

Formation of thin Cu_2S (chalcocite) films using reactive sputtering techniques

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Thin Cu_2S (chalcocite) films, which are of interest for solar cell fabrication, have been prepared using reactive sputtering techniques. The copper-sulfur system, which is multiphase and polymorphic, is difficult to form in the orthorhombic chalcocite phase. This phase can be achieved by careful control of substrate temperature and the partial pressure of H_2S in the sputtering atmosphere. Sulfur-rich atmospheres produce the sulfur-rich Cu_xS phases which are unsuitable for solar cell fabrication, whereas sulfur-lean atmospheres result in precipitated copper cones on the surface. Epitaxial chalcocite films have been formed on single-crystal CdS substrates. Charge transport studies in polycrystalline Cu_xS films formed on polycrystalline CdS indicate minority carrier diffusion lengths of 100 nm which are adequate for solar cell operation. The sputtering parameters affecting film formation (H_2S concentration, substrate temperature and bias, and substrate material) have been studied and are discussed.

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INTRODUCTION

Chalcocite (Cu_2S) films function as the active region of the Cu_xS -CdS heterojunction solar cell. Several methods have been considered for chalcocite formation and, of these, physical vapor deposition schemes utilizing sputtering techniques appear promising.^{1,2} Our investigation has centered on the formation of Cu_xS films utilizing reactive sputtering techniques. Of critical importance for the solar application of these films is the attainment of crystalline chalcocite (Cu_2S), which has good solar spectrum optical absorption characteristics, diffusion lengths for minority carriers in excess of 100 nm, and can be epitaxially grown on CdS substrates. This has been achieved, and the influence of the sputtering parameters on these properties will be discussed in the following sections.

Cu_xS FORMATION PARAMETERS

We have studied the formation of Cu_xS by sputtering copper in an atmosphere of H_2S and argon in a 4-in. planar diode, rf-driven sputtering system. The substrate was 5 cm from the cathode and was normally grounded by the metal mask unless an external dc bias was applied. A number of parameters can be varied including (1) the effective partial pressure of H_2S (ppH_2S), (2) substrate temperature, (3) substrate biasing, (4) sputtering rate, and (5) substrate material. The properties of the films which are expected to vary include the copper-to-sulfur ratio, the phases present in the film where the Cu/S ratio is ≤ 2 , the film resistivity, the optical absorption characteristics, and the minority carrier diffusion lengths. In analyzing the films, measurements have been made which are specific to the film properties of interest. Microprobe analysis has been used to measure the chemical Cu/S ratio in the films. This has been particularly useful in determining the

copper-rich phase diagram limits for small values of ppH_2S and for analyzing the chemical composition of topographical features on the Cu_xS films. Direct sheet resistance measurements have been useful in estimating the mineral-phase content of nominally Cu_2S films. Since copper vacancies in Cu_xS films contribute mobile-charge carriers (holes), i.e., they act as acceptors, average copper-vacancy concentration and stoichiometry can be estimated on the basis of the film resistivity. Additional verification of mineral content has been obtained by x-ray diffraction measurements on 1- μm -thick sputtered Cu_xS films.

Optical transmission versus wavelength measurements are also used as an indication of the mineral-phase mix of the film since variations in the optical absorption characteristic are known for chalcocite, djurelite ($\text{Cu}_{1.96}\text{S}$) and digenite ($\text{Cu}_{1.8}\text{S}$). The most important sputtering parameter is the effective partial pressure of H_2S (ppH_2S) in the sputtering atmosphere. The ppH_2S was estimated by measuring the total pressure ($P_{\text{tot}} = P_{\text{Ar}} + P_{\text{H}_2\text{S}}$) for a known gas mixture where $P_{\text{H}_2\text{S}}/(P_{\text{H}_2\text{S}} + P_{\text{Ar}}) = 0.07$. The experimental measurements, which were made with a Pirani gauge, were verified by simultaneous measurements with a gas-insensitive electronic manometer (an MKS Baratron) and both readings were found to be within 15% of each other. It should be noted that since the ppH_2S readings are based on the source gas mixture ratio and on the total system pressure, actual values in the plasma during sputtering are not known but are qualitatively related to the ppH_2S values reported. The expected film compositions are expected to range from pure copper films for $\text{ppH}_2\text{S} = 0$ up to sulfur-rich films (likely CuS) for higher values of ppH_2S . Several series of films have been sputtered as a function of substrate bias and substrate temperature for values of ppH_2S ranging from 0.13 to 0.2 Pa. Measurements of the copper to sulfur ratio using microprobe analysis are plotted in Fig. 1 for

