Effect of Heat Treatment on Phase Transformation of TiO$_2$ and Its Reflectance Properties

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Abstract

Titanium dioxide (TiO$_2$) anti reflection coating film applied for solar cell application, gains more interest due to the insufficient energy problems today. Titanium dioxide can be found in several forms, and the most stable phase is rutile. This research aims to study effect of heat treatment on phase transformation of TiO$_2$ and its effect on reflectance property. Titanium dioxide film was coated on silicon wafer by DC magnetron sputtering to obtain 190 nm and 420 nm thicknesses. Then, it was heat treated at 900°C for 1 and 4 hours under ambient atmosphere. Phases and surface morphologies before and after heat treatment are investigated by X-ray diffractometer (XRD) and atomic force microscope (AFM). Cross-sectional microstructures of all samples were also observed by field emission scanning electron microscope (FESEM). It can be seen that heat treatment at elevated temperature induces phase transformation of TiO$_2$ from anatase to rutile. The heat treatment holding time also affects phase transformation. The thicker film requires longer holding time to completely transform anatase to rutile. The 420 nm thick TiO$_2$ requires 4 hours to completely transform to rutile, while, only 1 hour is needed to transform the 190 nm thick TiO$_2$. Besides phase transformation, agglomeration of rutile grain also takes place. Hence, after heat treatment, rutile TiO$_2$ film has coarse columnar structure. The existence of rutile TiO$_2$ film can reduce reflectance percentage of light from silicon surface by destructive interference. The reflectance percentage can be reduced to less than 10% when combining TiO$_2$ coating and etched surface.

Keywords : TiO$_2$, Phase transformation, Heat treatment, Reflectance

Introduction

Nowadays, energy crisis is one of the most critical problems. Insufficient gasoline production and pollution due to usage of energy from combustion become severe problems. Alternative energy source with low environmental burden has to be considered to replace energy from combustion. Solar cell is an attractive energy conversion device which produces the least amount of pollution. However, the main limitation of solar cell is its low efficiency due to much energy loss from conversion to heat and high reflection of light from solar cell shiny surface. Anti reflection coating (ARC) is coated on the top surface of solar cell to improve its efficiency[1].

Several candidate materials can be used as an ARC film such as TiO$_2$, SiO$_2$ and so on. Among those materials, TiO$_2$ is the most attractive material since it does not only have suitable reflective index but it also can be a self cleaning layer due to its super-hydrophilic property[2]. TiO$_2$ film can be found in several forms which are rutile, anatase, brookite and amorphous. Although TiO$_2$ with different structures can be produced by controlling coating and annealing condition, anatase, brookite and amorphous TiO$_2$ are metastable forms. The most stable form of TiO$_2$ is the rutile form at all temperatures due to the lowest standard free energy of formation[3,4]. In this research, the effect of heat treatment on transformation of anatase TiO$_2$ to the most stable form of rutile TiO$_2$ is studied including its anti-reflection property.

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2. Experimental procedure

2.1 Sample preparation

Single crystal p-type silicon wafer with (100) crystallographic orientation and 280 μm thick was used as substrate to be coated with TiO_2 by DC magnetron sputtering. The silicon wafer was cut into rectangular shape with 20 mm in width and 20 mm in length. All samples were rinsed in acetone for 15 minutes following by de-ionized water for 15 minutes using ultrasonic cleaner. Then, all samples were rinsed by ethanol for 5 times and dried. All samples were kept in desiccator prior to coating.

2.2 Texturing and coating

In order to simulate the silicon wafer that is used for solar cell application, surface texturing must be done. In this research, surface texturing was done by anisotropic etching using mixture of NaOH and IPA (Iso Propy l Alcohol) solution with 10 M concentration. During anisotropic etching, the etching solution with the samples was heated up to 60°C with 1 deg/minute heating rate and also was 150 rpm stirred. The total etching time was 40 minutes. After surface texturing, TiO_2 was coated onto the Si substrate. The coating parameters are listed in Table 1. All coated samples were annealed in ambient atmosphere at 900°C for 1 and 4 hours holding times to investigate phase transformation of TiO_2 film.

