monochromatic illumination by light of wave length λ , the photocurrent, J_n , is due to electrons generated in the depletion layer, W , and the electrons which are generated in the bulk beyond the edge of the depletion layer and which diffuse to the depletion layer.

$$\text{Thus } J_n = q \alpha \phi_0 (1-R) \eta \left[\int_0^W \exp(-\alpha x) dx + \int_W^{\ell} \{\exp(-\alpha x)\} \{\exp(-\frac{x-W}{L_n})\} dx \right]$$

Where q = electronic charge, α = absorption coefficient, ϕ_0 = incident light intensity, R = reflection coefficient, η = quantum efficiency, ℓ = sample thickness, W = depletion layer thickness, and L_n = electron diffusion length.

$$\text{Then } J_n = \eta q \alpha \phi_0 (1-R) \left[\frac{1}{\alpha + \frac{1}{L_n}} \right] \left[\exp(-\alpha W) - \exp\left(-\alpha \ell - \frac{\ell-W}{L_n}\right) \right]$$

Since $\exp\left(-\alpha \ell - \frac{\ell-W}{L_n}\right) \approx 0$ from $\ell \approx 200 \mu\text{m}$ $L_n \approx 5 \mu\text{m}$

$$J_n = \eta q \phi_0 (1-R) \left[1 - \exp(-\alpha W) / (1 + \alpha L_n) \right]$$

For λ 610 nm, $\alpha = 300 \text{ cm}^{-1}$. If we assume

$$W \approx 0.5 \mu\text{m}, \text{ then } \alpha W = 0.015 \ll 1$$

$$\text{Then } J_n = \eta q \phi_0 (1-R) \left[1 - \frac{1 - \alpha W}{1 + \alpha L_n} \right]$$

$$\text{Or } J_n = \eta q \phi_0 (1-R) \frac{\alpha}{1 + \alpha L_n} (L_n + W)$$

The width of the depletion layer is varied by varying the voltage applied to the junction. For each applied voltage, W can be evaluated by measuring the depletion capacitance $C_d = \epsilon_0 kA/W$ where A = area, k = dielectric constant, and ϵ_0 is the permittivity of free space. Also at the same voltage bias, the photocurrent J_n is measured using a light chopper and a lock-in amplifier. The plot of J_n vs W is extrapolated to $J_n = 0$ to yield $-L_n$ as the intercept.

The photocurrent method has an advantage over the SPV method in that accurate values of the absorption coefficient are not required. Also it is possible to probe the surface with a light spot in order to determine the variation of L_n across the sample and near grain boundaries.

V EXPLORATIONS OF LASER ANNEALING

In order to increase the approaches to preparing better junctions on Cu_2O , some explorations of laser annealing were made. Through laser annealing it may be possible to obtain some structures which are not attainable with the longer thermal annealing. Thus it may be possible to introduce impurities under unusual conditions, such as by ion implantation, while avoiding shifts in stoichiometry. This may lead to higher quality junctions or perhaps even to p-n junctions.

The first experiments were designed to test the feasibility of the laser annealing of Cu_2O with the equipment available. These were done both with a pulsed laser and with a continuous laser.

For the pulsed laser, the instrument used was a Quanta-Ray Model DCR-1 which uses a pulsed Nd:YAG laser. This produces pulses of light at 1064 nm. By use of a frequency doubling crystal, the beam was converted to $\lambda = 532$ nm. The pulses were ~ 7 ns (FWHH) at 10 Hz. The laser power at 532 nm was obtained with the oscillator at ~ 70 J and the amplifier at ~ 90 J and 160 mJ/pulse, with

horizontal polarization through a Pellin Broca prism. The laser beam was focussed with a 0.75 D biconvex lens located at 1 m in front of the laser and the sample was 0.5 m in front of the lens. A variety of oscillator and amplifier power settings were tried. Annealing was obtained for an oscillator power of 60 J and an amplifier power of 90 J. The surface melting of the Cu_2O was verified by microscopic examination.

The cw laser instrument was a Coherent Radiation Model CR 3000 K Super-graphite Ion Laser. The wavelength used was 530.9 nm which is at a favorable part of the absorption spectrum of Cu_2O . The laser power was ~ 1 W and the beam was focussed with a lens. The sample was moved across the beam and thus produced a path of melted and regrown material.

Through these preliminary experiments it was shown that the surface of Cu_2O can be melted either by pulsed or cw lasers with the equipment that is available.

VI. SUMMARY AND CONCLUSIONS

Section II describes some improvements in the surface analysis of photovoltaic junctions. By high resolution Auger techniques using the Cu MVV peak at ~ 56 eV, it is possible to distinguish between Cu(0) and Cu(I) at the junction. The method can be applied during continuous sputter etching, which allows more rapid analysis than the earlier ESCA technique. The new method will be used to characterize heterojunctions on Cu_2O , in particular to detect possible chemical degradation at the interface.

A program was begun to study the effect of impurities and potential dopants by additions to the starting copper. Apparatus has been assembled and techniques have been developed for the melting, casting and rolling of the dilute Cu alloys. These samples were oxidized and tested for resistivity and solar cell characteristics. Preliminary testing was done with Se and Si, and some promising results were obtained with Si at 0.05%. It is planned to make an extensive survey of a number of elements to be added to Cu.

The investigation of diffusion lengths in Cu_2O , originally done with the SPV method, has been broadened to consider other methods, such as the measurement of the photocurrent under bias. Preliminary testing of some methods was made. Further measurements of the absorption coefficient of Cu_2O are planned in order to improve the SPV method also.

Explorations were made of the laser annealing of Cu_2O . The experiments show that it is possible to do surface melting of Cu_2O at ~ 530 nm using either a pulsed laser, Nd:YAG with frequency doubling, or a continuous krypton laser. It is planned to develop the techniques further by diffusing the beam over a larger area or by using scanning. The laser annealing techniques will be used to

introduce impurities into the surface layers of the Cu_2O , possibly to prepare useful junctions. Some tentative plans have been made to use ion implantation to introduce the impurities and then to follow this with laser annealing.

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