Reactive sputter deposition of pyrite structure transition metal disulfide thin films: Microstructure, transport, and magnetism

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I. INTRODUCTION

The pyrite structure transition metal (TM) disulfides, i.e., the TMS₂ family with TM = Mn, Fe, Co, Ni, Cu, or Zn for example, are a fascinating and under-explored family of materials. The extraordinary diversity in their physical properties is aptly illustrated by the electronic and magnetic ground states observed across the first row transition metal disulfides.¹ MnS₂ for instance is an antiferromagnetic semiconductor undergoing a rare pressure-driven transition from a high-spin t₂g⁶e₅g⁴ state for the d⁶ Mn²⁺ ions to a low-spin t₂g⁴e₅g⁰ configuration.² In FeS₂ on the other hand, increased dominance of the crystal field splitting leads to a low-spin t₂g⁶e₅g⁰ configuration for the d⁶ Fe²⁺ ions and semiconducting behavior with an indirect band gap around 0.95 eV, closely followed by a direct gap at slightly higher energy.³ Due to the fact that this gap is well suited for solar absorption and that the absorbance exceeds 10⁵ cm⁻¹ in the visible, the potential for thin film solar absorber applications has long been acknowledged.⁴ Realization of this potential has proven difficult (see Refs. 3 and 4 for example), although interest in this material has recently been renewed due to its identification as a candidate for thin film solar cells synthesized from earth-abundant, non-toxic elements.⁵ Moving further along the first row transition metals, CoS₂, a t₂g⁶e₅g¹ system, is a ferromagnetic metal with a Curie temperature (TC) near 120 K.⁶ Recent work has shown that this material forms a substitutional solid solution with FeS₂ yielding Co₁₋₋ₓFeₓS₂, a material in which the position of the Fermi level with respect to the exchange-split d bands can be fine-tuned by x.²⁻⁴ This leads to a composition-tunable highly spin-polarized ferromagnet of considerable interest for fundamental studies in spintronics. NiS₂ is similarly interesting as its TM=Ni is a diamagnetic wide gap (≈2.5 eV) semiconductor.⁶

Development of reliable and reproducible methods for the controlled deposition of these TMS₂ materials in the form of high quality thin films would enable us to fully capitalize on these extraordinary properties in heterostructured devices. The desire to exploit the high conduction electron spin polarization of Co₁₋₋ₓFeₓS₂ in heterostructured devices for fundamental studies in spintronics provides a good example.⁸⁻¹⁰ In this case, the availability of closely lattice-matched, thermodynamically compatible transition metal...
disulfides with such a wide variety of electronic and magnetic ground states opens up the exciting possibility of a new class of “all sulfide” epitaxial heterostructures. Obvious opportunities include the potential for large magnetoresistive phenomena in Co$_{1-x}$FeS$_2$/FeS$_2$/Co$_{1-x}$FeS$_2$ or Co$_{1-x}$FeS$_2$/ZnS$_2$/Co$_{1-x}$FeS$_2$ magnetic tunnel junctions, or efficient spin injection in Co$_{1-x}$FeS$_2$/FeS$_2$ or Co$_{1-x}$FeS$_2$/CuS$_2$-based spin transport devices. FeS$_2$ provides another good example as the fabrication of solar cells from this material will require that FeS$_2$ layers, with precisely engineered electronic and optical properties, be integrated into complex film stacks incorporating dissimilar materials such as metals, transparent conductors, and other semiconductors. While the potential for solar cell applications has motivated a significant effort to apply various deposition techniques to FeS$_2$, thin film growth studies of other TMS$_2$ systems remain scarce. In the CoS$_2$ case, for example, although some progress has been made using synthesis methods such as ex situ sulfidation of metals, development of methods to deposit high quality low roughness thin films for use in spintronic heterostructures has not yet matured. Moreover, development of methods that are broadly applicable across the entire family of pyrite structure TMS$_2$ compounds would be distinctly advantageous as it would facilitate exploitation of their rich functionality in all-sulfide-based structures. Little, if any, progress has been made in this direction.

For a number of reasons, sputter deposition is an attractive method for transition metal disulfides. Sputtering is a highly versatile and scalable method for controlled deposition of a tremendous variety of materials, including metals, insulators, magnets, oxides, nitrides, carbides, etc. [see, e.g., Ref. 32]. There are two obvious approaches to sputtering TMS$_2$ films: Deposition from stoichiometric compound TMS$_2$ targets or reactive deposition from the relevant transition metals in a sulfur-containing gas. Sporadic reports of both approaches have appeared, primarily for FeS$_2$. Significant disadvantages with the former approach (i.e., sputtering from compound targets) include the difficulties associated with synthesizing large TMS$_2$ targets and the fact that it does not actually preclude the need for a reactive gas, as S deficient films are obtained otherwise. The second method (i.e., reactive deposition from metals) is advantageous in terms of circumventing the need for TMS$_2$ target fabrication, improved flexibility, pursuing deposition of thermodynamically unstable compounds (e.g., CuS$_2$), and the ability to simply deposit alloy films of varied composition (e.g., Co$_{1-x}$FeS$_2$ from Co and Fe targets). The obvious disadvantage is the need to work with S-containing reactive gases, such as S, SO$_2$, H$_2$SO$_4$, or H$_2$S. Of these, S vapor (generated by a thermal source) and H$_2$S (vapor phase delivery) have been explored in preliminary reports. Reactive sputtering of FeS$_2$ in a S/Ar environment has in fact been demonstrated but obvious technical issues exist, including difficulties with S evaporation rate control, poisoning of the vacuum system due to the high vapor pressure of S, and issues related to the multiple stable S vapor species. To our knowledge, reactive sputtering of TMS$_2$ films from transition metal targets in an Ar/H$_2$S environment has been reported only for FeS$_2$. Although toxicity and flammability of H$_2$S and the need for a purpose-built deposition system are obvious concerns, it seems clear that this method is worth pursuing as a generally applicable growth method for a wide variety of pyrite films and heterostructures.

In this manuscript, we report on the use of a purpose-built sputter deposition system for reactive growth of pyrite structure transition metal disulfides from metal targets in an Ar/H$_2$S environment. Optimization of deposition temperature ($T_{Dep}$), Ar/H$_2$S pressure ratio ($P_{Ar}/P_{H2S}$), and total working gas pressure ($P_{Tot}$), with the assistance of plasma optical emission spectroscopy, reveals significant windows over which deposition of single-phase, polycrystalline, smooth TMS$_2$ films can be achieved. This is illustrated for the test cases of CoS$_2$ and FeS$_2$, which we have argued are of particular interest. It is further argued that fine-tuning the sputtering conditions for FeS$_2$ could provide a means to controllably manipulate doping levels and conduction mechanisms—critical issues in solar cell applications. Also, although it is not the focus of the current work, conditions for deposition of phase-pure TM monosulfides and thiospinels are also identified.

