Preparation of Cuprous Oxide, Semiconductor by Thermal Oxidation Method

5.1. Introduction

There is a steady increase in the expenditure of energy resulting from the effect of man’s continuous struggle to survive. We consume energy in the form of food, clothing, shelter and tools, and use energy for transportation, heating, cooling and entertainment. A large part of the world’s population has not shared the benefit of modern energy utilization and energy consumption is on the increase for those that have enjoyed the benefits of modern technology. Since the present dependence on fossil fuels will be depleted in the long run, no country can depend on these indefinitely. One aspect which must be considered in connection with the energies of the future is pollution and possible measures to prevent it. This is especially true for nuclear generating plants. These factors, coupled with the increasing world population, create a need for more energy than traditional energy sources can supply. Solar energy utilization will play a great role in solving the world’s energy needs of the future. The direct conversion of sunlight to electricity is likely to be a prime method of the future, assuming that practical economic means of direct conversion can be developed. In operational practice, solar cells have an advantage over thermal conversion modes in that a solar cell responds linearly to the flux. There is no inertia to a solar-cell system, it immediately produces its output at the level appropriate to the solar intensity unlike solar thermal systems that need time to reach operating temperature. Fuel transport and storage problems are eliminated in a photovoltaic-power system. Solar energy can also be efficiently stored in batteries. The future
development of photovoltaic cells, such as silicon, is hampered by the present cost of the materials and fabrication.

There has been continuous search of new materials and refinement of existing semiconductors as photovoltaic active materials to design these cells that can be a low cost, efficient, durable and a long lasting. In this respect, certain semiconductors like I-VI, II-VI, IV-VI compounds, metal oxides, organic materials, and semiconducting polymers have been identified as potential materials for energy conversion applications due to ease of formation and processing [2]. Majority of these are prepared both in their bulk and nanostructure forms to reduce the cost and to increase the efficiency of solar cells.

In the recent years the transition metal oxides have attracted much attention because of their ease of synthesis and size dependent optoelectronic properties [3]. Among these are zinc oxide (ZnO), titanium oxide (TiO₂) and cupric oxide (CuO) etc. stand as prominent ones. The ZnO and TiO₂ are wide band gap materials and they lack effective absorption of solar spectrum and they must be combined with certain organic dyes and polymers to make them photovoltaic active in the visible region of spectrum. These structures work mainly under electrochemical environments and hence are classified as photo electrochemical solar cells, or a simply Gratzel cells [4]. The cupric oxide (copper monoxide (CuO)) is an interesting semiconductor of oxide family. Its optical band gap is 1.2 eV that is most suitable for solar cell applications and it can easily be converted as p-type material [5]. Further its advantage is that it is low cost, abundant, environmentally benign, and easily synthesizable and having direct band gap with high absorption coefficient [6]. In fact, Braver et al. had designed first kind of humidity sensor of CuO semiconductor way back in 1931. Recently this material has generated renewed interest due to its potential applications
Production of cuprous oxide, a solar cell material, by thermal oxidation

in other areas such as optoelectronics [7], flexible supercapacitors [8], catalysis [9],
lithium ion batteries [10], gas sensors [11] and good absorbent to remove highly toxic
ions from ground water [12].

5.2. Synthesis of Copper Oxide

Copper oxide exists in two stoichiometric forms, one is cuprous oxide (Cu$_2$O) and
another is cupric oxide (CuO). The former has a more band gap that is 2.137 eV and
hence is less suitable for photovoltaic applications, still there are certain reports of
using this material to constitute solar cells [13]. A simple thermal oxidation of copper
is a straightforward method of obtaining these oxide semiconductors. It has been
suggested that outward lattice diffusion and grain boundary diffusion or defect
assisted diffusion are two main mechanism for driving copper ions from bulk
copper (substrate) to the interface for thermal oxidation process. The former
process favors the formation of Cu$_2$O phase and latter CuO phase.

We have studied the thermal oxidation of copper under different pre-treated
conditions of copper powder to control the second mechanics and its effect on the
formation of CuO and Cu$_2$O phases.

