1P1-11
Proceedings of Symposium on Ultrasonic Electronics, Vol. 34 (2013) pp. 35-36
20-22 November, 2013

Characterization of poly-Si nanowire by photoacoustic spectroscopy
多結晶シリコンナノワイヤーの光音響分光による評価

Hisashi Miyazaki[1†], Jun Morimoto[1], Shinya Kato[2], Tatsuya Yamazaki[3], Ryousuke Ishikawa[2], Shinsuke Miyajima[3], and Makoto Konagai[2,3,4] ([1]Dept. Mat. Sci. Eng., Natl. Def. Acad.; [2]JST., [3]Dept. Phys. Electro., Tokyo Tech.; [4]PVREC, Tokyo Tech.)
宮﨑尚 [1†]，守本純 [1]，加藤慎也 [2]，山崎竜也 [3]，石川亮佑 [2]，宮島晋介 [3]，小長井誠 [2, 3, 4] ([1] 防衛大機能材料, [2] 科学技術振興機構, [3] 東工大院理工, [4] 東工大太陽光発電システム研究センター)

1. Introduction

Silicon nanowire (SiNW) have intensively studied as a material for optoelecronic devices, such as solar cells, FETs, and thermoelectric conversion elements. Especially for thin-film solar cell applications, the strong optical absorption of SiNW arrays is very effective to improve performance of the solar cells. In addition, there is a potenatil to control the bandgap by changing the diameter of the SiNW. Bandgap engineering of silicon is the key factor to realize all silicon tandem solar cells.[1)] The fabrication method of the SiNW for solar cell application has already been established.[2)] This technique is called MAE (Metal Assisted Etching) process.[3)] The MAE process is an etching technique in which electroless silver-plating and silver-catalytic etching are combined. This method was developed for SiNW arrays on a silicon substrate. However, SiNW arrays on heterogenous substrate are important to develop thin-film SiNW solar cells.

Ishikawa et al. has reported the application of the MAE technique to amorphous Si (a-Si) film.[4)] Amophous siliocn nanowire (a-SiNW) arrays were successfully prepared on glass substrate by using the MAE technique. They also reported that the crystallization of the a-SiNW arrays by thermal annealing. After the thermal crystalliation, a-SiNW arrays changed to polycrystalline slicon nanowire (poly-SiNW) arrays. They also investigated the optical absorption properties of the SiNW arrays by using transmitance and reflectance masured using an UV-VIS specrometer. Although the above-mentioned optical characterizations clarified important features of the SiNW arrays, strong optical scatterting caused by the nanowire structure significantly influenced the measurements. It is important to use a characterization technique which can avoid the influence of the optical scattering for more precise and detailed characterizations. Photoacoustic spectroscopy (PAS) is one of the suitable techniques to avoid the influence of the optical scattering.

In this study, we report the PA spectra of three kinds of samples; a-Si thin film, a-SiNW array film, and poly-SiNW array film. Based on the PA spectra, optical characteristic of these films are discussed.

2. Experimental Details

The a-Si films were deposited on a glass substrate by plasma enhanced chemical vapor deposition (PECVD) using silane (SiH_4) and hydrogen (H_2) gas. The thickness of the films was approximately 1 μm. The hydrogen concentration of the films estimated by Fourier transform infrared absorption (FT-IR) was about 15%. The MAE process was employed to form a-SiNWs.[4)] The diameter of the nanowire is about 50 nm. Solid-phase crystallization of a-SiNW arrays was carried out by thermal annealing under forming gas for 30 minutes at 800°C. We observed that the a-SiNW arrays were converted into the poly-SiNW arrays after annealing process using Raman spectroscopy and transmittance electron microscopy.[4)]

Figure 1 shows the schematic diagram of PA spectroscopy system. The photoacoustic (PA) spectra were measured by using a MEMS cantilever and laser interferometer. A monochromatized light was irradiated onto the samples. The light source was a halogen lamp. The wavelength of the

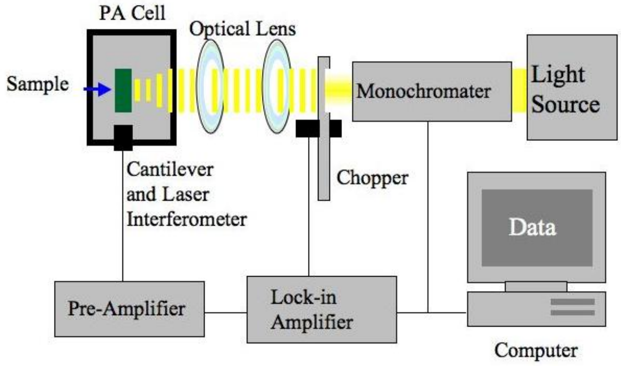

Fig. 1 Schematic diagram of photoacoustic spectroscopy system.

excitation light beam was scanned from 400 nm to 1600 nm with a 5 nm step. The modulation frequency was about 10 Hz. The PA signal intensity was normalized by the PA signal intensity from carbon black. All samples were measured at room temperature.