II. EXPERIMENTAL CONSIDERATIONS

The sulfide reactive sputter deposition system is illustrated in Fig. 1. The system is comprised of a stainless steel high vacuum chamber (base pressure $\sim 1 \times 10^{-7}$ Torr) equipped with three 2" magnetron sputtering sources arranged in a “confocal” geometry. High strength magnetron sources were used for Co and Fe targets. Pumping is achieved via a corrosive series turbomolecular pump backed with a dual-stage rotary vane pump modified for reactive gas compatibility. A leak valve introduces a stream of N$_2$ into the exhaust line of the turbomolecular pump to dilute the reactive gas below flammability limits, and the backing pump itself is situated in a fume hood. The H$_2$S reactive gas is delivered from a “lecture bottle” size cylinder in an exhausted gas cabinet through double-walled delivery lines to a corrosive series mass flow controller. In combination with a three-position gate valve between the chamber and the pumping system, a parallel Ar delivery system (directed to the individual sources) enables precise and independent control over $P_{H2S}$ and $P_{Ar}$, up to $P_{Tot} \approx 65$ mTorr, limited by the capacity of the backing pump. A pneumatic valve in the H$_2$S delivery line is interlocked to the N$_2$ leak valve in the backing line preventing use of H$_2$S without safe dilution. Together with H$_2$S sensors in the gas cabinet, fume hood, and laboratory, this completes the safety features associated with the system. All gauges can be isolated from the main chamber via valves and the system is outfitted with an internal bake-out heater and residual gas analyzer. The sample stage is equipped with a heater/thermocouple system capable of over 500°C.

For all depositions, 2 in. diameter, 0.125 in. thick metallic source targets (Co, 99.95%; Fe, 99.9%; Kurt J. Lesker Inc.) were used. Three primary parameters were optimized; i.e., $T_{Dep}$, $P_{Tot}$, and the $P_{H2S}/P_{Ar}$ ratio. The pressures were controlled via the gas flow rates. For most depositions, the sources were energized using dc power, although rf power was also explored for FeS$_2$. For the majority of the work reported here
the dc sputtering power was held at 100 W and the deposition time was fixed at 60 min (unless otherwise noted). The films were deposited on Al2O3(0001) substrates, primarily due to their low reactivity with S. During specific depositions, as described below, plasma optical emission spectra were recorded from 275 to 850 nm with an Acton Research Corporation spectrophotograph/monochromator (1.3 nm resolution) and a photomultiplier tube. Spatially averaged optical emission from the glow near the target was collected using an optical fiber coupled to the monochromator input slit. The resulting films were characterized structurally and chemically via wide-angle x-ray diffraction (WAXRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), grazing-incidence x-ray reflectivity (GIXR), confocal Raman spectroscopy, and atomic force microscopy (AFM). WAXRD employed a Bruker-AXS microdiffractometer equipped with a 2D area detector and a Cu Kα source. The films were examined using SEM and EDS in a JEOL 6500 field emission gun SEM equipped with a Thermo-Noran Vantage EDS system.

GIXR was measured on a Panalytical X’tal high resolution x-ray diffractometer using Cu Kα radiation, Raman spectra were obtained using a Witec Alpha300R confocal Raman microscope with an Argon ion laser, and AFM images were acquired using a Digital Instruments Nanoscope III in tapping microscope with an Argon ion laser, and AFM images were obtained using a Witec Alpha300R confocal Raman microscopy (SEM), energy dispersive spectroscopy (EDS), grazing-incidence x-ray reflectivity (GIXR), confocal Raman spectroscopy, and atomic force microscopy (AFM). WAXRD employed a Bruker-AXS microdiffractometer equipped with a 2D area detector and a Cu Kα source. The films were examined using SEM and EDS in a JEOL 6500 field emission gun SEM equipped with a Thermo-Noran Vantage EDS system.

A. CoS2

At all values of Ptot, Pgas, and PAr studied, a strong TDep dependence of the film morphology and growth mode was observed. This is illustrated in Fig. 2 for PAr = 15 mTorr and Pgas = 36 mTorr, i.e., Ptot = 51 mTorr with Pgas/Ptot ≈ 0.7. From 200 to 300 °C the SEM images reveal a surface morphology typical of sputtered polycrystalline films, the apparent lateral grain size simply increasing with TDep. An obvious change occurs above TDep ≈ 325 °C, however, where we observe formation of remarkably large crystallites with clear facets. Deeper insight is provided by the data shown in Fig. 3, which collates the TDep dependence of the film structure, composition, and physical properties, again at PAr = 15 mTorr and Pgas = 36 mTorr. Fig. 3(a) shows that the average lateral grain size (ξ) extracted from SEM image analysis increases slowly from ≈10 nm at 200 °C to ≈30 nm at 300 °C, followed by rapid growth above 300 °C coincident with the formation of the faceted crystallites (see Fig. 2). The crystallite sizes approach a micron at the highest TDep studied. Consistent with Figs. 2(f) and 2(g), the size distribution was found to be bimodal in this higher TDep range.

Fig. 3(b) (left axis) plots the TDep-dependence of the S atomic % from EDS, from which it can be seen that at 200 °C ≤ TDep ≤ 300 °C the stoichiometry is consistent with CoS2 formation, as indicated by the horizontal dashed line. Above 300 °C, however, coincident with the large crystallite formation, the S:Co ratio drops quickly, leveling off around 55% S, strongly suggestive of the formation of S-deficient compounds. This conclusion is confirmed by the WAXRD data of Fig. 3(c). Although all observed reflections are monitored, in this plot, for simplicity, diffraction from CoS2, Co3S4, and CoS (Ref. 36) phases is quantified by plotting the intensities of the (200), (220), and (311) reflections, respectively (i.e., the most intense peaks in the powder pattern of each phase), normalized by the substrate intensity and film thickness. This quantification of the ”crystallinity”, χ, of

III. RESULTS AND DISCUSSION

Initial depositions and optimization of sputtering conditions were done for CoS2, primarily due to our prior experience with this material in bulk form and in films synthesized by ex situ sulfidation of Co.
each phase is shown as a function of TDep in Fig. 3(c).

