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Abstract

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Cover Page Footnote
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Thin Film semiconductors were created through the methods of electrochemistry to produce a copper, indium and sulfur metal alloy that could be placed on a stainless steel substrate. We observed other properties regarding the relative indium to copper relationships and both the macro and micro structure of the final product. X-ray diffraction, SEM imaging, and atomic absorption spectroscopy data suggest a relatively intact metal alloy, but also an inaccurate ratio of indium to copper.

Introduction

The exigency regarding research in renewable energy has aggrandized every year with the constant reminder of an international energy crisis due to a depleting amount of cheap and convenient fossil fuels. This has not only affected the developed world, but such a practice is also argued to have devastating consequences for the developing world as well. Among the many alternatives to fossil fuels, solar energy has remained a popular option due to the near endless supply of light radiation from the sun without harmful effects to the earth. Nonetheless, solar energy remains an expensive alternative compared to fossil fuels, with large amounts of materials and space required. Moreover, the relative efficiency of solar cells remains low in comparison. However, with the advent of thin film solar cells, these problems have the ability to go away. Although thin films have less efficiency than more traditional solar cells, much less materials and space are required.

One of the most promising Solar Thin Films is copper indium gallium diselenide ($CuInGaS_{2)}$. Having a band gap vacillating between 1.0 and 1.7 eV[2], this semiconductor material has great potential to be a flagship for the next generation of solar technology. Its forerunner, copper indium diselenide ($CuInSe_2$) currently holds the highest efficiency of any other thin film solar cell at around 20 percent[1][2] with a band gap of just 1.0 eV. Band gaps for these material are strikingly low compared to other competitors. Such band gaps ranges mean the average eV value would be very close to the Shockley-Queisser Efficiency Limit . Still, working with $CuInSe_2$

until moving into the final product has not been the most ideal way towards studying the properties of these photovoltaic semiconductors. Instead, another semiconductor must be used that contains the same general properties as the previously mentioned materials, but also have more accessibility in terms of safety and economic value. This is due to the relative toxicity of selenium extraction from sulfide ore deposits; economically, pure selenium also requires large amounts of manufacturing and refinement before it can be commercially used.

The answer to this dilemma comes with copper indium disulfide ($CuInS_2$) and contains a band gap between the two extremes of the gallium and non-gallium semiconductor. Previous studies [2][4] have stayed with more traditional methods of preparing this material, using a vacuum deposition-like approach to the creation of an absorber layer for a solar cell. Making the material this way still contains the issue of a fairly high cost towards the production of thin film solar cells. Other studies, fortunately, have been experimenting with other methods that could provide a more inexpensive alternative. One of these ideas involved using electrochemical [3] depositions to create $CuInS_2$ and, in doing so, cut down costs by a significant amount.

Our analysis decided to build upon this idea of using electrochemistry to produce $CuInS_2$. Going a step further, our study involved the elimination of the more traditional molybdenum medium that the semiconductor is placed upon, and using a more inexpensive material. Historically, molybdenum has been applied due to the relative rigidity of its structure when exposed to heat. Stainless steel became the primary medium due to its very low cost in comparison to other metals available and its relative inertness to many other compounds.

The previous phase of this experiment, done at Macalester College as an Undergraduate Senior Capstone Project in 2012, sought purely to show it was possible to make $CuInS_2$ on stainless steel. The experiment, overall, was a relieving success in the fact that the alloy was created through electrochemical depositions. However, the final product was not intact. The final product could be visibly seen, but was more or less physically similar to dust in appearance.

Overall, we had proof that the process could be done but overcoming this result would need a proper revaluation of all the steps taken to make the copper indium alloy. The previous work suggested that pH would be a large indicator in the overall procedure. Other studies [2][5] confirm this to be true but also list other factors that should be considered.

Experimental

Creating the copper indium alloy would have been possible at the very beginning, but this was avoided so some reevaluation could take place. From the beginning to end, the hope was to examine the copper and indium as it evolved through each step was given much more consideration.

