

High-yield production and manipulation of Si/Ge nanoparticles for energy applications

Seongbeom Kim^{1*}, Dong Suk Kim², Jeong Chul Lee², Jin Young Kim^{1*}

¹Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

²Korea Institute of Energy Research (KIER), Republic of Korea

exebac@gmail.com, jykim@unist.ac.kr

Keywords: CO₂ laser pyrolysis, silicon, germanium, nanoparticles, nanocrystals

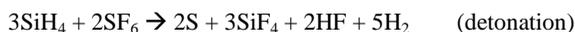
Abstract

Photosensitizer-assisted CO₂ laser pyrolysis for Si/Ge nanoparticles (Si/Ge-NPs) is presented in conjunction with practical manipulation of nanoparticle products. In particular, complete conversion from SiH₄ to Si-NPs was achieved using SF₆ photosensitizer during the laser pyrolysis implying the possibilities scale-up production of Si-NPs to meet the industrial demands. In addition, the size of as-produced Ge-NPs was tailored in a manner of precise and practical way using aqueous dispersions.

1. Photosensitizer-assisted CO₂ laser pyrolysis for Si-NPs production

An experimental set-up for laser pyrolysis is illustrated in Figure 1 (a).[1] Coupling of laser beam (10.6 μm, continuous wave CO₂ laser, max. power 60 W) with SiH₄ molecules induces dissociation of Si-H bonds and nucleation of silicon clusters. Further growth of silicon clusters leads to 10 – 50 nm size of crystalline Si-NPs and the Si-NPs are quenched as soon as they escape from the reaction zone.

Incorporation of SF₆ photosensitizer increases gas-so-solid conversion ratio during the process dramatically as shown in Figure 1 (b), however, the reaction is prone to proceed detonation[2] process which might provoke fatal failure in producing Si-NPs. The competing reactions could be simply summarized as follows;



Dilution of reactive gas mixtures with H₂ gas could suppress detonation successively and complete conversion from SiH₄ gases to Si-NPs was achieved. Emission of reaction flame was analyzed using spectroscopy showing detonation evidences.

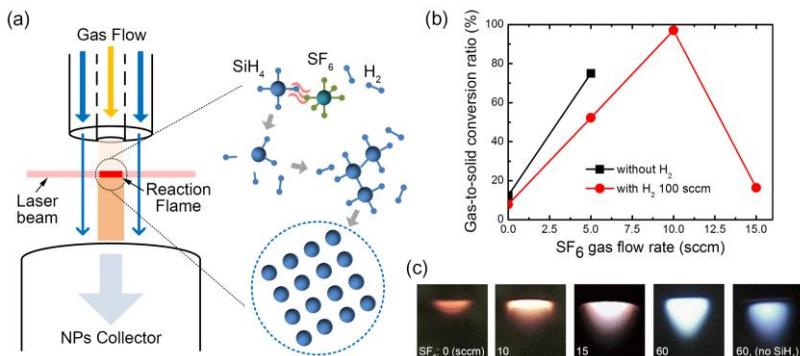


Figure 1: (a) A schematic of photosensitizer-assisted CO₂ laser pyrolysis of SiH₄. (b) Gas-to-solid conversion ratio. (c) Digital images of reaction flame during the laser pyrolysis.

As-produced Si-NPs are characterized by transmission electron microscopy (TEM) along with energy-dispersive X-ray spectroscopy (EDX), Brunauer-Emmett-Teller specific surface area measurement, X-ray diffractogram and X-ray photoelectron spectroscopy disclosing Si-NPs products are well crystalline, free-standing and spherical shape.

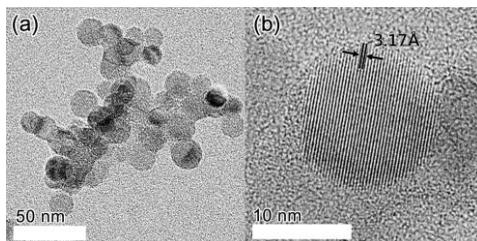


Figure 2: TEM images of as-produced Si-NPs

Significance of this results is that design of laser pyrolysis system for Si-NPs can have more degree of freedom in an industrial perspective. Required power of laser source for Si-NPs production can be reduced by directing laser beam energy to conversion from gas to Si-NPs efficiently, therefore, costs of production, loss in feedstock and he risks in optical elements can be reduced.

