Preparation and properties of polycrystalline silicon seed layers on graphite substrate*

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Abstract: Polycrystalline silicon (poly-Si) seed layers were fabricated on graphite substrates by magnetron sputtering. It was found that the substrate temperature in the process of magnetron sputtering had an important effect on the crystalline quality, and 700 ℃ was the critical temperature in the formation of Si (220) preferred orientation. When the substrate temperature is higher than 700 ℃, the peak intensity of X-ray diffraction (XRD) from Si (220) increases distinctly with the increasing of substrate temperature. Moreover, the XRD measurements indicate that the structural property and crystalline quality of poly-Si seed layers are determined by the rapid thermal annealing (RTA) temperatures and time. Specifically, a higher annealing temperature and a longer annealing time could enhance the Si (220) preferred orientation of poly-Si seed layers.

Key words: polycrystalline silicon; graphite; rapid thermal annealing; preferred orientation
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1. Introduction

Polycrystalline silicon (poly-Si) films are considered as one of the most prospective materials in microelectronics and photovoltaic technology because of their similar electrical properties to bulk crystalline silicon, high optical absorption coefficient and light stability[1,2]. Varieties of promising techniques have been proposed to fabricate poly-Si films, including chemical vapor deposition (CVD)[3], liquid phase epitaxy (LPE)[4] and magnetron sputtering (MS)[5]. CVD technology is widely used in deposition of poly-Si films for its low cost, high output, and ease of scaling-up. However, direct deposition of poly-Si films by using CVD technology on heterojunction substrates typically results in small grains[6,7]. Therefore, solid phase crystallization (SPC) of conventional annealing[8], rapid thermal annealing (RTA)[9] crystallization, and laser annealing crystallization (LAC)[10] techniques are often used to obtain larger grains. Another possible way is the so-called "seed layers approach". The seed layers approach involves a two-step process in which very thin poly-Si seed layers are fabricated firstly, and then thick films are epitaxially grown on the seed layers by CVD technology.

Seed layers have a great influence on the crystalline quality of subsequently grown thicker poly-Si films. Seed layers, with a large grain size and certain preferred orientation, can be used to produce large-grained poly-Si thick films with the same preferred orientation[11]. In addition, poly-Si films are usually fabricated on low-cost substrates, such as glass[12], mullite[13], and graphite[14]. In recent years, graphite substrate has become a research focus due to its high temperature endurance, low resistance, and similar thermal expansion coefficient to silicon.

In this paper, poly-Si seed layers were firstly fabricated on the graphite substrates by magnetron sputtering, and further crystallization were carried out by using the RTA method. The effects of the substrate temperatures, RTA temperatures, and time on the structural properties of poly-Si seed layers were systematically investigated. The results revealed that the Si (220) preferred orientation and the grain size of poly-Si seed layers in the process of magnetron sputtering were greatly affected by the substrate temperatures. Moreover, during the process of RTA, the Si (220) preferred orientation became enhanced with increasing RTA temperatures and time.

2. Preparation of poly-Si seeds on graphite substrates

The poly-Si seed layers were prepared on graphite substrates by use of the magnetron sputtering technique. The graphite substrates were 50 × 50 mm^2, and 1 mm thick. Both sides of the graphite substrate were polished and cleaned before the sputtering.

The pressure in the magnetron sputtering chamber is 0.5 Pa, and under a flowing argon ambience of 60 sccm (standard-state cubic centimeter per minute). The graphite substrates are placed in parallel to the target of un-doped silicon. The sputtering power is fixed at 200 W, and the reverse sputtering power is lower than 2 W. The sputtering period is also fixed at 2 h. The sputtering speed of the magnetron sputtering equipment had been calibrated. Under the sputtering power of 200 W, the sputtering speed is about 0.7 μm per hour. So, the thickness of poly-Si films sputtered for 2 h is about 1.4 μm. In order to obtain the optimal substrate temperature, a series of

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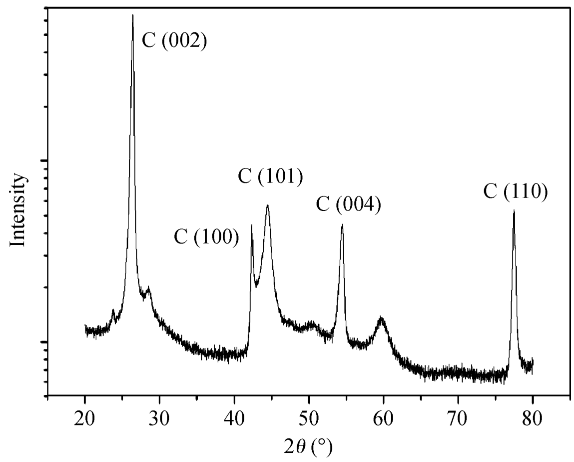

Fig. 1. XRD profile of as-sputtered silicon film on graphite substrates.

