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Progress in the development of $CuInS_2$ based mini-modules

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Abstract

A sequential process is used to synthesise $CuInS_2$ absorber layers for photovoltaic application. In this process CuIn precursor layers sputtered on molybdenum coated float glass are converted to $CuInS_2$ via sulphurisation in an elemental sulphur vapour ambient. A re-evaluation of process parameters has been performed including fine tuning of numerous minor aspects. Using optimised process conditions has lead to improved device performance, especially a narrowed distribution at higher module efficiencies is achieved. At the same time the process yield is improved resulting in fewer devices with poor electrical quality.

Keywords: $CuInS_2$, thin film, solar cell, module, efficiency

1. Introduction

Beside $Cu(In,Ga)Se_2$ a second thin film material from the chalcopyrite family, $CuInS_2$, has recently been introduced into industrial production [1]. Although still somewhat lower in efficiency than $Cu(In,Ga)Se_2$, a robust process has been developed that allows

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rapid and reliable $CuInS_2$ device production. Different methods to prepare $CuInS_2$ are currently under investigation, such as metal organic decomposition (MOD) [2], evaporation from a $CuInS_2$ powder source [3], aerosol-assisted chemical vapour deposition (AACVD) [4] or $CuInS_2$ on Cu-tape (CISCuT) [5]. To the best of our knowledge none of these techniques has reached solar cell efficiencies that are obtained by the sequential process that we apply [6]. In this work we report on the optimisation of process parameters and the resulting progress in mini-module performance.

2. Experimental

For the fabrication of $CuInS_2$ modules a sequential process is used [7,8,9]. In a first step copper and indium are sputtered on molybdenum coated soda lime float glass. In a second step these metallic precursor layers are converted to the $CuInS_2$ semiconductor by chemical reaction in elemental sulphur vapour at temperatures of 500 - 600 °C. This step is performed by rapid thermal processing (RTP) which allows fast temperature ramp-up and short process times [6].

Modules are completed by wet chemical removal of the secondary copper sulphide phase, chemical bath deposition of a CdS buffer-layer, and sputter deposition of a ZnO window layer. To achieve an integrated series connection of the solar cells to modules, three patterning steps are used, P1 after molybdenum deposition by laser, P2 after CdS deposition and P3 after ZnO sputtering, the latter two made by mechanical scribing.

This $CuInS_2$ process is used to prepare single solar cells of 0.5 cm^2 or larger and mini-modules on 5x5 or 10x10 cm^2 substrates having 7 or 13 integrated series connected cells, respectively. In this paper we will concentrate on the influence of process parameter variations on the performance of 5x5 cm^2 modules. Most of the correlations, however, apply to single cells in the same way.

3. Results

A number of process parameters have been evaluated on their impact on device performance. They will be discussed in the following sections.

3.1 **Precursor Cu/In atomic ratio**

Only copper-rich precursors are used with our $CuInS_2$ process. This means that considering $CuInS_2$ stoichiometry there is excess copper compared to indium, which forms the secondary copper sulphide phase with sulphur that is used in excess, too. Afterwards this copper sulphide phase is removed by wet chemical etching, thereby accurately adjusting stoichiometry. Fig. 1 shows the dependence of module efficiency on Cu/In ratio. For Cu/In $\geq$ 1.6 module efficiency is independent from the Cu/In ratio for a sufficiency large range, opening a wide process window for metal layer deposition. This is convenient as the sputter deposition rates vary differently for copper and indium with the abrasion of the sputtering targets. Modules with Cu/In = 1.4 perform somewhat inferior due to lower fill factors (not shown) but for even smaller Cu/In ratios only poor module efficiency can be achieved. Too large Cu/In ratios, e.g. > 2.0, have no advantage as the surplus copper only forms additional copper sulphide that will be removed later on. Besides a waste of target material adhesion problems may arise from too high Cu/In ratios.

3.2 Temperature ramp rate

It has been mentioned above that RTP allows fast heating up to top temperature. We have applied different ramp rates to reveal its influence on module performance. Fig. 2 shows module efficiencies as a function of temperature ramp rates between 5 and 20 K/sec. There is only a weak dependence within this range. On the other hand, former work has been performed with conventional heaters of less power output and thus lower ramp rates, but also achieved more than 11% cell efficiency [9].

