SOME METHODOLOGIES USED FOR THE SYNTHESIS OF CUPROUS OXIDE: A REVIEW

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ABSTRACT
Cuprous oxide, a semiconductor material has a direct band gap of about 2 eV. Since it is a direct band gap material this imparts higher efficiency especially when used for light emitting diodes (LED). For a long time it was believed that cuprous oxide is a p-type semiconductor but later on n-type cuprous oxide was also prepared. Both these types of cuprous oxides are useful in the fabrication of homo junctions instead of hetero junctions which give rise to higher efficiency of the solar cells. Different researchers have reported different semi-conducting properties of cuprous oxide. Since these properties not only depend upon the nature of the material but also upon the way they are synthesized. The reasons for different properties of the same material are because there may be different number of defects in the same material prepared through different routes. If we compare single crystal silicon to poly crystalline silicon, both have not exactly the same properties. Same is the case in fine and coarse grained materials. It is also noted that depending upon the synthesis conditions; the grain growth will take place at different preferred orientations and hence may result in different conductivity types. Therefore methods adopted for the synthesis of cuprous oxide by various researchers are discussed in this paper.

INTRODUCTION:
Cuprous oxide is a semiconductor with a direct band gap of about 2 eV. Before the application of silicon, the use of cuprous oxide, in transistor industry has been reported since long. In 1916, photoconductivity of cuprous oxide was observed. After that its semiconductor properties were investigated. In 1942, Angello studied the Hall Effect and conductivity of cuprous oxide. He showed that the exponential law of temperature dependence was not obeyed and that the departure from this law was caused by a loss of conduction holes with time and an enormous decrease in the mean free path in the vicinity of 100 °C. In 1959, Weichman found that the photo-conductivities versus wave-length of cuprous oxide were strongly dependent on the oxygen content of the material. In 1965, Heletemes studied the far-infra red properties of cuprous oxide. The transmission and reflectance was measured from 6-250 µm. The maximum values of excitation coefficient were shown to be 2.7 and 4.0 for vibrational frequencies of 613 cm⁻¹ and 1460 cm⁻¹. The high-frequency and static dielectric constants were found to be 6.6 and 7.6 respectively. In 1975, Polak studied the effect of transient and steady state illumination on the electrical properties of a single crystal. This study was carried out in the temperature range of 230 to -20 °C. Within the stability zone of cuprous oxide, the conduction was proved to be governed by an acceptor level at 0.4 eV. Near the CuO-Cu₂O phase boundaries, the conduction was governed by the same acceptor level of 0.4 eV. Near the Cu-Cu₂O phase boundaries, both a high-hole density and a high-mobility with an acceptor level energy of 0.16 eV was observed.

SYNTHESIS TECHNIQUES
Several methods have been used for the production of cuprous oxide. Musa et al produced cuprous oxide by thermal oxidation and studied its physical and electrical properties. During this process the copper foils were heated in the range of 200 to 1050 °C. It was noted that in the temperature range of 1040-1050°C, only one phase i.e. cuprous oxide existed while in the temperature range of 200-950 °C, the mixture of cuprous and cupric oxide was observed.

Wang synthesized cuprous oxide from a 0.4 M solution of copper sulphate mixed with a 3 M lactic acid. The lactic acid was to stabilize Cu (II) ions at a bath pH higher than 7.0. The bath pH could be controlled between 5.8 and 12 by
addition of 4 M NaOH. The effect of deposition condition on the properties of cuprous oxide was studied. It was shown that the growth rate was a function of deposition time at constant temperature of 60 °C and a constant pH of 9.0, 10.0 and 12.5 an increased thickness of the deposited film. With the increase in time, the growth rate was decelerated in contrast to that in a physical vapor deposition method. The reason behind this phenomenon was that with increasing film thickness, the effect on conductivity in the cell by indium tin oxide (ITO) was replaced by a less conductive material i.e. cuprous oxide. The effect of bath temperature and pH was also studied and was shown that by increasing both of these parameters, the film thickness was increased. The most interesting feature of this method is that both n-type and p-type cuprous oxide are synthesized. This has helped in the formation of a homo junction. This homo junction results in the increased efficiency of the solar cell. Before the research work performed by Wang, only a hetero junction formation was possible which had a lower efficiency.