3. Results and Discussion

The typical PA signals of the samples are shown in Fig. 2. Three peaks at 0.9, 1.1 and 1.3 eV originate in our PAS system. The bandgap of a-Si film and a-SiNW array film are about 1.7 eV, and poly-SiNW array film is 1.1 eV. This demonstration of the bandgap determination of a-SiNW and poly-SiNW array film is the most important result of this study because it is very difficult to determine the bandgap of silicon-based nanowire materials by using simple transmittance and reflectance measurements. This result also suggests that the PAS technique is a useful tool to investigate bandgap engineering of poly-SiNW with very small diameters.

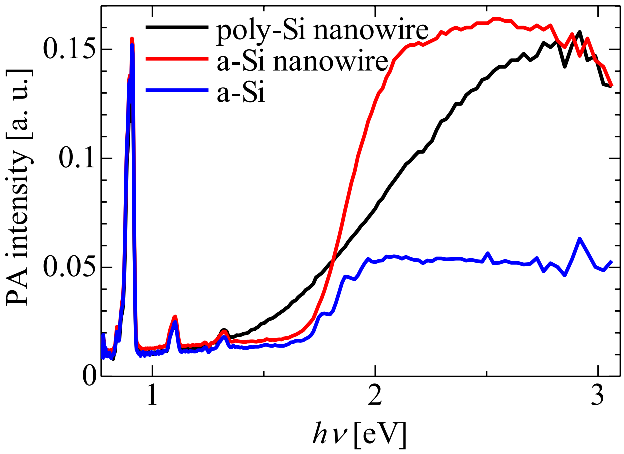

Fig. 2 Photoacoustic spectra of a-Si, a-SiNW array and poly-SiNW array films.

The PA signals can be assumed to be proportional to the optical absorption coefficients of a material. For a-Si films, absorption coefficients near and less than the bandgap are mainly determined by bandtail absorption. The bandtail absorption is strongly influenced by bulk defect states and surface states and can be expressed by using the Urbach's law.[6] The bandtail absorption of can be given by:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu - E_0}{E_u}\right)$$

α_0 and E_0 are fitting parameters. E_u is Urbach energy which reflects the slope of the absorption spectrum. The value of E_u for a-SiNW array film is found to be 0.134 eV. This value is very similar to that of the a-Si film.

We also found that the PA spectrum of the a-SiNW array film slightly shifted to lower energies compared with that of a-Si film. The reason of the shift is not clear at present. A possible explanation of the spectrum shift is the influence of the surface states. It is well known that subgap absorption of a-Si film is significantly enhanced by surface states.[5] The surface area of the a-SiNW array film is more than 100 times larger than that of a-Si film. Higher subgap absorption of a-SiNW would lead to the shift of the PA spectrum.

4. Conclusion

We measured the absorption spectra of the a-Si, a-SiNW array and poly-SiNW array films by using the photoacoustic spectroscopy technique. The experimental results clearly indicate that the PAS technique is suitable to investigate optical properties of a-SiNW and poly-SiNW array films. The PAS technique is also important to investigate the surface states of the films.

Acknowledgment

The authors would like to thank Dr. Aono for her useful suggestion. This work was supported in part of Ministry of Education, Culture, Sports, Science and Technology (MEXT), FUTURE-PV Innovation.

References

1. E. Cho, M. A. Green, G. Conibeer, D. Song, Y-H. Cho, G. Scardera, S. Huang, S. Park, X. J. Hao, Y. Huang, and L. V. Dao, Advances in OptoElectronics 2007 (2007) 69578.
2. V. Sivakov, G. Andrä, A. Gawlik, A. Berger, J. Plentz, F. Falk, and S. H. Christiansen, Nano Letters **9** (2009) 1549.
3. Z. P. Huang, N. Geyer, P. Werner, J. de Boor, and U. Gosele: Adv. Mater. **23** (2011) 285.
4. R. Ishikawa, T. Yamazaki, S. Miyajima, and M. Konagai: Abst. EM-NANO 2013. SS1-3.
5. Z.E. Smith, V. Chu, K. Shepared, S. Aljishi, D. Slobodin, J. Kolodzey, S. Wagner, and T.L Chu: Appl. Phys. Lett. **50** (1987) 1521.
6. F. Urbach, Phys. Rev. **92** (1953) 1324.