[논 문] 한국재료학회지
Kor. J. Mater. Res.
Vol. 19, No. 2 (2009)
DOI: 10.3740/MRSK.2009.19.2.102

RF 스퍼터를 이용하여 제작된 a-Si:H 박막의 어닐링 효과에 관한 연구

김도윤 · 김인수 · 최세영†
연세대학교 신소재공학과

Effect of Annealing on a-Si:H Thin Films Fabricated by RF Magnetron Sputtering

Do Yun Kim, In Soo Kim and Se-Young Choi†
School of New Materials Science and Engineering, Yonsei University, 134 Shinchondong, Seodaemungu, Seoul 120-749, Republic of Korea

(Received December 16, 2008 : Received in reviced form February 8, 2009 : Accepted February 9, 2009)

Abstract The effect of annealing under argon atmosphere on hydrogenated amorphous silicon (a-Si:H) thin films deposited at room temperature and 300 °C using Radio Frequency (RF) magnetron sputtering has been investigated. For the films deposited at room temperature, there was not any increase in hydrogen content and optical band gap of the films, and as a result, quality of the films was not improved under any annealing conditions. For the films deposited at 300 °C, on the other hand, significant increases in hydrogen content and optical band gap were observed, whereas values of microstructure parameter and dark conductivity were decreased upon annealing below 300 °C. In this study, it was proposed that the Si-H_X bonding strength is closely related to deposition temperature. Also, the improvement in optical, electrical and structural properties of the films deposited at 300 °C was originated from thermally activated hydrogen bubbles, which were initially trapped at microvoids in the films.

Key words hydrogenated amorphous silicon, hydrogen bubbles, microvoids, annealing, deposition temperature

1. Introduction

Recently, hydrogenated amorphous silicon (a-Si:H) thin films have attracted noticeable attention because of a large number of applications including photovoltaic solar cells,[1)] photo diodes,[2)] and thin film transistors.[3)] Particularly, a-Si:H makes it possible to fabricate solar cells of only a few hundred nanometers thick due to its high absorption coefficient, therefore reducing production cost compared to single crystalline silicon solar cells. In order to increase energy conversion efficiency of a-Si:H solar cells, it is required to make high quality absorber layers. In general, there are numerous defects in a-Si:H films, such as dangling bonds compared to single crystalline silicon which forms defect levels in the forbidden gap. This results in high dark conductivity by the thermal excitation of carriers at room temperature. For a-Si:H films having many defect levels in the forbidden gap, it is difficult to obtain an absorber layer having high photosensitivity. At the same time, photo-generated electron-hole pairs cannot be separated and collected efficiently due to recombination at these defect sites. At the moment, these problems have been minimized by incorporation of hydrogen into amorphous silicon films as a means of passivating dangling bonds during deposition. Another common approach used to improve material properties is to increase the amount of hydrogen in a-Si:H by hydrogen plasma treatment after deposition.[4)]

In this study, effects of annealing under argon atmosphere on optical, electrical, and structural properties of a-Si:H thin films grown by Radio Frequency (RF) magnetron sputtering were investigated.

2. Experimental procedure

The a-Si:H thin films were prepared by RF (13.56 MHz) magnetron sputtering method using silicon target (99.999% purity), hydrogen gas (99.999% purity) and

†Corresponding author
E-Mail : sychoi@yonsei.ac.kr (S. Y. Choi).

argon gas (99.999% purity). The as-deposited films having thickness of 200 nm were deposited on both glass and silicon substrates, whose temperature was kept constant at room temperature and 300 °C, respectively. During deposition, hydrogen flow ratio ($r_H=P_{H2}/(P_{H2}+P_{Ar})$) and working pressure were also kept constant at 0.1 and 2mTorr respectively. After deposition process, an annealing was carried out under argon atmosphere in the temperature range of 200 - 500 °C for 1 hour and the heating rate was 5 °C/min. Thickness of the samples was measured by a stylus type instrument, alpha step (Alpha step 500, KLA-Tencor). For transmittance and reflectance measurements, UV/Vis spectrometer (V-750, Jasco) was used. Absorption coefficient was calculated from the values of transmittance and reflectance, from which the optical band gap was deduced using the method established by Tauc et al.[5)]

