Identification of marcasite in pyrite FeS_2 thin films and their carrier transport characteristics

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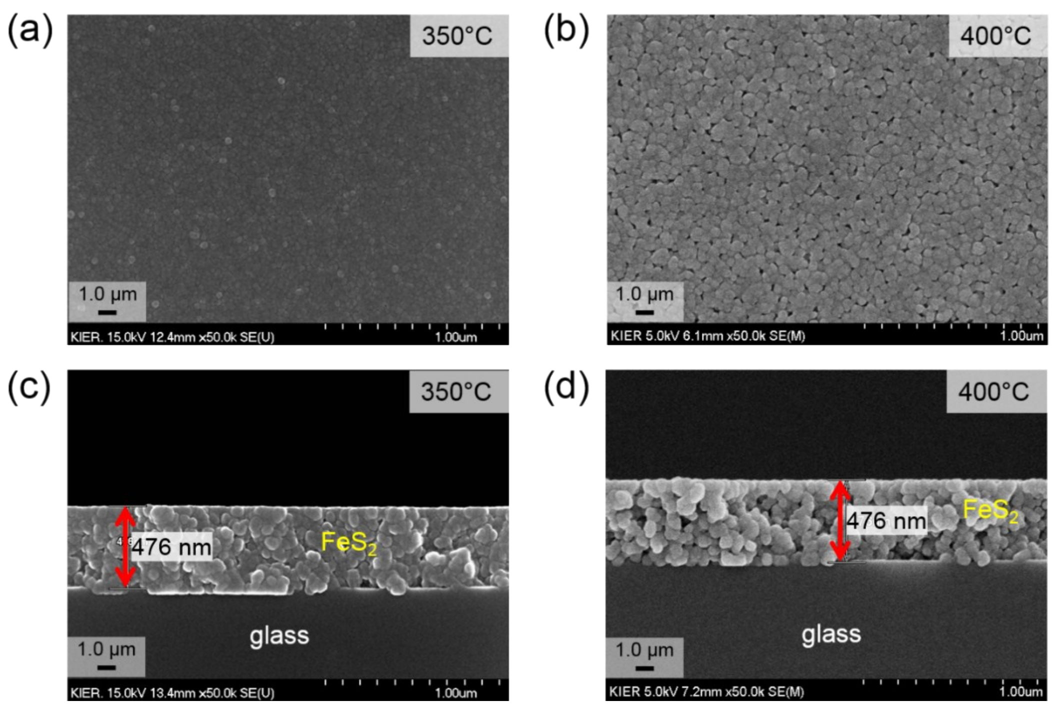
Supplemental material



Figures S1. (a) and (b) SEM images of FeS_2 thin film surfaces, and (c) and (d) cross-sectional SEM images of FeS_2 coated on glass.

Figure S1(a) and (c) show surface and cross-sectional SEM images of the FeS_2 thin film sulfurized at 350 °C. Figure S1(b) and (d) show surface and cross-sectional SEM images of the FeS_2 sample sulfurized at 400 °C. Comparing Fig. S1(a) and (b), it is clear that the higher sulfurized temperature results in spherical grains on the surface. This is because of less S concentration of 350 °C sulfurized sample. In the surface SEM images, the grain size of each sample seems to be vague. However, comparing Fig. S1(c) and (d) shows that the 400 °C sulfurized sample forms discernible grains even inside the precursor film, developing grain boundaries (GBs) for better conducting behavior in the light absorber layers.

In terms of the phase impurity, marcasite is considered to be a structural defect in pyrite. According to several previous studies, there are planar defects in pyrite, which are considered to be antiphase boundaries.[S1] Additionally, Fleet *et al.*[S2] reported that these defects produce marcasite lamellae. Dodony *et al.* stated the marcasite lamellae are located at GBs and limit the growth of pyrite.[S3] Accordingly, we presume that marcasite of mixed phase sample cannot be converted to pyrite on account of the low sulfurization concentration. The marcasite phase is known to have lamellae and to hinder the pyrite formation. Therefore, mixed-phase thin film shows unclear GBs. Thus, close inspection of the surface SEM image of the FeS_2 thin film sulfurized at 350 °C (Fig. S1(a)) shows extremely tiny grains on the surface.