Single-phase CoS$_2$ was observed for TDep/C$_{20}$/$\leq$ 300°C, the diffraction intensity growing with increasing TDep, consistent with $\zeta$(TDep) from Fig. 3(a). Above 300°C, however, S-deficient secondary phases form and the CoS$_2$ diffraction intensity decreases rapidly. This general trend is observed independent of the diffraction peak monitored. We thus associate the micron-scale crystallites seen in Figs. 2(g) and 2(h) with CoS and Co$_3$S$_4$, the hexagonal/triangular crystal habit being consistent with their crystal structures (CoS crystallizes in the P6$_3$/mmc space group, while Co$_3$S$_4$, a normal cubic spinel, crystallizes in the Fd-3m space group). According to WAXRD 2D detector scans, films exhibiting this large crystallite formation are also highly textured. It should be emphasized that this behavior, i.e., the onset of large, oriented crystallites of S-deficient phases (e.g., TMS and TM$_3$S$_4$) at a certain TDep, for fixed values of $P_{Ar}$ and $P_{H2S}$, was found to be general, occurring for TM = Fe, Co, Ni, and Cu. We interpret the onset of S deficiency at higher TDep in terms of the competition between sulfidation by the reactive S species in the plasma, and thermal decomposition of CoS$_2$. Further details on the mechanisms of S-deficient crystallite formation, and the potential opportunities it provides, will be provided elsewhere. We should also point out that while formation of Co$_3$S$_4$ is expected from the bulk phase diagram, CoS is not thermodynamically stable at room temperature. It has nevertheless been observed in nanoparticles, and as a secondary phase at low sulfidation temperature in sulfidation...
of Co films. Its detection here is thus not entirely surprising.

Basic magnetic and electronic transport properties were also probed as a function of $T_{\text{Dep}}$, as shown in Figs. 3(d) and 3(e), for films with thickness 45–49 nm. In order to place these results in an appropriate context, note that bulk polycrystalline specimens have saturation magnetization, $M_S = 0.87 \mu_B/\text{Co}$ at low $T$, $T_C = 120$ K, residual resistivity, $\rho_0 \approx 31 \mu\Omega\text{cm}$, and residual resistivity ratios near 12. For these reactively sputtered thin films, Fig. 3(d) shows that the $M_S$ value at 10 K gradually approaches the bulk value (horizontal dashed line) with increasing $T_{\text{Dep}}$, reaching 0.83 $\mu_B$/Co, i.e., very close to bulk, at 300 $^\circ$C. It should be noted that accurate determination of $M_S$ requires knowledge of the film density, $D$. Densities were thus determined via standard simulations of GIXR data, paying particular attention to the region around the critical angle. The results are shown on the right axis of Fig. 3(b), where it can be seen that $D$ gradually increases with $T_{\text{Dep}}$ (ascirable to grain growth), reaching 96% of the theoretical density at 325 $^\circ$C. The fact that $D$ exceeds the theoretical value for CoS$_2$ (4.82 g/cm$^3$) at the highest $T_{\text{Dep}}$ is expected as the densities of the phases we believe to form in this region (i.e., CoS and Co$_3$S$_4$) are 5.45 and 4.88 g/cm$^3$, respectively. The precipitous drop in $M_S(T_{\text{Dep}})$ beyond 300 $^\circ$C is also unsurprising as neither CoS nor Co$_3$S$_4$ are ferromagnetic. The 10 K coercivity, $H_c$, was also measured and is shown on the right axis of Fig. 3(d). This parameter slowly decreases (from 350 to 200 Oe) up to $T_{\text{Dep}} = 325$ $^\circ$C, as expected from the crystallinity and grain size improvement, at which point it decreases quickly as the volume fraction of ferromagnetic CoS$_2$ is rapidly diminished. These $H_c$ values are close to those obtained in films with similar thicknesses synthesized by ex situ sulfidation (250–300 Oe). Fig. 3(e) displays the results of basic electrical characterization, plotting the $T_{\text{Dep}}$ dependence of the 5 K conductivity, $\sigma$. The low-$T$ conductivity increases by more than two orders of magnitude from $T_{\text{Dep}} = 200$ to 300 $^\circ$C, which we ascribe to decreased defect density concomitant with the increases in $\xi$ and $D$. At $T_{\text{Dep}} = 300$ $^\circ$C the low-$T$ conductivity exceeds $10^5$ $(\Omega\text{cm})^{-1}$, within a factor of 2 of that obtained in bulk polycrystals (horizontal dashed line). At $T_{\text{Dep}} \geq 300$ $^\circ$C $\sigma$ saturates, consistent with the fact that CoS and Co$_3$S$_4$ are reported to be metallic. Films of the type shown in Figs. 2(g) and 2(h) are thus electrically continuous, which is not obvious from SEM.

To summarize the results from Figs. 2 and 3 it is clear that there exist two distinct regimes of $T_{\text{Dep}}$, at the typical conditions of $P_{\text{Ar}} = 15$ mTorr and $P_{H_2S} = 36$ mTorr, as delineated by the vertical dashed line in Fig. 3. $T_{\text{Dep}} < 300–325$ $^\circ$C results in phase-pure, smooth, continuous, polycrystalline CoS$_2$ films with bulk-like magnetic and transport properties in the 300 $^\circ$C range. Grain sizes up to 30 nm are obtained at these deposition rates (≈0.72 nm/min). $T_{\text{Dep}} > 300–325$ $^\circ$C on the other hand leads to formation of large (micron scale), heavily faceted crystallites of S-deficient phases such as CoS and Co$_3$S$_4$. In terms of high quality polycrystalline CoS$_2$ film growth, it is thus clear that $T_{\text{Dep}} = 300$ $^\circ$C represents a good starting point for further refinement of other deposition parameters.