Using FT-IR spectrometer (FT-IR 300E, Jasco), we confirmed the changes in hydrogen content in the films and the bonding configuration of the films annealed at various temperatures. Infrared spectra of a-Si:H consist of three absorption regions – wagging, doublet and stretching mode.[6-8)] The films have major peaks at 615cm^{-1}, 640cm^{-1}, 2000cm^{-1} and 2100cm^{-1} which indicate Si-Si phonon mode, Si-H wagging mode, Si-H stretching mode, and Si-H_2 stretching mode, respectively. Hydrogen atomic concentration, C_H, was calculated from the integrated intensity of the ~640 cm^{-1} wagging band infrared peak.[7-8)] Also, bonding configuration of the samples has been estimated from the relation

$$R = I_{2100} / (I_{2000} + I_{2100}), \quad (1)$$

where R is the microstructure parameter.[9)]

The dark conductivity and photoconductivity was measured on the films deposited on glass substrate using I-V measurement system (HP4145B) with Al coplanar electrodes at room temperature.

3. Result and discussion

Fig. 1 (a) shows the IR absorption spectra of the films deposited at room temperature as a function of annealing temperature. It can be seen that IR absorption intensity begins to decrease as annealing temperature increases. Such a behavior is closely related to broken Si-H_X bonds caused by thermal energy which is greater than the binding energy of Si-H_X bonds. This result is in good agreement with the literature on the relationship between hydrogen concentration and annealing temperature, which presented evolution of hydrogen in the films with increasing temperature, thereby decreasing hydrogen concentration in the films.[10)] Therefore, the decrease in IR absorption intensity can be explained by the fact that a number of Si-H_X bonds in the films were broken because of such a high annealing temperature, thereby decreasing significantly the bonding vibration intensity of these bonds detected by FT-IR spectrometer. On the other hand, as shown in Fig. 1 (b), IR absorption intensity of the films deposited at 300 °C tends to increase until the annealing temperature reaches over 300 °C. The increase in IR absorption intensity indicates that there was an increase in the content of bonded hydrogen in the films.

Fig. 2 (a) and (b) present the variation of Si-H wagging mode by annealing for the films deposited at

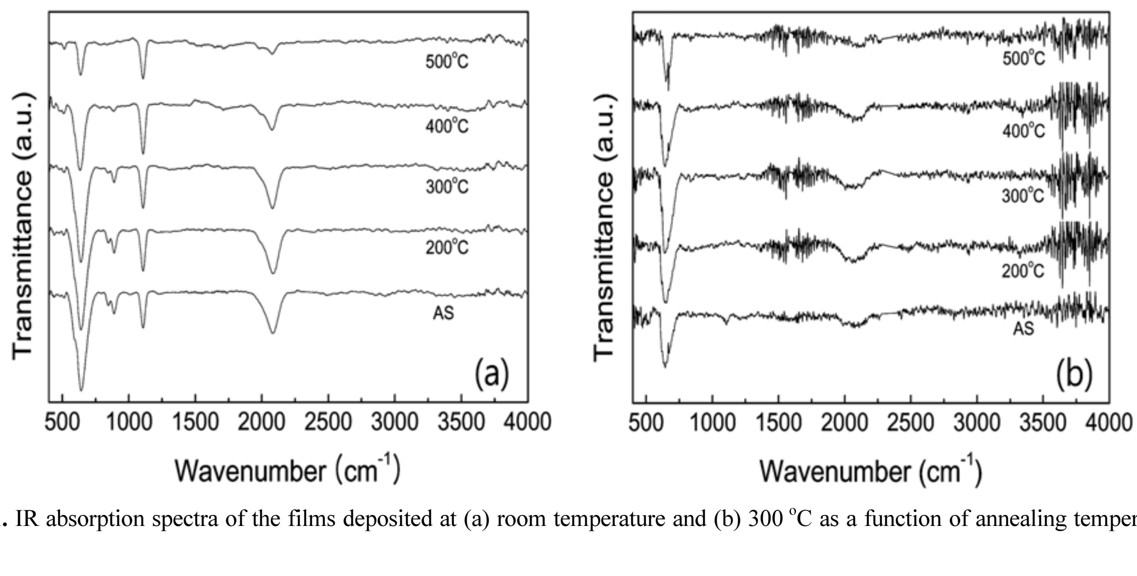

Fig. 1. IR absorption spectra of the films deposited at (a) room temperature and (b) 300 °C as a function of annealing temperatures.