The condition of the copper were deemed the most important due to the fact it would be placed on the stainless steel substrate first and be the layer that would contain all the imperfections with each new step in the alloy creation process. The previous capstone project made special notes in their research that clumping of the copper was occurring, in contrasted to the expected thin and

smooth layer. The general surface that the copper would lay on was examined heavily for the most suitable conditions the copper could exist on in a uniform and thin manner.

The efforts to find a suitable surface of stainless steel involved the intuitive idea that a smooth surface of steel let the copper spread itself uniformly on the surface. All stainless steel substrates were cleaned with a concentrated nitric acid for about 40 minutes before anything else happened to them. Methods of hand tools such as polishing the steel were considered first. Other ideas included sandpaper of various grits to be applied to the surface and various combinations with polishing. A laser system was used to give a rough estimate of the relative smoothness of the surface. Seeing a vivid "laser mark (i.e. seeing how much of the laser was reflected from the surface) represented a rough surface, so minimizing this mark could give a fairly quick result. Unfortunately, due to the empirical nature of this system, no numeric data was taken.

Nonetheless, other methods of cleaning the stainless steel came up when copper depositions came out in relatively poor conditions. Electrolytic methods were inevitably used by bathing the stainless steel in a combination of sulfuric and phosphoric acid in an effort to chemically smooth the surface and eliminate human error. Eventually, it was discovered that a combination hand polishing of 3 grit followed by 1200 micron grit sandpaper was best steel preparation for the copper depositions.

Due to the importance of the copper layer providing the overall base to the alloy, it was examined the most. Many variables were tested with in combinations of and including the pH increasing and decreasing from the earlier established pH of 3 standard, deposition time, current

(i.e. the rate the copper was stuck to the stainless steel), voltage, temperature (figure three), and general stirring of the $CuSO_4$ mixture were all changed and slowly changed as peaks in performance were found in each category. These variables, tested daily, over the course of three weeks found that a pH of around 2.5, a deposition time of 20 minutes, a current of 10 mA, and a voltage of 3V gave the best samples of copper as shown in figure two. Efficacy of copper transfer was determined through relative morphology of the copper to the naked eye, and through using SEM and X-Ray Diffraction to determine relative concentrations of elements and existence of compounds that may have formed in the process.

Next came the indium layering on top of the copper layer. This step, fortunately, took a much shorter time to accomplish. Research [2][3][4][7] indicates that indium has better "behavior" than copper, meaning the indium consistently came out in a high quality without many variables needing to change; however, the main caveat with the indium is that it will evaporate during the annealing process. To compensate, a relative ratio of 1.2:1 In:Cu was taken from another study [5] to use for the process. From trial and error, it was found that a deposition that was the same as the copper would be used, but with a much longer deposition time of 75 minutes to allow for a rough ratio of 20 percent more indium than copper.

Many studies [5][7] that use an electrochemical technique also use an annealing technique that was not utilized in this experiment here. Rather than using a "flash annealing" of exposing the metal, a two-step method of annealing was to be used. First, using a furnace, the indium and copper sample was placed inside and heated to a temperature of about 100 degrees Celsius for about an hour while a continuous current of argon gas flowed through the furnace to purge out

any oxygen. This step was taken to both see if any copper indium alloy was forming but also to remove the possibility of oxidation of the environment.

Finally, argon was quickly applied into the furnace, and the copper, indium, and sulfur were placed into a furnace that was now going to be at 540 degrees Celsius for about 3 minutes as advised in one study [6]. Sulfur annealing was followed by physical inspection by the naked eye, SEM visualizing, X-Ray Diffraction, and finally Spectroscopy to determine relative ratio of indium to copper in the final process.

Results and Discussion

Due to time constraints, only two samples were able to make it all the way to the final annealing phase. The first sulfur annealing yielded exciting results: $CuInS_2$ was successfully produced and somewhat intact. Although very brittle, the overall structure was able to stay together throughout each and every step. The second sulfur anneal was less successful. Although it was intact, it mostly came apart with each and every touch or locomotion from its location. Relative proportions starting from approximately 1.2:1 were reduced as expected, but went below the ideal value of a 1:1 ratio. Instead, the more successful ratio came out to approximately 0.73127:1 and the other sample came out to 0.57174:1. Although not perfect, this does seem to imply a ratio closer to 1:1 may invite a better semiconductor material.