Nair et al deposited cuprous oxide on glass substrate using chemical technique. The glass slide was dipped first in a 1-Molar aqueous solution of NaOH kept at 50-90°C for 20 s and then in a 1-Molar aqueous solution of copper complex. After three immersion cycles, a 30 nm thick film having a bright silvery color appeared. Borgohain et al synthesized cuprous oxide quantum particles and studied its properties. Two methods were used for the purpose. The first method involved the conventional chemical route. This was done by heating copper tartarate complex with glucose in the presence of a capping agent i.e. polyvinyl pyrrolidone (PVP), resulting the precipitation of cuprous oxide precipitated. Since the sizes of quantum dots reflected the colors of a quantum dot, these phenomena could be seen during the production of quantum dots during this process. In the other method, the originally reported method of Reetz was followed. In this method, cuprous oxide was synthesized using a modified electrochemical route. Copper and Platinum electrodes were used as the anode and cathode respectively. The electrolyte bath contained acetonitrile and tetrahydrofuran in the ratio of 4:1. Tetra-n-octyl ammonium bromide was also used as a stabilizer. Nitrogen bubbles were passed through the solution so as to remove the dissolved oxygen from the electrolyte. Upon application of current, copper ions were formed which were oxidized to form cuprous oxide. It was noted that the size of the quantum dot so formed depended upon the applied current. Quantum dot sizes of 2.0±0.5 and 8.0±2.0 nm were obtained by applying a current density of 50 and 2mA/cm². The Bohr’s excitation radius for cuprous oxide is 0.7 nm or in other words, its diameter is 1.4 nm. So it is clear that the quantum dot so formed had a size close to the Bohr’s excitation radius. The band gap and color of the quantum dot is sensitive to size in this range of size.

Armelao et al used a sol-gel method to synthesize nanophasic copper oxide thin films. Copper acetate monohydrate was used as precursor in ethanol as a solvent. The same precursor with glycerol as a solvent could also be used. The films were obtained by dip-coating at room temperature in air. The substrates used in this case were silica slides. The films were deposited in air at room temperature by keeping a controlled withdrawal speed of 7 cm sec⁻¹. Coatings were obtained by means of a multi-dipping process. Up to 7 depositions were carried out without any heat treatment among them.

Ghosh et al used radio frequency reactive sputtering for the synthesis of cuprous oxide thin film and characterized it. Deposition was carried out under the condition that first a pressure of 4×10⁻⁶ T was established in the chamber and then high purity oxygen was introduced with a mass flow rate of 7.5 sccm. It was noted that a coating thickness of 120, 172.5 and 210 nm were obtained corresponding to a substrate temperature of 30, 150 and 300 °C. The time of deposition in all the cases was kept to be 15 min. At a temperature of 30 and 150°C, the oxide formed was cuprous oxide while that formed at 300°C was cupric oxide.

Valtierra et al coated fiber glass with copper oxides, particularly in the form of 6CuO.Cu₂O with the help of chemical vapor deposition (CVD). As shown in table 1, it is clear that at a temperature of 320 °C only cuprous oxide is formed but at a higher temperature of about 340 °C cupric oxide is formed. At a temperature of 325 °C 6CuO-Cu₂O is formed. The precursor used for the purpose was (acac)₂ Cu(II) which was sublimated and transported along with oxygen which acts as oxidizing agent. The decomposition of precursor results in the
Table 1: XRD data for Cu$_2$O and CuO films on fibre glass [After Valteria et al. 2002]

<table>
<thead>
<tr>
<th>Deposition Temperature ($^\circ$C)</th>
<th>Reflection</th>
<th>2θ ($)</th>
<th>Planes and reflection of the copper compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>111</td>
<td>36.4</td>
<td>Clearly defined peaks of Cu$_2$O Crystallite size of 83 Å</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>42.3</td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>202</td>
<td>35.9</td>
<td>Small peaks of 6CuO.Cu$_2$O, crystallite size of 70 Å</td>
</tr>
<tr>
<td></td>
<td>004</td>
<td>36.5</td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>[111]</td>
<td>35.6</td>
<td>Clearly defined peaks of CuO, crystallite size of 79 Å</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>38.7</td>
<td></td>
</tr>
</tbody>
</table>

formation of a zero valent copper which upon oxidation at different temperature give different oxides as shown in Table 1.

Figures 1, 2 and 3 show the X-Ray diffraction peaks of copper oxides. From the peaks, the types of oxides, the volume fractions and grain sizes can be determined. Figure 1 shows that only cuprous oxide is formed. The peak is wider which indicates that the sizes of the grains are smaller.

Figure 1: XRD pattern of the films with substrate at room temperature [after Ghosh et al. 2000]

Figure 2: XRD pattern of the films with substrate at 150 $^\circ$C [after Ghosh et al. 2000]

Figure 3: XRD pattern of the films with substrate at 300 $^\circ$C [after Ghosh et al. 2000]

Figure 4: AFM image of a 6CuO.Cu$_2$O film grown at a temperature of 332 $^\circ$C [After Valteria et al. 2002]

CONCLUSIONS
A few methods are discussed in this paper for the synthesis of cuprous oxide. There are some other methods for the synthesis of this material. Each of these methods has its own advantages and disadvantages. In my view the simplest
method for the synthesis of cuprous oxide thin film for solar cell applications seems to be the electroless chemical deposition method. It is more important because it can give both p-type and n-type cuprous oxides. Although the electro deposition of cuprous oxide also gives the same advantage, but it is complicated as compared to the first one. Both of the methods mentioned above can produce homo junctions which are more efficient than hetero junctions.

REFERENCES