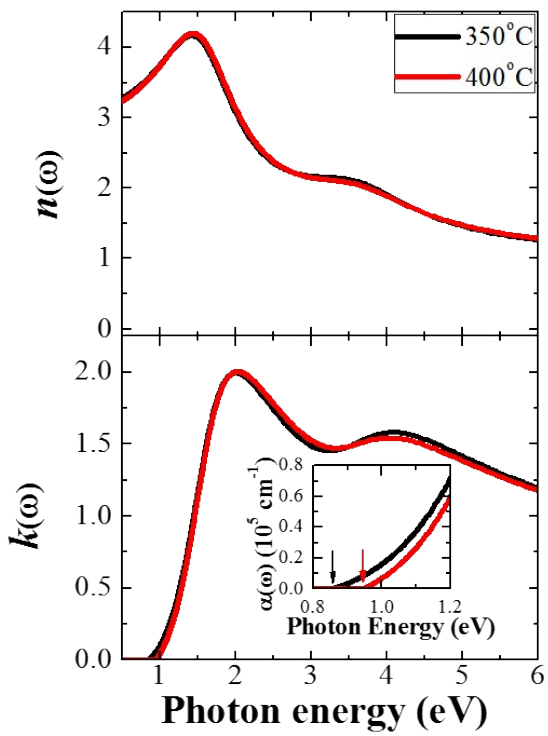


Figure S2. Complex optical constants of the FeS_2 films: (a) Refractive index spectra $n(\omega)$ and (b) extinction coefficient spectra $k(\omega)$. The inset in (b) shows the absorption coefficient spectra $\alpha(\omega)$ determined directly from $k(\omega)$. The arrows indicate the bandgap values.

The optical spectra of the two films show common features. First, two strong interband transitions are observed near 2 and 4 eV. The optical bandgaps are estimated to be 0.86 and 0.94 eV for the marcasite-containing and pure pyrite FeS_2 film, respectively, as shown in the inset in Fig. S2. The relatively small bandgaps of both phases are closely associated with the high refractive index (3.2 at 0.5 eV).

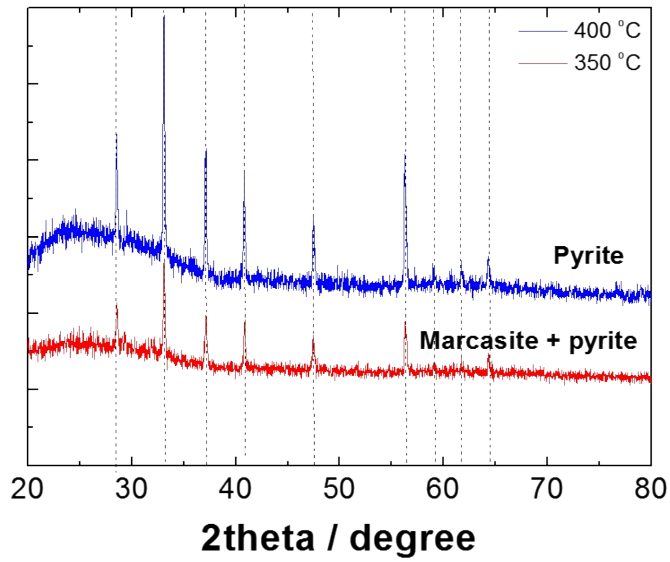


Figure S3. XRD patterns of 350 °C and 400 °C sulfurized iron pyrite samples.

As shown above, the XRD patterns of the two sample shows no differences, though the marcasite phase is detectable through micro-Raman scattering spectroscopy. This is because the marcasite phase exists in the mixed-phase pyrite thin film and has weak a crystalline state. Thus, we can observe only pyrite peaks in the patterns. We could obtain same results through several XRD measurement.

Reference

S1. L. Van Goethem, J. Van Landuyt and S. Amelinckx, *Am. Mineral.*, 1978, **63**, 548.

S2. M. E. Fleet, P. J. MacLean and J. Barbier, *Econ. Geol. Monogr.*, 1989, **6**, 356.

S3. I. Dódony, M. Pósfai and P. R. Buseck, *Am. Mineral.*, 1996, **81**, 119.