Doping in Spray-Deposited Fe_2O_3 for Next-Generation Photovoltaics

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Abstract:

The purpose of this experiment was to find optimal and simple parameters for fabrication of highly efficient solar cells with earth rich materials, which are capable of large scale deployment. Spray pyrolysis is a simple method for the creation of thin film solar cells. In this process, a solution is "atomized" into small droplets. A heated substrate evaporates the solvent, leaving behind a precipitated thin film. This technique was used to deposit a film of doped iron oxide (Fe_2O_3) onto a heated glass substrate, with a 100% ethanol solvent. The Fe_2O_3 was doped with zinc from zinc chloride ($ZnCl_2$). The samples were then analyzed for optimal morphology/film quality, resistivity, and transmittance using 4-point probe, SEM, and spectrophotometer. There was found to be no correlation between morphology patterns of doped and un-doped samples with the same deposition parameters. The optimal doped film structure was found to be amorphous. Optimal doping was at 9%, with a resistivity of 250 Ω-cm.

Introduction:

Current solar technologies are not sustainable at the terawatt scale of energy harvesting and storage. This is because they rely on either silicon (Si) or rare earth metals. Si requires massive amounts of energy for isolation, as well as notoriously harsh chemicals in the manipulation of the Si wafers, such as hydrofluoric acid or "piranha." Rare earth metals are just that: rare. Should solar energy seek to be a main energy source for society, the materials need to be in abundance and easy to isolate and manipulate. The optimal cell would also be easily translatable to large scale production.

Experimental Procedure:

A solution was prepared with a molarity varying from 0.1-1.0 M ferric chloride ($FeCl_3$) in a solution of water, ethanol, or a 50/50 mixture of the two. The solution was then mixed with $ZnCl_2$ to be 4-20% by mass. The solution was sucked into a titanium bodied Fuso Seiki STA-5N atomizing mister (Figures 1 and 2). The solution was sprayed onto a heated substrate (glass slides). On the glass slides, a small shard of Si wafer was pinned down to cover a section of the thickest part of the film (Figure 3), so that its thickness could be measured via profilometry. As the solvent evaporated, a thin film was deposited onto the substrate [1]. Following an experimentally derived "recipe," approximately 1 μm of film was deposited, with varying temperatures, but leaving the liquid consumption rate (LCR) and the nozzle-substrate-distance constant. This combination was used because these three variables all affect the rate at which the solvent is evaporated [1]. The sample was then allowed to cool to a temperature below 150°C before it was removed from the hotplate.

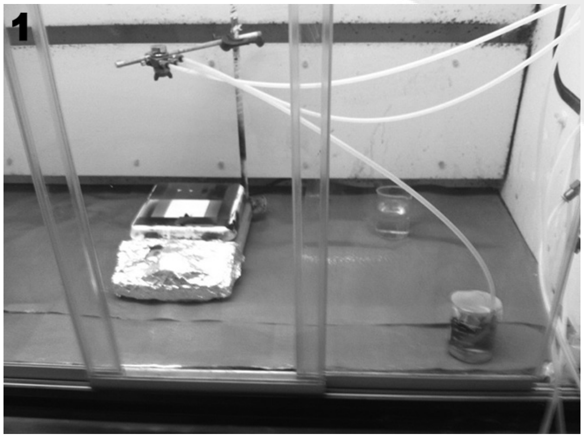
Results and Conclusions:

When the molarity of the $FeCl_3$ was varied, a correlation between that and film quality was found; the lower the molarity, the better the film quality [1] and the longer the deposition time was required to be. Film quality was judged by the crystallinity. In balancing these factors, 0.11 M $FeCl_3$ was found to be optimal [2, 3]. Solvent was varied from pure water to pure ethanol. The latter of these extremes yielded both highest film quality and shortest deposition time — 8:00 for 900 nm. Amorphous films (Figure 4) proved to have drastically lower resistivity than crystallized films, by at least two orders of magnitude.

After initial testing, continuous deposition produced lower resistivity than a pulsed deposition (rounds of :20 deposition and 1:00 re-heat period). The optimal resistivity was calculated to be 250 Ω-cm. This was found at 9% doping, which conflicts with literature values [2, 3]. This may be because we used an air carrier gas, rather than pure oxygen, and could also be due to a difference in spray techniques. This result is within three orders of magnitude of the goal 1-5 Ω-cm, which is encouraging, and this resistivity indicates that the material, still in its rudimentary stages, has the potential to be a sustainable and easily produced replacement for Si-based technologies.

Future Work:

Thermal annealing needs to be explored to see if resistivity can be lowered through that route. Sulfurization of the samples also needs to occur to tune the band gap of the film, as well as to lower the resistivity of the film. The p-type doped half of the solar cell also needs to be designed and produced.



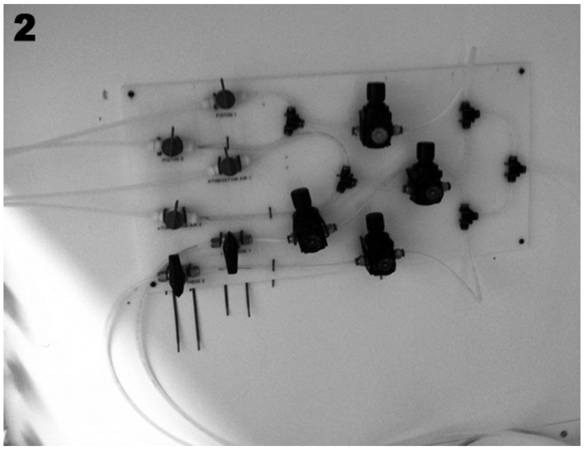


Figure 1, top left: Solution is sucked into the atomizer main body, where it is then sprayed as a mist towards the heated glass substrate.

Figure 2, bottom left: A system of valves and tubing directs pressure to the atomizer piston (controlling liquid flow), the main body (adding pressure to the solution), and to a carrier gas source (air).

Figure 3, right: Sample 7/23-2. Has lowest resistivity. Clearly visible is the section covered by the shard of silicon.

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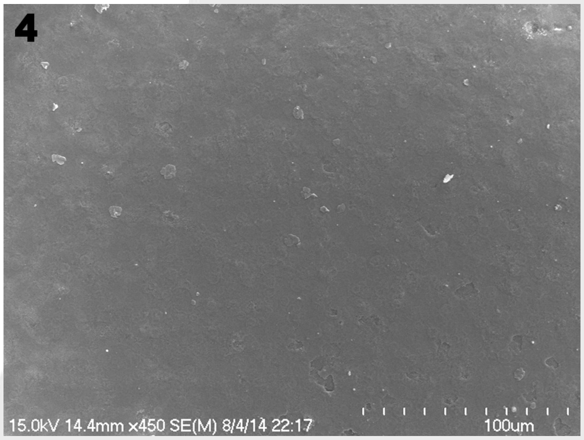

Figure 4: Sample 7/23-2. Amorphous film allows for even distribution of the dopant. Ethanol allows for fewer surface defects (e.g., pores, cracks, etc.).

References:

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