The results of experiments aimed at optimization of $P_{\text{Ar}}$, $P_{H_2S}$, and $P_{\text{Tot}}$ at $T_{\text{Dep}} = 300$ $^\circ$C are shown in Fig. 4(a). In such a deposition “phase diagram”, the obtained film phase(s) are depicted by symbol(s) plotted at the relevant point in the $P_{H_2S}$-$P_{\text{Ar}}$ plane. Crosses are used for CoS$_2$, circles for Co$_3$S$_4$, and plus signs for CoS. Additional information on the overall S content of the films (from EDS) is depicted via the color scale shown in the top left of the figure. Within this scheme, stoichiometric CoS$_2$ would appear as a blue cross, and slightly S deficient CoS$_2$ as a green cross. The maximum value of $P_{\text{Tot}}$ (≈65 mTorr, limited by the backing pump arrangement in our system) is shown by the solid line $P_{H_2S} + P_{\text{Ar}} = 65$ mTorr. Two exploratory depositions were made above this limit (at $P_{H_2S} = 36$ mTorr; $P_{\text{Ar}} = 36$ mTorr and $P_{H_2S} = 36$ mTorr; $P_{\text{Ar}} = 55$ mTorr), but these are not sustainable operating conditions in our current configuration due to backing pressures exceeding specifications for the turbomolecular pump (≈400 mTorr) and the possibility of subsequent overheating. From the data shown in Fig. 4(a) we see that there are essentially three important regions of parameter space. The first region (labeled region I on Fig. 4(a)) occurs at low $P_{\text{Tot}}$, i.e., the bottom left corner of the diagram. In this region we observe S-deficient phases such as CoS and Co$_3$S$_4$. In the very lowest $P_{\text{Tot}}$ range of this region Co$_3$S$_4$ is obtained, but as $P_{\text{Tot}}$ is increased the S content slowly increases and the films are
found to be mixed phase. Most importantly, we observe a roughly circular region, labeled region II in Fig. 4(a), where single-phase CoS$_2$ films form. At the center of this region single-phase CoS$_2$ films with nominally perfect stoichiometry$^{32}$ are obtained, the S content decreasing slightly towards the perimeter of region II. Finally, at the highest $P_{\text{Tot}}$ values, we observe a third region of parameter space, labeled region III. This region also results in S-deficient CoS phases, but with distinctly different surface morphology than region I. These distinct morphologies are illustrated by the SEM images of Figs. 4(b)–4(d), for regions I, II, and III, respectively. In region II (Fig. 4(c)), the single-phase stoichiometric CoS$_2$ film, we find low roughness continuous films with surface morphology typical of sputtered polycrystalline films. In region III (Fig. 4(d)), where single-phase CoS is obtained, we again find low roughness polycrystalline films. In region I on the other hand (Fig. 4(b)), we find much higher surface roughness and indications of the formation of faceted crystallites, much like the films deposited at higher $T_{\text{Dep}}$ with $P_{\text{Ar}}=15$ mTorr and $P_{H2S}=36$ mTorr (see Fig. 2). Thus, while regions I and III both result in the formation of S-deficient phases, they are very different morphologically and therefore likely involve different growth modes.

The trends depicted in Fig. 4(a) are further illustrated by the data of Fig. 5 (again for $T_{\text{Dep}}=300$ °C), where parameters from structural characterization, and optical emission spectroscopy of the sputtering plasma, are plotted as a function of $P_{\text{Tot}}$. Two sets of data are shown; one with $P_{\text{Ar}}$ fixed at 15 mTorr and $P_{H2S}$ varied, and another with $P_{H2S}$ fixed at 36 mTorr and $P_{\text{Ar}}$ varied. These correspond, respectively, to horizontal and vertical cuts through the “phase diagram” of Fig. 4(a), as indicated by the dashed lines. The parameters plotted in Fig. 5 are (a) the deposition rate ($r$), (b) the previously defined CoS$_2$ crystallinity parameter ($\zeta$), (c) the film S content, (d) the lateral grain size ($\xi$), and (e) the concentration of atomic H (from plasma optical emission), as well as the integrated emission intensity associated with H$_2$S dissociation. The first noteworthy point is that $r$ decreases with increasing $P_{\text{Tot}}$, as expected, but also that the three distinct regions of Fig. 4(a) are clearly reflected in $r(P_{\text{Tot}})$, independent of whether $P_{\text{Ar}}$ or $P_{H2S}$ is fixed, i.e., $r$ is controlled primarily by $P_{\text{Tot}}$ rather than $P_{\text{Ar}}/P_{H2S}$. The rate decreases quickly with $P_{\text{Tot}}$ in region I, levels off in region II, where single-phase CoS$_2$ is obtained, then falls again in region III. Figs. 5(b) and 5(c) show the expected trend based on Fig. 4(a) in that the CoS$_2$ diffraction intensity reaches a broad maximum in region II, accompanied by attainment of close to ideal S content (horizontal dashed line). In regions I and III, the CoS$_2$ diffraction intensity vanishes, and the S content drops to 50%–55%, consistent with the formation of CoS and Co$_3$S$_4$. Fig. 5(d), which plots $\zeta(P_{\text{Tot}})$, clearly illustrates the abovementioned morphological differences between regions I and III. Deposition in region I yields large $\xi$ associated with the formation of faceted crystallites, whereas region III yields much smaller $\zeta$, more typical of sputtered polycrystalline films with low roughness. Note that the weak decrease in $\zeta$ with $P_{\text{Tot}}$ above $\approx40$ mTorr is at least in part due to the decreasing film thickness due to the behavior of $r(T_{\text{Dep}})$ (Fig. 5(a)).

The results of the plasma optical emission spectroscopy are summarized in Fig. 5(e). For each spectrum (i.e., for each of the various combinations of $P_{\text{Ar}}$ and $P_{H2S}$), the intensities of a set of peaks uniquely assigned to S ($\lambda=534$ nm),

![FIG. 5. Total pressure ($P_{\text{Tot}}$) dependence of (a) the deposition rate ($r$), (b) the CoS$_2$ crystallinity (same definition as for Fig. 3), (c) the S atomic %, (d) the lateral grain size from SEM ($\xi$), and (e) the concentrations (based on optical emission) of atomic H (diamonds) and S (circles) on the left axis, and the integrated emission intensity associated with H$_2$S dissociation (triangles) on the right axis, at a deposition temperature of 300 °C. The thicknesses ranged from 15 to 148 nm (strongly dependent on $P_{\text{Dep}}$). Data were obtained by fixing $P_{H2S}$ at 36 mTorr and varying $P_{Ar}$ (black circles), or fixing $P_{Ar}$ at 15 mTorr and varying $P_{H2S}$ (red open circles). These correspond to vertical and horizontal cuts through Fig. 4, as indicated by the dashed lines on that figure. The dashed horizontal line in (c) indicates stoichiometric S content for CoS$_2$ and the vertical shaded region indicates region II from Fig. 4(a).](https://example.com/fig5)
H (λ = 656 nm), or Ar (λ = 738 nm) were measured, the large background emission intensity associated with H2S dissociation (not seen in the pure Ar case) integrated, and the intensities normalized to the Ar concentration (the non-reactive species). We then define $C_n = (I_n/I_A)\cdot(P_{Ar}/P_{Tot})$, where $C_n$ is the concentration of reactive species $n$, and $I_n$ is the intensity of the spectral peak associated with that species. The background intensity associated with H2S dissociation was normalized in a similar manner. For fixed $P_{H2S}$ ≅ 36 mTorr (closed points), a clear maximum in both the H and S concentration can be seen in Fig. 5(e) as $P_{Ar}$ is increased through region II, concurrent with a maximum in the integrated intensity due to H2S dissociation. This data indicates that conversion of H2S to reactive H and S is maximized in this region. Conversely, for fixed $P_{Ar}$ = 15 mTorr (open points) the integrated intensity due to H2S dissociation increases monotonically with increasing $P_{H2S}$, while the concentration of atomic S decreases, and the atomic H exhibits a weak maximum. These trends will be discussed in the context of other characterization data below, although we note at this stage that the decrease in the concentration of atomic H and S at high $P_{Ar}$ likely reflects formation of stable non-reactive species (e.g., $S_x$, or $S_xH_y$).