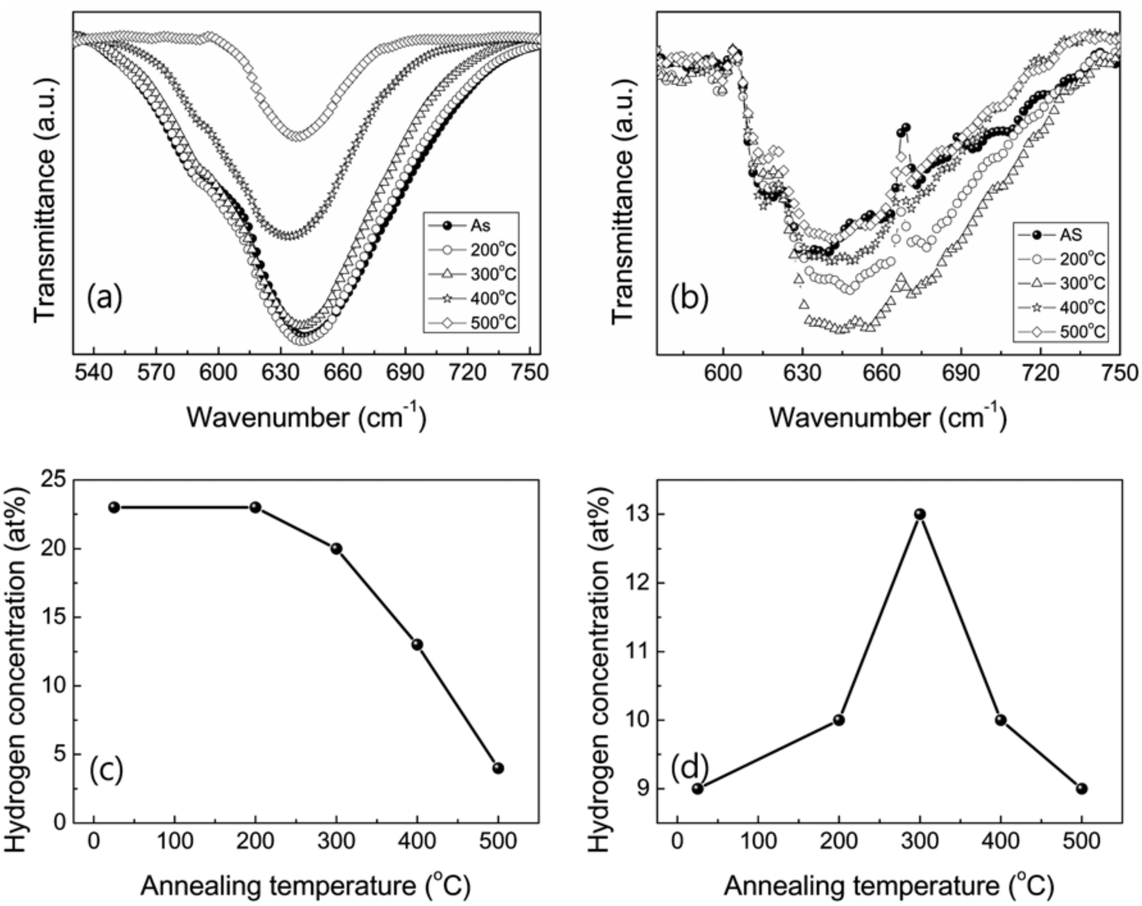

Fig. 2. Variations in IR absorption spectra of rocking-wagging mode in the films fabricated at (a) room temperature and (b) 300 °C upon annealing treatment. Hydrogen content of the films deposited at (c) room temperature and (d) 300 °C, obtained by numerical integration of the Si-H rocking-wagging mode at 640 cm^{-1}.