Thermal oxidation of pristine copper powder and chemically treated copper
powder with amines has been carried out. Thermal oxidation was carried out in a
muffle furnace for period of about 60 min. Copper metal powder (99.999%)
purity, was used as the starting material. The copper powder was loaded into the
crucible, which was then placed in a conventional muffle furnace for thermal
oxidation under open conditions. Here heating was carried out at two different
temperatures, one at 500 °C and another is still higher temperature that is 700 °C.
After heating, the copper powder gets converted into gray/black material that was
collected and stored for further characterization.
Similarly, amine treated copper powder is also subjected to the oxidation process. Here the required amount of copper powder was grinded sequentially for six hours with ETA and OA separately to achieve the through mixing and reaction. Again the amine treated copper were fired at 500 °C and 700 °C for 60 min in open conditions. After annealing the powder were collected and washed thoroughly with copious amount of double distilled water and dried, this material is used for further characterization.

5.3. Results and Discussion

X-ray diffraction was employed to study the conversion of copper to copper oxide by thermal annealing. Figure 5.1 shows the XRD patterns of pure copper, DETA and OA treated copper powders that were annealed at 500 °C.

The standard reported line patterns of CuO and Cu$_2$O compounds are also shown along with these patterns as vertical lines for the comparison (ICSD no.087126). The standard patterns for CuO is monoclinic (a= 4.689 Å, b=3.420 Å, c= 5.130 Å) and Cu$_2$O is cubic (a=4.27 Å). The observed patterns clearly indicate that annealing of untreated copper powder shows more sharp peaks as compared to amine treated annealed powder. Hence the amine treatment prior to oxidation of copper suppresses the crystallization process of oxide formation. The particle size in three different cases was estimated using Debye-Scherrer formula $d = \frac{0.9λ}{βCosθ}$ and they are 72 nm, 69 and 65 nm for untreated, DETA treated and OA treated oxides, respectively. The pattern of untreated copper oxide matches quite well with CuO rather with Cu$_2$O phase, almost all the peaks of former phase are clearly and distinctly seen. Among these peaks (111), (200), (202) and (113) are the intense peaks of this pattern.
Production of cuprous oxide, a solar cell material, by thermal oxidation

Figure 5.1: X-ray diffraction patterns of copper oxide of pure, diethylenetriamine (DETA) treated and oleamide (OA) treated copper powders oxidized at 500 °C for 60 minutes.
The peaks belonging to Cu$_2$O are almost absent in case of untreated copper converted to copper oxide. Hence, it can be concluded that oxidation of pure copper powder in open conditions at low temperature 500 °C leads to formation of pure CuO phase that is more active photovoltaic material due to its low band gap (1.2 eV) as compared to Cu$_2$O. However, the patterns of the amine pre-treatment before annealing show a reasonable change in the oxidation process of copper. The two patterns of DETA and OA show the emergence of certain new peaks in addition to the peaks of CuO phase. Notable changes in DETA annealed pattern are the appearance of new peaks at 2θ = 36.41°, 43.36° and 61.50° which belong to the (111), (200) and (220) set of planes of CuO$_2$ phase. These observations are clear indication that DETA treated annealing at 500 °C favors the formation of Cu$_2$O phase against the CuO phase, hence in this pattern (figure 5.1) both the phases CuO and Cu$_2$O are coexisting and the material becomes biphasic. Similar observations can be noted in case of OA treated annealing of copper, it shows that (111), (200) and (220) peaks of Cu$_2$O are more stronger as compared to DETA annealed and also these peaks are stronger than the prominent peaks of CuO phase. To study the effect of further increase in annealing temperature on the formation of copper oxide phases, the above exercise was repeated at 700 °C heating. These patterns along with standard patterns of two different phases of copper oxide are shown in figure 5.2.
Production of cuprous oxide, a solar cell material, by thermal oxidation

It can be noticed that in case of untreated copper the Cu$_2$O phase starts emerging and this process becomes more prominent in case of amine treated oxidations. Further, these patterns were also matched with pure copper powder pattern to see whether there is unreacted material. No such matching is observed. Hence it
can be concluded from the X-ray phase analysis that the prior to amine treatment and increase in annealing temperature of pure copper powder favor the growth of \( \text{Cu}_2\text{O} \) phase against the \( \text{CuO} \) phase.

