Observation, Characterization, and Mitigation of the Internal *p*-*n* Junction in Pyrite FeS_2, a Potential Low-cost Solar Absorber

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Pyrite FeS_2 is widely acknowledged as an ideal semiconductor for thin film solar cells due to its earth-abundance, low toxicity, low cost, suitable band gap (0.95 eV) and minority carrier diffusion length, and high visible light absorptivity. Power conversion efficiencies of FeS_2 heterojunction solar cells, however, have never exceeded 3% due to low open-circuit voltages (V_{OC} <0.3 V). One hypothesis emerging from recent temperature (T)-dependent transport measurements of high quality single crystals is that this low V_{OC} is due to a conductive pyrite surface with a carrier type (*p*-type) inverted from bulk (*n*-type) [1,2]. This could create a leaky (*i.e.*, low-V_{OC}) internal *p*-*n* junction, thus limiting heterojunction solar cell efficiencies. These studies established conduction through a 1-3 nm-thick, *p*-type surface upon freeze-out of *n*-type bulk carriers [1,2]. Two parallel resistors representing surface and bulk conduction can describe the T-dependence of resistivity across a wide T range (50-500 K) [1] and the non-linear Hall effect observed near the crossover between bulk- and surface-dominated conduction upon cooling below 300 K [2]. Notably, what has neither been observed nor characterized, however, is the internal *p*-*n* junction implied by this *p*-type surface and *n*-type bulk. Here, we directly observe this internal junction for the first time. In-plane sheet resistance (R_S) measurements of polished crystals doped heavily *n*-type *via* sulfur vacancies are shown to display an effect where metallic-like transport abruptly transitions to rapidly increasing R_S below ~175 K, eventually transitioning to surface conduction at lower T (<100 K). We show that this very unusual T-dependence can be well described by incorporating an exponentially-T-dependent junction resistance into the parallel resistor model. Junction barrier heights extracted from the model are typically 0.15 – 0.30 eV, in good agreement with typical V_{OC} values in past heterojunction solar cells, suggesting that this internal junction may, in fact, be limiting conversion efficiencies. Interestingly, while junction influence in $R_S(T)$ is independent of contact materials such as In, Ag, Fe, Co, and Ni, CoS_2 contacts mitigate this junction, allowing the first characterization of bulk properties to low T. Access to bulk properties at low T unveils rich phenomena, such as the onset of a smaller donor activation energy below 175 K, non-linear Hall effect near 100 K, and an unusual resistivity anomaly at $T \leq 10$ K, showcasing CoS_2 contacts as a way to both mitigate this junction and advance understanding of electronic transport in FeS_2. This work was supported by the customers of Xcel Energy through a grant from the Renewables Development Fund.

[1] M. Limpinsel *et al.*, Energy Environ. Sci. **7**, 1974 (2014).
[2] J. Walter, *et al.*, Phys. Rev. Mater. **1**, 065403 (2017).
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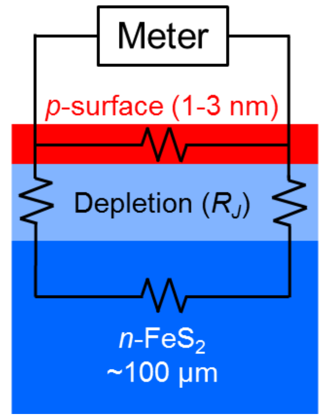
Supplementary Pages

Figure 1. Expected resistor network in horizontal transport measurements of a pyrite FeS_2 single crystal (~100 µm thick) with an *n*-type interior (shown in blue) and a degenerately-doped, *p*-type surface (shown in red). The depletion region on the *n*-type side of the internal junction, and the resistance associated with it (R_J), is shown in light blue.



