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Structural, optical and electrical impacts of marcasite in pyrite thin films

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ABSTRACT

The structural and electro-optical influence of marcasite on the properties of solution-processed iron pyrite thin films was investigated. Marcasite has a strong tendency to form simultaneously with pyrite upon sulfurization of amorphous iron-oxide precursor films, leading to a mixed-phase structure in which pyrite grains are surrounded by nanocrystalline marcasite boundaries. The optical analysis in combination with spectroscopic ellipsometry revealed that marcasite should have a bandgap of approximately 0.85–0.88 eV with a higher absorption coefficient than pyrite, differing strongly from the prior belief that marcasite has a bandgap of less than 0.4 eV. In addition, the pyrite/marcasite film has been found to have a larger diffusion coefficient for photogenerated minority carriers than the phase-pure pyrite film from electrochemical impedance analyses, resulting in a higher photocurrent density, as determined through photoelectrochemical measurement. The facile transport of a minority carrier along the marcasite boundaries is the putative origin of the observed improvement in the photoactivity of the pyrite/marcasite mixture films.

1. Introduction

Iron pyrite (cubic FeS_2) has attracted renewed attention as the most promising light-absorbing material for low-cost thin-film photovoltaic devices due to its abundance in the earth and lack of toxicity (Wadia et al., 2009a; Ennaoui et al., 1986, 1993). In addition, the intrinsic properties of pyrite necessary for efficient solar energy conversion, i.e., a modest energy bandgap ($E_g \sim 0.95$ eV), very large optical absorption coefficient ($\alpha > 10^5$ cm^{-1} for $h\nu > 1.4$ eV), long minority carrier diffusion length (100 ~ 1000 nm) and high majority carrier mobility (up to 360 cm^2 V^{-1}s^{-1}), make it ideal for use as a light-absorbing material in photovoltaic devices (Ennaoui et al., 1986, 1993; Altermatt et al., 2002; Seefeld et al., 2013; Berry et al., 2012). Several promising device results, such as a large short-circuit photocurrent density (> 40 mA cm^{-2}) and quantum efficiency of over 90%, were demonstrated in photoelectrochemical and solid-state Schottky solar cells based on pyrite single crystals (Ennaoui et al., 1986, 1993; Buker et al., 1992).

Despite excellent photocurrent generation, for decades, the power conversion efficiency of pyrite single crystals has been limited to 2.8% (Ennaoui et al., 1993). This poor performance is due to the very low open-circuit voltage (< 200 mV). Furthermore, a polycrystalline pyrite thin film with a detectable photovoltage has not been reported to date.

The generally accepted explanations for this low or non-existent photovoltage are the presence of secondary phases (Ennaoui et al., 1986; Yu et al., 2011; Wadia et al., 2009b), surface states (Bronold et al., 1994; Murphy and Strongin, 2009; Rosso et al., 1999; Limpinsel et al., 2014; Andersson et al., 2014; Liang et al., 2014) and/or intrinsic defects (Cabán-Acevedo et al., 2014; Hu et al., 2012). In particular, the phase purity issue should be considered prior to other issues not only because numerous iron sulfide phases exist in nature, each with unique properties depending on the stoichiometric ratios between iron and sulfur (Takeno et al., 1970; Jagadeesh and Seehra, 1980), but also because the characteristics of these phases, such as their metallic nature or significantly lower bandgaps, can significantly degrade solar cell performance (Wadia et al., 2009b; Jagadeesh and Seehra, 1980).

Based on the stoichiometric S/Fe ratio, these secondary iron sulfide phases can generally be divided into two groups: metallic iron sulfides, e.g., troilite FeS, pyrrhotite $Fe_{1-x}S$, smythite Fe_9S_{11}, and greigite Fe_3S_4, which are sulfur-deficient compared to pyrite (Sridhar et al., 2001) and a polymorph of pyrite (orthorhombic marcasite, FeS_2).

Since the formation of metallic iron sulfide phases is caused by an insufficient sulfur partial pressure, control of the sulfur partial pressure

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during the fabrication process is expected to prevent their formation. Several authors have already reported the prevention of the growth of metallic iron sulfides by employing a longer duration for sulfurization (Soukup et al., 2011), high sulfur partial pressure (Ennaoui et al., 1993; Yu et al., 2011; Thomas et al., 1998) and additional sulfurization processing step (Ennaoui et al., 1993; Nakamura and Yamamoto, 2001). As an alternative approach, a route using iron oxides instead of metallic iron as precursors has been suggested (Ennaoui et al., 1993; Morrish et al., 2012; Smestad et al., 1990) based on the thermodynamic consideration that iron oxides can be converted directly to pyrite, forming SO_2 gas as a byproduct, while sulfurization of metallic iron always occurs via the formation of intermediate metallic $Fe_{1-x}S$ prior to complete transformation to pyrite. Because the $Fe_{1-x}S$ phase is believed to be dealt with successfully by these methods, it is unlikely that the presence of metallic iron sulfide in the bulk of the film is the primary reason for the reported low or non-existent photovoltage.

However, the polymorphic marcasite phase has been considered to be the most deleterious secondary phase in pyrite. The coexistence of marcasite with pyrite is highly plausible due to their similar free energy of formation (Chase et al., 1985; Spagnoli et al., 2010; Sun et al., 2011) and small difference in relative stability (Gudelli et al., 2013). Indeed, marcasite is commonly found attached to pyrite crystals in natural minerals (Richards et al., 1995; Rakovan et al., 1986) and marcasite has frequently been observed as an intermediate metastable phase during transformation of precursor materials to pyrite in the thin-film fabrication process (Berry et al., 2012; Sun et al., 2011).