3.3 **Sulphurisation temperature**

Fig. 3 shows module efficiencies as a function of sulphurisation temperature. Between 520 and 580 °C the spread in module efficiency is about 0.5% absolute and best modules were obtained at 560 °C. While V_{oc} and j_{sc} have a slight tendency to show best values for highest temperatures, the fill factor drops about 4% absolute for 580 °C compared to 520 - 560 °C. One should not overestimate, however, these small differences. Using 550 °C as standard top temperature for sulphurisation results in a sufficiently large process window of about ± 20 °C without strong influence on device performance. The little difference that shows in Fig. 3 between 540 and 560 °C is not observed for 0.5 cm^2 solar cells for a larger number of devices.

Temperatures given in Fig. 3 are relative temperatures to compare different process runs in the same machine. As absolute temperature measurement is not easy in RTP where there are never steady state conditions for short process times, we content ourselves with relative temperature measurement and accept some offset from absolute temperature.

3.4 **Sulphurisation time at top temperature**

The chemical reaction between metal precursor layers and elemental sulphur is rather fast allowing short process times of only a few minutes. Fig. 4 shows module efficiencies for reaction times between 1.5 and 4.0 minutes. For too short times (≤ 2 minutes) the reaction has not yet been completed and no useful devices are possible. Within 2.5 minutes good devices are possible but not sure. For times longer than 3 minutes module efficiencies decrease significantly. Best sulphurisation time thus is 3 minutes resulting in module efficiencies of above 10%.

Fig. 5 – 7 show infrared thermography images of three mini-modules sulphurised for 2.5, 3 and 4 minutes, respectively. Light areas indicate higher temperature than dark areas. Shunts show as bright spots as can be found on Fig. 5 and especially on Fig. 7.

In Fig. 5 only 3 of the 7 cells are relatively homogeneous medium bright indicating relatively homogeneous power dissipation and thus homogeneous current distribution in these 3 cells. At the opposite end of the module 3 cells are almost invisibly black. They are completely shunted and have only a small ohmic resistivity, thus only little heat dissipation takes place. The middle cell is only partially operating but has 3 localised shunts, indicated by 3 bright spots. For all 7 cells of the module I(V) measurements have been made separately as single cells under AM1.5 and the electrical parameters approve the findings from the thermography image: the first 3 cells have efficiencies between 8% and 9%, the last 3 cells show ohmic I(V) characteristics. The conclusion is that the precursor layers have not yet completely been sulphurised to $CuInS_2$ within 2.5 minutes but still contain metallic fractions.

After 3.0 minutes of sulphurisation time the metallic precursors are completely converted to $CuInS_2$, the module is ready, the thermography image (Fig. 6) shows relatively homogeneous power dissipation indicating a laterally homogeneously operating module. Its efficiency is above 10%.

Extending sulphurisation to 4.0 minutes generates a lot of localised shunts indicated by numerous bright spots in Fig. 7. Some of them could be detected with an optical microscope and mechanically be removed by isolating them with a sharp needle from the surrounding area, now showing as dark spots, but the majority of the shunts remained undetected and the resulting module efficiency is only 5.7%.

4. Discussion and Conclusion

All of the parameters discussed so far influence the performance of $CuInS_2$ solar cells and modules, but all of them have sufficiently large ranges where they do not or not significantly affect device quality. That means for all parameters there is a sufficiently large process window to allow stable production. On the other hand these parameters are not independent from each other, e.g. we have seen that 2.5 minutes sulphurisation time may give good modules but not for sure. Using 20 °C higher sulphurisation temperature, however, which still is within the temperature window, will accelerate the reaction so that in this case 2.5 minutes are sufficiently long. Thus optimisation of the whole set of parameters is a multi-dimensional task.