**Table 1.** TiO_2 coating conditions by magnetron sputtering

| Parameter	Condition
Sputtering gas	Argon
Reactive gas	Oxygen
Gas flow rate	Ar:O 5:15 sccm
Total pressure	7×10^{-3} mbar
Base pressure	3×10^{-5} mbar
Sputtering current	500 mA
Target-substrate	8 cm
Substrate temperature	Room temperature
Coating time	72 and 168 minutes
Growth rate of film	2.6 nm/minute

2.3 Characterization

Surface morphology after etching, coating and annealing was observed by field emission scanning electron microscope (FESEM) and atomic force microscope (AFM). Phase of TiO_2 was investigated by X-ray diffractometer (XRD) using Cu Kα radiation. UV-visible spectrometry with integrated sphere mode was employed to measure percent of reflectance. Wavelengths of visible light used in this experiment were varied from 400 to 800 nm.

3. Results and Discussion

Figure 1 shows the silicon surface after texturing by anisotropic etching. It can be seen that there are a lot of pyramids formed on the surface which is due to the different etching rates of Si in (111) and (100) planes. The formation of pyramids on Si surface is well-known and widely used as a method to improve efficiency of silicon solar cell by creating texturing on solar cell surface. According to AFM results shown in Figure 2, the surface area of silicon after etching was increased up to 32.43% comparing to the surface area of silicon prior to etching which was about 10.74%. The increasing of surface area would reduce the reflection by light trapping in the valley areas between pyramids. AFM analysis also shows that thicknesses of film coated on the samples were 190 nm and 420 nm for coating holding time of 72 and 168 minutes, respectively.
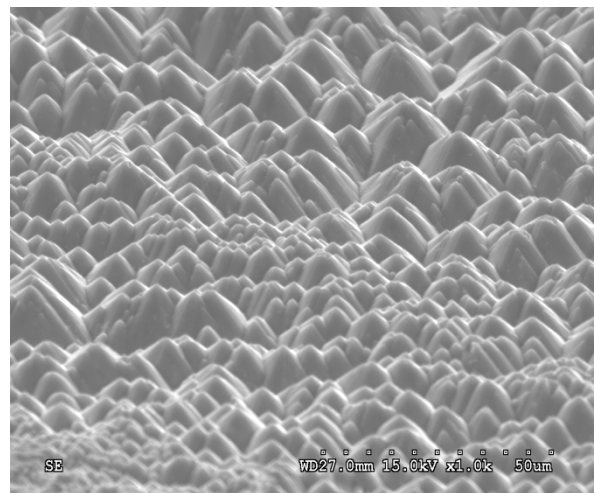

**Figure 1**. SEM microstructure of etched Si surface.

(a)

