Optical properties and growth mechanism of rock-like structured black silicon

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Abstract
In this study, rock-like black silicon is prepared by using plasma enhanced hot-wire chemical vapor deposition (PE-HWCVD). The average grain sizes of polysilicon for 10-min, 20-min and 40-min growth time was about 12.4, 14.3 and 15.5 nm, respectively. As the growth time increased, the surface morphology had more rock like structures all over the surface which can be seen in the scanning electron microscope (SEM). Growth mechanism of developing crystallline silicon is studied along with the optical property. The results showed that the PE-HWCVD silicon have low reflectivity 6.4% better than wet etch textured silicon 12.5% in the range of 400–800 nm. The black silicon has low reflectance than the wet etch textured silicon which can be perfectly used as an anti-reflective coating substance.

Introduction
For the solar cells to work effectively, the surface coating should absorb as much as light. There are very few materials which work as an anti-reflective coating and black silicon is one of the few materials which can be used in solar cells [1, 2]. Black silicon is a silicon surface which is covered by the fine Nano or micro crystal structures [3]. This property helps in suppressing the reflection and enhancing the scattering and absorption of light. The main function is to act as an anti-reflective coating layer [4]. Also, black silicon has high absorption rate in the visible and infrared regions, due to this property black silicon can be used in the visible and infrared photodetectors and also in night vision cameras [5]. Silicon is also used as an electrical source for the Surface Plasmon polariton (SPP) [6] and related electronic devices [7, 8]. Crystalline silicon is very effective in the solar cell application. Some reports suggested that the Si films deposited by CVD process contains the amorphous form of thickness around 200 nm which in turn required various amount of extra time and extra processes to become crystalline [9, 10].

To counter effect these extra steps, there are new techniques which are improving the crystalline nature of deposited material. Hot-wire chemical vapor deposition (HWCVD) [11, 12] and Hot-wire Implantation doping (HWID) [13] are the simplest methods to obtain crystalline form. In this research, silicon is being deposited over the Si wafers by using the Inductively Coupled Plasma (ICP)–assisted HWCVD technique which showed excellent properties over various tests. Hot wire technique can improve the crystallinity of the Si structure and Plasma is helpful for the uniform deposition of Si over the substrate. Test results showed the crystalline nature of the deposited silicon can be improved by increasing the growth time in deposition silicon. The deposited silicon appeared to be as black over the surface after the depositing, which when tested for reflectance, showed low reflectance than the wet etch textured silicon. This property of this black silicon can be used as an anti-reflective coating over numerous applications.

Experimental procedure
The rock-like polysilicon was deposited on p-type (100) 625 μm-thick Si wafers with area (2 cm × 2 cm) using an Inductively Coupled Plasma (ICP)-assisted HWCVD system (Syskey Technology co., Ltd). The hot-wire system was used to deposit the polysilicon film on the polished single-crystal silicon, and the filament
temperature, substrate temperature, SiH₄ flow rate, argon flow rate, distance between the hot wire filament and the substrate, and chamber pressure were 1800 °C, 400 °C, 100 sccm, 60 sccm, 5.0 cm and 20 mTorr, respectively. The ICP system was also used to assist polycrystalline silicon film deposition with 75 W working watts and deposition time is 10, 20, 40 min. The crystallinity and crystal orientation of polysilicon films were measured by x-ray diffraction (XRD, Rigaku D/MAX2500). The structures of rock-like polysilicon film were measured by transmission electron microscopy (TEM, Philips Tecnai G2F20). The surface morphology of films was measured by Atomic force microscopy (AFM, NT-MDT SFC050L). The AFM measurements were obtained using a conductive probe with a tip radius of 20 nm. The optical of polysilicon film were measured by ultraviolet-visible-NIR (UV−vis-NIR, JASCO V-670) spectrophotometer.

**Results and discussion**

The figure 1 shows the x-ray diffraction for the PE-HWCVD coated silicon wafer. Three different variations for the growth time have been done and all the samples have the silicon peaks of (111), (220) and (311) formed at the respective angles 28.4°, 47.28° and 56.8° [1]. When the growth time is increasing, a Si peak (400) at 70° is begun to form. Also, as the growth time increases, the peaks are getting stronger and changing from amorphous form to crystalline form. The growth time of Poly-Si-10 (10 min growth time of Si) indicates less grain size when compared to the growth time of Poly-Si-20 (20 min growth time of Si) and Poly-Si-40 (40 min growth time of Si). The XRD pattern shows the polycrystalline form of Si peaks (JCPDS file 27-1402). From the values of 2θ and β of the (111) peak, the grain size (D) can be estimated by Scherrer’s formula \( D = \frac{0.9λ}{β\cosθ} \) [14], where λ is the x-ray wavelength equal to 0.1542 nm, θ is the (111) peak angle, and β is half the peak width. The average grain sizes of thin film grown for 10, 20 and 40 min was about 12.4, 14.3 and 15.5 nm, respectively. Figure 2(a) shows the top-view SEM image for the Poly-Si-10 by PE-HWCVD process. This is a low-resolution image which shows the silicon is deposited uniformly all over the surface. As the deposited Si is in crystalline form, the structure morphology consists of small grains like structure which is crystalline form of
silicon and the rest of the surface is filled with nano crystalline form of silicon. Figure 2(b) shows the top view SEM image for Poly-Si-20 deposition in which the size of solid form silicon has been increased and accumulated all over the surface. In figure 2(c) SEM image shows the top view of Poly-Si-40. As the growth time is very high, silicon is formed as small rock like structures all over the surface. The size of the rock grain structures is also increased highly when it compared to figure 2(b). The cross-sectional image of Poly-Si-40 is shown in figure 2(d). The figure shows that the base of Si deposition is a solid form without the formation of rock like structures. As the growth time increases, the solid form like rocks are formed on the surface layer due to thermal heating which can be seen from the cross-sectional view. In this process, thermal deposition will generate rock-like silicon when the film was grown thick enough and the role of plasma and hot wire have a very limited impact on formation of rock-like structure.