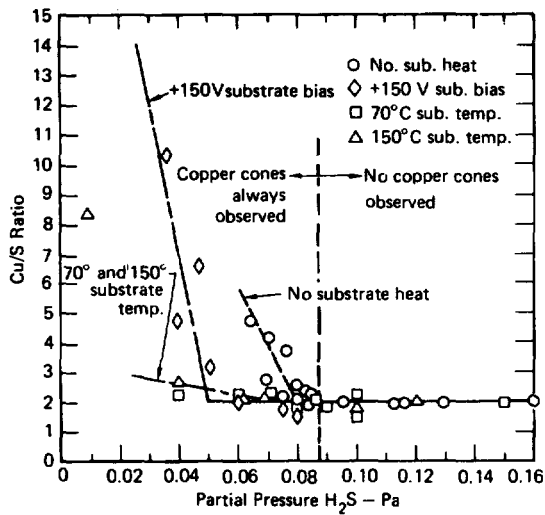


FIG. 1. Cu/S Ratio as a function of ppH_2S for different substrate temperatures and biasing conditions.

glass substrates clamped to a water-cooled plate but with no special provision to ensure thermal contact. Thermal dots were utilized to estimate the maximum substrate temperatures which were found to be between 100° and 145°C . The films were sputtered by holding all conditions as constant as possible while varying the ppH_2S value which was determined as outlined earlier. The ppH_2S value was set prior to sputtering by bleeding in a 7% mixture of $\text{H}_2\text{S}/\text{Ar}$ with the pump orifice restricted at a present point to a preset given pressure as indicated by the Pirani vacuum gauge. Additional Ar was then admitted to reach an equilibrium pressure of 2 Pa for sputtering. The sputter discharge was first established with a closed shutter for about 15 min, and then Cu_xS was formed on the substrate by this sputter-plasma discharge at a rate of $0.1\text{--}0.15\text{ nm s}^{-1}$. Film thicknesses of $150\text{--}300\text{ nm}$ were usually fabricated.

As can be seen in Fig. 1, small values of ppH_2S result in copper-rich films. Increasing the ppH_2S above 50 mPa results in Cu/S values approaching 2, at which point the accuracy of this measurement ($\sim\pm 10\%$) is insufficient to unambiguously determine the specific mineral phase. A series of films was also sputtered wherein the substrate was biased at +150 V to minimize positive ion bombardment of the Cu_xS film. As can be seen, the result was a shift of the Cu/S vs ppH_2S curve to the left of the unbiased curve. While definitive measurements have not been done to understand this effect, one possible explanation is that the positive bias accelerates the negative sulfur ions into the anode substrate surface. An alternate explanation is that the positive bias reduces the loss of sulfur ions due to backspattering.

The effects of substrate heating on film formation were studied using a temperature-controlled substrate holder installed in the sputtering system. Indium foil (which melts above 156°C) was sandwiched between the holder and the glass substrate. At temperatures greater than 156°C , the indium melts but still provides an excellent liquid metal contact. Cu/S vs ppH_2S runs were then made at substrate temperatures of 70° and 150°C and the results are also shown plotted in Fig. 1. The apparent effect of increasing substrate

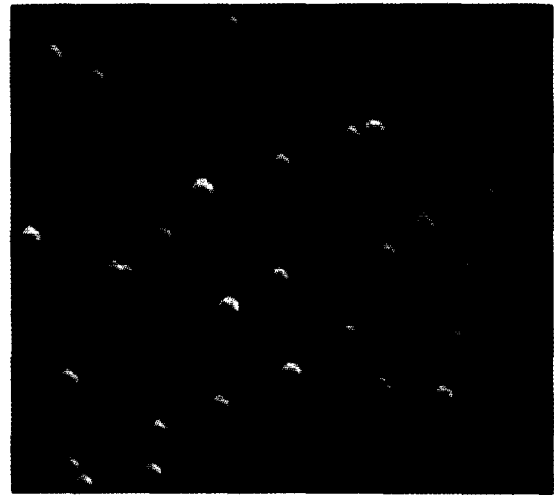


FIG. 2. Cu precipitate cones formed on the Cu_xS film for small ppH_2S values.

temperatures is to shift the formation of very copper-rich films to lower values of ppH_2S .

