Annealing treatment of a-Si:H films deposited by PECVD and their properties

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Abstract. The hydrogenated amorphous silicon (a-Si:H) films have been grown on the glass substrates by plasma enhanced chemical vapor deposition (PE-CVD) employing silane (SiH₄) with hydrogen (H₂) dilution. The as-deposited films were then annealed at various temperatures of 200, 300 and 400°C for 30 minutes. Annealing process at 300°C was also performed for 60 and 90 minutes. Examinations using X-ray diffractometry, infrared and UV-Vis spectroscopy demonstrated that the annealed films show an increasing crystallinity of 3.26 – 6.80% and reduced dangling bond content down to more than one order of magnitude (from 2.3x10¹⁹ to 1.2x10¹⁸ cm⁻³). Meanwhile, the energy bandgap and Urbach energy of the films are around 1.71 – 1.75 eV and 0.21 – 0.27 eV respectively.

1. Introduction
Among the solar cell material, hydrogenated amorphous silicon is a promising material in photovoltaic technology today. Initial efficiency ranges between 9-10% achieved in the laboratory for a single connection, then the value rises to 13% with multiple structure and silicon alloy (mostly with Ge). Crystalline silicon (c-Si or mc-Si) are more stable and have higher efficiency, but the production costs for both are very expensive [1]. Therefore, although the efficiency of a-Si: H is lower compared to c-Si (and mc-Si), a-Si: H has the potential to be cheaper so that it will be able to replace crystalline silicon technology which has a more stable efficiency. However, the Si-H bond formed easily separated by the effect of irradiation with high intensity, which is then left dangling bond defect. Dangling bond is a prime candidate causes a decrease in the efficiency of solar cells based on a-Si: H, which is known as the Staebler-Wronski effect [2]. Another defect is the addition of the bond length deviation of 1.9% and a bond angle of about 10º from its crystal structure [3].

Although it has been shown clearly that hydrogen is the trigger of the state of the defect within a thin layer of amorphous silicon, however, the study of the fundamental properties of defects and their interaction with hydrogen is still being conducted in a serious and profound. For example, how the contributing role of dangling bond defects that arise and changes in particle size on properties of thin layers. This paper discusses the process of anneal after deposition, aims to determine the effect of heat treatment on the bond between the silicon and hydrogen (SiH, SiH₂), the value of the energy gap, the size of the particle, and its relationship with the phase change. This is related to the stability and density of states bonds are made. When the bonds between silicon and hydrogen is lost due to the heat treatment, it will form a dangling bond in the structure of the film. Dangling bonds is a major defect that resulted...
in losses on the solar cell material based a-Si: H, and it is one factor contributing to the Stabler-Wronski effect.

2. Experiment Methods
Layer deposition of a-Si: H is done by using RF-PECVD, by diluting the silane gas with hydrogen, namely R=H$_2$/SiH$_4$=36. Other deposition parameters are P= 2 torr, T=150°C, RF=5 watt, and t=60 minutes. Anneal is one of the heat treatment process in which the sample is heated and held at a given temperature, then allowed to cool at room temperature. This anneal process aims to determine the effect of heat treatment on the energy gap, defects in thin layers, particle size, and its relationship with the phase change. At the time of the annealing process, the sample is placed in a furnace with a thin layer facing up, to avoid the deposition layer is not damaged. In this anneal process, used furnace apparatus, with variations in temperature, T = 200ºC, 300ºC, 400ºC and variations of time, t = 30 minutes, 60 minutes and 90 minutes.

To determine the character of the results of deposition and annealing, performed three types of characterization, ie UV-Vis spectrometer, X-ray diffraction (XRD), and Fourier-Transform Infra-Red (FTIR). XRD characterization is done by firing angle 3° over a range of angles (2θ) = 5°-60°. XRD characterization is used to determine the level of crystallinity layer. Determination of the crystallinity of the films using XPert HighScore Plus software (HSP). FTIR characterization performed at wave number 400–4000 cm$^{-1}$. While UV-Vis performed at a wavelength of 250 – 800 nm.

3. Results and Discussion
Figure 1 shows the transmittance of the wave function for the effect of temperature anneal 200ºC, 300ºC, and 400ºC with anneal time is 30 minutes. Seems that the anneal temperature of 200ºC, 300ºC, and 400ºC, a thin layer that transmits visible light respectively by 0.29% - 86.73%, 0.05% - 86.99%, and 0.13% - 76.23% in the wavelength range 500nm – 800 nm. In the anneal temperature of 300ºC, transmittance increased and decreased in temperature anneal 400ºC. Layers with anneal time variation of 30, 60 and 90 minutes, transmit light at 0.05% - 92.22%, 0.09% - 87.28%, and 0.002% - 69.05% in the wavelength range 500nm - 800 nm. The longer the anneal time, the transmittance decreases. The increase and decrease in transmittance certainly is not caused by the thickness of the layers, because of the interference fringe pattern seen relatively the same layer thickness. The increase and decrease in transmittance be linked to changes in crystallinity, energy gap, Urbach energy and particle size.

Figure 1. The transmittance of a thin layer of Si:H as a function of wavelength and anneal temperature.