Future work includes working with the material the alloy is placed on. $CuInS_2$ has a different differential thermal stress than the stainless steel, and this could have contributed to the weak

structure of the final product as seen in figure four. Ideas, besides revisiting the copper and indium depositions to stop further delamination include sputtering molybdenum on glass for the copper and indium to be deposited on, and also possibly using indium tin oxide (ITO) coated glass that would stop much of the hypothetical differential thermal stress. Lastly, using the "flash" annealing could be another viable option, as the researchers using this method reported no loss to any thermal stress.

Conclusion

Production of $CuInS_2$ onto a stainless steel medium has been found to be plausible bringing some interesting insights to the future of thin film technologies for solar energy. Still, many properties need to be worked out still as the final products did not come out as ideally as predicted as shown in figure one, and even then only one of the samples could retain its general structure. This may be due to the thermal stress experienced when using a slower annealing technique compared to a very quick flash technique used in other studies that do not report any problems.

Acknowledgements

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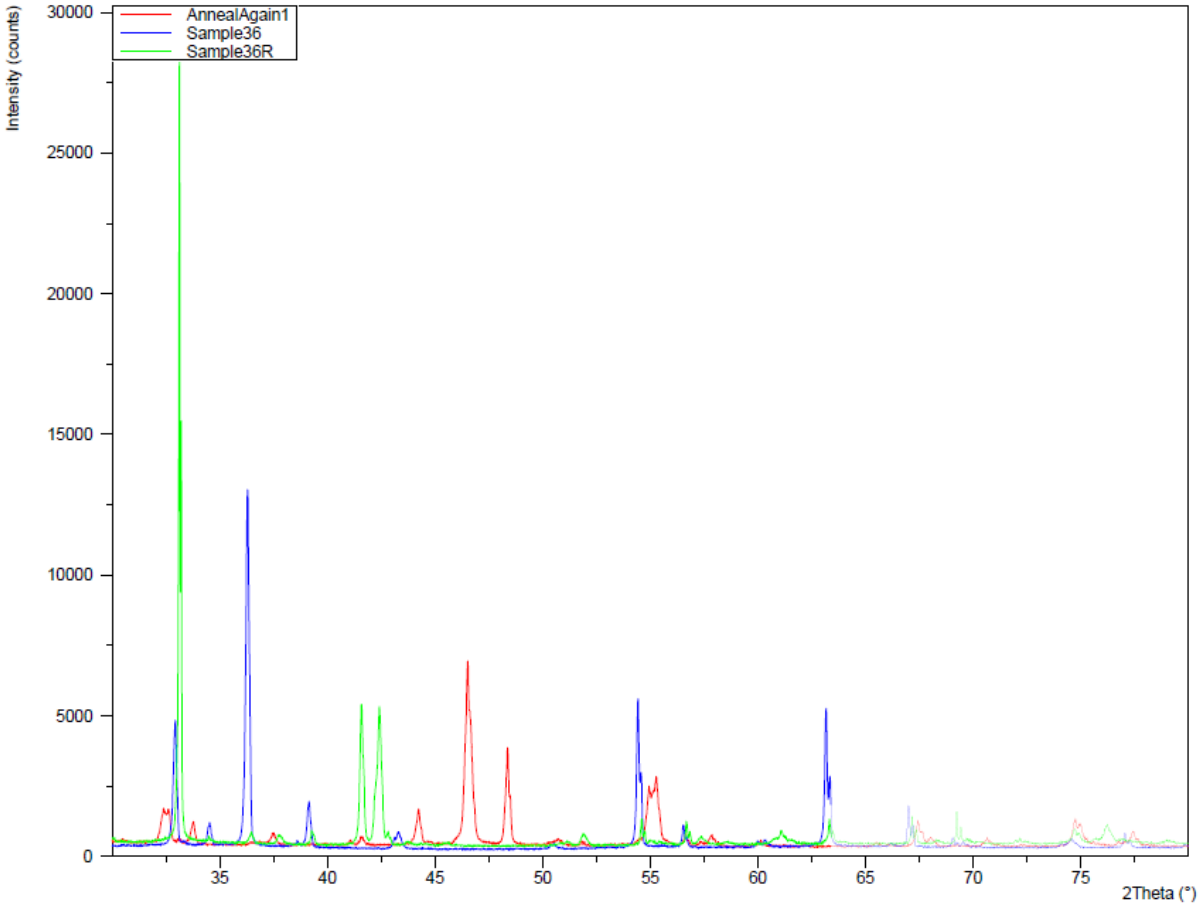

