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Insights into the Mechanism of In-Plasma Photo-Assisted Etching

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Recently, we discovered that, in addition to ion-assisted etching, vacuum ultraviolet (VUV) photons (<180 nm) generated in the plasma also substantially contribute to etching of Si in halogen containing plasmas, especially at ion energies lower than the ion-assisted etching threshold.[1] This in-plasma photo-assisted etching (PAE) could be detrimental to the development of self-limiting processes required for atomic layer etching. It is therefore important to understand the role of VUV photons in etching silicon, particularly at low ion energies.

Various mechanisms have been proposed to explain PAE of Si, including photogenerated carrier-mediated etching, photon-stimulated desorption, and photon-induced damage (breaking of Si-Si bonds) produced by VUV photons irradiating the substrate.[2] In this study, we used optical emission spectroscopy to gain insights into possible in-plasma PAE mechanisms. Optical emission from Cl, Si, SiCl, and Ar were recorded as a function of power while etching p-Si in Faraday-shielded inductively coupled plasmas sustained in Ar/Cl_2 at a pressure of 60 mTorr with no substrate bias. Under these conditions, ion-assisted etching was negligible. The ratio of optical emission from Si with respect to Ar, I_{Si}/I_{Ar} (proportional to the etching rate of Si), substantially increased with power. Accounting for the contribution to this signal from the dissociation of $SiCl_x$ (x=1-3) etch products, the residual increase in the emission indicated that the rate of PAE also increased with power. Time resolved emissions were also recorded in a pulsed plasma where power was modulated between 500 W and 300 W. Normalized intensities are shown in Fig. 1. I_{Cl}/I_{Ar} is hardly modulated due to the long time scale of Cl atom recombination compared to the period of plasma modulation. In contrast, I_{Si}/I_{Ar} is modulated with the instantaneous power. This result rules out the the proposed mechanism that PAE results from photon-induced damage. If this mechanism were dominant, the I_{Si}/I_{Ar} signal would not be modulated since the damaged surface would persist throughout the pulsed period.

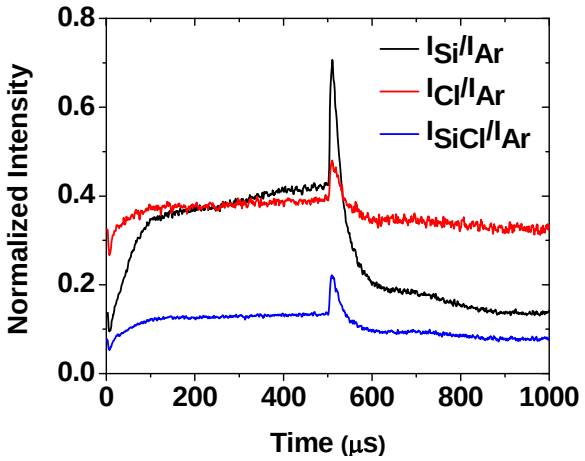


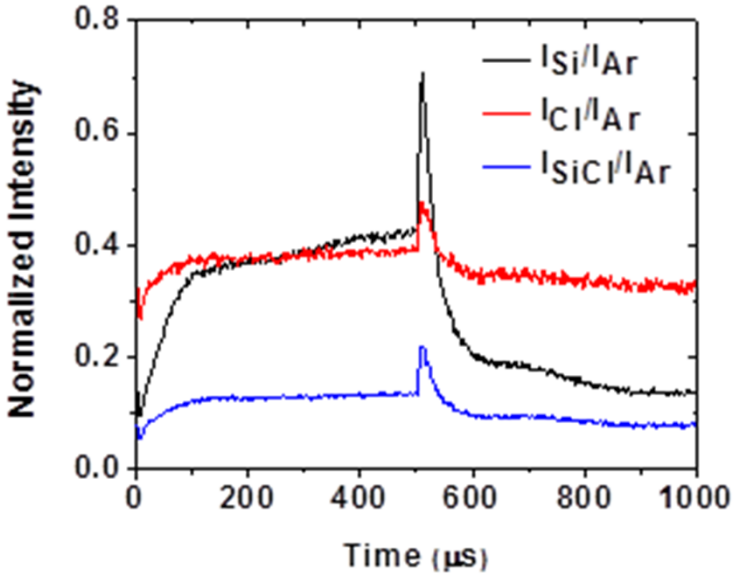
Figure 1 – Time resolved, normalized emission intensities during Si etching in an Ar/Cl_2=50/50 plasma. Power is modulated between 500 W and 300 W.

References

[1] H. Shin, W. Zhu, V.M. Donnelly, and D.J. Economou, J. Vac. Sci. Technol. A **30**, 021306 (2012).
[2] S. Samukawa, B. Jinnai, F. Oda, and Y. Morimoto, Jpn. J. Appl. Phys. **46**, L64 (2007).

INSIGHTS INTO THE MECHANISM OF IN-PLASMA PHOTO-ASSISTED ETCHING

- Possible mechanisms of photo-assisted etching (PAE) include photon-induced: (a) creation of e-hole pairs and reaction of these carriers, (b) product desorption, (c) crystal damage (broken Si-Si bonds).
- Use optical emission spectroscopy during Si etching in Ar-Cl_2 plasmas under PAE conditions to gain insight into mechanisms.
- *Continuous wave* plasma experiments showed that PAE increases with power.



- Normalized Intensity vs. time in a pulsed plasma.

