

Size effect of silicon nanocrystals on Seebeck coefficient of phosphorus-doped Si nanocrystals/silicon oxide multilayers

Hisayoshi Kobayashi¹, Shinya Kato², Masashi Kurosawa¹, Kazuhiro Gotoh¹,
Noritaka Usami¹ and Yasuyoshi Kurokawa¹

¹ Nagoya Univ.

Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Phone: +81-52-789-3246 E-mail: kobayashi.hisayoshi@c.mbox.nagoya-u.ac.jp

² Nagoya Inst. Tech.

Gokiso-cho, Showa-ku, Nagoya, 466-8555, Japan

Phone: +81-52-735-7966

Abstract

Phosphorous-doped silicon nanocrystals (Si-NCs)/silicon oxide (SiO_y) multilayers were prepared by plasma enhanced chemical vapor deposition (PECVD) and post-annealing. The diameter of Si-NCs were changed by varying the thickness of Si-rich amorphous silicon oxide (a-SiO_x) layer from 3 to 50 nm. The absolute value of Seebeck coefficient (S) of Si-NCs/SiO_y multilayers were increased to 600.99 μ V/K drastically with decreasing the diameter (d) of Si-NCs to $d=3$ nm. The power factor (PF) was estimated using the S and the electrical conductivity measured in previous studies. Maximum PF was 1.53 μ W/cm \cdot K at $d=5$ nm. The drastic increase of S is likely to be a result of activation rate of dopants and the localization of electrons due to quantum confinement.

1. Introduction

Wireless sensor network technology based Internet of things (IoT) is getting important to realize the enhancement of the security and convenience in our society. Conventional batteries in IoT produce environmental concerns and have limited operational life. Harvesting ambient environmental energy is important for sustainable green power used in wireless and portable devices in IoT. Solar cells, electret, rectenna, thermoelectric devices, and so on are studied as candidates of energy harvesting devices. Silicon is one of abundant materials on the earth and nontoxic. Therefore, there are huge infrastructure and know-how available for its production and processing. It is also possible to combine silicon-based thermoelectric devices with other IoT devices. However, bulk Si is a poor thermoelectric material since it has high thermal conductivity (κ). Many researchers have tried nanostructuring of thermoelectric materials to obtain high S and low thermal conductivity [1-4].

In previous research, silicon nanocrystals (Si-NCs)/SiO_y multilayer were prepared by PECVD and post-annealing [4]. The diameter of Si-NCs can be controlled by varying the thickness of Si-rich layer. Therefore, the diameter of Si-NCs can be adjusted below phonon mean free path, leading to the reduction of thermal conductivity. Moreover, as the density of Si-NCs becomes higher in the Si-NCs layers, power factor

of the Si-NCs layer will approach to that of polycrystalline silicon. Therefore, it is expected that Si-NCs/SiO_y multilayers realize high dimensionless figure of merit ($ZT=S^2\sigma/\kappa$). In our previous research, it was revealed that electrical and thermal conductivity of Si-NCs/SiO_y multilayers were decreased with decreasing the diameter (d) of Si-NCs, and thermal conductivity at $d=3$ nm was estimated at 1.48 W \cdot m⁻¹ \cdot K⁻¹, which is much lower than bulk Si [5]. In this study, we prepared phosphorous doped amorphous silicon oxide (a-SiO_x) single layers and stacks of Si-NCs embedded in a-SiO_y as n-type thermoelectrical materials, and evaluated the effect of the size of Si-NCs on their S and calculated their power factor.

2. Experimental method

Phosphorous-doped a-SiO_x was prepared by PECVD. Setting substrate temperature, pressure, and RF power density were kept at 285 $^{\circ}$ C, 25 Pa, and 0.0325 W/cm², respectively. Both of CO₂ and SiH₄ flow rates were fixed at 10 sccm, and PH₃ flow rate was varied from 1 to 50 sccm. After the deposition, the samples were annealed at 900, 950, and 1000 $^{\circ}$ C for 30 minutes under forming gas atmosphere (N₂: 97%, H₂: 3%). Silicon oxide multilayers (a-SiO_x:H/a-SiO_y:H) were also prepared by PECVD. The oxygen composition of each layer was purposely designed as x is less than y so that the a-SiO_x and a-SiO_y layer were converted into Si-NCs layer and phonon scattering layer after annealing, respectively. Thickness of a-SiO_x was varied from 3 to 50 nm and that of a-SiO_y was fixed at 2 nm. The flow rates of SiH₄, CO₂ and PH₃ were 10, 10 and 10 sccm for the a-SiO_x layer, and 4, 50 and 0 sccm for the a-SiO_y layer. After the deposition, the samples were annealed at 900, 950, and 1000 $^{\circ}$ C for 30 minutes under forming gas atmosphere. Raman scattering spectra were measured and crystal volume fraction of Si-NCs was calculated. Electrical conductivity (σ) was measured by I - V measurement. S was measured by an original equipment [6].

3. Results and discussion

Figure 1 shows the result of crystal volume fraction calculated from Raman scattering spectra. For samples with large crystal size ($d \geq 20$ nm), these crystal volume fractions were saturated at about 0.6. However, for samples with small crystal size ($d \leq 10$ nm), as the thickness of the a-SiO_x layer becomes thinner, the distance between crystal nuclei and interfaces also becomes closer, and the increase of the free energy of interface between a-SiO_x and a-SiO_y interferes the growth of crystal nuclei. Therefore, the crystallization rate decreases with the thinning of a-SiO_x layer. That is why in the range of $d \leq 10$ nm, the crystal volume fraction was decreased with decreasing the size of Si-NCs and we could expect that Si-NCs were scattered throughout the Si-NCs layer.