room temperature and 300 °C, respectively. For the films deposited at room temperature, it is observed that the quantity of Si-H_X bonds decrease as annealing temperature exceeds 300 °C. However, there is no significant decrease in IR absorption intensity when annealing temperature is below 300 °C. This result can be regarded as the two reasons. First, there are not any changes in bonding structures at relatively low annealing temperature of under 300 °C. Second, the broken Si-H_X bonds by thermal energy counterbalance the newly generated Si-H_X bonds by thermally activated hydrogen bubbles which were initially trapped at microvoids in the films. In Fig. 2 (b), there is significant enhancement of Si-H wagging mode by annealing at temperature below 300 °C although annealing was performed under argon atmosphere, which means that there was no source of hydrogen to be incorporated into the films. Using BCC method, variations in bonded hydrogen contents were calculated and presented in Fig. 2 (c) and (d) for the films deposited at room temperature and 300 °C, respectively. It might be hard to understand that there is an increase in the content of bonded hydrogen in the films deposited at 300 °C. Regarding the fact that we have calculated the content of bonded hydrogen in the films using Si-H_X vibration mode excluding H_2 vibration mode, one can conclude that the source of incorporated hydrogen in the films existed in the film itself. It is well known that a-Si:H films have a number of microvoids, where hydrogen could be trapped without forming bonds, which is called hydrogen bubbles.[11] The hydrogen atoms, which are not bonded with silicon atoms, are not detected by FT-IR spectrometer at 640 cm^{-1} from which the content of bonded hydrogen is calculated. However, they are only detected when bonded with silicon atoms. Therefore, it can be estimated that hydrogen bubbles trapped at microvoids were activated by annealing and these hydrogen bubbles began to move through the crevices caused by activation of atomic oscillation due to thermal