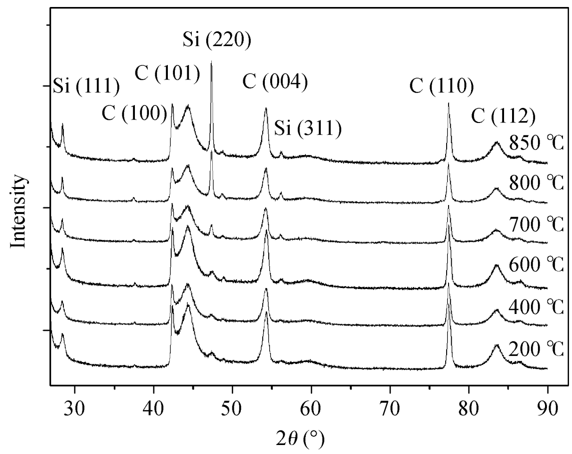

Fig. 2. XRD profiles of the samples prepared at different substrate temperatures and annealed at 800 ℃ for 200 s.

sputtering experiments under different substrate temperatures of 200, 400, 600, 700, 800, and 850 ℃ were carried out, respectively.

The samples sputtered at different temperatures were evaluated by X-ray diffraction (XRD) measurements, and the results showed that only the peaks from the substrates were detected, as shown in Fig. 1. These results indicated that the as-sputtered silicon films were amorphous. In order to crystallize the sputtered Si seeds, the samples of sputtered Si films on graphite were further annealed by using the RTA method under the same temperature of 800 ℃, and the same time of 200 s.

The optimal annealing temperature and time were obtained by changing the annealing temperatures and time, respectively, for the same sputtering samples at a fixed substrate temperature.

3. Results and discussion

3.1. The influence of substrate temperatures on sputtered poly-Si seed layers

Because the as-sputtered silicon films were amorphous, as shown in Fig. 1, the samples of sputtered Si films on graphite were annealed by using the RTA method under the same temperature of 800 ℃, and the same time of 200 s. Figure 2 shows the XRD profiles of the samples with different substrate temperatures. In Fig. 2, the diffraction peaks corresponding to the (111), (220) and (311) crystal planes of silicon were clearly observed, which demonstrated that the samples were highly crystallized. All of the sputtered-Si on graphite with different substrate temperatures transformed into poly-Si by annealing at 800 ℃ for 200 s. It can also be seen in Fig. 2 that the diffraction peak from Si (220) increased obviously for the samples with substrate temperatures higher than 700 ℃.

Further analyses indicated that the peak intensity and sharpness of Si (220) were strongly influenced by substrate temperatures. A critical temperature was found in the diffraction of Si (220). That is, the peak intensity and sharpness of Si (220) did not significantly change below 700 ℃. While the substrate temperature was higher than 700 ℃, the peak intensity and sharpness of Si (220) was increased obviously with increasing substrate temperature. However, Si (111) and Si (311) diffraction peaks were barely influenced by the substrate temperatures. The diffraction peak from the sample sputtered under 850 ℃ was the sharpest which indicated the Si seed layers were Si (220) preferred orientation after the annealing.

Table 1. Structural parameters of the Si (220) diffraction peak of poly-Si seed layers deposited at different substrate temperatures and annealed at 800 ℃ for 200 s.

Substrate temperature (℃)	FWHM (°)	Grain size (nm)
200	0.584	14.849
400	0.528	16.413
600	0.485	17.892
700	0.322	26.929
800	0.267	32.425
850	0.195	38.941

To evaluate the grain size of the poly-Si seed layers, Scherrer's formula[15] was used to calculate the size of the crystallite oriented along (220) plane. Scherrer's formula is

$$D = k\lambda/\beta\cos\theta, \tag{1}$$

where D is the grain size, k is the correction factor taken as 0.90 in the calculation, λ (1.5 Å) is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg diffraction angle. The calculation results of FWHM and the grain sizes of Si (220) are shown in Table 1. It can be seen from Table 1 that the grain size was small and did not change significantly below 700 ℃. However, the grain size became much larger and increased obviously when the substrate temperature was higher than 700 ℃. It indicated that 700 ℃ was the critical substrate temperature in the formation of Si (220) preferred orientation.