(b)
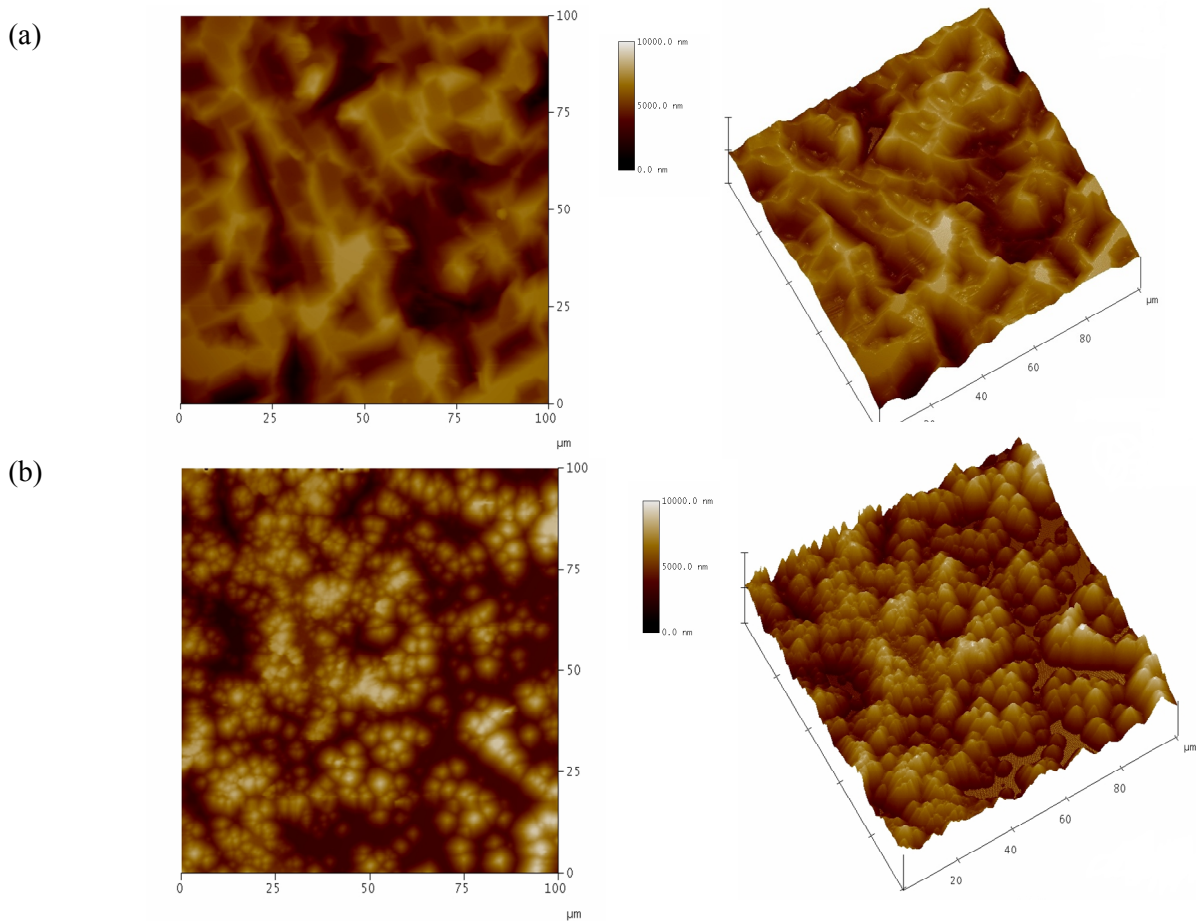
Figure 2. Surface morphology of Si samples by AFM (a) as received Si and (b) after anisotropic etching.

After coating, all samples were analyzed by XRD. The XRD profiles in Figure 3 and 4 show that anatase TiO_2 film formed on the top surface of Si samples according to JCPDS No. 78-2486. Si peak is also detected at the angle (2θ) of 33.038 (JCPS No.71-1088) coexisting with peaks of anatase. This is because TiO_2 film formed by DC magnetron sputtering in this research is very thin.
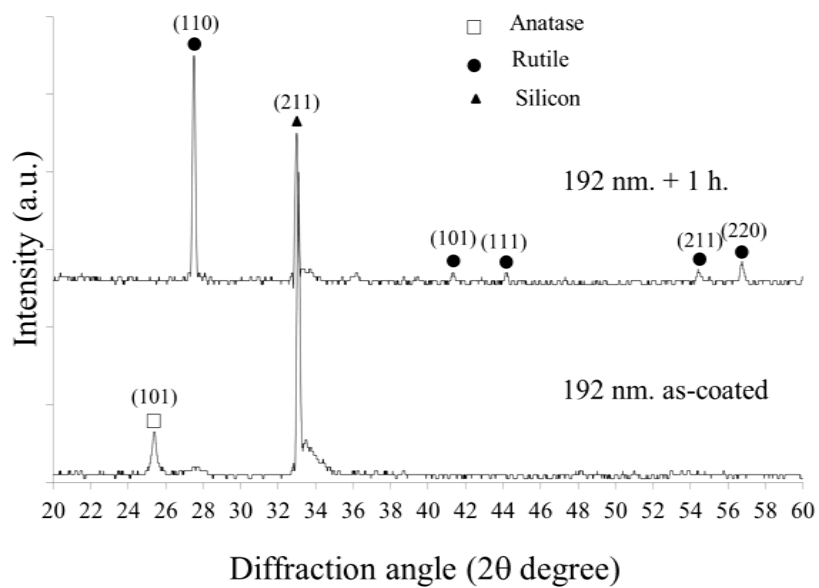