Within two half year periods, July - December 2004 and July - December 2005, about 130 mini-modules have been fabricated, each, by a baseline process. Baseline means, that all devices are included in the statistics that have been processed using a set of parameters that are considered optimum at the time of processing. Thus not included are experiments with deliberately using different parameters. In Fig. 8 the result is given as a histogram, showing the number of modules as a function of module efficiency. The improvement within one year is quite obvious, the peak of the histogram has shifted by more than 1% beyond the 10% limit, the best module having 11%. The improvement can also be seen from the yield curve: in 2004 only 20% of all modules had efficiencies higher than 9%, in 2005 about 85% of all modules were better than 9% efficiency. Applying this statistics to the electrical parameters V_{oc}, j_{sc} and fill factor (not shown here) it is found that all three contribute to this improvement, predominantly current and fill factor.

5. Summary

We have used our $CuInS_2$ baseline process to fabricate integrated series connected mini-modules on 5x5 cm^2 glass substrates. A number of process parameters have been optimised, such as Cu/In atomic ratio, temperature ramp rate, sulphurisation temperature and sulphurisation time. These parameters are not independent but influence each other. The result of this optimisation is an improvement of module efficiency by more than 1% absolute within one year period.

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References

[1] N. Meyer, I. Luck, U. Rühle, J. Klaer, R. Klenk, M.C. Lux-Steiner, R. Scheer, in: W. Hoffmann, J.L. Bal, H. Ossenbrink, W. Palz, P. Helm (Eds.), 19th European Photovoltaic Solar Energy Conference, Proceedings of the International Conference, Paris, June 7-11, 2004, p. 1698.

[2] T. Hashimoto, S. Merdes, N. Takayama, H. Nakanishi, S.F. Chichibu, S. Ando, in: W. Palz, H. Ossenbrink, P. Helm (Eds.), 20th European Photovoltaic Solar Energy Conference, Proceedings of the International Conference, Barcelona, June 6-10, 2005, p. 1926.

[3] M. Zribi, M. Kanzari, B. Rezig, in: W. Palz, H. Ossenbrink, P. Helm (Eds.), 20th European Photovoltaic Solar Energy Conference, Proceedings of the International Conference, Barcelona, June 6-10, 2005, p. 1890.

[4] J.S. NcNatt, J.E. Dickman, A.F. Hepp, C.V. Kelly, M.H.C. Jin, K.K. Banger, in: Conference Record of the 31st IEEE Photovoltaic Specialists Conference, Lake Buena Vista, Florida, January 3-7, 2005, p. 375.

[5] M. Winkler, J. Griesche, I. Konovalov, J. Penndorf, J. Wienke, O. Tober, Solar Energy, 77 (2004), p. 705.

[6] K. Siemer, J. Klaer, I. Luck, J. Bruns, R. Klenk, D. Bräunig, Sol. Energy Mater. Sol. Cells 67 (2001) 159.

[7] J. Klaer, J. Bruns, R. Henninger, K. Siemer, R. Klenk, K. Ellmer, D. Bräunig, Semicond. Sci. Technol. 13 (1998) 1456.

[8] J. Klaer, J. Bruns, R. Henninger, M. Weber, K. Ellmer, R. Klenk, R. Scheer, D. Bräunig, in: H.A. Ossenbrink, P. Helm, H. Ehmann (Eds.), 14th European Photovoltaic Solar Energy Conference, Proceedings of the International Conference, Barcelona, June 30-July 4, 1997, p. 1307.

[9] J. Klaer, J. Bruns, R. Henninger, K. Töpper, R. Klenk, K. Ellmer, D. Bräunig, in: J. Schmid, H.A. Ossenbrink, P. Helm, H. Ehmann, E.D. Dunlop (Eds.), 2nd World Conference on Photovoltaic Solar Energy Conversion, Proceedings of the International Conference, Vienna, July 6-10, 1998, p. 537.

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Fig. 4: Module efficiency as a function of sulphurisation time.

