Surface thermal stability of iron pyrite nanocrystals: Role of capping ligands

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ABSTRACT

Iron pyrite (FeS$_2$) is a promising photovoltaic absorber material with a high natural abundance and low cost, but surface defects and low photoresponse inhibit sunlight energy conversion. The surface stability of pyrite FeS$_2$ nanocrystals synthesized in oleylamine (OLA) with trioctylphosphine oxide (TOPO) as an additional capping ligand was investigated using Fourier transform infrared spectroscopy, Raman spectroscopy and X-ray diffraction. Tunable laser exposure during Raman spectroscopy measurement was developed for convenient and systematic evaluation of the stability of FeS$_2$ nanocrystals. The surface stability of 100–200 nm diameter cubic nanocrystals with long-chain (OLA, TOPO) or small-molecule (pyridine) capping ligands was evaluated after high-intensity laser exposure as well as after thermal annealing in air and N$_2$. While increasing surface coverage with OLA and TOPO capping ligands provided additional protection against oxidation, FeS$_2$ nanocrystals capped with pyridine showed good stability at temperatures up to 200 °C in air and 400 °C in N$_2$. These results provide greater understanding of the processing of nanocrystal-based iron pyrite thin films for photovoltaic applications.

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1. Introduction

Due to its high natural abundance, nontoxicity, low cost and the high absorption coefficient of $1–5 \times 10^5$ cm^{-1}[1,2], an attractive application of iron pyrite (FeS$_2$) is as a photovoltaic (PV) absorber material. The estimated highest attainable efficiency of pyrite PV energy conversion is as high as that of single crystal silicon solar cells [3]. This prospectus is further promoted with the recent development of highly crystalline, phase-pure iron pyrite nanocrystal (NC) inks that enable large through-put and low cost fabrication of solar panels using established solution-based techniques [4–11]. Despite the huge promise iron pyrite holds, this material has not yet been developed into efficient PV devices. The highest pyrite PV device efficiency has been obtained in a photoelectrochemical cell with a reported short circuit current (I_{sc}) of 42 mA/cm^2, open circuit voltage (V_{oc}) of 187 mV, and fill factor (FF) of 50%, yielding an efficiency of 2.8% [2,12]. The limiting factor for high efficiency is the high dark current that leads to the very small V$_{oc}$, less than 20% of its bandgap (0.95 eV) [2,12–16].

Natural bulk pyrite and synthetic thin films generally have common traits of high carrier concentrations in excess of 10^{19} cm^{-3} and strong sub-bandgap absorption [17–19]. Photoresponse (e.g., photoconductivity) of these grown films has barely been observed at room temperature [20,21]. There are two types of possible factors that lead to the high dark carrier concentrations in iron pyrite: impurity phases and surface

defects. Previously it was believed that impurity phases such as marcasite and hexagonal troilite have much smaller bandgaps (0.34 eV for marcasite and 0.04 eV for troilite) [22]. More recently Law et al. declared that marcasite had band gap comparable to pyrite [23]. They also suggested that the high conductivity and low mobility of pyrite films might be caused by nanoscale amorphous impurities and surface effect and excluded the intrinsic bulk defects [23]. The surfaces of iron pyrite are terminated with S dimmers, that tend to segregate to the surface and cause the vanishing of the hybridized band at the top of the Fe layer, making the surface effectively similar to 1S terminated troilite or FeS$_{2-x}$. This results in large density-of-defect states in the middle of pyrite bandgap that reduced the bandgap energy at the surface to nearly zero [5,24]. Pyrite films may be heavily hole doped due to a hole-rich layer formed at the surface resulted from a large concentration of surface states located near the valence band edge and even in pyrite single crystals there might exist an n-type bulk layer and a p-type surface layer according to recent experimental work [23]. Although not conclusive, more and more evidence shows that the surface defects dominate the generation of large density of background charge density. It is suggested by theoretical calculations that FeS$_2$ is actually a stoichiometric compound because of the high energy required to generate S vacancies in bulk FeS$_2$, and thus, bulk defects are unlikely to cause the large carrier concentrations [19]. Instead of bulk S vacancies, the presence of high-density S vacancies at the surface has been calculated to be favorable in CoS$_2$ which has the same structure with FeS$_2$ [25,26]. Recent high resolution transmission electron microscopy studies of sulfurized pyrite films clearly revealed a S-deficient amorphous surface

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despite annealing in a very S-rich environment [19]. The pyrite crystal surfaces suffer incomplete coordination of iron by S due to the loss of S from the surface [27].

