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<td>Citation</td>
<td>Journal of Applied Physics, 110(1): 016103</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2011-07-01</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/46883">http://hdl.handle.net/2115/46883</a></td>
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<td>Type</td>
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<td>JAP110-1_016103.pdf</td>
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Thin-film solar-chemical battery: Photo-charging and discharging in amorphous AgAsS\textsubscript{2} films

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(Received 6 May 2011; accepted 8 June 2011; published online 7 July 2011)

We have fabricated a rechargeable photochemical battery using ion-hole conducting AgAsS\textsubscript{2} films. An asymmetrically-electroded Al/AgAsS\textsubscript{2}/SnO\textsubscript{2} yields photocurrents and upon illumination it is concomitantly charged up. When the illumination is stopped, the stack discharges electricity into an external circuit. This photo-charging and discharging phenomenon is attributed to a photo-chemical modification of Ag-ion distribution in amorphous AgAsS\textsubscript{2}. © 2011 American Institute of Physics. [doi:10.1063/1.3606426]

There is a great demand for solar cells in the world, although one of the limitations of a solar cell is that it cannot store the electricity it generates. In many cases, solar-power systems are connected with separate storage batteries to resolve this problem.\textsuperscript{1, 11} A solar cell that can simultaneously generate and store electricity in a single device has also been invented.\textsuperscript{2-5} However, in such single devices reported so far, the battery contains liquid electrolytes as a polysulphide solution,\textsuperscript{5} which is not suitable for applications where monolithic and all-solid state cells are preferred. Furthermore, in many of these devices, photocells are sensitized by dyes, which may not be stable under prolonged light illumination.

Yoshida et al. have reported an interesting phenomenon,\textsuperscript{6} which may be applied to develop a solar-chemical battery. They have found that, in amorphous ion-hole conducting AgAsS\textsubscript{2} films with coplanar Ag electrodes, a persistent voltage appears after nonuniform illumination where only half of the AgAsS\textsubscript{2} area around one side of the Ag electrode was illuminated. They interpreted that this persistent voltage arises from the relaxing motion of Ag ions, when the spatial distribution varies through a photo-chemical modification effect in amorphous materials.\textsuperscript{9} However, they did not detect any discharging current, or photo-generated power, because of the high sample resistivity (\(~10^{11}\) Ω cm)\textsuperscript{8} of amorphous AgAsS\textsubscript{2} and the coplanar electrode structure. In addition, an electric potential change by photodoping of Ag electrodes\textsuperscript{9} has not been considered in their analysis.

In the present study, we have applied the aforementioned idea to fabricate an all-solid energy-storable solar-battery, or solar-chemical battery. For this purpose, we have considered a cell structure with AgAsS\textsubscript{2} films sandwiched between two asymmetric electrodes of Al and SnO\textsubscript{2} as Al/AgAsS\textsubscript{2}/SnO\textsubscript{2}. This structure possesses a much lower electrical resistance and hence, yields first observation of discharging electrical power in a monolithic thin-film photocell.

The cell structure, illustrated in the inset of Fig. 1(b), was prepared as follows: First, AsS\textsubscript{2} and then Ag films ~400 and ~80 nm in thickness, respectively, were sequentially evaporated onto the so-called NESA glass substrate, which is a transparent Sb-doped SnO\textsubscript{2} film deposited on a silicate glass plate. The sample was then exposed to prolonged illumination, which produced a homogeneous amorphous film with a composition of AgAsS\textsubscript{2} through the photodoping process.\textsuperscript{10} The AsS\textsubscript{2} and Ag films with the thickness ratio of 5:1 are known to produce a homogeneous AgAsS\textsubscript{2} film. An Al electrode (~10 nm thick) was evaporated onto this AgAsS\textsubscript{2} film. Finally, for stabilization the sample was annealed at 130 °C, just below the glass-transition temperature (~150 °C)\textsuperscript{11} of AgAsS\textsubscript{2} for 10 min in air. A typical sample resistance was measured to be 10\textsuperscript{8} Ω. In addition, for examining comparative characteristics, samples consisting of an Ag-free AsS\textsubscript{2} film with a thickness of ~400 nm and the same electrode structure were prepared. Excitation light was incident upon the bottom NESA side, and an electrometer (Advantest, R8240) with the meter resistances of 10\textsuperscript{13} and 10\textsuperscript{7} Ω was used to monitor voltages and currents. We hereafter define, as illustrated in the inset in Fig. 1(b), a current flow from the bottom NESA glass toward the Al electrode through the external circuit as positive.