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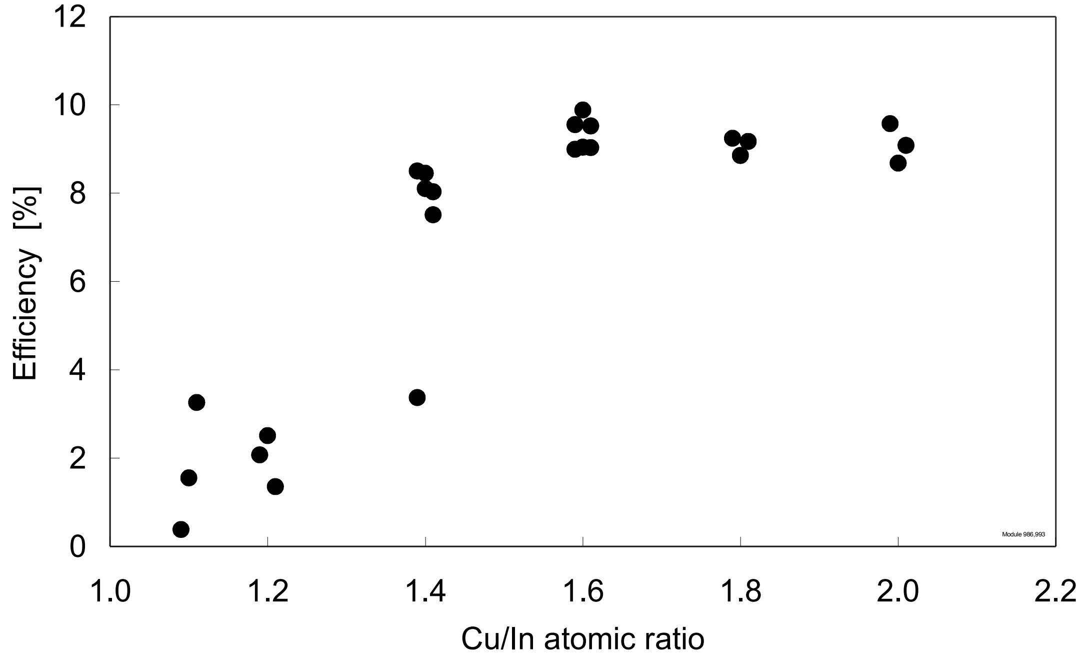
Fig. 8: Efficiencies of all baseline modules on 5x5 cm^2 processed during two different 6 months periods: July - December 2004 and July - December 2005, respectively. The total number is about 130 modules in each period. The histogram shows the number of modules in an efficiency range of 0.1%, respectively, the two lines give the accumulative yield at the corresponding efficiency.



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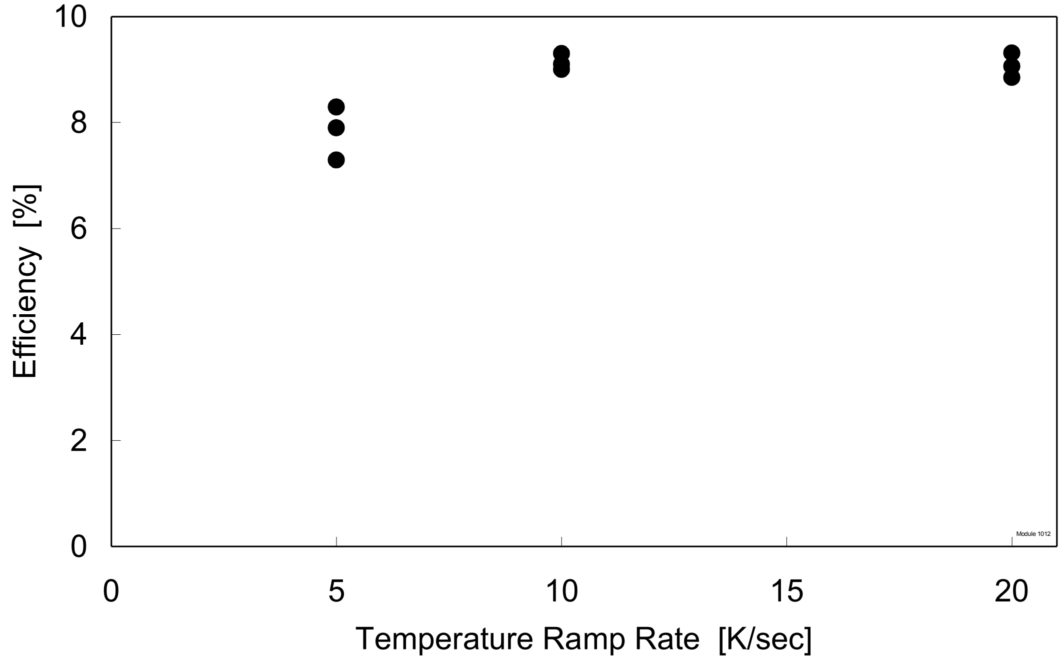


Fig. 2: Module efficiency as a function of the ramp rate to reach sulphurisation temperature.