However, even though marcasite has long been considered the most plausible secondary phase, its phase transformation behavior and influence on the structural, optical and electrical properties of pyrite are still not entirely clear. In the traditional view, both the marcasite and pyrite have n-type semi-conductivity (Sanchez et al., 2016; Moon et al., 2014) while marcasite has a much smaller bandgap than pyrite, measuring approximately 0.34 eV (Jagadeesh and Seehra, 1980), which is believed to impede the development of photovoltage. However, this value is based on an indirect resistivity measurement that was made on natural marcasite crystals in 1980, which is of doubtful reliability because the measurement has never been verified via more reliable direct measurements. Only recently was it suggested that marcasite may have a bandgap that is slightly smaller than or similar to the bandgap of pyrite based on an optical measurement on mixed phase thin films (Berry et al., 2012) or natural minerals (Sanchez et al., 2016). A marcasite bandgap that was even larger than the bandgap of pyrite was predicted by theoretical calculations (Sun et al., 2011). A paper from Wu et al. (2016) provided a completely different view of the role of marcasite based on the photoresponse of the marcasite/pyrite mixture film that was significantly higher than the photoresponse of the phase-pure pyrite film in their photoelectrochemical measurements. These researchers explained this improved photoresponse by the enhanced charge separation that occurs at marcasite/pyrite phase junctions. However, even with this new and interesting insight into the role of marcasite, more studies are still required to address the issue of marcasite effects fully for the following reasons: first, their pyrite film is not phase pure and contains FeS-type impurities, evidenced by the XRD patterns of their films (even though the authors did not mention it). Second, the authors attributed the improved photoresponse in the marcasite/pyrite mixture film solely to the improved charge separation based on the density functional theory (DFT) calculation without support of experimental results. Other possibilities, including a different degree of carrier generation, which can be caused by the different optical properties between marcasite and pyrite, and different carrier transport characteristics were not considered in their report and hence should be investigated. All of these literature surveys indicate that there is still a lack of understanding and consensus on the optical and electrical impact of marcasite on the characteristics of the pyrite/marcasite mixture films.

In this study, we report experimental results on the effects of the marcasite on the structural and opto-electrical properties of solution-processed iron pyrite thin films to provide more complete insight into the role of marcasite. First, we investigated the detailed phase transformation behavior of the precursor to pyrite upon sulfurization, particularly focusing on its distribution in the pyrite matrix. Marcasite was found to exist as a fine nanocrystalline form intimately attached to the relatively large pyrite crystals until the marcasite is completely converted to pyrite at high temperature. Based on the marcasite/pyrite mixture structure of the film, we performed optical measurements to extract the marcasite absorption coefficient and bandgap energy. Marcasite was found to have a bandgap energy of 0.85–0.88 eV with an absorption coefficient higher than the absorption coefficient of pyrite, differing from the prior belief that the bandgap of marcasite is less than 0.4 eV. In addition to the better light absorbing ability of the marcasite phase, we report direct experimental evidence supporting better efficacy of the pyrite/marcasite film for transport of photogenerated minority carriers than the phase-pure pyrite film, which is the presumable reason for the higher photocurrent density of the mixture film observed in the photoelectrochemical measurements. These results suggest that the existence of marcasite in the pyrite matrix is unlikely to be the main reason for the low or non-existent photovoltage of the current pyrite-based solar cells. In contrast, phase-pure marcasite or a properly controlled marcasite/pyrite mixture may be a new promising photoelectrode.

2. Experimental section

2.1. Preparation of the precursor solution

Iron(II) acetate ($C_4H_6FeO_4$; ≥99.99%), sulfur powder (≥99.98%), and monoethanolamine (MEA; ≥99.0%) were purchased from Sigma-Aldrich. Ethanol (C_2H_5OH; ≥99.6%) was acquired from Junsei Chemical. All chemicals were used as received. Approximately 0.53 mol of iron acetate was dissolved in 26 mL of ethanol in a glass bottle, and 3 mL of MEA was then added to this solution to obtain a suitable viscosity for spin-coating.

2.2. Thin film deposition

The precursor solution was coated by spin-coating (ACE-200, Dong Ah Trade Co., Korea) at 2200 rpm for 20 s on Mo (1 μm thick)-coated soda-lime glasses (SLGs) for the phase evolution study, on bare SLG substrates for optical investigation and on F-doped SnO_2 (FTO)-coated SLG substrates for electrochemical analyses. After spin-coating, the samples were immediately moved onto a hot plate pre-heated to 300 °C and dried for 10 min in air to evaporate the solvent and induce thermal decomposition of MEA. The thickness of the precursor film was controlled by repeating the spin-coating and drying steps. The entire process, including solution preparation and film deposition, was performed in ambient air.

2.3. Sulfurization

Sulfurization was carried out in a heat-treatment chamber in which a graphite container was placed. The chamber was equipped with a temperature and pressure controller. The precursor films were placed inside the graphite container with 0.3 g of sulfur powder located near the samples, and then, the container was covered with a graphite lid. After loading the samples in this manner, the chamber was initially evacuated to a base pressure of 10^{-3} Torr with a rotary pump and then, the background pressure was regulated by the injection of nitrogen gas. A value of 360 Torr was chosen as the background pressure at room temperature to obtain the highest sulfur vapor partial pressure inside the graphite container (approximately 500 Torr) at a final sulfurization temperature of 450 °C based on the quantitative estimation of the actual sulfur vapor partial pressure described in our previous paper (Moon