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Experimental Studies on FeS_2 Films Prepared on Si(100) Substrates by Synchrotron Radiation Surface X-Ray Diffraction Method*

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Abstract Both conventional X-ray diffraction (XRD) and synchrotron radiation surface X-ray diffraction methods were used to study FeS_2 films prepared by magnetron sputtering on Si (100) and glass substrates for comparison. The results show that the preferred orientation of FeS_2 along (311) direction, which might be due to the well-matched crystal lattice for FeS_2 and Si (100), is mistaken. The peak at about 56° with extremely strong intensity comes from the (311) crystal plane of the silicon substrate, other than the preferred orientation of FeS_2. The conclusion is proved by both calculation and experimental measurements in present paper.

Key words FeS_2, synchrotron radiation surface X-ray diffraction, semiconducting materials

1 Introduction

FeS_2 has been widely investigated because of its potential photovoltaic and photoeletrochemical applications stemming from its proper band gap ($E_g \approx$ 0.95eV) and large absorption coefficient ($\alpha > 10^5 cm^{-1}$ for $\lambda < 10^3$nm)[1, 2]. The high absorption coefficient, which is two orders of magnitude higher than that of crystalline silicon, would make it possible to allow for the application of very thin absorption layers less than 100 nm thickness. In addition, FeS_2, which consists of nontoxic and widely available elements, is a suitable semiconductor material for the environment. Therefore, FeS_2 is attracting more attention because of its promising potentials for applications as optoelectronic and photovoltaic materials[3—5]. A great variety of procedures have been used to investigate FeS_2 thin films[6—9] and their basic properties have been widely researched[10, 11]. Among these studies, single crystal silicon was employed as substrate in order to get high-quality films, however, the epitaxial layers of FeS_2 on silicon substrates should be paid more attention due to their close lattice constants (0.5418nm for FeS_2 and 0.5431nm for silicon) and low lattice mismatch. Naoyuki Takahashi et al.[12] have succeeded in the preparation of single crystal thin films of FeS_2 on Si(100) wafers by means of chemical vapor deposition under atmospheric pressure (AP-CVD) using $FeCl_3$ and CH_3CSNH_2 as starting materials. However, J. Oertel et al.[13] have grown polycrystalline FeS_2 films by metalorganic chemical vapour deposition (MOCVD) on the same wafers. Ennaoui[3] and Birkholz[4] have found that there was an extremely strong reflection of X-ray diffraction on (200) crystal face; they assigned it to the thin thickness of the film and a preferred orientation of crystallites along the (200) crystal plane parallel to the surface of the wafer. While D. Y. Wan et al.[14] have

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studied FeS_2 films by the synchrotron radiation surface XRD method, and given the results that the "strong (200) reflection" for the FeS_2/Si(100) sample measured by the conventional XRD was mainly from the contributions of both the FeS_2 film and the silicon substrate, other than the effect of the preferred orientation of FeS_2 crystal grains which was suggested in the previous reports. However, a strong preferred growth of FeS_2 along (311) crystal plane was detected due to the low lattice mismatch for FeS_2 and Si (100). In my point of view, any preferred orientation on silicon should be treated carefully and the effect of the substrate should be taken into consideration. In present paper, calculation and experimental measurements were performed to account for the results before.

2 Experimental procedures

The FeS_2 films were prepared in the following procedures: glass slides were boiled in acid solution (HCl: H_2SO_4=3:1) for 20 minutes to eliminate oxides and Si (100) wafers were cleaned in HF solution for about 2 minutes in order to get rid of SiO_2 on the surface, and then both slides and wafers were rinsed with de-ionized water at least five times after ultrasonic cleaning in ethanol and dried in vacuum chamber at 473K. Iron films of about 200nm[15] were deposited on Si (100) and glass substrates respectively at room temperature in a FJL560 magnetron sputtering system. An background pressure of about 2.0×10^{-4}Pa was reached and a Φ 60×2mm^2 Fe target of nominal 99.9% purity was employed. While sputtering, the argon pressure was about 1.0Pa. The Fe film along with sulfur powder (99.5% of purity) which was a little more than the mass required for the saturated sulfur vapor at the corresponding temperature were isothermally annealed in a vacuum sealed quartz ampoule at 673K for different time. Heating and cooling rate at about 2K/min and 1K/min were used respectively during the sulfidation.