Figure One: X-ray diffraction data depicting the evolution of the deposition solution. Here 36 represents the copper deposition, 36R is indium, and the AnnealAgain1 represents the post-sulfur anneal peaks.

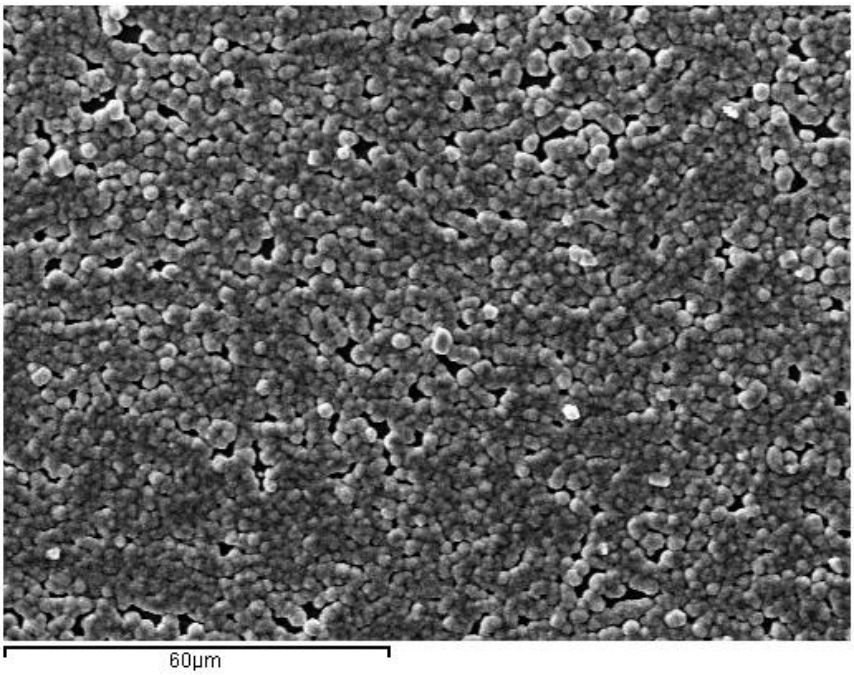

Figure Two: SEM image of the best performed copper Deposition sample

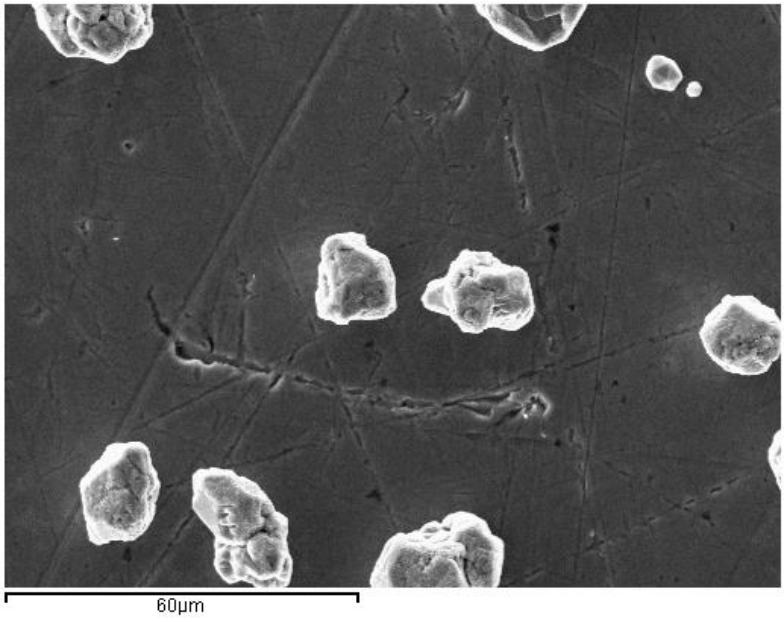

Figure Three: High temperature exposed copper sample. Although the copper did not stick much to the steel, the quality of the copper crystals was much higher.