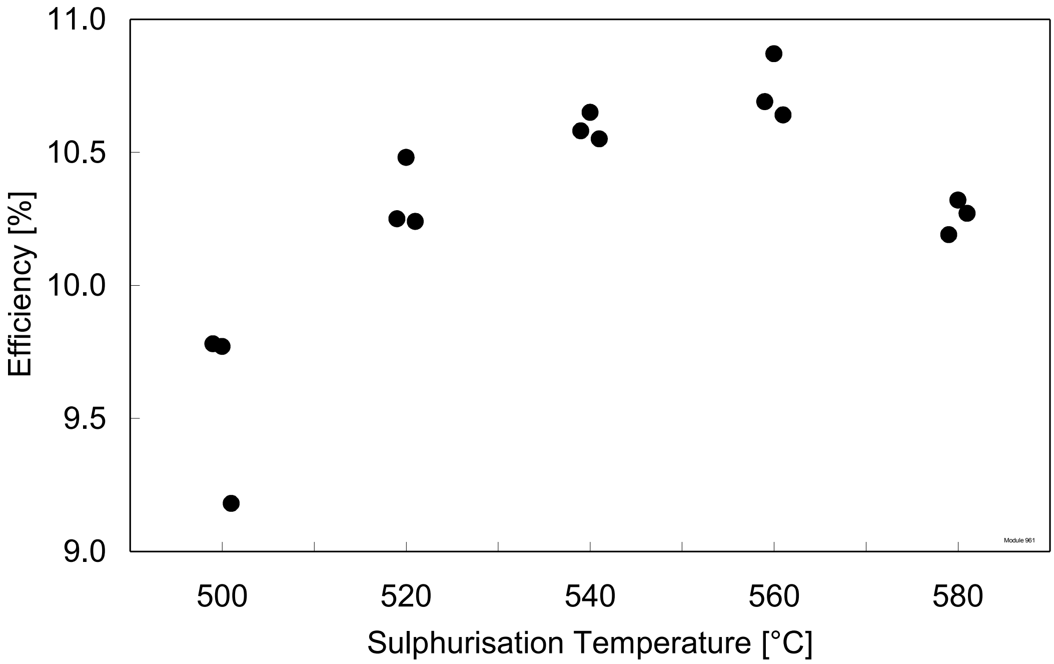
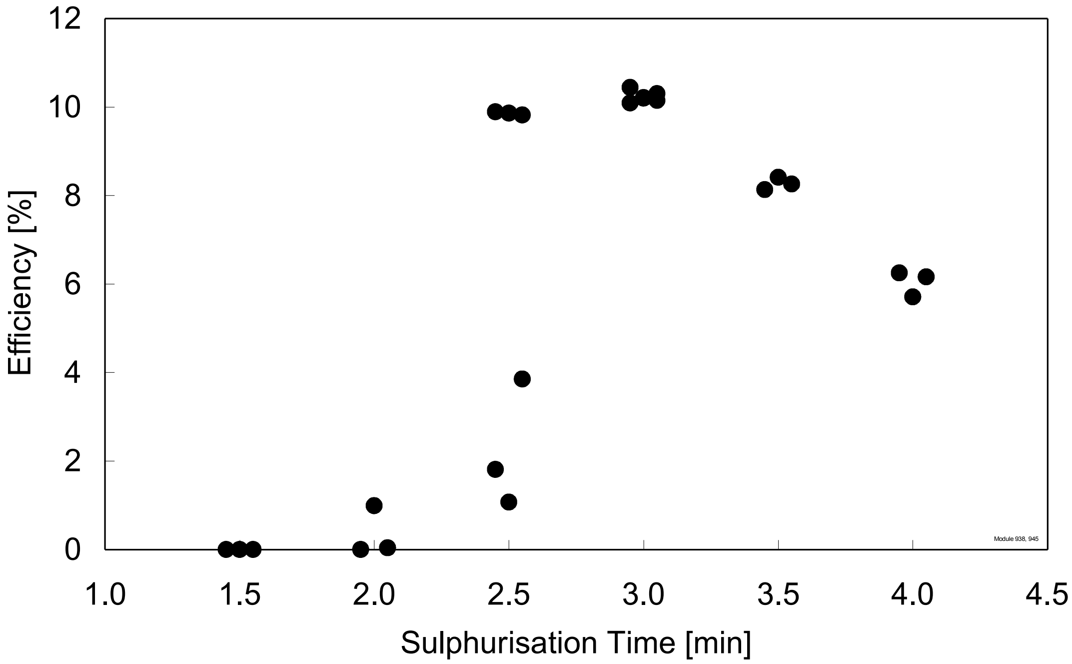