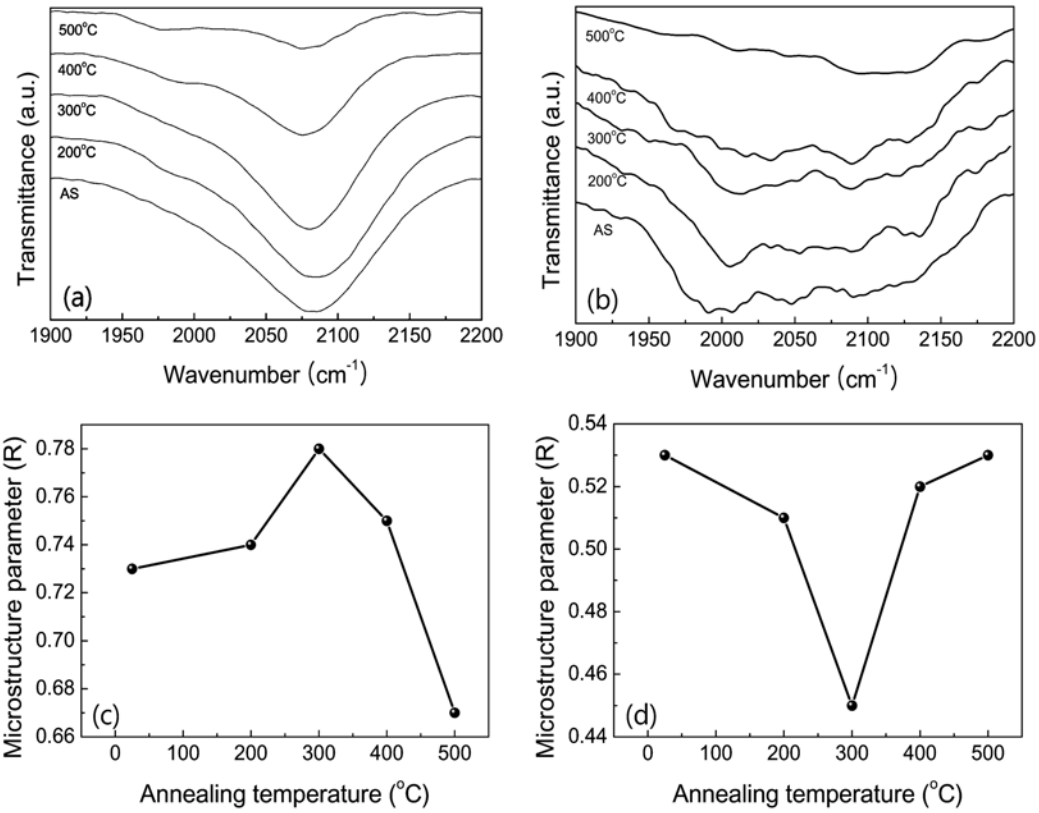

Fig. 3. Variations in IR absorption spectra of stretching mode in the films fabricated at (a) room temperature and (b) 300 °C upon annealing treatment. Changes in microstructure parameter of the films deposited at (c) room temperature and (d) 300 °C depending on annealing temperature.

energy. Then, these begin to passivate the broken bonds as hydrogen atoms meet with dangling bonds, thereby increasing the content of bonded hydrogen detected by FT-IR spectrometer. From this point of view, it is appropriate to conclude that increase in the content of bonded hydrogen originates from thermally activated hydrogen bubbles trapped at microvoids. It is also observed that the content of bonded hydrogen in the films decreases as annealing temperature increases over 300 °C for all the prepared films deposited at room temperature and 300 °C because Si-H_X bonds were broken rather than form stable bonds at such a high annealing temperature.

In Fig. 3 (a) and (c), it can be seen that there is a little change in the values of microstructure parameter for the samples deposited at room temperature so it is appropriate to conclude that there were changes in bonding structures. Considering Fig. 2 (a) and (c), this result supports the fact that the constant hydrogen concentration in the films was based on equilibrium between the broken Si-H_X bonds and the newly generated Si-H_X bonds. Fig. 3 (b) and (d) presents the changes in microstructure parameter and IR absorption intensity for the samples deposited at 300 °C. The IR absorption intensity at 2000 cm^{-1} was enhanced in contrast to 2100 cm^{-1} until the annealing temperature reaches over 300 °C. This result shows that newly generated bonding configuration in the films as a consequence of annealing was mainly Si-H rather than Si-H_2.

In Fig. 4 (a), optical band gap of the films prepared at room temperature decreases linearly with increasing annealing temperature. It is well known that reduction of hydrogen concentration in a-Si:H thin films leads a decrease in optical band gap. Changes in optical band gap of the films prepared at 300 °C as a function of annealing temperatures are shown in Fig. 4 (b). It is clearly seen that optical band gap of the films deposited at 300 °C tends to decrease when annealed at temperatures above 300 °C like those of the films deposited at room temperature. On the contrary, optical band gap of the films annealed at below 300 °C increases as temperature increases. The linear region in this figure, which is

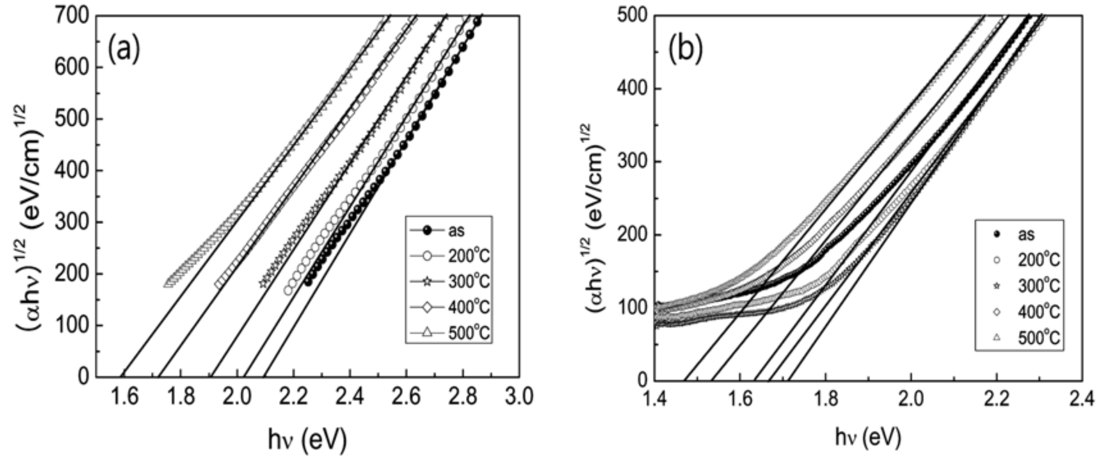

Fig. 4. Variation of $(ahv)^{1/2}$ vs. photon energy for the films deposited at (a) room temperature and (b) 300 °C with different annealing temperatures.