**Figure 5.3:** SEM images of pure copper powder (a) oxidized at 500 °C and (b) oxidized at 700 °C for 60 minutes.

Next, the scanning electron microscopy (SEM) images were recorded on all the samples to study the surface morphology of copper oxide. Figure 5.3 (a) and (b) show
these images for pure copper that was heated at 500 °C and at 700 °C temperatures, respectively. In case of 500 °C heating the structure appears more extended and hence could be better crystalline and of single phasic, whereas the heating at high temperature gives appearance of new phase as whisker. This could be related to the emergence of Cu$_2$O phase with increase in temperature. These observations are in accordance with X-ray phase analysis of these samples.

Figure 5.4: SEM images of copper powder treated with diethylenetriamine (DETA), (a) oxidized at 500 °C and (b) oxidized at 700 °C for 60 minutes.
Production of cuprous oxide, a solar cell material, by thermal oxidation

Figure 5.4(a) and (b) show similar SEM images for DETA annealed copper powder to form copper oxide. The extended structure of pure copper annealing breaks into small elongated like structures at 500 °C heating and it further breaks into smaller size structures at higher oxidation temperature 700 °C. These structures closely resemble to the pure copper annealing at 700 °C. Similar SEM patterns of OA treated oxides at two different annealing temperatures are shown in figures 5.5 (a) and 5.5(b).

Figure 5.5: SEM images of copper powder treated with Olelamine (OA), (a) oxidized at 500 °C and (b) oxidized at 700 °C for 60 minutes.
OA treated copper oxides show interesting morphology as compared to DETA treated powders. At 500 °C annealing the structure shows small dense rods, while at higher annealing temperature 700 °C a fine nanowires with some clusters of CuO phase appears. These nanowires possesses good apex ratio (length/diameter >20).

The oxidation of transition metals by heating process is of continued interest and is an interesting process, a lot of work has been carried out in this regards. The surface condition of a metal, the presence of catalysis, temperature of oxidation, oxygen availability, pressure and the time of annealing are some of the important parameters that decide the chemical nature and structure of grown metal oxide. The thermal oxidation of metals is an appealing technique due to fact that the precise control of the above parameters permits to grow bulk to nano-sized metal structures of different phases and such metal oxides find potential applications in varieties of electronic devices. Here, the interface between metal surface and open atmosphere is a critical place at which metal ion migrate from the bulk region to combine with the atmospheric oxygen to form the oxide phase. This process can be analysed in terms of Gibb’s free energy and by plotting Ellingham diagram (change in Gibb’s energy versus temperature under different pressure) [14]. A general whisker growth, formation of micrometer sized wires, has been well studied process in terms of vapour-solid, vapour-liquid-solid and Frank dislocation growth mechanisms [15]. A typical growth of wire-like structures in case of copper oxide and zinc oxide by thermal process has been analyzed in the literature and four important and independent mechanisms have been proposed [14,15]. These are (i) the absorption of atmospheric oxygen at the metal surface by diffusion process, (ii) nucleation of surface oxide by metal ion and oxygen reaction, this is a diffusion controlled process by which metal ions and oxygen gets
Production of cuprous oxide, a solar cell material, by thermal oxidation

agglomerated to reduce their surface energy, (iii) nuclear (seeds) arrangement process on the surface of metal to favor the further growth of metal oxide and (iv) morphologically controlled growth of metal oxide, this is mainly controlled by the difference of surface pressure of metal oxide nucleation and metal substrate.

In the recent time, the oxidation of copper has gained a lot of interest due to fact that a simple oxidation under the controlled conditions of temperature, purity of copper and oxygen partial pressure makes it possible to generate interesting nanostructures, particularly nanowires. This synthetic route is an extremely simple and has potential to generate a highly functional material with low cost of synthesis and that can be easily scalable for a large quantity synthesis. The issue of thermal oxidation of copper is not a well resolved issue. As mentioned above, the copper oxide has two stable phases, one is Cu$_2$O (Cu(I) oxide) and another is CuO (Cu(II) oxide), having standard enthalpy of formation -170 kJ-mol$^{-1}$ and -156 kJ-mol$^{-1}$ with melting points 1232 °C and 1326 °C, respectively. Among these, the latter is a more attractive material from photovoltaic application point of view. Hence, there has been a continuous effort to form this material in its purest form. A systematic study of thermal oxidation of copper has been carried out by Zhu et al. in the temperature range from 300 °C to 900 °C [16]. Based on this and the others work the thermal oxidation of copper can be divided into two distinct regime of temperatures, one is lower temperature (400 °C) and another is high temperature (800 °C), the former has low activation energy (40 kJ/mol) and latter has a high activation energy (111 kJ/mol). These processes follow parabolic rate law [17]. In many of the reports it has been claimed that the thermal oxidation of copper begins first with Cu$_2$O phase which is then converted to CuO phase. In both the regimes this phenomenon has been reported. In many cases it is claimed that at the highest possible temperature
Production of cuprous oxide, a solar cell material, by thermal oxidation