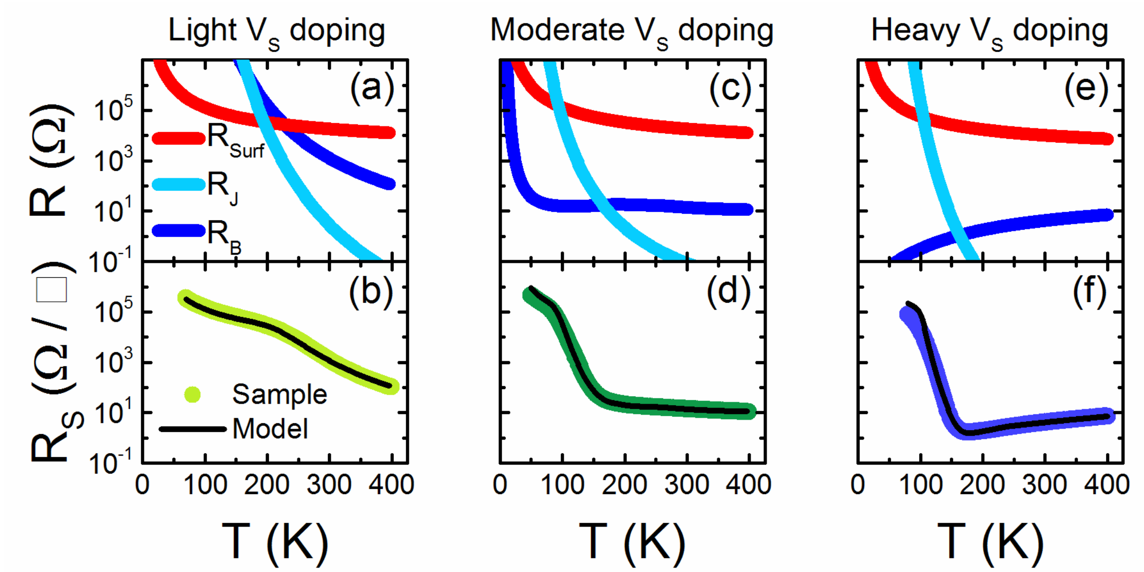


Figure 2. (a,c,d) The temperature (T) dependence of surface (R_{Surf}), junction (R_J), and bulk resistance (R_B) contributions to the total sheet resistance (R_S) of FeS_2 crystals grown under light (a), moderate (c), and heavy (e) sulfur vacancy (V_S) doping. The T-dependence of R_{Surf} (red data) is independent of V_S doping. $R_B(T)$ (blue data) is quantitatively described in each case using the Hall effect and the Drude model, by which the T-dependences of electron density and mobility are described by simple activated and power law behavior, respectively (data not shown). $R_J(T)$ (light blue data) is described assuming a Schottky junction, with $R_J(T) = R_{0,J} e^{q\varphi_B / k_B T}$, where $R_{0,J}$ is a pre-exponential factor, q is the electric charge, k_B is Boltzmann's constant, and φ_B is the Schottky barrier height (in eV). (b,d,f) Comparison of the T-dependence of measured sheet resistance (R_S, colored data) and calculated sheet resistance (black lines). In each case, the measured R_S is well described by the parallel resistor network shown in Figure 1, adjusted from previous work by including R_J. Interestingly, R_J is only made manifest in crystals doped with larger V_S concentrations, where R_B does not freeze out upon cooling to intermediate T (~200 K) due to donor band broadening and an evolution towards an insulator-metal transition.

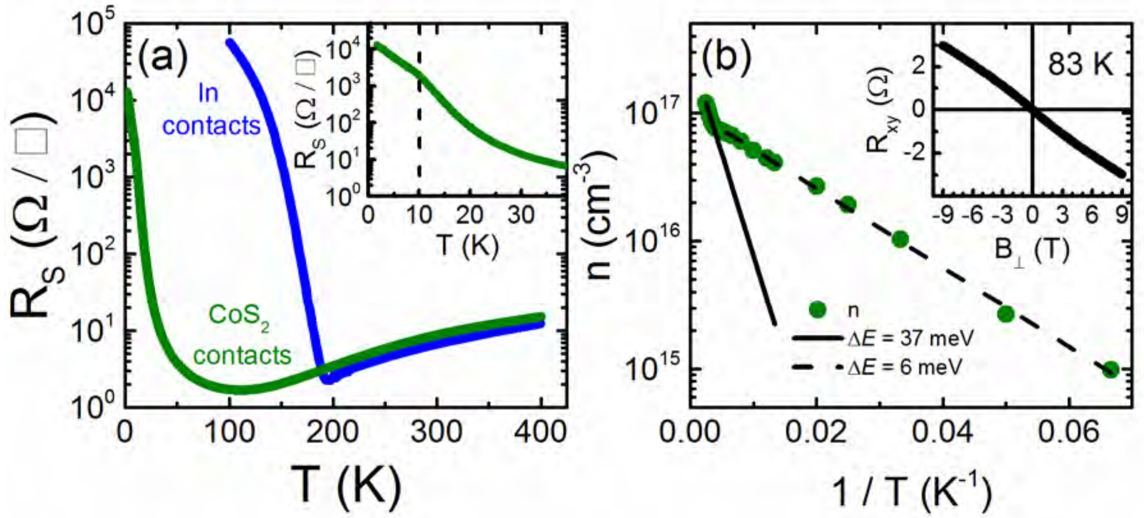


Figure 3. (a) $R_S(T)$ of an FeS_2 crystal heavily doped with V_S, contacted using In soldered (blue data) *vs.* CoS_2 (green data) contacts. CoS_2 contacts mitigate the strong *T*-dependent R_J, allowing access to bulk FeS_2 transport at lower *T*. Shown in the inset is bulk FeS_2 transport at low *T*, accessed using CoS_2 contacts, which highlights the resistivity anomaly near and below 10 K (vertical dashed line). CoS_2 is a ferromagnetic metal, also crystallizing in the pyrite structure, and Co is a known shallow donor in FeS_2. The current hypothesis is that, through the mild heat treatment (350 °C, 8 hrs, in S vapor) we use to sulfidize sputtered Co contacts into CoS_2, Co in-diffuses, strongly doping the near-surface region of the FeS_2 crystal and shorting the junction resistance. (b) Arrhenius plot of electron density (*n*) *vs.* 1/T, where the slope is proportional to the activation energy (ΔE) of the donor state contributing to extrinsic conduction. A smaller ΔE (6 meV) is observed below ~175 K; this is not accessible without CoS_2 contacts. Inset: the non-linear magnetic field dependence of the Hall resistance (R_{xy}) at 83 K.