- Pulsed plasma experiments showed that the normalized intensity I_{Si}/I_{Ar} modulates with *instantaneous* power.
- If photon-induced damage was the prevailing mechanism, the I_{Si}/I_{Ar} signal would not be modulated.
- PAE is likely not due to substrate damage.

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A Review Paper – "Nonthermal Plasma Synthesis of Nanocrystals: Fundamental Principles, Materials, and Applications"

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Plasma Science Center co-principal investigators Kortshagen, Aydil, and Girshick, together with co-authors Sankaran, Pereira, and Wu, published an invited review paper on the synthesis of nanocrystals with nonthermal plasmas titled *Nonthermal Plasma Synthesis of Nanocrystals: Fundamental Principles, Materials, and Applications*. The review will be included in a special issue on *Nanoparticle Chemistry* in the American Chemical Society journal *Chemical Reviews* (impact factor: 37.3). Over 67 pages, the authors present a comprehensive overview of the field of plasma synthesis of nanocrystals, reviewing 545 references.

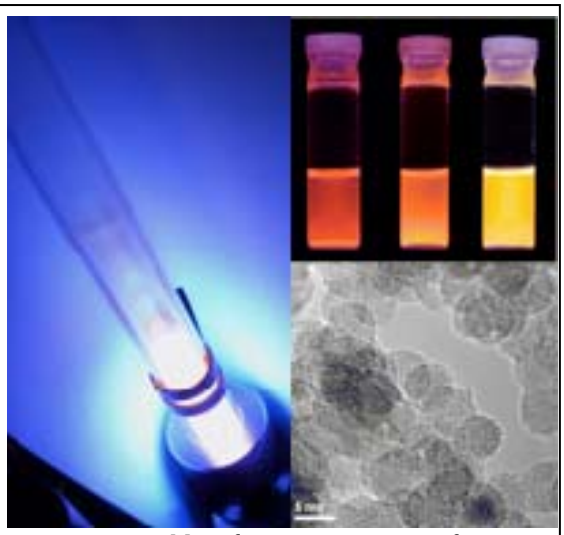


Figure 1 – Table of contents image of review paper: (left) image of plasma reactor for the synthesis of silicon nanocrystals. (upper right): plasma-produced photoluminescent silicon nanocrystals of various sizes, size decreasing from left to right. (lower right): transmission electron microscope image of plasma produced silicon nanocrystals.

Aimed at an audience of non-plasma scientists, the paper first presents a tutorial-style overview of the basic properties of nonthermal plasmas and of plasma-nanoparticle interactions. It then reviews various practical implementations of plasma reactors. The authors survey the significant body of literature on the plasma synthesis of group IV nanocrystals, a traditional domain of nonthermal plasmas. They then discuss the more recent progress in the synthesis of metal oxides, metal nitrides, and metal sulfides. As the ability to electrically dope nanocrystal materials is a particular strength of plasma synthesis compared to other synthetic approaches, the authors also pay particular attention to this topic. The review concludes with an overview of the applications of plasma produced nanocrystals in such diverse fields as thermoelectric energy conversion, electronic devices, solar cells, and light emitting devices. In the final outlook section, the authors present their view of future research challenges, which include the synthesis of core/shell nanocrystals, of multicomponent materials, and an increased control over the nanoparticle morphology.

The paper is available under digital object identifier: 10.1021/acs.chemrev.6b00039 (http://dx.doi.org/10.1021/acs.chemrev.6b00039).

DOE Center for Control of Plasma Kinetics

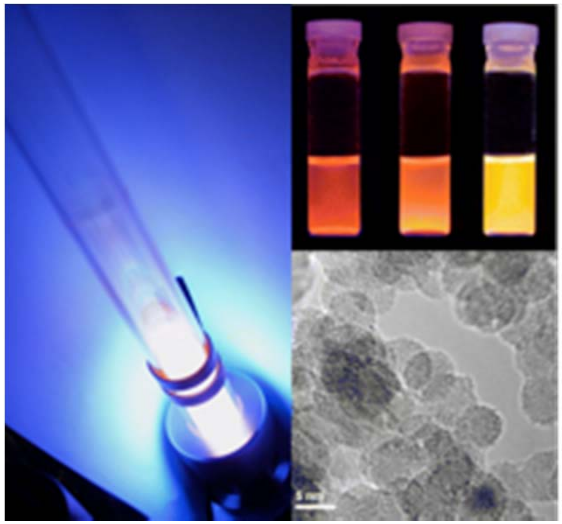
Highlight

Center for Predictive Control of Plasma Kinetics: Multi-Phase and Bounded Systems

PSC Department of Energy Plasma Science Center

A REVIEW – "NONTHERMAL PLASMA SYNTHESIS OF NANOCRYSTALS: FUNDAMENTAL PRINCIPLES, MATERIALS AND APPLICATIONS"

- **Plasma Science Center co-PIs Kortshagen, Aydil, and Girshick with co-authors published an invited review paper on the synthesis of nanocrystals with nonthermal plasmas in *Chemical Reviews* (impact factor: 37.3).**
- **The 67 page review provides a comprehensive overview of the field of plasma synthesis of nanocrystals including 545 references.**
- **Topics in the review include: basic properties of nonthermal plasmas and plasma-nanoparticle interactions, plasma reactors, synthesis of group IV nanocrystals and other materials, nanocrystal doping, applications of plasma-produced nanocrystals, and future research challenges.**



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