of oxidation it is Cu$_2$O phase that in predominantly dominated in the material. However, Park et al. report that at low temperature (350-450 °C) oxidation of copper in their case directly yields CuO phase. Regarding the thermal oxidation of copper the following picture arises from these studies. With increase in temperature first there is a formation of Cu rich Cu$_2$O phase at the interface between copper substrate and atmospheric oxygen, due to a large difference in molar volume between copper and its oxide creates high compression stress that leads to high density of grain boundaries of this phase. These parameters with other favorable conditions convert the top layer of Cu$_2$O phase into CuO phase, particularly in the form of nanowires. Here the growth rate is controlled by two independent process of the supply of copper ions to the interface, one is by outward lattice diffusion of copper ions that usually occurs at higher temperature and another is grain boundary diffusion or defect mediated diffusion occurs at low temperature [18]. Recently, Goncalves et al. carried a detailed study on the thermal oxide formation of CuO nanowires [19]. These authors suggest that the fast supply of copper ions by the short circuit diffusion through grain boundaries favor the formation of CuO phase.

Most of the work in literature on the thermal oxidation of copper has been carried out on solid plates/discs and hence the formation of CuO phase above the Cu$_2$O phase must govern the lattice and grain boundary diffusion through the latter phase. In the present work we have chosen a fine copper powder as a starting material to facilitate the fast diffusion of copper ions by grain boundaries process and availability of large surface atoms on these particles to form photovoltaic active phase CuO. In order to suppress the grain boundary diffusion and availability of surface atoms for oxidation process, the starting material was
Production of cuprous oxide, a solar cell material, by thermal oxidation

chemically passivated with DETA and OA amines. The present results, that is the easy formation of CuO phase at low temperature oxidation (500 °C) and inhibition of this process in case of amine treatment clearly supports that the grain boundary diffusion or defect mediated diffusion process is primarily responsible for the formation of CuO phase. This process in case of amine treatment clearly supports that the grain boundary diffusion or defect mediated diffusion process is primarily responsible for the formation of CuO phase.

Nanowire-based (NW) solar cells have been reported to possess inherent advantages over traditional bilayer devices [20-24]. By separating the optimal length scales for light absorption and exciton diffusion, it is possible to create a device with a relatively thick absorbing layer (for full solar spectral absorption), yet small interwire spacing (for short exciton diffusion). In addition, oriented nanowire arrays have been shown to possess excellent charge transport (and therefore charge collection) characteristics in photovoltaic devices [24-27]. The potential for improved performance and cost reductions of NW arrays over their bulk photovoltaic counterparts is primarily due to (1) increased absorption due to diffuse light scattering in NW arrays, (2) short collection lengths of minority carriers that are radially separated and collected normal to the light absorption direction, and (3) flexibility of cell integration on a variety of low-cost carrier substrates. A key point is that single-crystalline NWs can be grown by the vapor-liquid-solid (VLS) method. The synthesis and application of nanostructures in solar cells have attracted much attention. Metal oxide nanowire (NW) arrays with large surface area and short diffusion length for minority carriers represent a new class of photoelectrode materials that hold great promise for photoelectrochemical (PEC) hydrogen generation applications. Thus this material synthesized with simple thermal oxidation
Production of cuprous oxide, a solar cell material, by thermal oxidation method will be implemented in photoelectrochemical cells, which will be discussed in chapter six.
Production of cuprous oxide, a solar cell material, by thermal oxidation

REFERENCES


Production of cuprous oxide, a solar cell material, by thermal oxidation