Figure 3. XRD patterns of as coated and 1 hour annealed at 900°C Si samples.
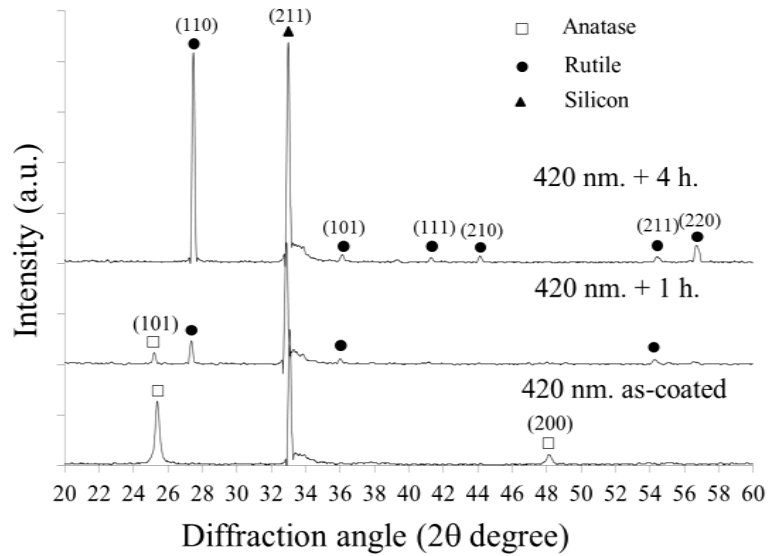
Figure 4. XRD patterns of samples with as-coated and annealing for 1 hour and 4 hours at 900°C.

Effect of heat treatment on phase transformation of TiO_2 can be seen in Figure 3 and 4. For sample coated with 190 nm TiO_2 film, after annealing for 1 hour at 900°C, all of anatase was transformed to rutile. This can be confirmed by XRD result in Figure 3 that shows only rutile (JCPDS No. 87-0920) and Si substrate peaks. However, in the case of 420 nm, small peak of anatase is still found at 2θ equals 25.307 degree. This suggests that transformation of anatase to rutile has not completed resulting in some amount of anatase left in the coated film. With increasing annealing holding time to 4 hours, it was found that there is no anatase peak detected which means that anatase completely transformed into rutile. Therefore, the optimum conditions for heat treatment to transform anatase to rutile are 1 hour and 4 hours for 190 nm and 420 nm thick films, respectively.
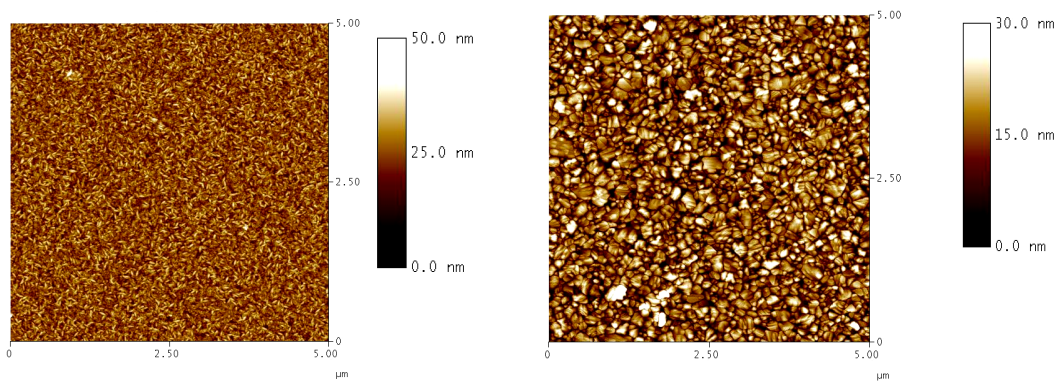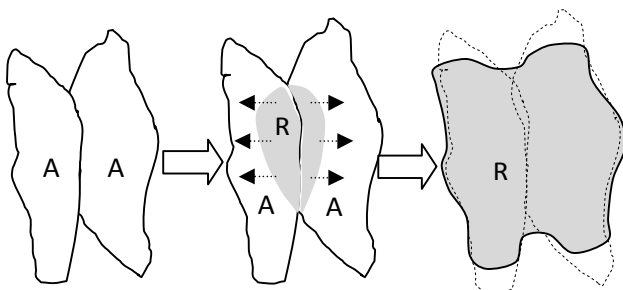