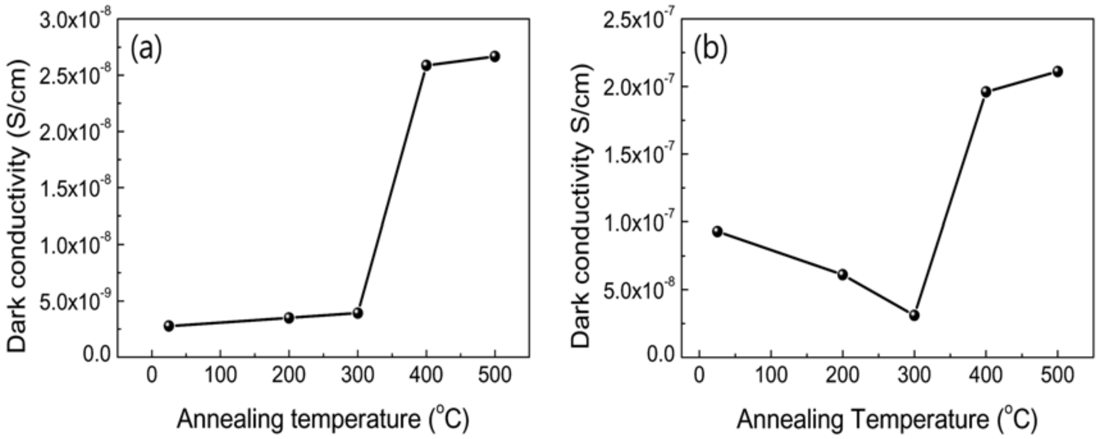

Fig. 5. Changes in dark conductivity for the films deposited at (a) room temperature and (b) 300 °C with different annealing temperatures.

generally called the Tauc region, is attributed to the optical electron transition between the extended valence band and the conduction band. Increase in the optical band gap can be interpreted as the following. First, the optical band gap increases with increasing contents of bonded hydrogen in the films.[12-13] This behavior can be explained by the partial replacement of Si-Si bonds with Si-H bonds of greater binding energy. The presence of hydrogen causes the valence-band edge to move towards the lower energy side by removing the Si-Si bonding orbitals in the neighborhood of the valence band edge. Consequently, the optical band gap is expanded as the content of bonded hydrogen increases.[14] Second, removal of mechanical compressive strain induces the increase in the energy band gap and band tails of the materials.[15-16] In conjunction with FT-IR results, it is appropriate to conclude that the increase in the optical band gap of the films, which is deposited and annealed at 300 °C, is attributed by the increase in content of bonded hydrogen in the films.

When a number of defects exist in a-Si:H films, such as dangling bonds, which form defect levels in the forbidden gap high dark conductivity is induced by the thermal excitation of carriers at room temperature. In this context, dark conductivity measurement is widely employed to estimate defect density of a-Si:H thin films. In Fig. 5 (a), dark conductivity of the films deposited at room temperature is shown with different annealing temperature. An increase in dark conductivity as annealing temperature increases can be clearly explained by the evolution of hydrogen in the films, which remains dangling bonds. Dark conductivity of the films deposited at 300 °C is presented as a function of annealing temperature in Fig. 5 (b). Samples show the lowest dark conductivity of 3.1×10^{-8} S/cm upon annealing at 300 °C. Above this temperature, dark conductivity of the films began to increase due to hydrogen evolution, which means that more dangling bonds were created in the films. As already shown above, optical band gap and contents of bonded hydrogen were increased by thermally activated hydrogen bubbles, whereas values of microstructure parameter were decreased in the films upon annealing below 300 °C, from which it can be inferred that dangling bonds of the films were efficiently passivated. Thus, dark conductivity of the films annealed below 300 °C was minimized due to improvement in the quality of the films. In conjunction with all of the experimental results in this study, increase in dark conductivity of the films annealed above 300 °C is due to the thermally induced broken bonds.