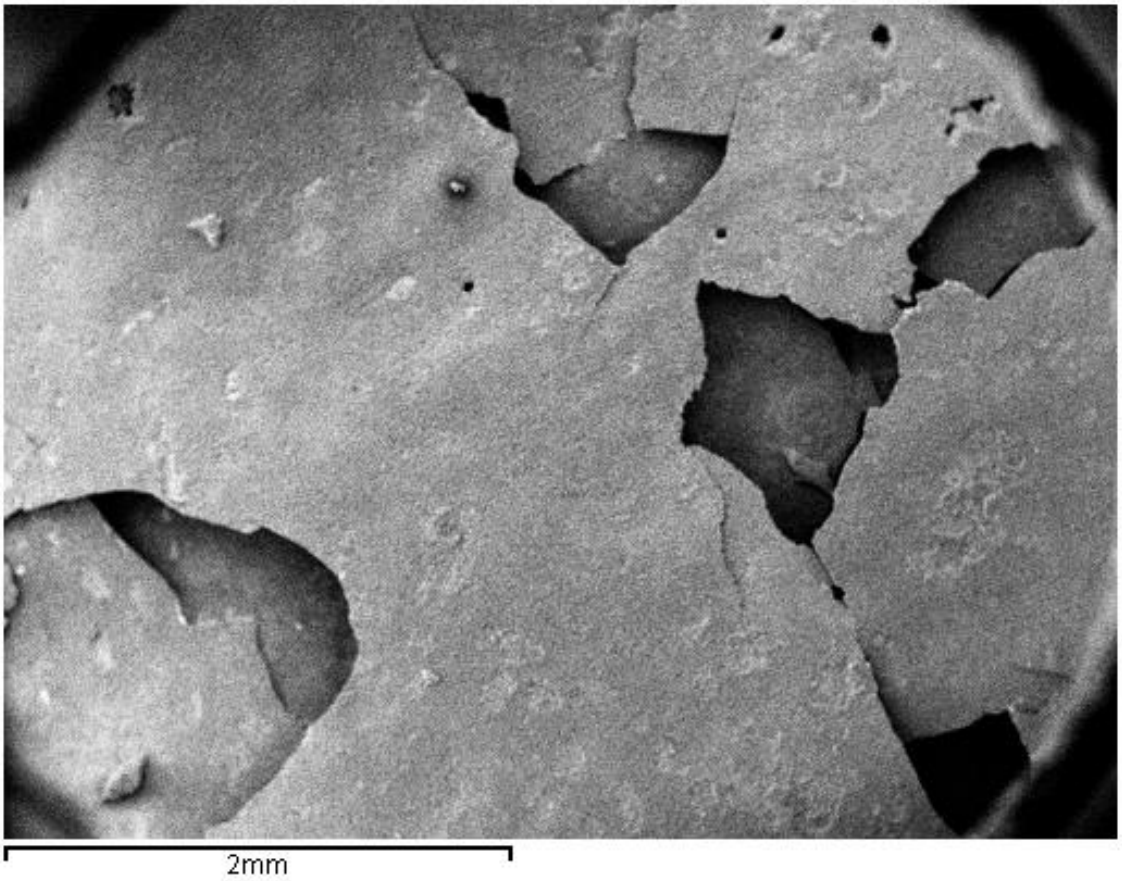

Figure Four: Image of the intact final product

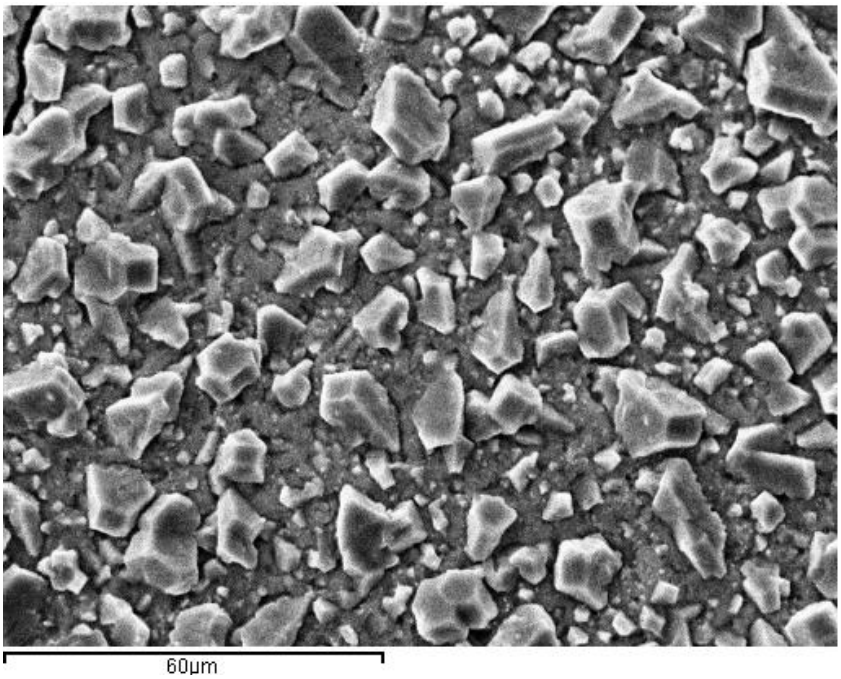