Films which were sputtered in lean atmospheres of ppH_2S and which showed Cu/S ratios >2 were covered to a varying extent with cones as shown in Fig. 2. The extent of cone coverage was proportional to the Cu/S ratio. Microprobe analysis of these cones and the surrounding films showed that the cones were nearly pure copper (Cu/S > 80) whereas the surrounding films were essentially chalcocite. The cones appeared on all copper-rich (lean ppH_2S) films. An important observation was that the onset for cone formation apparently occurred at the same value of ppH_2S (0.09 Pa) even though there were significant variations in substrate temperature and bias.

The resistivity of the chalcocite phase (Cu_2O) is known to be relatively high with the more sulfur-rich phases being significantly lower due to the increasing concentration of copper vacancy acceptors.³ Figure 3 shows the resistivity as a function of ppH_2S for the different substrate temperatures and bias. For very low values of ppH_2S , the films are highly conductive as would be expected for predominantly thin copper films. As the Cu/S ratio drops, the films suddenly become very highly resistive and essentially maintain this high

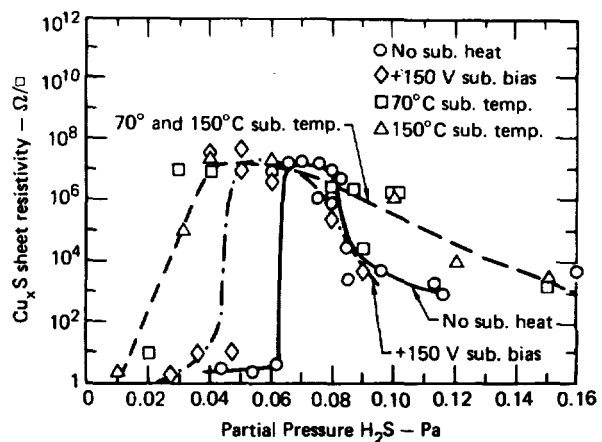


FIG. 3. Cu_xS film sheet resistivity as a function of ppH_2S for different substrate temperatures and biasing conditions.

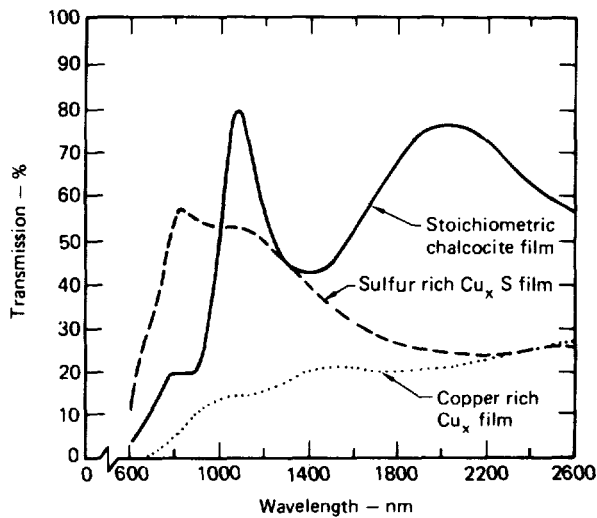


FIG. 4. Optical transmission as a function of wavelength measured at room temperature in air for different phases of Cu_2S films.

resistivity value up to $\text{ppH}_2\text{S} = 0.08$ Pa for all sputtering conditions studied. The onset of the high resistivity state, however, is dependent on substrate conditions as expected from the Cu/S vs ppH_2S curve. The interpretation is that Cu_xS is being formed in a two-phase regime of copper and chalcocite. The excess copper precipitates from the chalcocite and forms as cones which literally grow out of the surface of the film reaching dimensions of $10 \mu\text{m}$ for a $0.3 \mu\text{m}$ film. For high copper content films, these cones "grow" together providing a continuous conduction path. When separated, however, conductivity is controlled by the film which has the very high sheet resistivity of chalcocite.

As the ppH_2S is increased above 0.08 Pa, the cones disappear and the sheet resistance begins dropping. Here we see an apparent difference between the films prepared at different substrate temperatures. The films prepared at low substrate temperatures show a more rapid drop in sheet resistivity than those sputtered onto the higher temperature substrates. Since high resistivity is related to stoichiometric chalcocite, it would appear that increasing substrate temperature increases the chalcocite content of Cu_xS films formed at values of ppH_2S in excess of 0.09 Pa.