This behavior of crystalline with varying substrate temperatures can be explained by classical nucleation theory[16]. In the process of crystal nucleation, when the substrate temperature is higher than a certain temperature, the increase of the critical nucleus size induces the enlargement of the frequency for a single atom to join a critical nucleus. Meanwhile, the concentration of the critical nuclei is enhanced. Hence, the nucleation rate is increased[17].

Based on the theory of grain growth in thin films[18, 19],

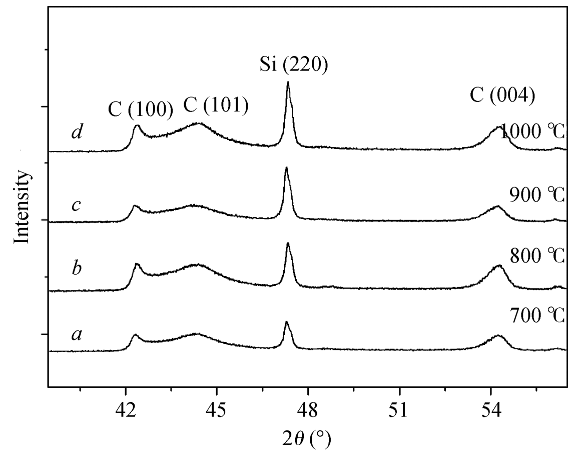

Fig. 3. XRD profiles of poly-Si seed layers annealed at (*a*) 700 ℃, (*b*) 800 ℃, (*c*) 900 ℃, and (*d*) 1000 ℃.

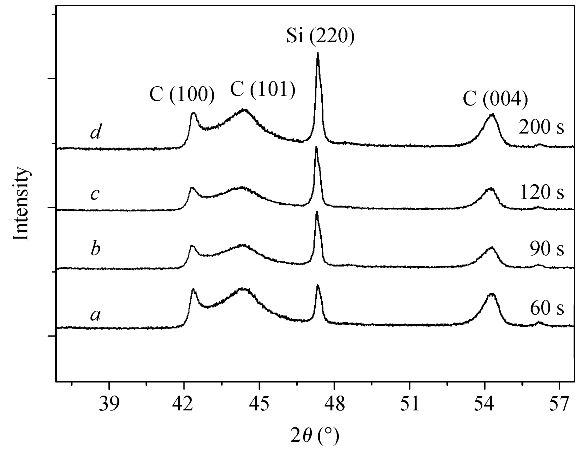

Fig. 4. XRD profiles of poly-Si seed layers annealed for (*a*) 60 s, (*b*) 90 s, (*c*) 120 s, and (*d*) 200 s.

grains of different orientations compete with each other. But grains with a lower surface energy tend to grow preferentially to minimize the total system energy. When the temperature was lower than 700 ℃, the close-packed Si (111) surface grew faster than the Si (220), because the Si (111) surface had the lowest surface energy. But when the temperature was higher than 700 ℃, the nucleation rate of Si (220) was distinctly enhanced. Meanwhile, Si (220) planes could form a tetragonal columnar structure, which restrained or inhibited the growth of Si (111)[20]. Thus, the Si (220) preferred orientation of poly-Si seed layers could be obtained.

3.2. The influence of annealing temperatures on poly-Si seed layers

As discussed above, the poly-Si seed layers had highly (220) preferred orientation when the substrate temperature was 850 ℃ after annealing. Consequently, samples prepared at 850 ℃ were further analyzed with the same annealing time (200 s) and different annealing temperatures, as illustrated in Fig. 3. Diffraction intensities of Si (220) were intensively influenced by annealing temperatures. It can be seen in Fig. 3 that the diffraction intensities of the Si (220) plane became obviously stronger and sharper with the increase of temperature. It indicated that the Si (220) preferred orientation of poly-Si seed layers was enhanced by increasing annealing temperatures.

3.3. The influence of annealing time on poly-Si seed layers

The samples that were sputtered at the substrate temperature of 850 ℃ and annealed at 1000 ℃ had the optimal Si (220) preferred orientation. To further explore the influence of RTA time, a series of experiments under different annealing times of 60 s, 90 s, 120 s, and 200 s were carried out, respectively.

Figure 4 shows the XRD profiles of poly-Si seed layers annealed at 1000 ℃ under different annealing times. The diffraction intensities of the Si (220) plane increased with prolonging the annealing time, which indicated that longer annealing time could also enhance the Si (220) preferred orientation of poly-Si seed layers.

4. Conclusions

In this paper, poly-Si seed layers were fabricated on graphite substrates by magnetron sputtering, and then annealed by using the RTA method under different temperatures and times. The effects of substrate temperatures, RTA temperatures, and time on the structural properties of the poly-Si seed layers were systematically investigated.