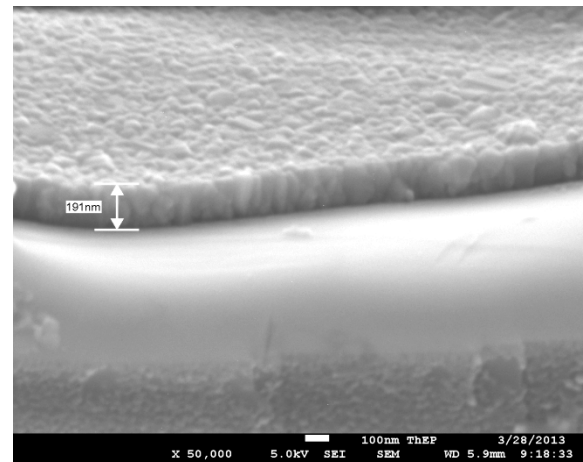**Figure 5.** Surface morphology of TiO_2 (a) before and (b) after annealing at 900°C for 1 hour.
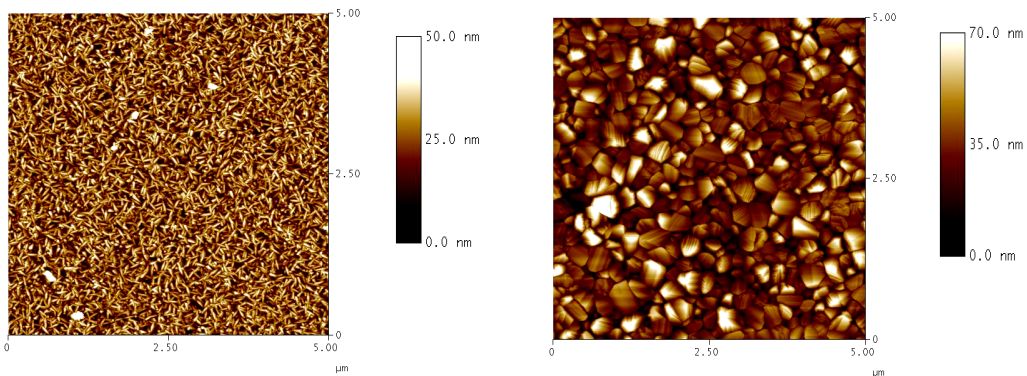
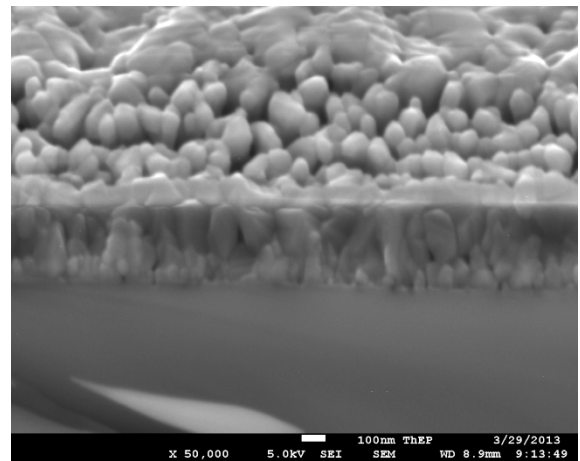**Figure 6**. Surface morphology of TiO_2 (a) before and (b) after annealing at 900°C for 4 hour