Conventional X-ray diffraction (Siemens D/MAX-2400 Automated X-ray diffractometer) was used to analyze the phase structure in the usual θ-2θ couple mode with monochromatized CuKα (λ=0.154nm) radiation, working at 40kV and 100mA. The surface X-ray diffraction measurements were performed by synchrotron radiation at the diffuse-scattering station on 4W1C beamline of Beijing Synchrotron Radiation Facility (BSRF), using a Huber five-circle diffractometer, the wavelength λ is 0.154nm. A focus spot size of 0.5mm(H)×0.3mm(V) with energy resolution of 4.4×10^{-4} and photon flux of 2×10^8 photons/s was obtained at the sample position. Two kinds of scanning mode were employed during the measurements, one was that the angle θ between the incident beam and the surface of the sample was fixed at 3°, 5°, 10° respectively, and 2θ was scanned in the range of 25° to 66°, using 5 seconds residence time every 0.02 radian step, the other was that the scanning angle 2θ was fixed with changeable incident angle θ from 1° to 60°.

3 Results and discussion

FeS_2 films were fabricated on glass slide substrates in order to compare with the films on Si (100) wafers under the same surfidation condition. Fig. 1 shows the XRD patterns of the FeS_2 films annealed in sulfur vapor at 673K for different time. The standard card ASTM 06-0710 for FeS_2 is given on the bottom of the figure for comparison. After annealing for 10 minutes, some main peaks such as (200), (210), (311) appear, whereas other peaks with high diffractive

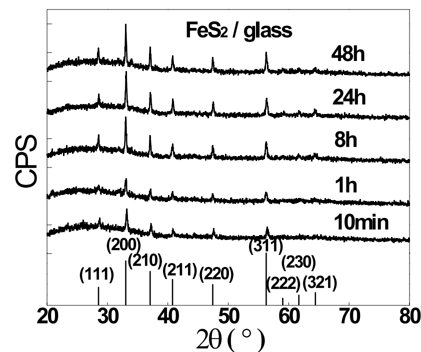

Fig. 1. XRD patterns of FeS_2 by sulfurizing Fe films prepared on glass substrates at 673K for different time. (Standard pattern ASTM06-0710 for FeS_2 was given on the bottom of the figure.)

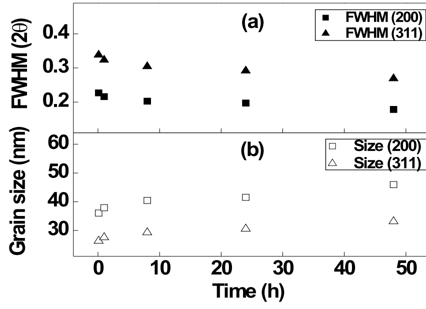

Fig. 2. (a) Dependence of full width at half maximum of (200), (311) peaks; (b) the average grain size with respect to the sulfidation time.

angles (222), (230) and (321) display with weak intensity while increasing annealing time. Fig. 2 can give an obviously impression that the FWHM decrease and the average grain size increase with prolonging the annealing time. The mean size of the crystallite is estimated to be 25—45nm from the XRD peak broadening according to the Scherrer's formula. As has been revealed above, there exists no preferential growth along (200) and (311) orientation for the FeS_2 films deposited on glass substrate, whereas the reflection in $2\theta = 33°$ showed more strong intensity than the other peaks[12]. XRD patterns on Si (100) wafers were given in that paper to assure that the strong (200) reflection was at least partly generated from the silicon substrate, which can be easily understood by Fig. 3(a). Fig. 3(a) shows the sketch of the conventional XRD. The sample was measured in θ-2θ couple scanning mode. The condition for constructive interference is given by the Bragg's law as mentioned below in Eq. (1):

$$2d_{hkl}\sin\theta_{\mathrm{B}} = n\lambda, \tag{1}$$

where d_{hkl} is the reciprocal lattice spacing and can be expressed by Eq. (2)

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}, \tag{2}$$

where a is the crystal lattice constant and $(h,\ k,\ l)$ is known as the Miller indices of the plane. Besides, θ_{B} is the incident angle, n is an non-zero integer representing the diffraction order and λ is the wavelength of the incident radiation. For a fixed incident X-ray wavelength λ, each crystalline solid has a characteristic X-ray diffraction pattern associated with it, which yields accurate information on its crystal structure and lattice spacing. So the Si (200) diffraction angle 2θ can be computed to be about 32.95° with a lattice constant $a = 0.543$nm, this is approximately equal to that of FeS_2, therefore, more strong diffractive intensity on (200) crystal plane can be easily understood.

