

Electrical Characterization of Heat-Treated Tin Monosulfide Thin Films

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Abstract and Introduction:

Tin monosulfide (SnS) thin films have generated much interest in recent years due to their potential application as an absorber layer in thin film photovoltaic cells [1]. Thus, the goal of this project was to improve the quality of SnS films through various methods of heat-treatment by means of grain growth, a reduction in bulk defects, and increased carrier mobility, which can increase the probability of charge collection and thus potentially improve cell efficiency. The effects of the annealing atmosphere (inert nitrogen (N_2) versus hydrogen sulfide (H_2S) gas), temperature (250-540°C), and annealing time (10 s versus 60 min) on the film's electrical properties were investigated. Scanning electron microscopy (SEM) and Hall measurement results revealed that annealing the films in H_2S atmosphere produced larger, columnar, and uniform grains with greater mobility as compared to the as-deposited and N_2 annealed SnS. While the heat-treatment of SnS films in H_2S for 10 s and 60 min both produced films of comparable mobility, the film that underwent the 10 s process had a relatively lower carrier concentration, which is an indicator of the amount of bulk defects present. Therefore, the most desirable SnS films were found to be produced through annealing in a H_2S atmosphere at 400°C for 10 s.

Experimental Procedure:

SnS films were deposited using atomic layer deposition (ALD), and annealed at various atmospheres (N_2 or H_2S), temperatures (between 250-540°C) and times (10 s or 60 min). These films were heated at an average ramp rate of 0.17°C/s before being held at the annealing temperature for the specified time. The heat-treated films were then studied using the SEM and x-ray diffraction (XRD). Square Hall samples of the heat-treated films 1 cm wide were then prepared through deposition of 200 nm of gold, and removal of excess film using a reactive ion etching (RIE). The various electrical properties of each film were then calculated from the measured Hall voltage of each prepared sample.

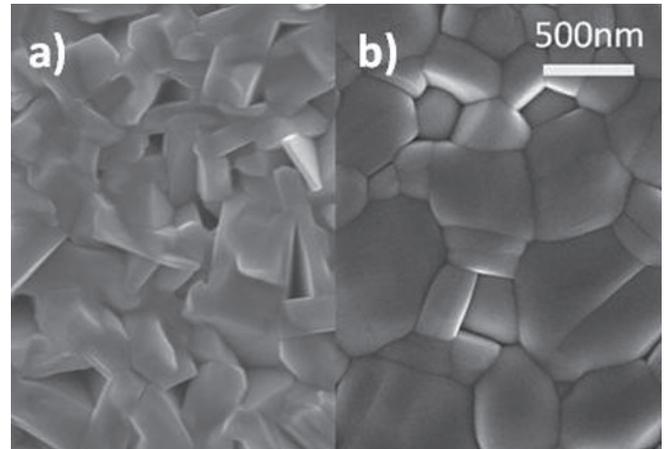


Figure 1: SEM comparison of SnS grains of (a) as-deposited and (b) heat-treated in H_2S for 60 min.

Results and Conclusions:

Cross-sectional SEM images of the heat-treated films demonstrated that when all other conditions were held constant, larger, more columnar grains were produced by annealing in H_2S as compared to N_2 and as-deposited films. Increasing the annealing temperature also produced an increased grain size.

Figure 1 demonstrates the significant change in grain size produced by such an annealing process, with the as-deposited film shown on the left in (a) and heat-treated film in H_2S at 400°C on the right in (b). Such grain growth is beneficial in the development of SnS films for use in photovoltaic devices, since it reduces the probability of charge scattering at the grain boundaries, potentially allowing for more efficient charge collection.

The results of characterization of the electrical properties are shown in Figure 2 and Figure 3 respectively. The as-deposited films are indicated in both graphs by the point at 200°C, which is the deposition temperature.

Figure 2 demonstrates that consistently high mobility can be achieved for films annealed in H_2S between 250-400°C at annealing times of 10 s and 60 min. However, mobility drops sharply above 250°C when annealed in N_2 . Since annealing in high temperatures is favorable in order to achieve larger grains, annealing in H_2S is preferred over N_2 because it produces significantly greater mobility at temperatures between 300-400°C. At temperatures above 400°C however, mobility drops significantly, although imaging under the SEM revealed that the grains continue to be significantly larger. Thus the drop in mobility could be a result of increasing amounts of point defects present at higher temperatures.

Carrier concentration is an important parameter because while the film must have sufficient carriers to conduct charge, an excess of carriers could serve as point defects causing unwanted recombination. Two distinct trends in the data shown in Figure 3 can be observed: when annealing was carrying out for 60 min, regardless of the annealing atmosphere, increasing the temperature generally produced an increase in the carrier concentration. For the annealing done for 10 s above 300°C however, increasing the temperature appeared to lower the carrier concentration to a value close to the as-deposited carrier concentration. In particular, a comparison of the two annealing times for H_2S at 400°C reveals that annealing for 10 s produced a lower carrier concentration, and thus is the more favorable process.