Fig. 3: Module efficiency as a function of sulphurisation temperature. Note that the efficiency axis has a strongly suppressed origin.



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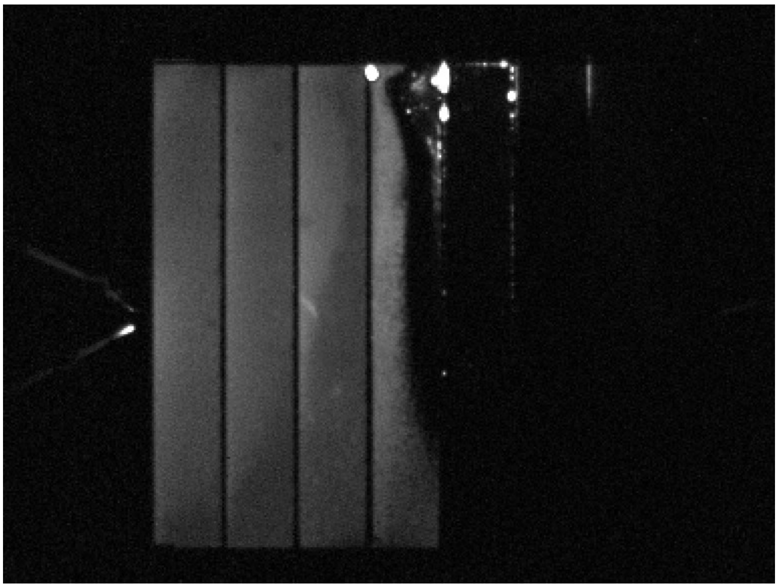


Fig. 5: Infrared thermography image of a module sulphurised for 2.5 minutes. For details refer to the text.

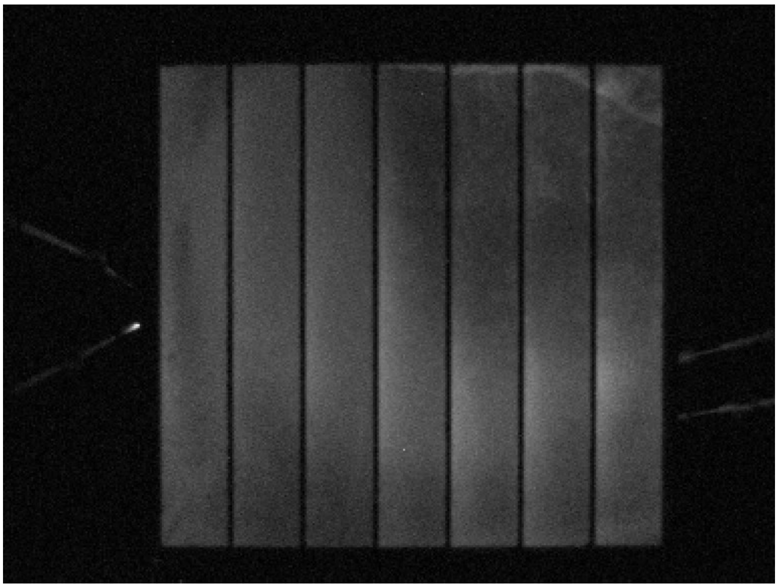


Fig. 6: Infrared thermography image of a module sulphurised for 3.0 minutes.