All the samples sputtered below 850 ℃ were amorphous evaluated by XRD measurements, and the samples showed post crystalline characteristics after they were annealed by using RTA methods. It could be concluded that with higher substrate and annealing temperatures, and longer annealing times, a better preferred orientation of Si (220) can be obtained. It should be emphasized that the Si (220) was not preferred if the substrate temperatures were lower than 700 ℃ regardless of the annealing temperatures, and the Si (220) became obviously preferred when the substrate temperatures reached 850 ℃ while sputtering.

References

[1] Pereira L, Barquinha P, Fortunato E, et al. Influence of metal induced crystallization parameters on the performance of polycrystalline silicon film transistors. Thin Solid Films, 2005, 487(1/2): 102

[2] Gall S, Schneider J, Klein J, et al. Large-grained polycrystalline silicon on glass for thin-film solar cells. Thin Solid Films, 2006, 511: 7

[3] Focsa A, Slaoui A, Pihan E, et al. Poly-Si films prepared by rapid thermal CVD on boron and phosphorus silicate glass coated ceramic substrates. Thin Solid Films, 2006, 511: 404

[4] Kim H, Lee G, Kim D, et al. A study of polycrystalline silicon thin films as a seed layer in liquid phase epitaxy using aluminum-induced crystallization. Current Applied Physics, 2002, 2(2): 129

[5] Jung M J, Jung M Y, Shaginyan R, et al. Polycrystalline Si thin film growth on glass using pulsed DC magnetron sputtering. Thin Solid Films, 2002, 420: 429

[6] Yang Deren. Solar cell materials. Beijing: Chemical Industry Press, 2006 (in Chinese)

[7] Beaucarne G, Bourdais S, Slaoui A, et al. Thin-film polysilicon solar cells on foreign substrates using direct thermal CVD: ma-

terial and solar cell design. Thin Solid Films, 2002, 403: 229

[8] He S, Hoex B, Lnns D, et al. Crystal quality improvement of solid-phase crystallized evaporated silicon films by *in-situ* densification anneal. Solar Energy Materials Solar Cells, 2009, 93(6/7): 1116

[9] Rau B, Weber T, Gorka B, et al. Development of a rapid thermal annealing process for polycrystalline silicon thin-film solar cells on glass. Mater Sci Eng B, 2009, 159/160: 329

[10] Park K C, Lee J H, Song I H, et al. Poly-Si thin film transistors fabricated by combining excimer laser annealing and metal induced lateral crystallization. Journal of Non-Crystalline Solids, 2002, 229: 1330

[11] Gall S, Becker C, Conrad E, et al. Polycrystalline silicon thin-film solar cells on glass. Solar Energy Materials Solar Cells, 2009, 93: 1004

[12] Gordon I, Vallon S, Mayolet A, et al. Thin-film monocrystalline-silicon solar cells made by a seed layer approach on glass-ceramic substrates. Solar Energy Materials Solar Cells, 2010, 94: 381

[13] Focsa A, Gordon I, Auger J M, et al. Film polycrystalline silicon solar cells on mullite ceramics. Renewable Energy, 2008, 33(2): 267

[14] Rostalsky M, Muller J. High rate deposition and electron beam recrystallization of films for solar cells. Thin Solid Films, 2001, 401(1/2): 84

[15] Cui L, Zhang H Y, Wang G G, et al. Effect of annealing temperature and annealing atmosphere on the structure and optical properties of ZnO thin films on sapphire (0001) substrates by magnetron sputtering. Appl Surf Sci, 2012, 258: 2479

[16] Chen L H, Chen C Y, Lee Y H. Nucleation and growth of clusters in the process of vapor deposition. Surf Sci, 1999, 429(1–3): 150

[17] Chen C Y, Chen L H, Lee Y H. Nucleation and growth of clusters on heterogeneous surfaces. International Communications in Heat and Mass Transfer, 2000, 27(5): 705

[18] He Y Z, Ding H L, Liu L F, et al. Computer simulation of 2D grain growth using a cellular automata model based on the lowest energy principle. Mater Sci Eng, 2006, 429(1/2): 236

[19] Frost H J, Thompson C V. Computer simulation of grain growth. Current Opinion in Solid State and Materials Science, 1996, 1(3): 361

[20] Wang Y Y, Kamins T I, Zhao B Y. Polycrystalline silicon thin films and their application in integrated circuits. 2nd ed. Beijing: Science Press, 2000 (in Chinese)