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Growth of Single-Crystal Pyrite Films by Atmospheric Pressure Chemical Vapor Deposition

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Pyrite of FeS_2 has attracted considerable attention as a potential candidate instead of amorphous and crystalline silicon films, which is applicable to photovoltaic and photoelectrochemical devices. It has not only excellent properties appropriate to absorb solar energy such as a band gap of 0.95 eV and a very high optical absorption coefficient equal to 5×10^5 cm^{-1} at $h\nu > 1.3$ eV but also rich abundance of the constituting elements in the earth. In addition, they are cheap and nontoxic as well. It is, therefore, thought that pyrite has been of interest as an alternative to silicon for the thin film solar cells.[1] There has been a number of investigations on the preparation of pyrite films with a variety of methods such as sulfurization of the electrodeposited[2] or evaporated[3] metallic iron films, ion beam sputtering,[4] spray pyrolysis,[5] electrodeposition,[6,7] and metal-organic chemical vapor deposition (MOCVD).[5,8] However, none of the reports concerning the growth of single-crystal films of pyrite has been published so far. In the previous papers,[9,10] we reported the preparation of pyrite films by atmospheric pressure chemical vapor deposition (AP-CVD) using $FeCl_3$ and CH_3CSNH_2 as starting materials. Although all the films deposited onto a glass substrate were of polycrystalline pyrite, it was confirmed that pyrite is formed by means of the AP-CVD utilizing a reaction of $FeCl_3$ and CH_3CSNH_2. An advantage that we found is that CH_3CSNH_2 is available for the sulfur source to form pyrite. In most cases $(NH)_2CS$, H_2S, and S are used as sulfur sources to prepare metal sulfide films, although our preliminary experiments suggested that they were not suitable for the preparation of pyrite films. Therefore, we extended the work to prepare single-crystal pyrite films on a Si(100) substrate by means of AP-CVD using the same starting materials.

A hot-wall horizontal quartz reactor used in the present study was the same as that described previously.[9,10] $FeCl_3$ and CH_3CSNH_2 were evaporated from the source boats at temperatures of 503 and 393 K, respectively, and were provided to the reactor. Purified N_2 was used as a carrier gas. Thin films of FeS_2 were deposited onto a Si(100) surface in the reactor by the reaction of $FeCl_3$ with CH_3CSNH_2 under atmospheric

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Table 1. Typical Growth Conditions

substrate	Si(100)
$FeCl_3$ source temperature	503 K
flow rate of $FeCl_3$	200 $cm^3\ min^{-1}$
CH_3CSNH_2 source temperature	383 K
flow rate of CH_3CSNH_2	200 $cm^3\ min^{-1}$
flow rate of counter gas	200 $cm^3\ min^{-1}$
carrier gas	N_2
total flow rate	600 $cm^3\ min^{-1}$
growth temperature	673 K
duration of deposition	1 h

pressure. Typical growth conditions are summarized in Table 1. It was confirmed by a number of experiments carried out under the conditions given in Table 1 that the films with the same quality described in this communication are reproducible. Thickness of films was examined by scanning electron microscopy (SEM) using Shimadzu superscan SS-550 microscopy. As-deposited films were characterized by X-ray diffractometry (XRD) with $\theta-2\theta$ scan using a Rigaku RINT 2000 X-ray diffractometer with Cu Kα radiation, double-crystal X-ray diffractometry (DCXRD) with ω scan, XRD pole figure analysis using Rigaku Denki ATX-G, and atomic force microscopy (AFM) using a Shimadzu SPM-9500. Chemical composition of the films was determined by energy-dispersive analysis of X-ray (EDAX) using a JEOL Ltd. JXA-8900R instrument in which the amount of each element obtained was calibrated with an FeS_2 single crystal of a known stoichiometry. XPS spectra were measured using a Shimadzu XRTOS-XSAM 800 X-ray photoelectron spectrometer. Electrical resistivity (ρ) was measured by means of a four-probe technique in which tungsten wire springs (0.5 mm ϕ) with platinum being soldered at the end of them were used to obtain ohmic contact between the film and the probes. Hall coefficient (R_H) was measured at a magnetic field of 0.7 T. Reflection spectra in the range of 400 and 1700 nm were measured using a conventional double-beam spectrophotometer in conjunction with Shimadzu UV3150.

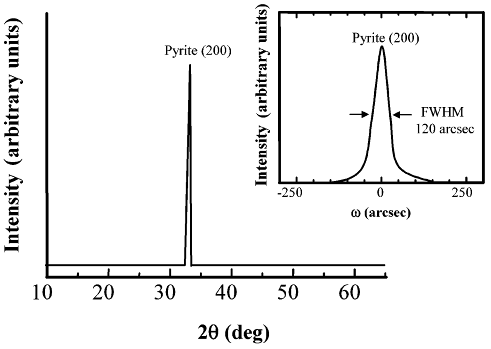

Figure 1. $\theta-2\theta$ mode XRD profile of the pyrite thin film grown at 673 K for 1 h shown in Figure 1. ω-mode DCXRD profile for the pyrite(200) plane is also shown, in the inset.