For two different crystal planes, the angle between them can be calculated from the Eq. (3) as mentioned below:

$$\cos\theta = \frac{h_1h_2+k_1k_2+l_1l_2}{\sqrt{h_1^2+k_1^2+l_1^2}\times\sqrt{h_2^2+k_2^2+l_2^2}}, \tag{3}$$

where (h_1,k_1,l_1) and (h_2,k_2,l_2) are the Miller indices of the two planes. The Si (311) and (200) crystal planes are plotted in Fig. 3(c), and the angle between them is 25.24° according to the Eq. (3). In other words, the Si (311) crystal plane has the same angular difference with the surface of the sample. If an horizontal incident beam focused on the surface of the sample which was tilted about 3° to the horizontal line, there would be a diffraction peak of Si (311) on the direction $2\theta = 56.48°$ relative to the horizontal line by the Bragg's law, this would donate to the intensity of FeS_2 (311) crystal plane.

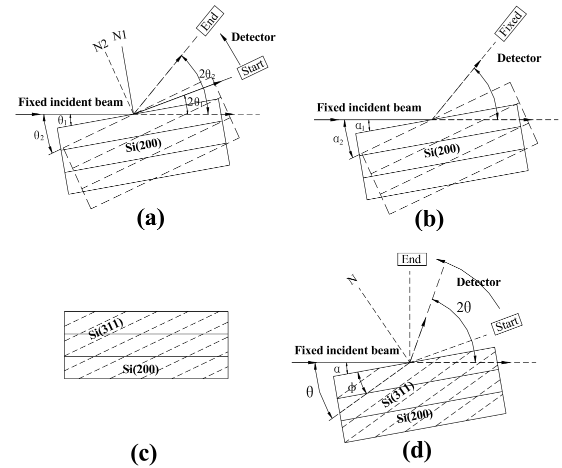

Fig. 3. Diagrammatic sketch for surface XRD measurements. (a) θ-2θ scanning mode with rotating the sample and the detector; (b) θ scanning mode with rotating the sample; (c) two different crystal faces of single-crystal silicon (200) and (311); (d) 2θ scanning mode with rotating the detector.

In order to prove the assumption discussed above, experimental measurements were carried out and another scanning mode was introduced. The detector

was fixed on the direction which was right 56.48° to the fixed horizontal incident beam as shown in Fig. 3(b), and the sample was changed within the range from $\alpha_1 = 1°$ to $\alpha_2 = 62°$ during the measurements. Fig. 4 shows the spectrum of FeS_2 films on Si (100) substrate measured by the synchrotron radiation surface X-ray diffractometer. A sharp peak appears at $\theta = 3°$, the inlet is an accurate scanning spectrum from 2.9° to 3.1° with 0.0025° per step. This is in good agreement with our prediction mentioned above. In order to assure the conclusion, another accurate θ-2θ scanning mode was used by synchrotron radiation surface XRD which is much more accurate than the conventional XRD. Fig. 5 shows the synchrotron radiation surface XRD spectrum for 2θ from 55° to 57° with an accurate scanning step. There is also a sharp peak located at $2\theta = 56.177°$, this is in accord with the results investigated in Fig. 4. The Bragg's law is satisfied when the incident beam is properly 3° to the surface of the sample, the peak at about 56° would be enhanced by the diffraction of Si (311) crystal plane. This is the main reason that leads to the mistaken conclusion made before.