Using iron pyrite NCs to fabricate the photovoltaic films avoids the formation of impurity phases as proven by their excellent phase purity and crystallinity [4,5,22,28]. However, the significantly larger surface-to-volume ratio of NCs is expected to bring challenges in maintaining stable iron pyrite surfaces. To our surprise, NC-based FeS_2 films show better stability than those made by other methods as indicated by the observed room temperature photoresponse in iron pyrite films [5]. The surface capping ligands on these NCs are proposed to play the major role in stabilizing the NC surface. Introducing surfactant capping ligands to stabilize NC surfaces is a commonly employed strategy in NC synthesis. The situation is especially complex for FeS_2 NCs because in addition to size and shape, the crystallinity and phase purity [22], colloidal stability against aggregation [29,30], stability of NC films [5], and optoelectronic properties [5,31,32], all have showed strong dependence on the surfactants used during NC synthesis or post-treatment.

In this paper, the function of ligands in stabilizing FeS_2 NC surface was studied by monitoring the thermal stability of FeS_2 NCs in air and N_2 after removing long alkane ligands by solvent wash, or exchanging the long ligand with short ligands of pyridine. The role of ligands in the oxidization behavior of FeS_2 NCs capped with different length ligands upon high-intensity laser irradiation and thermal annealing was investigated systematically using Raman spectroscopy and X-ray diffraction (XRD). Efforts were focused on determining the importance of the nature of the capping ligands, how they protect the thin films, and how these issues impact future device fabrication and processing.

2. Experimental details

2.1. Synthesis of FeS_2 NCs

Anhydrous iron (II) chloride (99.9%), sulfur (98%), trioctylphosphine oxide (TOPO), oleylamine (OLA), chloroform and methanol were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. Cubic shaped FeS_2 NCs were synthesized by the hot injection method reported previously with minor modifications [5]. In brief, a mixture containing 0.5 mmol of $FeCl_2$, 0.3 mmol of TOPO and 10 ml of OLA was heated to 170 °C and kept at that temperature for 2 h under N_2 to form Fe-surfactant precursor species. A solution of 3 mmol sulfur in 5 ml OLA was injected quickly into the Fe precursor and then the system was immediately heated to 220 °C and kept at that temperature for 2 h to complete the growth of the iron pyrite NCs. The reaction was terminated by removing the heating mantle and cooled down to room temperature naturally.

The FeS_2 NCs were precipitated by adding excess methanol and isolated by centrifugation at 3000 rpm for 10 min. For selected experiments, these as-prepared NCs were washed with chloroform/methanol, sonicated, and isolated by centrifugation to remove the excess of OLA and TOPO. These NCs were denoted as FeS_2-OLA/TOPO. To prepare pyridine-capped FeS_2 NCs (denoted as FeS_2-pyridine), the FeS_2-OLA/TOPO NCs were dispersed in 10 ml of pyridine, sonicated for 10 min and isolated by centrifugation. This process was repeated one more time to ensure the maximum exchange of the long-chain OLA and TOPO ligands by pyridine. Pyridine was chosen for ligand exchange because pyridine capped NCs are still dispersible in organic solvents, which are superior to ethanedithiol that causes aggregation of NCs and can only be applied for post-treatment of NC films. Both FeS_2-OLA/TOPO and FeS_2-pyridine NC samples were dispersed in chloroform and kept in a N_2 filled glove box for storage prior to further characterization.

NC-based thin films were formed on 1×1 cm^2 silicon wafers by drop casting from FeS_2 NC/chloroform dispersions. These films were annealed on a hot plate in air or in N_2 at different temperatures for 20 min, respectively. All of these FeS_2 films were stored in a N_2 filled glove box before

XRD and Raman measurements to avoid the unintentional gradual oxidation or decomposition of the FeS_2 NCs in air.