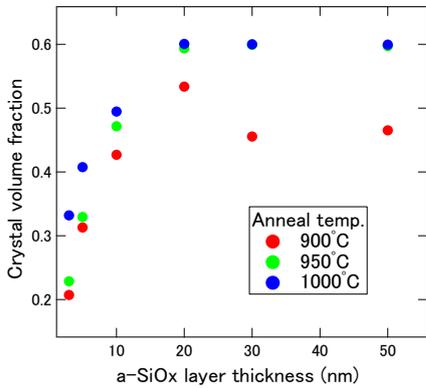


Fig. 1 Crystal volume fraction of the a-SiO_x:H/a-SiO_y:H multilayers after annealing at each temperature.

Figure 2(a) shows the results of S measurements. In the range above 20 nm, S is almost constant and the absolute value at annealing temperature of 900 °C is higher than 1000 °C. This can be explained by crystal volume fraction. In the range below 10 nm, absolute value of S was increased as Si-NCs was decreased. Especially, in the case of the sample of Si-NCs with the diameter of 3 nm after annealing at 900 °C, the S reached 600.99 μ V/K, which was comparable to that of bulk Si (≈ 600 μ V/K at impurity concentration of 10^{19} cm⁻³ [7]). The tendency between S and crystal volume fraction is very similar each other. This is likely to be a result of activation rate of dopants and the localization of electrons due to quantum confinement.

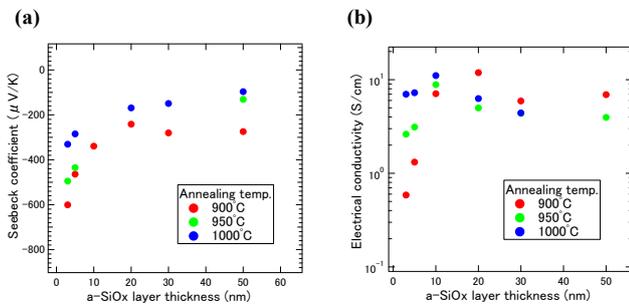


Fig. 2 (a) Seebeck coefficient and (b) electrical conductivity of the Si-NCs/SiO_y multilayers as a function of the a-SiO_x thickness.

In addition, from the σ obtained from previous studies

(Figure 2(b)) and the S measured in this study, the power factor (PF) was estimated as shown in Figure 3. S contributes to PF by the square. Therefore, the higher the S , the more the PF also tended to increase. However, as the nanocrystal size was reduced to 3 nm, the contribution to the decrease in σ overcomes and the PF decreases. Therefore, the results from this experiment showed that the maximum value of PF exists around $d=5$ nm.

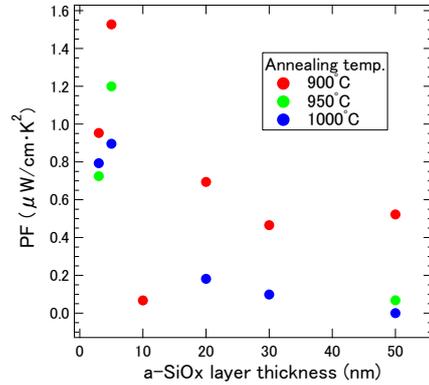


Fig. 3 Power factor of the Si-NCs/SiO_y multilayers as a function of the a-SiO_x layer thickness.

4. Conclusion

Phosphorus-doped Si-NCs/SiO_y multilayers were prepared by PECVD and post-annealing for use in thermoelectric devices. The absolute value of S was significantly increased as the size of Si-NCs was decreased. Especially, the maximum S of 600.99 μ V/K was obtained at $d=3$ nm. The power factor was estimated from the S and σ and 1.53 μ W/cm²·K was obtained at $d=5$ nm. The drastic increase of S with decreasing the size of Si-NCs contributes to the increase in PF significantly. The drastic increase of S is likely to be a result of activation rate of dopants and the localization of electrons due to quantum confinement.

References

- [1] Y. Nakamura, M. Isogawa, T. Ueda, S. Yamasaka, H. Matsui, J. Kikkawa, S. Ikeuchi, T. Oyake, T. Hori, J. Shiomi, A. Sakai, Nano Energy **12** (2015) 845.
- [2] M. Nomura, J. Nakagawa, Y. Kage, J. Maire, D. Moser, O. Paul, Appl. Phys. Lett. **106** (2015) 143102.
- [3] Z. Wang, J. E. Alaniz, W. Jang, J. E. Garay, C. Dames, Nano Lett. **11** (2011) 2206.
- [4] Y. Okamoto, H. Uvchino, T. Kawahara, J. Morimoto, Jpn. J. Appl. Phys. **38**, L945 (1999).
- [5] H. Kobayashi, R. Akaishi, S. Kato, M. Kurosawa, N. Usami, Y. Kurokawa, Jpn. J. Appl. Phys. **59** SGGF09 (2020)
- [6] M. Kurosawa, K. Liu, M. Izawa, I. Tsunoda, S. Zaima, ECS Trans. **75** 481 (2016)
- [7] F. Salleh, K. Asai, A. Ishida, H. Ikeda, Appl. Phys. Express **2** 071203 (2009).