



Synthesis of iron pyrite thin films by Russian Doll sulfurization apparatus



M.F.O. Silva ^{a,*}, L.P. Souza ^a, S. de Oliveira ^a, A.S. Ferlauto ^a, W.N. Rodrigues ^{a,b}

^a Departamento de Física, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, Brazil

^b Centro de Microscopia, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, Brazil

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ABSTRACT

In this work, we present a sulfurization apparatus, we call Russian Doll, which provides a quasi-stationary sulfur rich environment. We prepared several pyrite films using the technique to sulfurize iron oxide films. We studied the influence of the synthesis parameters in the phase composition and microstructure of the disulfide films. We found no traces of iron oxides nor of secondary iron sulfide phases, such as pyrrhotite. Nevertheless, we observed the formation of the marcasite polymorph at two different temperature ranges, due to the similarity in the thermodynamic properties of both disulfide phases. At temperatures lower than 550 °C, however, marcasite undergoes a transformation reaction to pyrite, which is completed after 4 h at 550 °C. At temperatures higher than 550 °C, pyrite slowly decomposes producing pyrrhotite and sulfur gas, due to the high sulfur equilibrium fugacity. During cooling, the sulfur equilibrium fugacity drops shifting the reaction inversely towards the formation of iron disulfide, resulting in a core-surface pattern of pyrite-marcasite. We also observed that oxide films with larger particles generated pyrite films also with larger particles.

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1. Introduction

Many authors have thoroughly studied iron pyrite (FeS₂) due to its potential use as absorber material in solar cells [1–6]. The fact that FeS₂ combines excellent physical properties, such as high optical absorption coefficient ($\alpha \sim 10^5 \text{ cm}^{-1}$) with environmental friendly characteristics – low toxicity and abundance of its constituent materials, Fe and S, – makes it a suitable material to be used in photovoltaic devices [1,7]. Such a favorable scenario was explored by Alivisatos et al. who compared the theoretical performance of several semiconductors as absorber materials in ideal solar cells, i.e., with minimum energy loss [3]. Iron pyrite excelled in their model surpassing all other semiconductors, including amorphous silicon. However, despite the many advantages, authors still struggle to achieve high power conversion efficiencies [2]. Recently, M. Law et al. found that a hole rich inversion layer exists at the surface of n-type pyrite single crystals [6]. The presence of such layer greatly reduces the open circuit voltage (V_{OC}) by creating a potential barrier between the n-doped bulk and the surface inversion layer. The formation of the inversion layer is attributed to sulfur vacancies, which reduce the iron coordination number, creating acceptor levels close to the edge of the valence band. The authors also suggest that such effect is intrinsic to pyrite regardless of the production method, and it is more pronounced in polycrystalline films, due to the higher surface to volume ratio. Therefore, it is of extreme importance

when producing films of pyrite, to ensure that large grains are formed to reduce the influence of the inversion layer.

Many techniques have been used to produce iron pyrite with different degrees of purity, such as spray pyrolysis [8], metal-organic chemical vapor deposition [9–12], aerosol assisted chemical vapor deposition [13], chemical vapor deposition [14–16], sulfidation reaction with iron salts [17], sequential evaporation [18], hydrothermal growth [19], chemical vapor transport [6,20–22], flash evaporation [23], chemical methods [5,24–26], reactive sputter deposition [27], and sulfurization of iron [4,28–35] and iron oxide [36–39]. The sulfurization of iron oxide is of particular interest because the reactions of iron oxides with sulfur do not pass through the FeS phase field. Instead, reacting hematite (Fe₂O₃) with sulfur produces only FeS₂ and SO₂ gas, and the reaction of magnetite (Fe₃O₄) with sulfur produces FeS₂ and Fe₂O₃ [36]. This fact reduces the possibility of formation of iron rich sulfides (like pyrrhotite) in the process.