2.2. Characterization

The presence and exchange of capping ligands on FeS_2 NCs were identified by Fourier transform infrared spectra (FTIR) using a Nicolet Avatar spectrometer. A drop of the FeS_2 NC/chloroform dispersion was mixed with dry KBr powder (FT-IR grade, Alrich), and the solvent was allowed to evaporate. This mixture was ground and pressed into pellets for FTIR measurements. Morphology and size of the NCs were characterized by scanning electron microscopy (SEM) using a Quanta 200 FEG SEM at high vacuum mode with the operating voltage of 15 kV. The thermal stability of FeS_2 samples was investigated by Confocal Raman spectroscopy (RenishawinVia) with a 514 nm laser source. To investigate the effect of light intensity on the oxidation of the FeS_2 NCs, lasers with power of 1.5, 7.5 and 15 mW were focused on sample spots of approximately 25 μm^2 with the irradiation time of 10 s. These laser powers corresponded to power intensities of 6.0×10^6, 3.0×10^7 and 6.0×10^7 mW/cm^2, respectively. The laser penetration depth is ~60 nm estimated by $1/\alpha$, where α is the absorption coefficient (~1.7×10^5 cm^{-1} at 514 nm) of the FeS_2 NCs [5,33]. Powder X-ray diffraction (XRD) patterns of the FeS_2 NC films were collected on a Rigaku D/Max-B diffractometer with Bragg–Brentano parafocusing geometry (Co Kα, $\lambda = 1.7902$ Å) with X-ray tube operating voltage of 40 kV and current of 30 mA.

3. Results and discussion

3.1. Ligand exchange studies

SEM images of the as-prepared pyrite FeS_2 NCs show that they had cubic shapes and diameters ranging between 100 and 200 nm (Fig. 1b). FTIR spectroscopy was used to identify the presence of OLA and TOPO capping ligands on the FeS_2 NCs (Fig. 1a). FTIR spectra of pure OLA and TOPO are also shown for comparison. The IR spectrum of OLA shows peaks at 2921 and 2852 cm^{-1} that correspond to the asymmetric ($\nu_a(-CH_2-)$) and symmetric ($\nu_s(-CH_2-)$) stretching modes, respectively, of the oleyl groups. The peak at 3315 cm^{-1} is due to the $\nu(N-H)$ stretching of the $-NH_2$ group. There is a small peak at approximately 1650 cm^{-1} due to $\nu(C=C)$ stretching in OLA molecules [34]. The peaks in the region below 1650 cm^{-1} correspond to complex combinations of the $\nu(C-C)$ stretching, CH_2 deformations and other motions [34]. All of these OLA peaks were seen in the FeS_2-OLA/TOPO NC spectrum (Fig. 1a, green curve) indicating the existence of this long-chain ligand on the NCs after washing.

For TOPO, there are also two peaks around 2900 cm^{-1} assigned to the stretching mode of $-CH_2$ in the octyl group. Characteristic vibration bands of P=O and P–C groups in TOPO are observed at 1149 cm^{-1} and 1411 cm^{-1}, respectively. The IR spectrum of the FeS_2-OLA/TOPO NCs clearly shows peaks that indicate the presence of OLA. While many of the TOPO P=O and P–C vibrational frequencies match those of OLA peaks, the presence of at least a small amount of TOPO is indicated in the 650–1250 cm^{-1} region of the spectrum. This evidence indicates that OLA and TOPO capping ligands are present on the FeS_2 NCs after three washing cycles with chloroform/methanol. After ligand exchange with pyridine, the FeS_2-pyridine NC IR spectrum (blue curve in Fig. 1a) exhibits very little signal from OLA and TOPO, indicating the removal of most of the long-chain ligands.

3.2. Stability study of the FeS_2 NCs by Raman spectroscopy

3.2.1. Thermal stability of FeS_2-OLA/TOPO NCs

Raman spectroscopy was employed to investigate the thermal stability and surface chemistry of the FeS_2 NC samples. Fig. 2 shows Raman spectra of FeS_2-OLA/TOPO NC samples after exposure to various