After cutting by focused Ion Beam (FIB), cross-sectional TEM images of top layer of rock-like polysilicon is detected at figure 3(a), which shown a columnar structure with a raised surface. We can clearly see the long grain boundaries in figure 3(b). It can be estimated that the direction of parallel grain boundaries is the growth direction of columnar polycrystalline silicon. The diameters of the nanocrystals are about 10–20 nm in figure 3(c), which agree with the XRD results. Figure 3(d) can be indexed into pure phase of well-crystallized Si with cubic structure (JCPDS No. 27-1402) and obtained the high purity of Si phase without other impurities.

Figure 4 shows the graph between different growth times and its corresponding roughness. The roughness is an important factor to consider because of the scattering losses which impact negatively on the propagation losses of the deposited layers [15]. From the graph, it can be seen that the roughness of PE-HWCVD deposited silicon is gradually increasing with the increase in the growth time. The roughness of Si film is very low around 46 nm when the growth time is 10 min. When the growth time is increased to 20 min, the roughness is tremendously increased to 116 nm which is very high when compared to 10-min growth time. At 40-min growth time, roughness remained at 138 nm which is almost similar to 20-min growth time. Thickness of different Si samples with different growth time is showed in the table 1.

Figure 5 shows the reflectance spectra for the PE-HWCVD deposited silicon wafers with comparison to wet etch textured silicon. For the Poly-Si-10, reflectivity is stable in the ultraviolet region and has a strong...
interference patterns after 550 nm region due to its microcrystalline Si form [16]. For Poly-Si-20 and Poly-Si-40, they show low reflectivity in the visible region due to the formation of crystalline nature when the growth time is increased. The average reflectance in the range of 400–800 nm was about 8.5%, and 6.4% for the Poly-Si-20 and Poly-Si-40, respectively. These values are lower than those for the wet etch textured Si and the Poly-Si-10, with
average reflectance of about 21.7% and 12.5%, respectively. Poly-Si-20 and Poly-Si-40 showed reflectance much lower than the wet etch textured silicon in the visible region which can be used as an anti-reflective coating agent for many purposes [17]. The Poly-Si-40 showed better light-trapping effect than the wet etch textured silicon in case of reflectivity.

Figures 6(a)–(c) shows the growth mechanism for the PE-HWCVD silicon on thick Si wafer. There are basically two types of growth mechanisms for crystalline structures which are primary crystallization and secondary crystallization. Primary crystallization occurs due to defect energy and secondary crystallization occurs due to grain boundary energy. However, in this case, grain structures gain the energy from the thermal
heating and small grains starts to grow into bigger grains forming a crystalline structure. So, the mechanism happened might be secondary crystallization via primary crystallization. Figure 6 (a) shows the 10-min growth time for the silicon deposition where the surface is occupied with amorphous form of silicon. In between the amorphous form, there are small traces of Nano crystalline form of silicon. When the growth time is increased to 20 min in figure 6 (b), these Nano crystalline structure tends to grow on the Si wafer and the amorphous silicon starts to disappear. The grain size of crystalline silicon also gets bigger. Figure 6 (c) represents the growth time of 40 min where the Nano crystalline form of silicon is completely occupies the surface and the grain size grows very big which forms into the shape of rock like structure.

Conclusion

Black silicon preparation process by the Hot-wire chemical vapor deposition process revealed that the deposited silicon can be formed as crystalline nature. The average grain sizes of PE-HWCVD polysilicon for 10, 20 and 40 min was about 12.4, 14.3 and 15.5 nm, respectively, from the x-ray diffraction. As the growth time increased, the surface morphology had more rock like structures all over the surface which can be seen in the SEM. The diameters of the nanocrystals are about 10–20 nm from TEM images. The growth mechanism also explains the amorphous deposition of silicon into the crystalline form. Most important property reflectivity is tested for PE-HWCVD silicon comparing to wet etch textured silicon. The results showed that the PE-HWCVD silicon have low reflectivity 6.4% better than wet etch textured silicon 12.5% in the range of 400–800 nm.

Acknowledgments

This work was financially supported by the Ministry of Science and Technology of Taiwan, with project numbers: MOST 107-2221-E-218-032-MY2 and MOST 107-2221-E-492-007. The authors would like to thank the Taiwan Semiconductor Research Institute (TSRI) and Ms. Hui-Jung Shih with the Instrument Center of National Cheng Kung University for supporting the use of high-resolution SEM (Hitachi SU8000).

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