From the behavior shown in Figs. 2 through 5 and additional insight gained from the Fe-S case presented below, the effect of varying $T_{Dep}$ on the “phase diagram” can also be deduced and qualitatively understood. In essence, we propose that the size of region II is strongly $T_{Dep}$-dependent. Due to the competition between sulfidation and thermal decomposition of CoS2 (i.e., the reversible reaction $CoS_2(s) \leftrightarrow Co(s) + 2S(g)$ being driven to the right), we propose that region II shrinks with increasing $T_{Dep}$, reflecting the increasing dominance of thermal decomposition. When the working gas pressures are fixed at values such as $P_{Ar}$ = 15 mTorr and $P_{H2S}$ = 36 mTorr, as in Fig. 2, this leads to a morphological transition from region II to region I as $T_{Dep}$ is increased, as observed in the SEM images. This explains the morphological similarities between, for example, Figs. 2(f), 2(g), and 4(b).

We now consider the extent to which the data of Figs. 2 through 5 can be understood in terms of growth mechanisms. Unfortunately, the understanding of the plasma physics and chemistry relevant to reactive sputter deposition from transition metal targets in an Ar/H2S environment is incomplete. Indeed, this is an area that could clearly benefit from additional work, particularly if reactive sputtering of TMS2 films is to be understood in sufficient detail to enable rational fine-tuning of electronic and optical properties. The complexity of the reactive sputtering process is exemplified by prior work applying plasma diagnostic tools to Fe sputtering in Ar/H2S, which found an extraordinarily complex range of S-H species, no doubt related to the unusual propensity of S to form $S_x$ molecules. Nevertheless, we believe that most of the major features of the $T_{Dep}$-dependent “phase diagram” of Fig. 4(a) can be rationalized to some extent. In essence, we believe that the key factors at work are (i) the $T_{Dep}$ and pressure-dependent decomposition of CoS2, (ii) the pressure-dependent plasma density, composition, and electron temperature, and (iii) the pressure-dependent density of reactive S species.

Briefly, the behavior in region I can be rationalized as follows. Weak dissociation of H2S (Fig. 5(e)) leads to insufficient generation of reactive S-containing species to form CoS2. The high electron temperature in such a low-pressure Ar-dominated plasma will also lead to higher plasma potentials and consequently high ion bombardment energies at the substrate surface. As the momentum transfer from Ar (40 amu) ions to S atoms (32 amu) is more efficient than the momentum transfer to the heavier Co atoms (59 amu), preferential resputtering of S is likely, further limiting sulfidation. Ion bombardment of WS2 and FeS2 surfaces has in fact been observed to result in S deficiency. Increasing $T_{Dep}$ exacerbates these problems as it favors thermal decomposition of CoS2. In the “sweet-spot” in region II on the other hand, higher H2S pressures and improved H2S dissociation lead (see Fig. 5(e)) to a plasma with higher densities of S-containing reactive species. This enables formation of the higher valence, phase-pure stoichiometric CoS2. The known tendency of H2S addition to reduce ion densities and ion energies in an Ar plasma may also play a role in this region by limiting re-sputtering effects, which are known to be important in reactive sputtering of materials such as oxides.

As pointed out by Ellmer and Lichtenberger, such effects could also play an important role in determining defect densities in FeS2 films and thus controlling electronic properties. Finally, in region III it is likely that a regime is entered where the density of S-containing reactive species is actually decreased at the highest pressures, due to the usual decrease in electron temperature with increasing pressure, increased importance of collisions between neutral species (atoms and molecular fragments). Indeed, the visible emission intensity from the plasma measurably decreases in this region. In addition, and as mentioned briefly above, the formation of non-reactive S-H species and S molecules through neutral-neutral collisions is quite likely, as evidenced by the decrease in atomic S and H concentrations in this region (Fig. 5(e)).

Having identified optimal conditions for reactive deposition of CoS2 (i.e., $T_{Dep}$ = 300°C, $P_{H2S}$ ≅ 36 mTorr, and $P_{Ar}$ ≅ 15 mTorr), 45 nm thick films were grown under these conditions for more detailed characterization of structure, microstructure, composition, and magnetic and electronic behavior, enabling comparisons with ex situ sulfidized CoS2 films, and bulk polycrystals. Structural and chemical characterization is summarized in Fig. 6. As expected WAXRD (Figs. 6(a) and 6(b)) confirms single-phase polycrystalline pyrite-structure films. Note that the data in Fig. 6(b) was obtained by integration of the background-subtracted 2D detector image shown in 6(a). The vertical lines indicate the expected peak positions and intensities for bulk pyrite CoS2 powder. Although some discrepancies arise in comparing observed peak intensities to the powder reference these vary randomly between various reflections and samples (likely due to the relatively low signal to noise ratio, and issues with background subtraction), and we thus conclude that no obvious texturing occurs. The film lattice parameter was determined to be $5.53 ± 0.01$ Å, in excellent agreement with the value for bulk CoS2 ($5.532$ Å (Ref. 10)), indicating negligible strain. AFM images (inset of Fig. 5(c)) indicate
\(\xi \approx 25 \text{ nm}\), consistent with SEM. Multiple 1 \(\mu\)m line scans of the type shown in the main panel of Fig. 6(c) (see caption for details) give an rms roughness value \(\langle R\rangle\) of 1.8 nm. In the context of prior work, this value is worthy of further comment, as \textit{ex situ} sulfidation tends to result in significant surface roughness.\(^{30}\) Indeed, rms roughness values (on the same lateral length scale) of 3.5 nm are found in \textit{ex situ} sulfidized CoS\(_2\) films of similar thickness.\(^{30}\) The values obtained by reactive sputtering thus represent a factor of 2 improvement, an encouraging observation for future work on all-sulfide heterostructures. EDS data (Fig. 6(d)) reveal the presence of only Co and S, and modeling of the data results in an extracted S/Co ratio of 2.00 ± 0.06, indicating nominally stoichiometric films.

Magnetic and electronic properties of this 45 nm thick film are summarized in Fig. 7, which plots (a) the \(T\)-dependence of the magnetization (with the field \(H\))-dependence at 10 K shown in the inset), and (b) the \(T\)-dependence of the zero magnetic field resistivity. The magnetization data of Fig. 7(a) were acquired on warming in a 1 kOe measuring zero magnetic field resistivity. The magnetization data of CoS\(_2\) films of similar thickness.\(^{30}\) The values obtained by reactive sputtering thus represent a factor of 2 improvement, an encouraging observation for future work on all-sulfide heterostructures. EDS data (Fig. 6(d)) reveal the presence of only Co and S, and modeling of the data results in an extracted S/Co ratio of 2.00 ± 0.06, indicating nominally stoichiometric films.