In this work, we first present a sulfurization apparatus called “Russian Doll” to produce iron pyrite films from hematite precursor films. Sulfurization is a well-known process that usually involves the use of glass or fused silica ampoules, which need to be destroyed after use, and may lead to condensation of sulfur on the surface of the films. Our apparatus provides a quasi-stationary sulfur environment without the use of ampoules, may be reused indefinitely without the need to break open, and eliminates the excess of sulfur, avoiding condensation of the material on the surface of the films, which may occur in the case of ampoules [30]. Another sulfurization technique commonly used consists of producing a continuous low sulfur flow (typically <100 sccm) by using either H₂S, which is highly toxic, or considerable amounts (hundreds of milligrams) of sulfur heated at temperatures

* Corresponding author.

E-mail addresses: mangos@ufmg.br (M.F.O. Silva), ligia@fisica.ufmg.br (L.P. Souza), sergio@fisica.ufmg.br (S. de Oliveira), ferlauto@fisica.ufmg.br (A.S. Ferlauto), wagner@fisica.ufmg.br (W.N. Rodrigues).

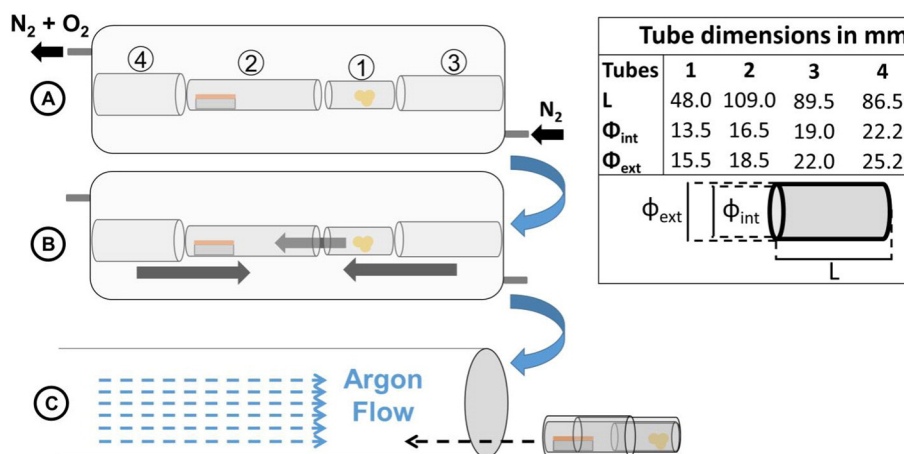


Fig. 1. Scheme illustrating the Russian Doll sulfurization apparatus.

slightly higher than the melting point (approximately 115 °C). Our method uses sulfur powder as well, but in lower amounts – when compared to the previous method mentioned above – (15 mg), to produce a sulfur rich atmosphere in an enclosed environment and, thus, it is a process both cleaner and safer. Finally, we present our results on the influence of the sulfurization parameters as well as the influence of the precursor microstructure on the phase composition and microstructure of the resulting pyrite films.

2. Materials and methods

Iron pyrite thin films were produced via a two-step process. In the first step, hematite thin films were grown by spin coating a 0.5 M solution of iron (III) nitrate nonahydrate [(FeNO₃)₃·9H₂O 98%, Sigma Aldrich] and ethanolamine [H₂N(CH₂)₂OH ≥ 98%, Sigma Aldrich] in 2-methoxyethanol [HO(CH₂)₂OCH₃, 99.8%, Sigma Aldrich] on soda lime glass or fused silica substrates, following a similar procedure for obtaining ZnO thin films as described elsewhere [40]. After spin coating the solution, we placed the substrates in a hot plate at 300 °C for 10 min and further annealed the films at different temperatures, hereinafter referred to as T_A.