4. Conclusion

The effect of annealing on optical, electrical and structural properties of the a-Si:H films deposited at room temperature and 300 °C using RF magnetron sputtering were investigated. It was estimated that silicon and hydrogen atoms of the films prepared at room temperature were weakly bonded compared to those of the films prepared at 300 °C, which indicates that bonding strength of Si-H_X in the films was quite affected by deposition temperature. So, there was not any increase in the content of bonded hydrogen in the films deposited at room temperature during annealing process.

For the films deposited at 300 °C, hydrogen bubbles trapped in microviods were activated by thermal energy with annealing at below 300 °C. As a result, they began to passivate the dangling bonds in the films. Therefore, the optical band gap and content of bonded hydrogen in the films were increased and, thus, the quality of the films was improved. In this study, we propose that the increase in the content of bonded hydrogen induced the increase in the optical band gap. Also, values of microstructure parameter were decreased because the newly induced bonding configuration of the films was mainly Si-H. The decrease in dark conductivity also supports the explanations in this study.

For all the prepared films, hydrogen atoms bonded to silicon atoms begin to break and hydrogen in the films are evolved upon annealing at temperatures of above 300 °C,, remaining as dangling bonds rather than forming stable bonds. As a result, optical, electrical and structural properties of the films were deteriorated continuously as annealing temperature increased above 300 °C.

Acknowledgment

This work was supported by the Second Stage of Brain Korea 21 Project in 2008.

Reference

1. K. Yamamoto, M. Yoshimi, Y. Tawada, Y. Okamoto and A. Nakajima, J. Non-Cryst. Solids, **266**(2), 1082 (2000).
2. H. Stiebig, E. Moulin and B. Rech, Thin solid films, **515**(19), 7522 (2007).
3. C. H. Lee, A. Sazonov and A. Nathan, Appl. Phys. Lett., **86**, 222106-1 (2005).
4. P. Danesh, B. Pantchev, B. Schmidt and D. Grambole, Semicond. Sci. Tech., **19**(12), 1422 (2004).
5. J. Tauc, R. Grigorovici and A. Vancu, Phys. Stat. Sol., **15**, 627 (1966).
6. G. Lucovsky, R. J. Nemanich and J. C. Knights, Phys. Rev. B, **19**(4), 2064 (1979).
7. M. H. Brodsky, M. Cardona and J. J. Cuomo, Phys. Rev. B, **16**(8), 3556 (1977).
8. A. A. Langford, M. L. Fleet, B. P. Nelson, W. A. Lanford and N. Maley, Phys. Rev. B, **45**(23), 13367 (1992).
9. H. Rinnert, M. Vergnat, G. Marchal and A. Bruneau, J. Appl. Phys., **83**(2), 1103 (1998).
10. A. Deneuville, A. Mini and J. C. Bruyere, Solid State Phys., **14**(30), 4531 (1981).
11. Y. J. Chabal and C. K. N. Patel, Phys. Rev. Lett., **53**(18), 1771 (1984).
12. W. Futako, T. Kamiya, C. M. Formann and I. Shimizu, J. Non-Cryst. Solids, **266**(1), 630 (2000).
13. C. M. Fortmann, Phys. Rev. Lett., **81**(17), 3683 (1998).
14. K. Tanaka, E. Maruyama, T. Shimada, H. Okamoto and T. Sato, Amorphous Silicon, p.106, John Wiley & Sons, England, (1999).
15. G. D. Cody, C. R. Wronski, B. Abeles, R. B. Stephens and B. Brooks, Sol. Cells, **2**(3), 227 (1980).
16. S. H. Won, J. K. Chung, C. B. Lee, H. C. Nam, J. H. Hur and J. Jang,, J. Electrochem. Soc., **151**(3), G167 (2004).