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Metallic behavior (i.e., \(\rho = 0\)) is important as it is well-established that it reflects, indirectly, the bulk spin polarization at the Fermi surface, high values of which are the main motivation for the study of Co\(_{1-x}\)Fe\(_x\)S\(_2\).\(^{8-10}\) Fig. 7(b) shows the \(T\)-dependence of the resistivity \((\rho = 1/\sigma)\) compared to bulk polycrystals. Overall, the behavior of reactively sputtered CoS\(_2\) films is very similar to bulk. Metallic behavior (i.e., \(d\rho/dT < 0\)) is observed at both high and low \(T\), with the well-known resistivity anomaly\(^{9,10,39}\) occurring at \(T_C\). A residual resistivity \((\rho_0)\) of 66 \(\mu\)\(\Omega\) cm and a residual resistivity ratio (RRR) of 5.3 are obtained for the reactively sputtered film. While these values in films with 30 nm grain size are inevitably worse than bulk polycrystals with micron-scale grains \((\rho_0 = 31\ \mu\)\(\Omega\) cm, RRR = 12 (Ref. 39)), they compare very favorably with \textit{ex situ} sulfidized films of similar thickness, which have \(\rho_0 = 530\ \mu\)\(\Omega\) cm and RRR \(\approx 1.\)\(^{31}\) Such \textit{ex situ} sulfidized films are thought to suffer from S accumulation at grain boundaries,\(^{31,41}\) leading to large intergranular tunneling magnetoresistance effects,\(^{31}\) of order 2.5% at 10 K for these thicknesses. By comparison, in the 45 nm thick reactively sputtered film shown in Fig. 7, we obtain only 0.5% tunneling magnetoresistance at 10 K. Furthermore, we also measured reactively deposited films at half this thickness (27 nm), yielding \(\rho_0 = 73\ \mu\)\(\Omega\) cm, RRR = 5.2, and \(M_S = 0.83\ \mu\)\(\Omega\)Co, barely degraded cf. the 45 nm thickness. These results are significant as \(\rho_0\) and RRR are widely acknowledged as excellent overall indicators of total defect density in metals. We thus conclude that the crystalline quality of CoS\(_2\) thin films deposited by reactive sputter deposition in an Ar/H\(_2\)/S plasma under optimized conditions exceeds that of films synthesized via \textit{ex situ} sulfidation of Co, and that issues with excess S accumulation at grain boundaries are largely circumvented.
Having optimized the growth of CoS$_2$ and demonstrated superior properties to \textit{ex situ} sulfidation, we subsequently explored the growth of FeS$_2$ to test the extensibility of the reactive sputtering approach to other transition metals. As discussed in Sec. I, FeS$_2$ is the subject of intense current interest as a potential next generation solar absorber, and this work is thus quite topical.

### B. FeS$_2$

As a first step, $T_{Dep}$ was fixed at 300 $°C$ (i.e., the optimal value for CoS$_2$) and a “phase diagram” was constructed in the PH$_2$S–PAr plane, as shown in Fig. 8(a). On the whole, the similarity to Fig. 4(a) for CoS$_2$ is substantial, a strong indication that similar growth mechanisms are at work. In particular, we again observe three distinct regions of behavior, labeled regions I, II, and III. Just as for the Co case, region I corresponds to deposition of faceted micron-scale crystallites (see Fig. 8(b)) of S-deficient phases. The very lowest $P_{Tot}$ values in this region result in single-phase FeS \cite{Ref. 52} crystallites, just as in the Co case. Mixed phase films composed of FeS and FeS$_2$ are then observed as region II is approached. One minor difference in comparison to the Co-S case is the absence of Fe$_3$S$_4$, greigite, a relatively unstable phase. At higher $P_{Tot}$, region II is entered, where WAXRD-phase-pure FeS$_2$ is obtained. There are however a number of important differences between region II for the Co-S case and region II for the Fe-S case. First, unlike the Co case, region II is roughly elliptical in shape, extending across a large area of the diagram, approximately centered on $P_{Tot} = 55$ mTorr. It is possible that this much larger area of region II reflects the higher reactivity of Fe with S than Co with S. Additionally, region II is in fact split into two distinct sub-regions, IIA and IIB, as shown in Fig. 8(a). In region IIA slightly S-deficient FeS$_2$ is found and cracking/delamination is apparent on a large lateral length scale (see Fig. 8(d)), while in region IIB nominally stoichiometric, smooth, continuous (see Fig. 8(c)) FeS$_2$ is obtained. Note that region IIB, the most important in the context of this work, is clearly shifted to higher $P_{Tot}$, higher $P_{H2S}$ at a fixed $T_{Dep}$ of 300 $°C$. The thicknesses ranged from 19 to 66 nm for continuous films (strongly dependent on $P_{Tot}$).

![FIG. 7. Magnetic and electronic properties of a 45 nm CoS$_2$ film deposited on Al$_2$O$_3$ (0001) under optimized conditions, i.e., $T_{Dep} = 300$ $°C$, $P_{H2S} = 36$ mTorr, and $P_{Ar} = 15$ mTorr). Panel (a) shows the temperature dependence of the dc magnetization (measured in 1 kOe), while panel (b) shows the zero field resistivity. The dashed vertical red line denotes the approximate Curie temperature of 122 K. For comparison panel (b) also shows data taken on a bulk polycrystal (from Ref. 39). The inset to (a) shows an isothermal magnetization hysteresis loop at 10 K. The horizontal dashed red line represents the saturation magnetization in bulk polycrystals.](image)

![FIG. 8. “Phase diagram” of observed Fe$_x$S$_y$ phases and associated S contents as a function of $P_{Ar}$ and $P_{H2S}$ at a fixed $T_{Dep}$ of 300 $°C$. The thicknesses ranged from 19 to 66 nm for continuous films (strongly dependent on $P_{Tot}$). The Fe$_x$S$_y$ phases are represented by symbols: Crosses for continuous FeS$_2$ films, circles for discontinuous FeS$_2$ films, and plus signs for FeS. The atomic % S is represented by color, according to the scale shown on the top left. The diagram is split into regions I, IIA (purple), IIB (orange), and III, based on phase and morphology. Note the additional 250 $°C$ data point indicated on the figure. Representative secondary electron SEM images in regions I, IIB, and IIA are shown in (b), (c), and (d), respectively. The vertical and horizontal dashed lines indicate the trajectories explored in Fig. 9.](image)
decomposition of FeS₂ occurs at a faster rate than CoS₂ at 300 °C, as the decomposition point of FeS₂ is approximately 740 °C, a significantly lower temperature than the equivalent for CoS₂ (1027 °C). Indeed, thermal decomposition of FeS₂ has been observed to begin around 300 °C in thermogravimetric measurements. Higher \( P_{\text{H}_2\text{S}} \) is thus required to achieve full sulfidation at a given \( P_{\text{Ar}} \). The cracking and delamination observed in region IIA is accompanied by a large increase in resistivity and has also been observed in prior work. It may reflect a gradual transition from region IIB (continuous polycrystalline FeS₂) to region I (S-deficient crystallites).