In the second step, the precursor hematite films were sulfurized using the Russian Doll apparatus, illustrated in Fig. 1 and described as follows. First, we place 15 mg of sulfur powder inside a glass tube (tube 1) and a hematite thin film inside another slightly larger glass tube (tube 2) [Fig. 1(A)]. Both tubes are placed inside a deoxygenating chamber with a third and fourth tubes (tubes 3 and 4, respectively), each slightly larger than the previous ones. The dimensions of the tubes are displayed in Fig. 1. The third and fourth tubes increase the enclosing of the system, providing a quasi-stationary sulfur environment during the sulfurization process. Then, the system is rinsed with a continuous nitrogen flow for 10 min in order to assure an inert atmosphere inside the Russian Doll tube set. Later, the tubes are nested inside the chamber [Fig. 1(B)] and transferred to a fused silica tubular furnace under 1000 sccm of argon flow [Fig. 1(C)]. The tube set is heated up to different sulfurization temperatures (T_S) for different times (t_S) under a constant argon flow of 500 sccm (note that the argon flow is used here only to prevent oxygen from outside the furnace to enter the tube set, and contaminate the films), and then allowed to cool down naturally. We also used a set of fused silica tubes when the process occurred at temperatures higher than 550 °C.

In this work, we analyzed the effect of t_S and of both T_S and T_A on the microstructure and phase composition of the resulting iron pyrite thin films. We determined the phase composition of the films firstly by X-ray diffraction (XRD) measurements carried out in the Crystallography Laboratory (LabCri) of UFMG, with a PANalytical EMPYREAN diffractometer using Cu K_α radiation (λ = 1.540598 Å), working in

continuous scan mode with grazing incidence. We used the same incident angles for each set of samples belonging to the same series, which were 1.75° for the first two series and 2.0° for the last two series of samples. We chose the incidence angles based on an optimum signal detection. The peaks were indexed using the Crystallography Open Database to compare with reference data. We also used Scanning Electron Microscopy (SEM) imaging to determine phase composition by analyzing the crystal habits present in the films. In addition, we investigated the effects of the synthesis parameters in the microstructure of the films with SEM. All, the SEM experiments were performed at the Microscopy Center of UFMG in a FEI Quanta 3D FEG FEI electron microscope, with a working distance of 10 mm and accelerating voltage of 15 kV.

3. Results

3.1. Experiments varying the sulfurization temperature

We first sulfurized hematite films at temperatures of 450 °C, 500 °C, and 550 °C for 1 h with 15 mg of sulfur powder. All the precursor iron oxide films were annealed at 500 °C for 30 min, and heated up to T_S with a heating rate of 10.5 °C/min. All the films were grown on soda lime glass substrates.

XRD results clearly show the presence of both FeS₂ polymorphs, pyrite and marcasite (indexed by “M” in the graphs), with a dominance of pyrite, as shown in Fig. 2. The presence of the marcasite polymorph is

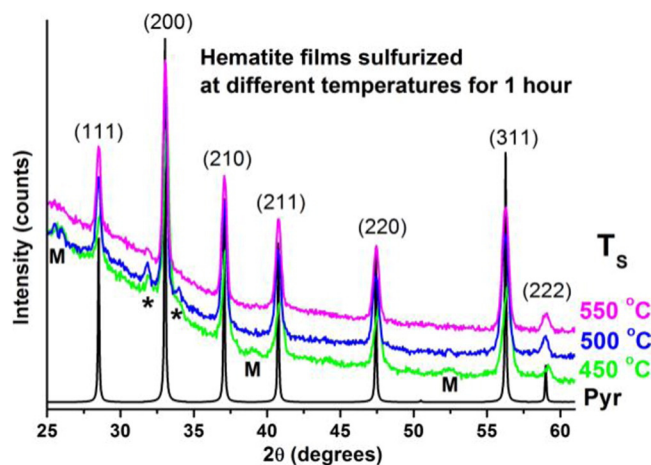


Fig. 2. XRD patterns of pyrite films sulfurized at 450 °C, 500 °C, and 550 °C. The “M” represents peak positions of the marcasite polymorph and the asterisks represent artifacts from the equipment.

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