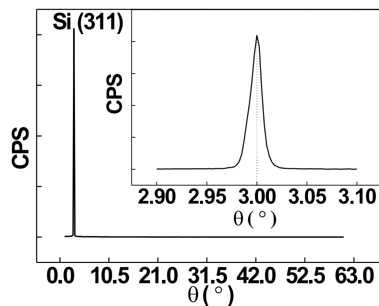

Fig. 4. The synchrotron radiation surface XRD spectrum for the FeS_2 film on Si (100) substrate with fixed detector at 56.48° and changeable incident angle θ from 1° to 60°. The inlet is an accurate scanning figure with the incident angle around 3°.

In turn, a fixed incident beam was focused on the sample, and the detector was moved in a wide range to collect the diffraction line. Fig. 6 shows the spectra while the angles between the surface of the sample and the fixed horizontal incident beam are 3°, 5°, 10° respectively. Two obvious distinctions can be recognized from the figure. One is that when the incident angle is 3°, the intensity of FeS_2 (311) peak is much higher than that in the conventional XRD. In that case, there happen to be the strongest diffraction for the Si (311), which will contribute to the intensity of FeS_2 (311). However, when the angle is 5° and 10°, the spectra are similar to the conventional ones in θ-2θ couple scanning mode. That is to say, there is not a peak with strong intensity at about 56° while the incident angle deviates from 3°, the diffraction of Si (311) crystal plane can not be satisfied according to the Bragg's law. This is why D. Y. Wan reported that there was a preferred orientation on FeS_2 (311) crystal plane in the paper. The other distinction is that there is a difference of about 0.38° in accurate scanning mode between FeS_2 (311) peak in Fig. 6(a) and peaks in (b), (c), but other peaks corresponding to (111), (200), (211), (220) crystal planes are located in the same angle. This prompts another evidence that both (311) crystal plane of the Si substrate and the FeS_2 film contribute to the intensity of the peak at about 56° in the figure.

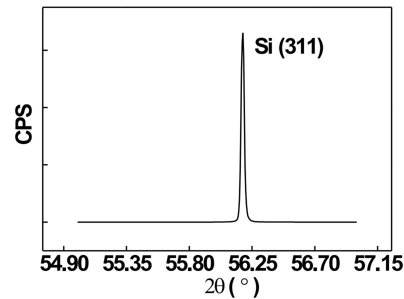

Fig. 5. The synchrotron radiation surface XRD spectrum for the FeS_2 sample on Si (100) substrate with θ-2θ couple scanning mode for 2θ from 55° to 57°.

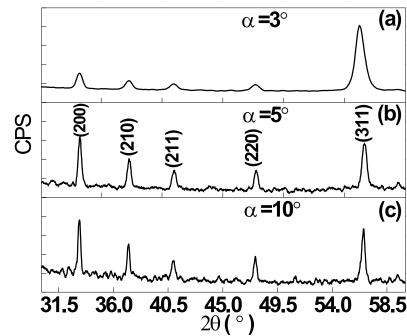

Fig. 6. The synchrotron radiation surface XRD spectrum of the FeS_2 samples with fixed incident angle θ equal to 3°, 5°, 10° respectively and changeable scanning angle 2θ from 25° to 66°.

4 Conclusion

FeS_2 films prepared by magnetron sputtering on Si (100) and glass substrates were studied by conventional XRD and synchrotron radiation surface XRD. A peak at about 56° with strong intensity was detected when the incident beam was about 28° to the Si (311) crystal plane, i. e., 3° to the surface of the silicon sample. This happened to lead to the mistaken conclusion that there was a remarkably strong preferred orientation of FeS_2 along (311) direction, which might be due to the well-matched crystal lattice for FeS_2 and Si (100). In fact, through calculation and experimental measurements, the peak with strong intensity on XRD patterns for FeS_2 comes from the (311) crystal plane of the silicon substrate, other than the preferred orientation of FeS_2.

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硅基底生长FeS_2薄膜的同步辐射表面X射线实验研究*

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摘要 通过对硅与玻璃衬底生长二硫化铁薄膜的常规X射线衍射和同步辐射表面X射线衍射研究比较, 结果发现, 硅衬底上生长二硫化铁薄膜时, 图谱中56°附近出现的衍射强峰并不是由于二硫化铁与硅有良好的晶格匹配导致的, 而是由于硅衬底(311)晶面的衍射造成的. 结合实验与计算论证了该结论.

关键词 二硫化铁 同步辐射表面X射线衍射 半导体材料

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