Based on observations of both substrate biasing and substrate temperature effects on the Cu/S ratio and chalcocite formation, it appears that an important portion of the reaction in the reactive sputtering of Cu in H_2S occurs at the substrate. If the reaction occurred only on the Cu cathode, or in the plasma, then film resistivity would be dependent only on the ppH_2S value, not on substrate bias or temperature. The effect of substrate-parameter changes appears to be a fine tuning of the film stoichiometry.

Studies of the optical transmission versus wavelength were also performed as a function of ppH_2S . Figure 4 shows transmission spectra for a sulphur-rich film, a copper-rich film, and a film which is predominantly chalcocite. The interference effects due to the thin films are clearly evident. Calculations of the expected transmission characteristics for the different mineral phases of Cu_2S closely match the experimental data.

X-ray diffraction data were also taken on selected films. Due to the need for sufficient material for x-ray diffraction, films of about $1 \mu\text{m}$ thickness were prepared with an unheated and grounded substrate at ppH_2S values slightly in excess of 0.09 Pa. Several of the films contained diagnostic peaks only for chalcocite ($\text{Cu}_{2.0}\text{S}$), while other films primarily contained diagnostic peaks for djurelite ($\text{Cu}_{1.96}\text{S}$). This is consistent with the data for resistivity versus ppH_2S above 0.09 Pa for the unheated substrates since a rather rapid change in the resistivity in this range (within ~ 0.01 Pa) indicates that film compositions ranging from $\text{Cu}_{2.0}\text{S}$ to $\text{Cu}_{1.96}\text{S}$ were formed. X-ray diffraction data have not been taken for the heated substrates, but resistivity data indicate that predominantly chalcocite films will be formed over a larger ppH_2S range above 0.09 Pa.

Measurement of the electron diffusion length L_e in the $p\text{Cu}_x\text{S}$ films formed without heating with an unbiased substrate at $\text{ppH}_2\text{S} = 0.09$ Pa is most easily accomplished by forming a $\text{Cu}_x\text{S-CdS}$ heterojunction cell using polycrystalline thin CdS films. These cells are then analyzed in terms of their photovoltaic and EBIC response characteristics. Photovoltaic analysis allows the direct measurement of heterojunction interface losses and permits an estimate of carrier diffusion length. In addition, EBIC response measurements using an SEM have also been used to estimate L_e . Data concerning electron gain and electron collection efficiency were taken as a function of electron beam penetration depth (using a variable beam energy) for the heterojunction. By curve-fitting the results using previously measured values for the interface loss, we have determined a value for L_e in the Cu_xS film of 100 nm.

Additional measurements made by Krishna Seshan of the Lawrence Berkeley Laboratory provided information on the $\text{Cu}_x\text{S-CdS}$ interface structure. In these measurements, Cu_xS films were reactively sputtered onto thin single-crystal CdS substrates for transmission electron microscope analysis. Seshan was able to discern the fine structure electron diffraction pattern for Cu_xS superimposed upon and in alignment with the coarser pattern attributed to the CdS substrate. Similar patterns have been observed elsewhere⁴ and have been interpreted to be a continuation of the sulfur lattice structure. It would appear, then, that we are achieving epitaxial growth of Cu_xS onto the CdS .

SUMMARY

We have shown that we can sputter films with controlled composition ratios by varying the ppH_2S value in our sputtering system. While differences in ppH_2S values will occur in other systems due to differences in pumping and leak rates, we have demonstrated that ppH_2S control is an important variable for chalcocite formation. Copper rich films form as a two-phase system of chalcocite and precipitated copper. For the conditions of flow in our sputtering system, chalcocite forms near $\text{ppH}_2\text{S} = 0.09$ Pa. Above $\text{ppH}_2\text{S} = 0.09$ Pa, Cu_xS phases are formed which become increasingly sulfur-rich with increasing ppH_2S values. The range of ppH_2S pressures over which chalcocite can form is controlled by the substrate temperature. The existence of chalcocite is confirmed by optical transmission, Cu/S chemical ratio, x-ray diffraction,

and sheet resistivity measurements. The Cu_xS films, which grow epitaxially on CdS, can be formed reproducibly and have electron diffusion lengths normally observed for Cu_xS formed by other processes.

ACKNOWLEDGMENT

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⁴W. F. Tseng and I. G. Greenfield, *Phys. Status Solidi* **26** 643 (1964).