Figure Five: Close up of the intact final product

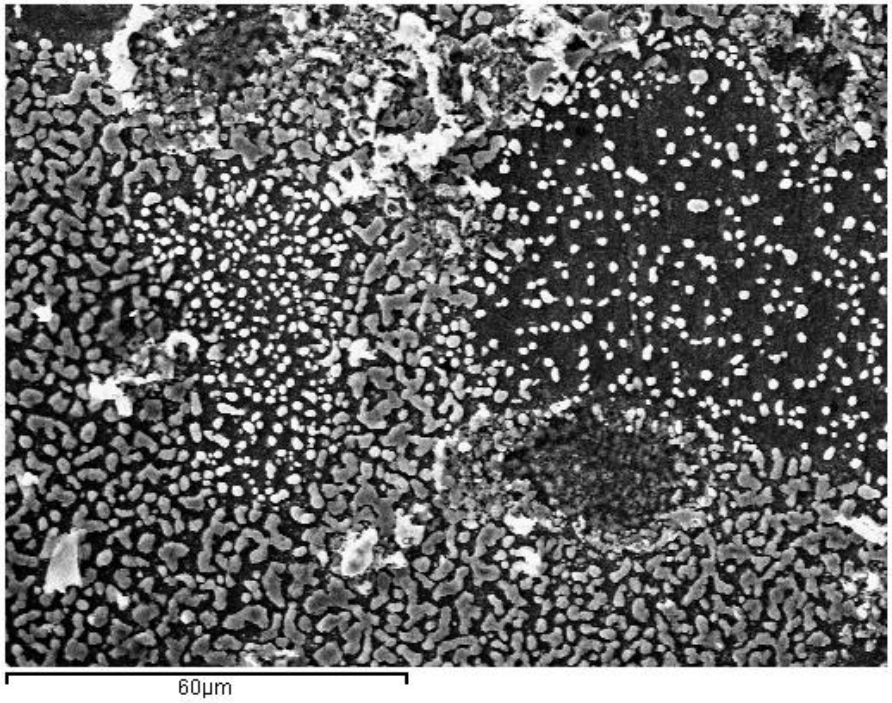

Figure Six: Close up of the region under the intact final product.