Surface morphologies of TiO_2 film with film thickness of 190 and 420 nm before and after annealing are shown in Figure 5 and Figure 6. Both figures reveal changing in surface morphology together with phase transformation during annealing. It can be seen that agglomeration of small needle-like anatase grain to be large coarse grain of rutile takes place. The longer annealing time, the larger grain of rutile is attained; therefore, the 420 nm thick film after annealing for 4 hours has rougher surface, with Ra equals 10.351 nm, when compared to those of 190 nm thick film which has Ra equals 4.590 nm after 1 hour annealing. The longer annealing time is necessary for thick TiO_2 film might be due to difficulty from constrain of volume that must be changed during phase transformation because of different densities of anatase and rutile (anatase density = 3.84 g/cm^3, rutile density = 4.10 g/cm^3). The agglomeration of TiO_2 occurs during anatase-rutile phase transformation as reported by B.S. Richards[1]. During annealing, two grains of anatase attached to each other following by nucleation of rutile phase. After that, growth of rutile begins resulting in phase transformation. Then agglomeration of rutile occurs as shown in schematic drawing in Figure 7. The main driving force of the agglomeration could be due to the higher surface energy of rutile comparing to anatase; therefore, agglomeration from small needle-like grain to larger coarse grain remarkably decreases surface energy of TiO_2. After phase transformation, the rutile has large columnar grain as shown in Figure 8. Although agglomeration indicates that some solid-state diffusion occurred during annealing, the rate of diffusion is not high enough to cause formation of equiax grain by recrystallization. The structures of both 190 nm and 420 nm thick TiO_2 are still in the Structure Zone Model II (SZM II).

(a)


(b)

Figure 8. Cross-sectional microstructure of rutile TiO_2 with thickness of (a) 190 nm and (b) 420 nm.

Figure 7. Schematic drawing of anatase to rutile phase transformation and agglomeration during annealing[1].