Figure 2. Energy gap, crystallinity, Urbach energy, and the particle size.
Figure 2 shows the crystallinity, energy gap, Urbach energy, and the particle size under the influence of temperature anneal. The increase in transmittance at the anneal temperature 300°C due to increased energy gap. Increased energy gap resulting in a reduction of crystallinity, and the particle size of the thin film, compared the effect of a decrease in energy Urbach. The influence of the presence of localized state is less sensitive when compared with the effect of particle size reduction (quantum confinement) [4,5]. When the anneal temperature is raised to 400°C, energy gap decreases and the crystallinity increases, so that the transmittance of the layer was decreased. Usually anneal temperature increases can result in the release of hydrogen bonds that result in increased localized state, because the dangling bond activation and increased the randomness due to changes in the length and angle of the chain bonding, and this is indicated by the increase in energy Urbach. However, due to changes in particle size is getting bigger, the energy gap decreases, although the Urbach energy is increasing.

At the time of annealing process to anneal time of 60 minutes, the resulting increase in energy Urbach and crystallinity in the layer. These two contradictory consequences that impact, due to rising energy Urbach will raise the energy gap, otherwise the increase in crystallinity lowers energy gap. Because two things are contradictory, then a large energy gap layer unchanged. Annealing process is carried out with anneal time of 90 minutes, resulting in increased crystallinity layer, Urbach energy decreases, and the particle size enlarged, so that the energy gap decreases. In general, when the dangling bond in the layer increases, the energy gap will increase. This is due to defect or localized state increased. But the energy gap was also strongly influenced by the particle size (grain).

Dangling bond density of states can be approximated by the density of electron spin state of unpaired. The density of states of the electron spin can be determined using the absorption coefficient values at hv = 1.2 eV [6]. Because UV-Vis characterization is only done for the value of hv between 1.55 eV to 3.1 eV, then the value of the absorption coefficient is determined by a mathematical equation based on Urbach energy trendline. Figure 3 shows the results of calculation of changes in the density of states of the dangling bond, after treatment anneal temperature of 200°C, 300°C and 400°C, using electron spin state density approach. At 300°C temperature, electron density of states or the dangling bond decreased compared with a thin layer on anneal temperature of 200°C, and increased in layers with anneal temperature of 400°C. This is due to the release of hydrogen atoms in SiH. Theoretically changes in the density of states Si-H, inversely proportional to the dangling bond. This is consistent with that seen from Figure 3, where the density of states of the SiH tends to fall when the dangling bond density of states increases.

![Figure 3](image1.png)  ![Figure 4](image2.png)

Figure 3. Normalized dangling bond (electron spin) and SiH (hydrogen) density of states.

However, Si-H and dangling bond has a relationship with the complex interplay. This is because during the anneal process will many possibilities happen. For example, For example, when SiH bond
breaking and H atoms is released, it is possible to form Si-H₂ and left dangling bond. Thus, the density of states of SiH is inversely proportional to the density of states of dangling bond and Si-H₂. However, when one of the H atoms in SiH₂ is released, it will form SiH and dangling bond, which is formed HSi-(db). Because it can be understood that the change in the density of dangling bond (electron spin state density) and SiH in layers with anneal temperature to 300°C decreased, compared to the anneal temperature of 200°C. It was expected because some of the dangling bond is released, most of the SiH and not all of them form a radical SiH. Others form a radical such as SiH₂, SH₃, and (SiH₂)n.

Figure 4 shows the FTIR spectrum in the wave number interval 500-1200 cm⁻¹, for layers with anneal temperature of 200°C, 300°C, and 400°C, and anneal time is 30 minutes. It is seen that the absorption peaks of silicon hydride compounds that are in wave numbers 598 cm⁻¹ (600/SiH wagging), 669 cm⁻¹ (667/SiH), 887 cm⁻¹ (890/SiH₃ bending) [7]. Aside from that shown in Figure 4, the absorption peaks are also on the wave number 1999 cm⁻¹ (2000/SiH stretching), and 2090 cm⁻¹ (2090/SiH₂ Stretching) The peak intensity at around 600 cm⁻¹ decreases with rising temperatures and anneal time. This indicates that the density of SiH bond at the position of the wave number decreases with increasing temperature and anneal time. The opposite occurs in the top position at wave number 669 cm⁻¹ and 887 cm⁻¹, wherein the peak intensity increases on rising anneal temperature. An increase in the density of SiH bond at the peak position. Nevertheless, SiH bond formation is dominated by changes in the position of the peak of 600 cm⁻¹, and is in accordance with the decreasing density of SiH in Figure 3. Shifting the top point of absorption also occurs around the wave number of 2000 cm⁻¹ to changes in anneal temperature, i.e [i] peak at 1997 cm⁻¹, [ii] at 1999 cm⁻¹, and [iii] the position of the wave number 1998 cm⁻¹ for layers with anneal temperature of 400°C. Shifting positions absorption peak can be associated with increasing regularity in the network silicon, and an increase in the fraction of crystalline [8].

4. Conclusions

Based on research that has been done can be concluded that the higher the anneal temperature and the longer the anneal time, there is generally a tendency to decrease transmittance. Decrease in transmittance due to changes in crystallinity, energy gap, Urbach energy and particle size. Theoretically changes in the density of states of the Si-H is inversely proportional to the density of dangling bonds. However, Si-H and dangling bond has a relationship with the complex interplay. Many possibilities occur.

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