XRD analysis of the heat-treated SnS films, shown in Figure 4, revealed that annealing in N_2 at higher temperatures produced a greater dominance of the <040> peak over the <111> crystal orientation. At 400°C in N_2 , the <040> peak had the greatest intensity, replacing <111> as the dominant crystal orientation. When the film was annealed in H_2S at 400°C however, no growth of the <040> peak relative to the <111> was observed. This could be due to the fact that annealing in N_2 results in a loss of sulfur from the film, causing the crystallites to rearrange in the most stable <040> orientation in order to accommodate the new sulfur defects formed. On the other hand, since H_2S is a source of sulfur, annealing in an atmosphere of H_2S would suppress the loss of sulfur, rendering reorientation unnecessary. Thus, these changes in crystallite orientation could be a further reason for the demonstrated difference in mobility and grain size when annealed in N_2 as compared to H_2S .

Acknowledgments:

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References:

- [1] Sinsermuksakul, P.; Heo, J.; Noh, W.; Hock, A. S.; Gordon, R. G., *Advanced Energy Materials* 2011, 1, (6), 1116-1125.

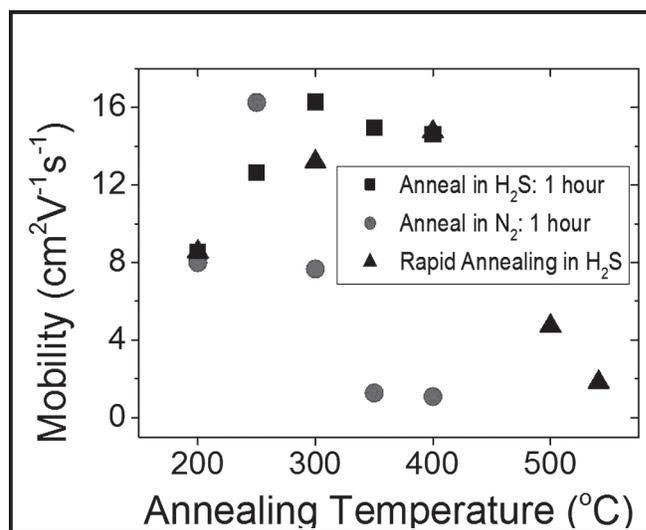


Figure 2: Effect of annealing conditions on carrier mobility in SnS films.

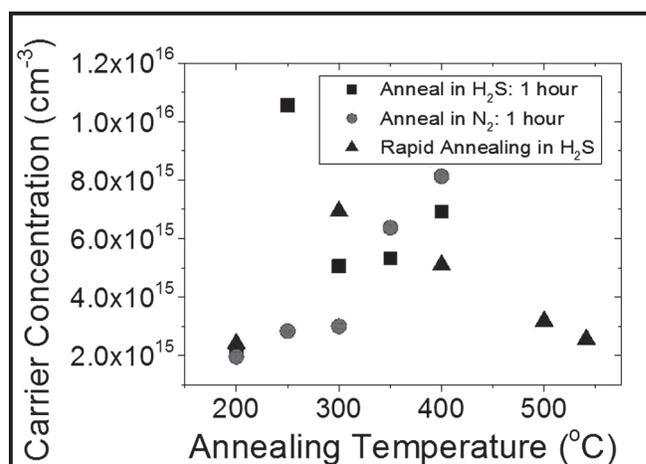


Figure 3: Effect of annealing conditions on carrier concentration.

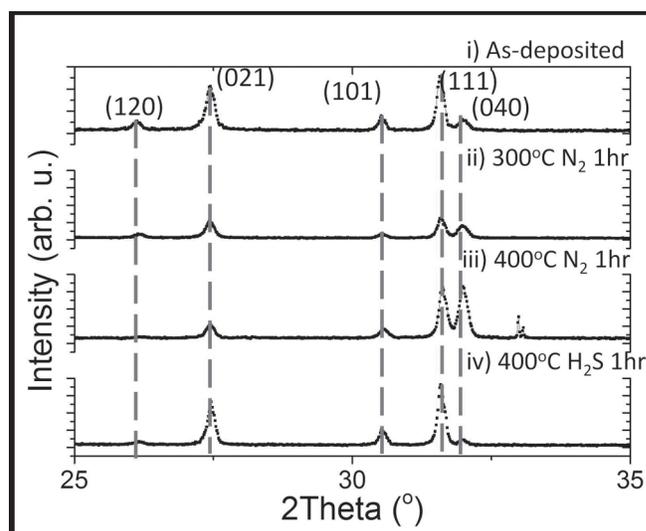


Figure 4: XRD Analysis of crystal orientation shifts due to heat-treatment.