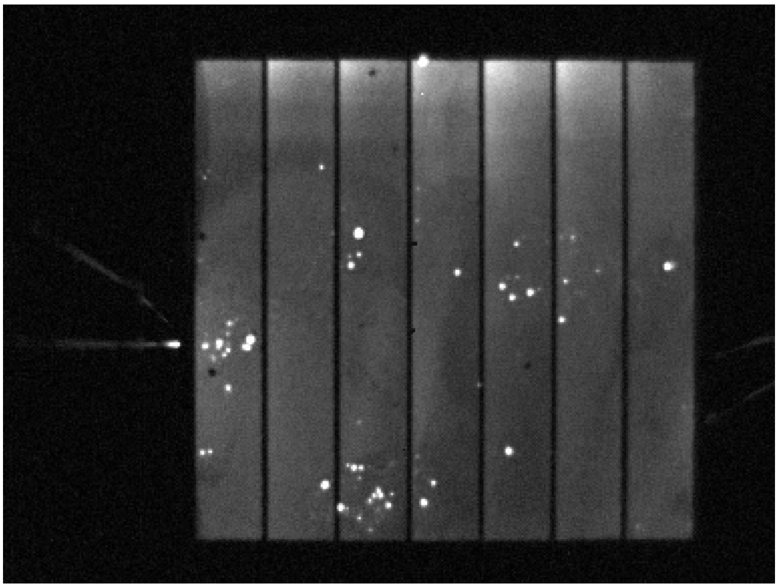
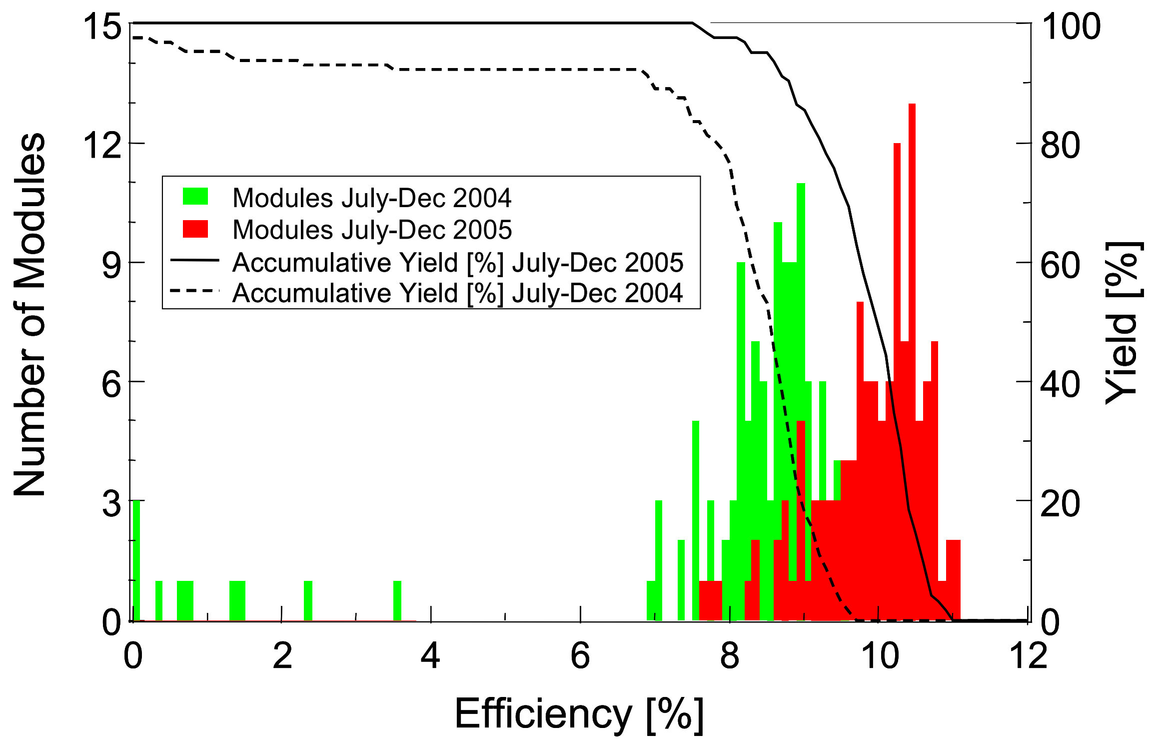


Fig. 7: Infrared thermography image of a module sulphurised for 4.0 minutes.



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