To further understand the role of \( T_{\text{Dep}} \) on the phase behavior shown in Fig. 8(a) and to gather additional information on the impact of secondary parameters, a series of additional exploratory depositions were performed. First, a number of growths were performed at \( T_{\text{Dep}} = 250 \) °C, using \( P_{\text{Ar}} = 8 \) mTorr and \( P_{\text{H}_2\text{S}} = 30 \) mTorr, i.e., pressure conditions that would lead to cracked S-deficient films at \( T_{\text{Dep}} = 300 \) °C. As indicated on Fig. 8(a) crack-free, smooth, continuous, and nominally stoichiometric FeS₂ was obtained, confirming the anticipated widening of region IIB towards lower pressures with reducing \( T_{\text{Dep}} \). Second, a number of films were deposited in region IIA (specifically \( P_{\text{Ar}} = 15 \) mTorr, \( P_{\text{H}_2\text{S}} = 36 \) mTorr) using rf excitation (as opposed to the dc employed thus far) at 100 W of power, developing a dc bias of 137 V. This was also found to result in phase-pure, nominally stoichiometric, crack-free FeS₂ films. Together, these observations indicate significant flexibility in terms of fine-tuning growth modes and microstructure via \( T_{\text{Dep}} \), \( P_{\text{Ar}} \), \( P_{\text{H}_2\text{S}} \), \( P_{\text{Tot}} \), and dc vs. rf excitation. In such a sensitive process it is further anticipated that fine-tuning of deposition rate could be important also. Thus, while our work certainly demonstrates growth of phase-pure (according to WAXRD) nominally stoichiometric, polycrystalline FeS₂ films via this method, it is clear that additional work is required to fully understand the intricacies of the interplay between the deposition conditions, the microstructure, and, in particular, the electronic and optical properties.

As in the Co-S case, plasma optical emission spectroscopy was used to gain insight into the pressure dependence of the concentration of atomic H and S in the plasma, and the extent of \( \text{H}_2\text{S} \) dissociation. Similar to Co-S, horizontal and vertical cuts were made through the “phase diagram” of Fig. 8(a) (dotted lines), passing through each region. As shown in Fig. 9, \( P_{\text{Ar}} \) was fixed at 8 mTorr and \( P_{\text{H}_2\text{S}} \) was varied, and \( P_{\text{H}_2\text{S}} \) was fixed at 55 mTorr and \( P_{\text{Ar}} \) was varied. The trends are near identical to those seen for Co-S (Fig. 5(e)). For fixed \( P_{\text{H}_2\text{S}} = 55 \) mTorr (closed points) and variable \( P_{\text{Ar}} \), a clear maximum in the concentration of both atomic H and S occurs in region IIB, concurrent with a maximum in the integrated intensity due to \( \text{H}_2\text{S} \) dissociation. Conversely, for fixed \( P_{\text{Ar}} = 8 \) mTorr (open points) a monotonic increase in the integrated intensity due to \( \text{H}_2\text{S} \) dissociation occurs with increasing \( P_{\text{H}_2\text{S}} \), along with weak maxima in the concentration of atomic S and H. Again, this behavior is likely due to atomic S and H forming stable species (e.g., \( S_x \) or \( \text{H}_2\text{S}_x \)) at higher \( P_{\text{Tot}} \), which are not detected in the optical emission spectra.

The structural, microstructural, chemical, and electronic properties of FeS₂ films deposited under these preliminarily optimized conditions \( T_{\text{Dep}} = 300 \) °C, \( P_{\text{Ar}} = 12 \) mTorr, \( P_{\text{H}_2\text{S}} = 48 \) mTorr, and 100 W dc power \((r = 0.24 \text{ nm/min})\) were investigated. Note that quantitatively similar results were obtained at \( T_{\text{Dep}} = 250 \) °C, \( P_{\text{Ar}} = 8 \) mTorr, \( P_{\text{H}_2\text{S}} = 30 \) mTorr, and 100 W dc power \((r = 0.71 \text{ nm/min})\). WAXRD (Figs. 10(a) and 10(b)) confirms polycrystalline FeS₂ films. Note that the data in Fig. 10(b) were obtained by integration of the background-subtracted 2D detector image shown in Fig. 10(a). The vertical lines indicate the expected peak positions and intensities for bulk pyrite FeS₂ powder, from which it can be seen that no obvious texture is evident. The film lattice parameter was determined to be \( 5.41 \pm 0.01 \) Å, similar to the bulk value of \( 5.418 \) Å. This is potentially important, as significant deviations from the bulk lattice parameter have been observed in thin films in prior work \([\text{e.g., Refs. 17 and 21}]\). It can be seen from Figs. 10(a) and 10(b) that an additional reflection occurs near 52°, likely a relatively weak contribution from the well-known marcasite polymorph. This indication of marcasite formation was found for all FeS₂ films sputtered at \( T_{\text{Dep}} = 250–300 \) °C, slightly diminished for rf sputtering. In these cases, Raman spectra revealed the expected signatures for both pyrite and marcasite FeS₂, although a quantitative determination of the phase fraction of each polymorph is difficult. Fig. 10(c) shows peaks at 343, 379, and 435 cm⁻¹ for pyrite (labeled p) in addition to a marcasite peak (labeled m) at 324 cm⁻¹. SEM images (see Fig. 8(c)) reveal \( \zeta \approx 47 \) nm, the grain size and structure being clearly different from the more typical CoS₂ case (see Figs. 4(c) and 6(c)). As touched upon above we believe that further exploration of the influence of deposition conditions on the grain structure, and the subsequent effect on electronic and optical properties, is clearly warranted as it...
provides a potential path to tunable opto-electronic properties of FeS₂ films. EDS data (Fig. 10(d)) reveal the presence of only Fe and S, and modeling of the data results in an extracted S/Fe ratio of 2.00 ± 0.06, indicating nominally stoichiometric films. Finally, to explore the T_{dep}-dependence of the resistivity, depositions at these pressure conditions were also performed at T_{dep} = 190°C. Under these conditions marcasite was not detected by WAXRD or Raman spectroscopy (see Fig. 10(c)), another demonstration of the feasibility of additional fine-tuning of FeS₂ film properties with growth conditions.