Figure 1(a) shows a time variation of the open-circuit voltage, V, measured in the Al/AgAsS\textsubscript{2}/NESA cell under monochromatic illumination. The excitation light has an intensity of 20 µW, a spot area of ~1 mm\textsuperscript{2}, and wavelength of 545 nm. The photon energy is 2.3 eV, being comparable to the Tauc optical gap of AgAsS\textsubscript{2}, which is ~2.2 eV.\textsuperscript{12} The penetration depth of this light is estimated to be ~400 nm, which is nearly the same as the film thickness. We see that, before illumination (t < 0), the cell exhibits a nonzero voltage of ~250 mV, which appears when an electrolyte is sandwiched in between two electrodes having different ionization potentials. This is probably a type of the so-called voltaic cell effect.\textsuperscript{13} Upon illumination, the voltage increases by ~100 mV and when the illumination is stopped after 1 min, it decreases to 20–50 mV with a long decay time.

Figure 1(a) also shows a response of an Ag-free cell with the structure Al/AsS\textsubscript{2}/NESA. The illumination

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The discharging capacity in the AsS₂ cell is negligibly small (~1 nC), which strongly suggests that the Ag ions are responsible for the photo-charging and discharging behaviors.

Figure 2 strongly suggests the total discharging capacity, $Q$ and a quantum efficiency, $N_e/N_{ph}$, as a function of the illumination duration, $t_{ill}$. Here, $N_e(=Q/e)$ is the discharging carrier number and $N_{ph}$ is the total number of photons absorbed in the AgAsS₂ cell during the time, $t_{ill}$. We see that $Q$ increases steeply at $t_{ill} \leq 1$ sec, which becomes a gradual increase at longer $t_{ill}$. In correspondence to this behavior, the quantum efficiency exhibits a maximum of ~0.1% at $t_{ill} = 1$ s.

The mechanisms of the photo-charging and discharging characteristics can be understood on the basis of the band diagram. Figure 3(a) shows a schematic energy-band diagram of the Al/AgAsS₂/SnO₂ cell before illumination. It is to be noted that, in order to focus upon the potential change by light illumination, the initial voltage [~250 mV in Fig. 1(a)] probably arising from the voltaic cell effect is neglected here. In this figure, it is assumed that Sb-doped SnO₂ (NESA glass) is an n⁺-type (degenerate) wide-gap semiconductor and amorphous AgAsS₂ is roughly an intrinsic semiconductor having an energy gap of 2.2 eV.

On one hand, the band at the SnO₂/AgAsS₂ interface bends upward, reflecting a higher work function (~5.6 eV) of Sb-doped SnO₂ than that (~5.4 eV) of AgAsS₂. On the other hand, the band at the AgAsS₂/Al interface bends downward, due to the fact that the work function of Al is ~4.2 eV, which is substantially smaller than that of AgAsS₂. As it is difficult to estimate an effective carrier number in amorphous AgAsS₂, the widths of these Schottky barriers are only illustrated as estimates.

In this short-circuit condition, the behavior of the excited charge carriers under illumination can be understood as follows: In Fig. 3(b), light with photon energies greater than ~2.2 eV impinging upon the NESA glass excites the electrons and holes in the AgAsS₂ film. The excited electrons and holes in AgAsS₂ flow toward the Al and SnO₂ electrode, respectively, as indicated by the (blue) $e^-$ and (red) $h^+$ arrows, in response to the interfacial electric fields at the Schottky barriers. This rectification behavior causes a net current flow toward the left-hand side, which appears as positive, which is consistent with the observation in Fig. 1(b).