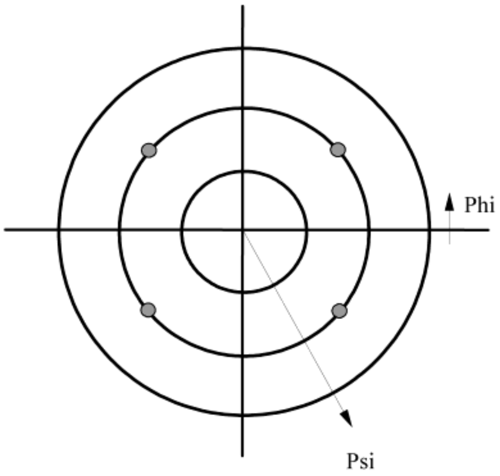

Figure 2. X-ray pole figure of a pyrite thin film grown on Si(100) at 673 K using AP-CVD.

The film thickness was found to be about 1.0 μm. Figure 1 shows a typical XRD profile with $\theta-2\theta$ scan of the as-grown film at 673 K along with its DCXRD ω-scan profile. In the $\theta-2\theta$ scan profile, an intense diffraction line appears at 33.1° assigned to the (200) diffraction of the pyrite with cubic structure. It is worth noting that there is no indication of the formation of marcasite and $Fe_{1-x}S$. This implies that the film deposited under the conditions given in Table 1 is of epitaxially grown pyrite. A lattice constant calculated to be $a = 0.5420$ nm is slightly larger than the reported one of 0.5417 nm.[11] In the DCXRD ω-scan profile for the (200) reflection of pyrite shown in Figure 1, a symmetric diffraction line with a full-width at half-maximum (fwhm) value of 120 arcsec is observed. The obtained value is 33% smaller than that of the polycrystalline films deposited by MOCVD.[12]

Further examination was carried out using XRD pole figure analysis to elucidate the in-plane alignment of the pyrite film. Pyrite has a cubic structure so it is 4-fold along the a-axis. Therefore, four spots with C_4 symmetry should be observed in the pole figure with a 2θ fixed at the (111) reflection of pyrite if the film on the Si(100) substrate is grown along the a-axis. As is illustrated in Figure 2, four spots, separated by an angle of 90°, are observed. This gives clear evidence that the a-axis of the as-grown pyrite film is perpendicular to the Si(100) surface. In other words, the epitaxial pyrite is grown homogeneously with in-plane alignment.

The surface roughness of the pyrite film with a 1.0-μm thickness was evaluated by AFM. The mean square roughness evaluated for $30 \times 30\ \mu m^2$ was <5.5 nm, suggesting that the surface is flat and smooth. From the comparison of the surface morphology between the pyrite films prepared by CVD,[8,12,13] it is found that the former film has a smoother surface than the latter one.

Regarding chemical composition, EDAX analysis suggested that the as-deposited film has an atomic ratio of Fe:S of 1.00:1.98. In the XPS measurement, other elements such as C, N, O, and Cl, which may be trapped in the pyrite film as impurities during the film growth, were not detected.

Table 2 shows the electrical properties of as-deposited pyrite film together with those of a balk pyrite single crystal. The as-deposited pyrite film showed a resistivity, carrier concentration, and hall mobility of 0.97

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Table 2. Electrical Properties of Pyrite Sample

	resistivity (Ω·cm) at 293 K	carrier concentration (cm^2/V·s) at 293 K	Hall mobility (cm^{-3}) at 293 K
Echarri and Sanchez[14]	0.29	1.28×10^{17}	164
Marinace[15]	0.65	0.97×10^{18}	98
Marinace[15]	1.85	2.6×10^{18}	1.3
Ovchinnikov and Krivoshein[16]	0.03	9.6×10^{18}	20
Ovchinnikov and Krivoshein[16]	9.09	6.6×10^{18}	0.1
Horita[17,18]	0.52	0.75×10^{17}	159
this work	0.97	5.5×10^{17}	280

Ω·cm, 5.5×10^{17}cm^{-3}, and 280 cm^2/V·s at 298 K, respectively, which are similar to those of the balk single crystal of pyrite prepared by other methods.[14−18]

Optical properties of the pyrite film with a 1.0-μm thickness are shown in Figure 3. Strong absorption occurs in the photon energy range higher than 1 eV and then reaches a plateau with an absorption coefficient of about 5×10^4 cm^{-1} at $E > 2$ eV, in which the absorption coefficient was calculated using the reflectance spectra. Both the obtained spectral pattern and the absorption coefficient are similar to those of polycrystalline pyrite films prepared by other methods.[13,19,20]

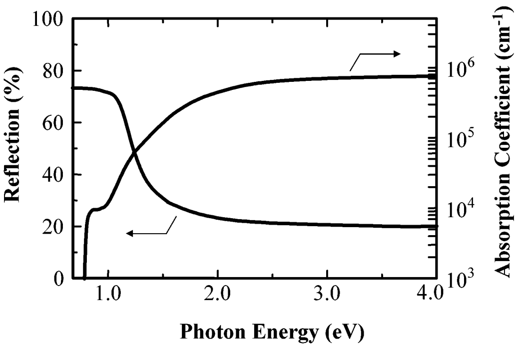

Figure 3. Optical reflection and absorption of a pyrite thin film grown on Si(100) at 673 K.

We have succeeded in the preparation of a single-crystal thin film of pyrite. Its electrical conductivity, carrier concentration, and Hall mobility at 298 K were 0.97 Ω·cm, 5.5×10^{17}cm^{-3}, and 280 cm^2/V·s, respectively. A band gap energy of 1.0 eV and an absorption coefficient of 5×10^{-4} cm^{-1} at $h\nu \geq 1.3$ eV were estimated by the optical reflectance measurements. Consequently, it is concluded that the AP-CVD with a reaction of $FeCl_3$ and CH_3CSNH_2 is an excellent method for preparing single-crystal pyrite thin films.

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