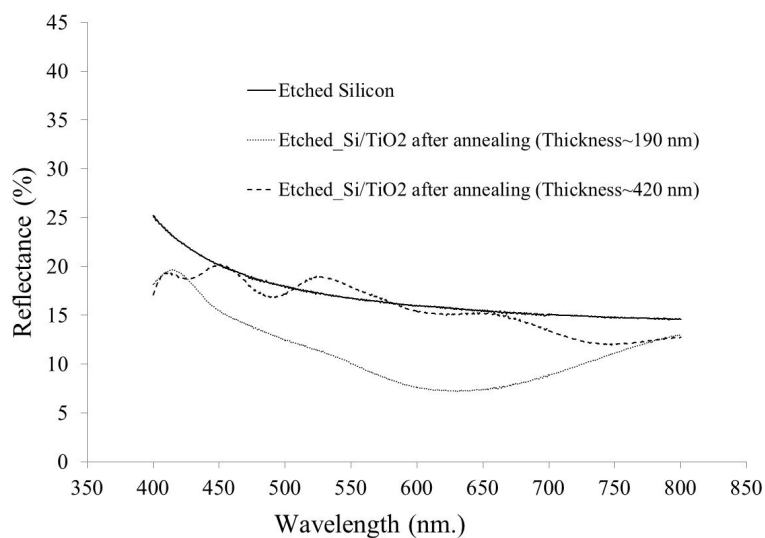Formation of rutile, both 190 nm and 420 nm thicknesses, on the as-received silicon surface significantly reduces reflectance percentage in all wavelengths as can be seen in Figure 9. In the case of etched silicon, shown in Figure 10, formation of TiO_2 also can lower reflectance percentage; however, its effect is not foremost as in the case of as-received silicon. This is because the reduction of reflectance percentage in etched silicon is mainly influenced by pyramid formation as described previously. The reduction of reflectance percentage is due to the formation of rutile with reflective index about 2.3, leading to destructive interference[5]. This destructive interference also creates wave form of the reflectance graphs as seen in Figure 9 and 10. Since the reduction of reflectance percentage is governed by interference, the thickness of TiO_2 film plays an important role on degree of phase difference of reflected light. It can be seen from the result that the rutile film with thickness of 190 nm exhibits lower reflectance percentage for both as-received silicon and etched silicon; hence, the 190 nm thickness can be considered as the appropriate thickness for rutile coating. Comparing the reflectance percentages achieved from Figure 9 and 10, it was found that the effect of anisotropic etching significantly impacts on anti-reflectance properties of all samples.
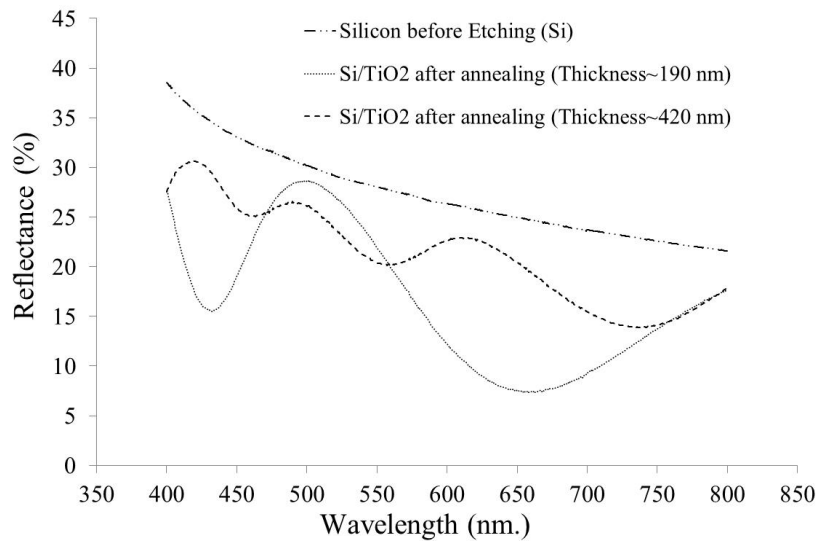
Figure 9. Reflectance percentage of as-received silicon and rutile TiO_2 coated silicon with 190 nm and 420 nm thick TiO_2.

Figure 10. Reflectance percentage of etched silicon and rutile TiO_2 coated silicon with 190 nm and 420 nm thick TiO_2.

4. Conclusion

Heat treatment by annealing at 900°C can induce phase transformation of TiO_2 from anatase to rutile. The holding time of annealing also affects amount of phase transformation. The thicker anatase TiO_2 film requires longer holding time to completely transform to rutile TiO_2. During anatase to rutile transformation, agglomeration of grain also takes place. Rutile obtained from annealing has coarse columnar structure. The longer annealing time, the larger columnar is attained. Rutile is an effective anti-reflection coating especially for as-received silicon. The reflectance percentage of light can be reduced for all wavelengths in the range of 400 to 800 nm. The thickness of TiO_2, which is the important parameter for destructive interference, needs to be considered to minimize light reflectance. In this experiment, coating of 190 nm thick rutile TiO_2 film on etched silicon substrate is the most appropriate condition to reduce the reflectance of light to be less than 10%

Acknowledgement

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