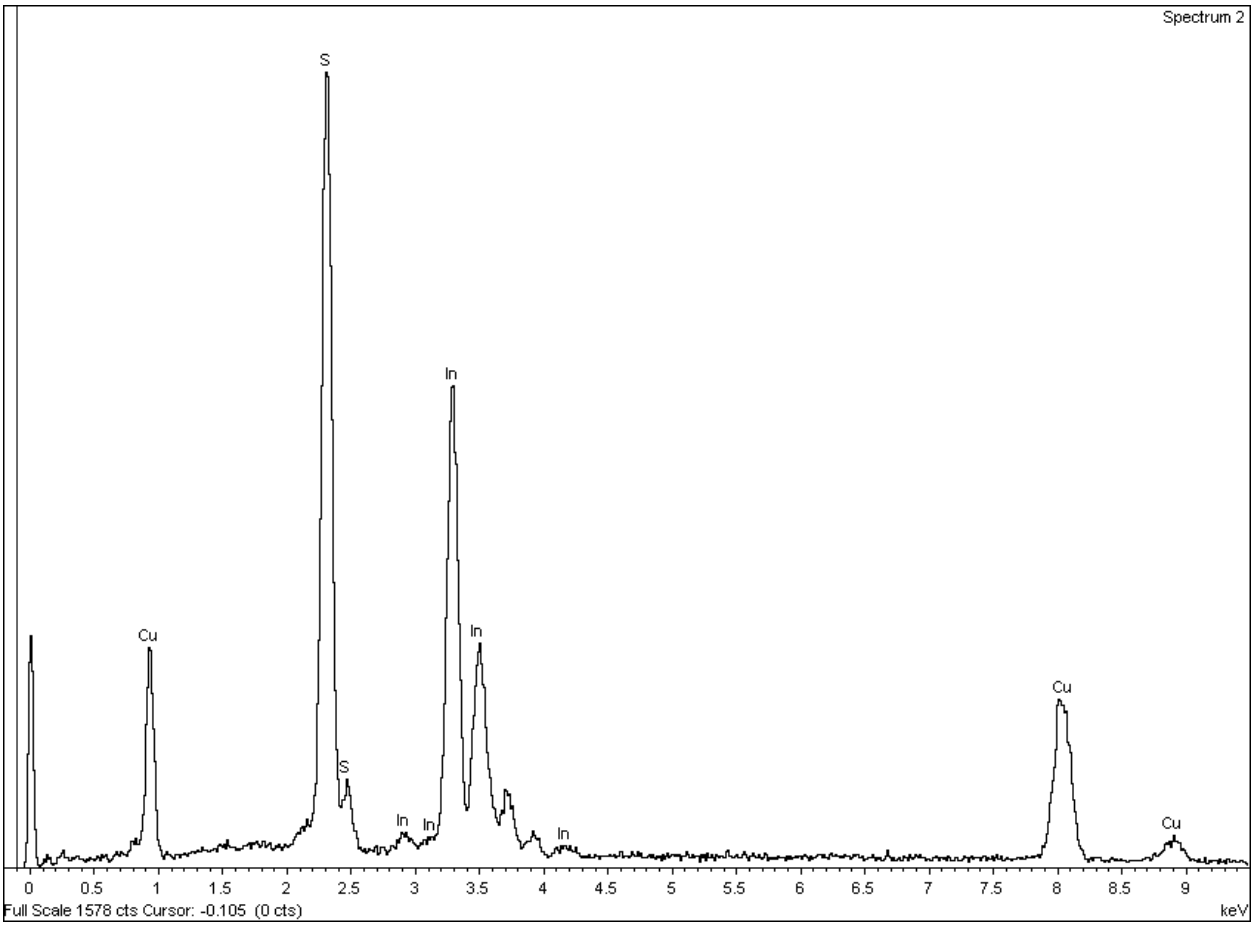

Figure Seven: SEM data showing relative concentrations of elements found in the alloy.