However, it is known that in amorphous AgAsS₂, holes are more mobile than electrons. Consequently, to satisfy a charge-flow balance, Ag⁺ ions will move toward the right-hand side through a kind of hole-ion interaction. This microscopic view is only speculative at present. Practically, this ion flow may be assisted by electric fields, which can be generated by trapped electrons and holes at the interfaces and/or by the finite internal resistance ($10^7$ Ω) of the current meter. The flow makes Ag⁺ ions denser in the right-hand (Al) side in the AgAsS₂ film. After the illumination is stopped, the ion diffuses toward the left-hand (NESA) side, giving rise to a positive discharging current in the dark. The stretched exponential decay may be connected to this diffusion motion. In fact, applying $L \sim (D\tau)^{1/2}$ for a diffusion motion ($L$ is the diffusion length, $D$ the diffusion constant, and $\tau$ a typical diffusion time) and using $L = 400$ nm and $\tau = 10^2$ s [Fig. 1(b)],
we get \(D = 10^{-11} \text{cm}^2/\text{s}\), which is consistent with the Ag diffusion constant in the AgAsS\(_2\) glass obtained using a tracer diffusion method.\(^{17}\)

Now we discuss the factors which govern the storage capacity of the cell. Figure 2 shows that the storage charge seems to become saturated at \(\sim 1 \mu\text{C}\). Assuming that this charge, which reflects the number of mobile Ag\(^+\) ions, is distributed uniformly in the AgAsS\(_2\) film before the illumination, we estimate the ion density to be \(10^{20} \text{cm}^{-3}\), which is consistent with that \((\sim 10^{19} \text{cm}^{-3})\) in AgAsS\(_2\) obtained from an electric time-of-flight measurement.\(^{18}\) This agreement suggests that the density of mobile ions, not the total Ag density, determines the storable capacity.

To understand the behavior of the quantum efficiency, we consider three characteristics. First, Fig. 2 shows that the maximum quantum efficiency of \(\sim 0.1\% \ (\sim 10^{-3})\) is obtained at the illumination duration of \(\mu\text{s} \sim 1 \text{ s}\), when the absorbed photon number is estimated to be \(10^{20} \text{cm}^{-2}\). We then envisage that similar numbers of electrons and holes are excited, and the electronic carriers induce the flow of Ag\(^+\) ions of \(10^{17} \text{cm}^{-3} \ (= 10^{-3} \times 10^{20})\). This number reduction of three orders should be attributed to an insufficient electro-ionic interaction. In addition, the electronic leakage current in the dark will necessarily reduce the efficiency, which is inevitable in the present monolithic cell operating at a fixed temperature. Second, the efficiency reduction at a longer exposure duration shown in Fig. 2 may be ascribed to the recombination of excess photo-excited electrons and holes. If the density of mobile ions were higher, longer exposures could be more efficiently utilized. Finally, under the present model, the reduction in efficiency after repeated illumination-discharging cycles can be attributed to a gradually degrading electro-ionic interaction and lowering ion mobility, both of which may arise from some structural changes in AgAsS\(_2\) amorphous networks.

In summary, we have demonstrated electric power generation in the dark using an all-solid solar-chemical battery. The cell employs an amorphous ion-conducting photoconducting film, AgAsS\(_2\), which is sandwiched in between two asymmetric electrodes as Al/AgAsS\(_2$/SnO\(_2\). The electrode structure governs the flow direction of the photoelectric carriers, and the Ag\(^+\) ionic charge \((\sim 300 \text{nC})\) can be stored through the photo-chemical modification effect. The maximum quantum efficiency obtained at present \((\sim 0.1\%)\) is insufficient for practical use, and further exploration to find new electro-ionic semiconductors is needed. For instance, an electro-ionic semiconductor having dense mobile ions (as Ag or Li), a low electron-hole recombination rate, and high electro-ionic interaction can be a candidate for preparing a more efficient device.

The authors are grateful to Professor Jai Singh for making valuable suggestions that substantially improved the quality of the paper.

\(^{13}\)C. M. A. Brett and A. M. O. Brett, Electrochemistry: Principles, Methods, and Applications (Oxford University Press, Oxford, 1992), Chap. 2.