

## General Introduction

The study of thin films of materials in recent years has greatly interest of material scientists due to discovery of new device applications . A great variety of insulating, metallic and semiconducting thin films have already found key applications by physicists and engineers. Thermal, optical , magnetic and electronic properties of thin films are finding new and varied applications in industry, medical science, space science, .. etc. Consequently , thin film technology continues to attract the interest of scientists.

At present, a wide variety of thin film deposition techniques are in use, physical vapour deposition, chemical vapour deposition, solution growth, electro-chemical deposition or hybrid techniques involving combinations of two or more of these (1-3). The solution growth of thin films is the cheapest and most reliable technique for obtaining thin films of high quality and good reproducibility. Chemical methods of depositing thin films of soluble compounds have been studied and developed by empirical methods (4-10).

I-III-VI<sub>2</sub> semiconductors were proposed as viable candidates for applications of photovoltaic energy production. These materials offer cost advantages and higher efficiencies over the present silicon and CdS/ Cu<sub>x</sub>S systems. Several research groups have studied these compounds and their properties (11,12,13). CuInS<sub>2</sub> was chosen because the constituent elements are plentiful and easily obtained in the required purities. The absorption coefficient permits the device to be made in thin film form and its band gap of 1.55 eV is near the optimum value for photovoltaic applications (14) .

The I-III-VI<sub>2</sub> sulfides are ternary analogs of the familiar II-VI compounds ZnS and CdS. Very little is known of either the electrical or optical properties of this class of materials<sup>(11)</sup>. They are tetrahedrally coordinated semiconductors which crystallize in the uniaxial chalcopyrite structure<sup>(15)</sup> figure (1.1). The ternary ABC<sub>2</sub> chalcopyrites ( A=Cu and Ag, B=Al, Ga and In, and C=S, Se and Te) form a large group of semiconducting materials with diverse optical, electrical and structural properties <sup>(16)</sup>. One can define a binary analog to each ternary compound, by taking the cation that is situated in the periodic Table between the A and B atoms (e.g., ZnS is the binary analog of CuGaS<sub>2</sub>, or Zn<sub>0.5</sub> Cd<sub>0.5</sub> S is the binary analog of CuInS<sub>2</sub>). Despite the overall structural similarity between the ternary I-II-VI<sub>2</sub> compounds and their II-VI binary analog, the band gaps of the former compounds are smaller than those of the latter <sup>(17)</sup> Table (1.1).

Ternary chalcopyrite have some interesting structural anomalies relative to their binary analogs figure (1.2). For comparison of the crystal structure, first, the binary have a single cation while the ternary have two cations, starting from the A atom and translating in the vertical direction through intervals of  $c/2$ , it was found the sequence ABAB..., whereas, translating horizontally with interval of  $a$ , its was found the sequence AAA..... Second, these crystals often shew a tetragonal distortion where the ratio between the lattice parameters  $\eta = c/2a$  (tetragonal deformation) differ from 1 by as much as 12%. Third, the anions are displaced from their Zinc-blend sites. In binary AC Zinc-blend compounds each cation A has four anions, C, as nearest neighbours, while in ternary chalcopyrite ABC<sub>2</sub> each cation A and B has four anion, C as nearest neighbours, and each anion has two A and B cations as nearest neighbours. As a result, the anion C usually adopts an equilibrium position closer to one pair of cations than to the other, that is , unequal bond lengths  $R_{AC} \neq R_{BC}$  ( bond alternation) <sup>(17)</sup>.