Basic characterization of the electronic properties of these films (T_{dep} = 300°C, P_{Ar} = 12 mTorr, P_{H₂S} = 48 mTorr, and 100 W dc power) is shown in Fig. 11(a), which plots the T-dependence of the resistivity (log scale) from 300 K down to the lowest temperature at which the measurement could be performed (approximately 20 K). Clear semiconducting behavior is observed, the resistivity increasing by 4 orders of magnitude on cooling by a single order of magnitude, from 0.2 Ωcm at 300 K to 4 × 10⁸ Ωcm at 20 K. Figs. 11(b) and 11(c) demonstrate that simple activated transport does not occur; rather, the natural logarithm of the resistivity is linear in T^{−1/2} (see solid line) over one decade in T and four decades in resistivity (Fig. 11(b)). The absence of a simple activated behavior can also be seen from the obvious nonlinearity on a ln(ρ) vs. T^{−1} plot (Fig. 11(c)). A more quantitative and unbiased determination of the actual temperature dependence is shown in the inset to Fig. 11(a), which plots ln[−dln(ρ)/dln(T)] vs. ln(T). If the resistivity follows ρ = ρ₀ exp(T₀/T)^a, this plot generates a straight line with slope negative a. The solid line through the data in the inset to Fig. 11(a) results in a = 0.498, T₀ = 3560 K, and ρ₀ = 7.54 × 10⁻³ Ωcm. This behavior (i.e., a = 0.5) clearly indicates some form of hopping conduction, the most obvious conclusion being Efros-Shklovskii variable-range hopping. However, in recent work on FeS₂ films synthesized via ex situ sulfidation of Fe (Ref. 54), via detailed analysis, we have identified this form of conduction with intergranular tunneling transport due to the Coulomb energy penalty associated with tunneling between nanoscopic high carrier density regions. These high charge density regions are believed to be S-deficient cores in individual grains, below the WAXRD detection limit. We thus believe a similar mechanism is at work here, further motivation for more detailed studies fine-tuning the electronic properties via close control over the deposition parameters.

The extent to which additional fine-tuning may be possible is hinted at by similar measurements (also shown on Fig. 11) on films deposited under different conditions. The ρ(T) behavior was in fact found to be quite sensitive to the deposition rate. For example, deposition at T_{dep} = 300°C with 100 W rf power, which results in the substantially slower rate of 0.12 nm/min (half the rate of dc sputtering) shows semiconducting behavior but with quantitatively different ρ(T) behavior (also shown in Fig. 11). Specifically, Figs. 11(b) and 11(c) show that ρ(T) in this case no longer closely follows T^{−1/2}, the logarithmic derivative method (analysis not shown) yielding a significantly larger a of 0.65. Similarly, deposition at 250°C with 25 W of dc power, which results in a deposition rate of 0.09 nm/min, again yields deviations from T^{−1/2}, a logarithmic derivative analysis (not shown) giving a = 0.65. The increase in a towards the value expected for simple activated transport (i.e., a = 1) is very reminiscent of that seen as a function of sulfidation temperature in ex situ sulfidized FeS₂ films, a trend that was
IV. SUMMARY

We have demonstrated synthesis of single-phase polycrystalline CoS$_2$ and FeS$_2$ thin films on Al$_2$O$_3$ (0001) substrates via reactive sputtering from metallic Co and Fe targets in a purpose-built sputtering system using H$_2$S as the reactive gas. Detailed structural and chemical characterization, aided by plasma optical emission spectroscopy, reveals significant windows for the primary deposition parameters (i.e., substrate temperature and Ar/H$_2$S pressures), over which low roughness single-phase TM$_2$S$_2$ films can be deposited. Optimized CoS$_2$ films exhibit bulk-like magnetic and electronic transport properties, distinctly superior to films synthesized by ex situ sulfidation in terms of both surface roughness and magnetic/electronic properties. This is promising in terms of future work devoted to all-sulfide heterostructures for fundamental studies in spintronics. Although on the whole similar to the Co-S case, microstructural details and electronic properties of reactively sputtered FeS$_2$ were found more sensitive to the deposition parameters. Preliminary data suggest considerable potential for fine-tuning doping levels and transport mechanisms via careful manipulation of the deposition conditions, which is encouraging for solar absorber applications. Finally, although not the focus of the current study, growth conditions for single phase transition metal monosulfides and thiospinels were also identified.

ACKNOWLEDGMENTS

This work was supported primarily by the MRSEC Program of the NSF Under Award DMR-0819885. We also acknowledge partial support from the UMN’s Initiative for Renewable Energy & the Environment under Award RL-0004-11. M.J. was funded by the NSF through Grant No. CBET-0931145. Parts of the work were carried out in the UMN Characterization Facility, which receives partial support from NSF through the MRSEC and NNIN programs.


FIG. 11. Temperature dependence of the zero magnetic field resistivity, $\rho$, of three reactively sputtered FeS$_2$ films. As shown in the legend, black solid points are for a 33 nm thick film deposited dc at 100 W on Al$_2$O$_3$ (0001) at $T_{Dep} = 300$ °C, $P_{H_2S} = 48$ mTorr, and $P_{Ar} = 12$ mTorr; red open points are for a 19 nm thick film deposited rf at 100 W on Al$_2$O$_3$ (0001) at $T_{Dep} = 300$ °C, $P_{H_2S} = 36$ mTorr, and $P_{Ar} = 15$ mTorr; blue solid points are for a 26 nm thick film deposited dc at 25 W on Al$_2$O$_3$ (0001) at $T_{Dep} = 250$ °C, $P_{H_2S} = 30$ mTorr, and $P_{Ar} = 8$ mTorr. Panel (a) shows $\rho$ (log scale) vs. $T$, panel (b) shows $\ln(\rho)$ vs. $T^{-1/2}$ and panel (c) shows $\ln(\rho)$ vs. $T^{-1}$. The inset to (a) shows a linearized form of $\rho = \rho_0 \exp(T_0/T)^a$, with slope negative $a$, for the $T_{Dep} = 300$ °C dc sputtered sample.
As noted in Ref. 20 the influence of the magnetic field strength can be significant.

Although a small number of depositions were performed at pressures exceeding this level, these are not sustainable conditions of usage of the deposition system.

We use the phrase “nominally stoichiometric” to make clear that we are discussing TMS$_2$ that is, within the resolutions of the various characterization techniques applied here, stoichiometric. We are aware, as discussed in Ref. 4, that the issue of FeS$_2$ stoichiometry has generated some controversy. Optical emission lines were obtained from the NIST Atomic Spectra Database Lines Form: See http://physics.nist.gov/PhysRefData/ASD/lines_form.html.

**References**


23. As noted in Ref. 20 the influence of the magnetic field strength can be significant.