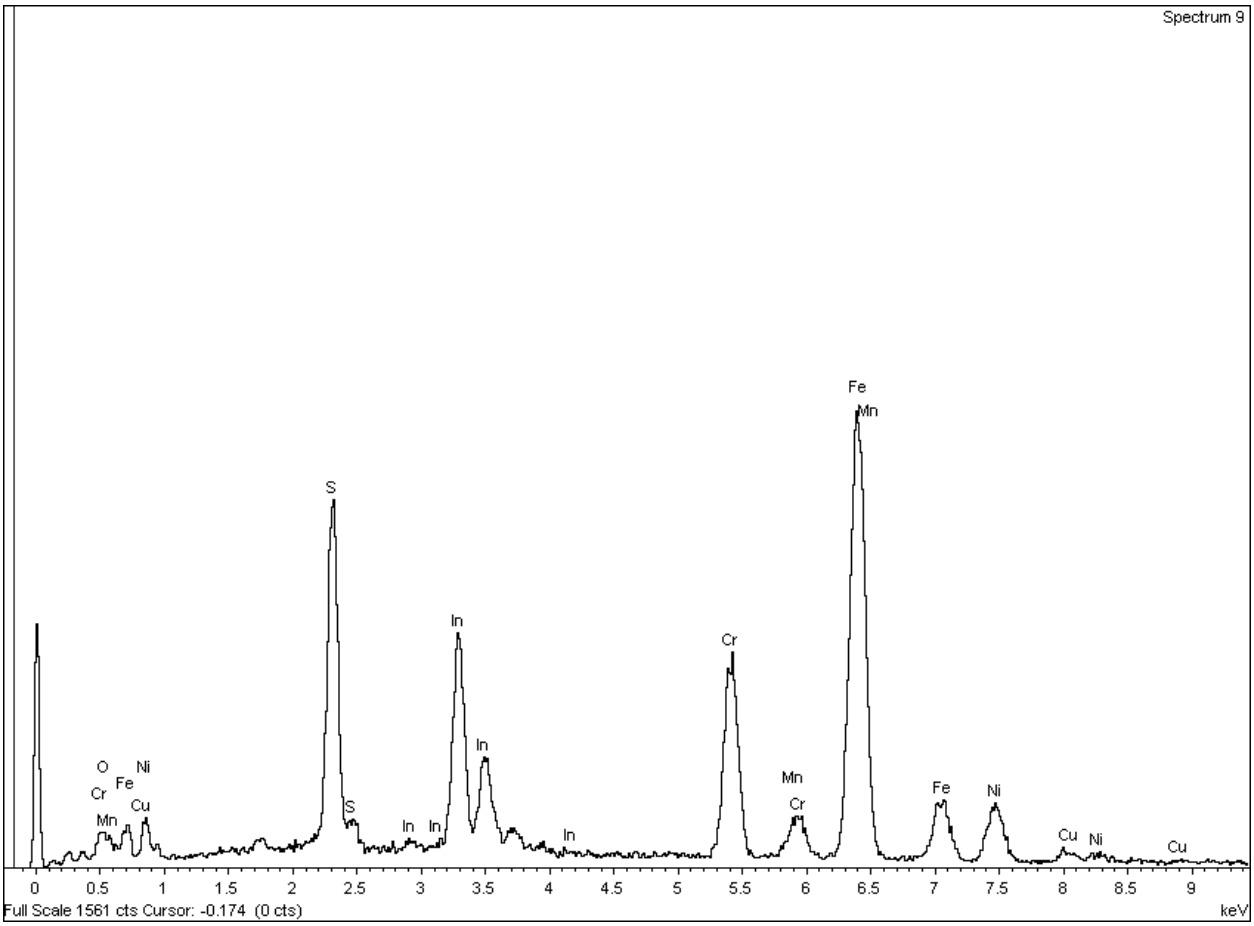

Figure 8: SEM data showing relative concentrations of elements found in the final product's surface.