2. Facile and precise size control of Ge-NPs

Introduction of GeH₄ gas instead of SiH₄ into laser pyrolysis facilitates production of pristine Ge-NPs. Compared to silicon, germanium exhibits higher charge carrier

mobilities[3] and greater absorption coefficient[4], interestingly oxide can be dissolved in water. By the preliminary studies on Ge-NPs dispersion in various solvents showed that the water dispersion is the most stable for Ge-NPs. The observed preferential solubility of Ge-NPs in water likely arises from the presence of a thin negatively charged oxide layer on the particle surfaces.[5] We sought to take advantage of this oxidative etching process as a method to control the size of the NP dispersions. The size of the Ge-NP dispersed in water can be precisely controlled via the volumetric addition of H_2O_2 as shown in Figure 3.

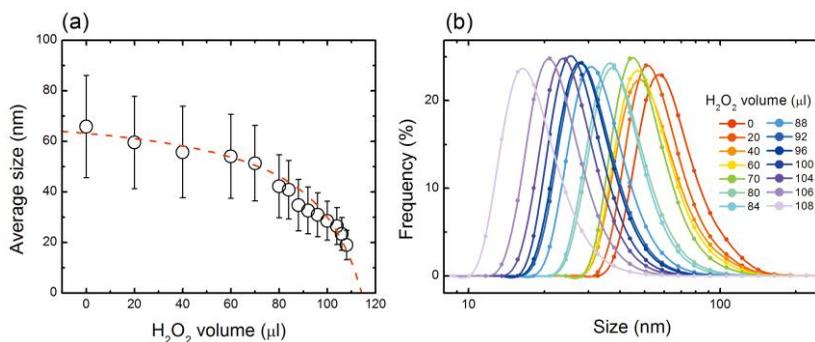


Figure 3: Effect of H_2O_2 etching on (a) particle size (dotted red curve : estimated Ge NPs size as a function of specific surface area) and (b) size distribution.

The average diameter (measured by dynamic light scattering method, DLS) of the Ge-NPs decreases as the volume of H_2O_2 is increased as shown in Figure 3 (a). The rate of oxidation is proportional to specific surface area, therefore, the smaller sizes of Ge-NPs are oxidized faster. The tendency of experimental results roughly matches the estimation which is plotted in red-dotted line in Figure 3 (a) as a function of specific surface area. Small diameter Ge-NPs which are quite far from the average diameter oxidize quickly and dissolved into water, leaving Ge-NPs with lower polydispersity as shown in Figure 3 (b). To confirm the diameter of Ge-NPs measured by DLS, the particle sizes were counted from TEM images by measuring the diameter of more than 80 NPs. The average particle diameter from the sample treated with 88 μl of H_2O_2 was found to be 34.4 ± 9.1 nm, consistent with the diameter obtained by DLS (34.8 ± 10.1 nm). The absorption spectra of size-controlled Ge-NPs and the surface investigation using XPS are disclosed in this study.

3. Conclusion

Silicon and germanium are representatives of semiconductive materials which has been used several decades and 3-dimensionally confined Si and Ge NPs have been broadening their potential due to inherited properties from bulk materials and emerging properties as quantum dots. In industrial perspective, a laser pyrolysis technique can be one option for producing Si/Ge-NPs. We have demonstrated complete conversion of gas-to-solid using photosensitizer-assisted laser pyrolysis of SiH₄ proposing cost-effective strategy. In addition, practical manipulation in terms of precise size control of Ge-NPs have been studied. It is believed that the suggested production engineering and manipulation of Si/Ge NPs can contribute to wide applications covering optoelectronic, energy and biomedical devices.

References:

- [1] S. Kim, J. H. Lee, M. T. Swihart, J.-C. Lee, J. Y. Kim, *Curr. Appl. Phys.*, **14**, 127, 2014.
- [2] S. Bauer, J. Haberman, *IEEE Journal of Quantum Electronics*, **14**, 233, 1978.
- [3] S. M. Sze, K. K. Ng, *Physics of semiconductor devices*, Wiley, 2006.
- [4] W. C. Dash, R. Newman, *Phys. Rev.*, **99**, 1151, 1955.
- [5] F. H. Frimmel, R. Niessner, *Nanoparticles in the water cycle: properties, analysis and environmental relevance*, Springer, 2010.