

Photo-oxidation of Ge Nanocrystals: Kinetic Measurements by *In Situ* Raman Spectroscopy

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ABSTRACT

Ge nanocrystals are formed in silica by ion beam synthesis and are subsequently exposed by selective HF etching of the silica. Under ambient conditions, the exposed nanocrystals are stable after formation of a protective native oxide shell of no more than a few monolayers. However, under visible laser illumination at room temperature and in the presence of O₂, the nanocrystals rapidly oxidize. The oxidation rate was monitored by measuring the Raman spectra of the Ge nanocrystals *in-situ*. The intensity ratio of the anti-Stokes to the Stokes line indicated that no significant laser-induced heating of illuminated nanocrystals occurs. Therefore, the oxidation reaction rate enhancement is due to a photo-chemical process. The oxidation rate varies nearly linearly with the logarithm of the laser intensity, and at constant laser intensity the rate increases with increasing photon energy. These kinetic measurements, along with the power dependencies, are described quantitatively by an electron active oxidation mechanism involving tunneling of optically excited electrons through the forming oxide skin and subsequent transport of oxygen ions to the Ge nanocrystal surface.

INTRODUCTION

Oxidation phenomena can have a significant impact on the structural and electronic properties of nanoscale materials because of their large surface to volume ratios. For example, oxidation of Si nanocrystals is commonly used to passivate surface states and enhance optical activity [1]. Furthermore, size-dependent self-limiting oxidation has been observed and is used to control the size distributions of nanomaterials [2]. Although nanocrystals are often embedded in a host matrix, such as silica, a number of synthesis routes lead to the formation of exposed nanocrystals. Therefore, it is of significant importance to understand oxidation processes that occur upon exposure of nanocrystals to ambient atmospheric conditions. In this work, we show that exposed Ge nanocrystals can be rapidly photo-oxidized. This oxidation process is monitored by *in situ* Raman spectroscopy and a quantitative mechanistic model is proposed.

EXPERIMENTAL DETAILS

Ge nanocrystals were formed by ion implantation of ⁷⁴Ge⁺ at 150 keV to 3×10¹⁶ cm⁻² into 500 nm thick SiO₂ layers on Si substrates followed by thermal annealing at 950 °C for 1 h under Ar. Transmission electron microscopy (TEM) shows nanocrystals located in the near surface region of the oxide film and with an average diameter of 6.3 nm. High resolution TEM (HR-TEM) images (not shown) demonstrate that silica-embedded Ge nanocrystals are spherical with sharp interfaces to the surrounding matrix [3].

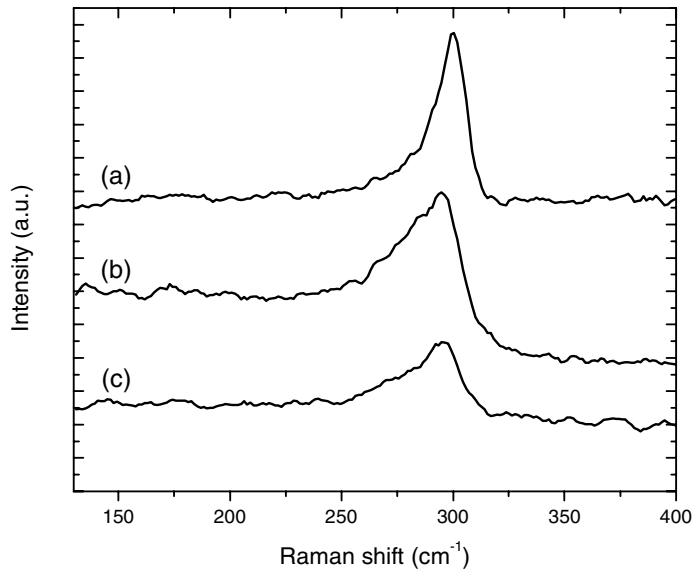


Fig. 1: Raman spectrum of ^{74}Ge nanocrystals embedded in silica (a). Raman spectra of air-exposed ^{74}Ge nanocrystals after 2 s (b) and 1250 s (c) of 488 nm laser illumination with a flux of 1.16×10^{21} photons $\text{cm}^{-2} \text{s}^{-1}$. Spectra are offset along the y-axis for clarity, but the relative intensities of spectra (b) and (c) have not been adjusted. The intensity reduction observed between spectra (b) and (c) is attributed to photo-oxidation.

Exposed nanocrystals were obtained by selective etching of the silica matrix with 1:1 49% HF:H₂O, followed by immersion in methanol and drying under flowing nitrogen. As described previously, this selective etching process does not significantly alter the nanocrystal size distribution from the silica-embedded state [3]. Though all nanocrystals were fully exposed by this procedure, etching was terminated prior to complete removal of the oxide film in order to suppress direct electronic interactions between nanocrystals and the Si substrate. Previous experiments showed that oxidation of exposed nanocrystals, in the absence of laser illumination, is suppressed by hydrogen termination after HF etching for at least 2 h. In the present work, photo-oxidation experiments were performed within 30 s of initial exposure to air.

Raman spectroscopy was performed in a macroscopic optical setup using the 488 nm of an Ar laser and spectra were collected using a LN₂-cooled CCD detector. The spot size was $2.6 \times 10^{-4} \text{ cm}^2$ at the sample, as measured using a photodiode array, and the intensity was varied by insertion of neutral density filters into the beam path. The extent of oxidation was determined by monitoring the evolution of the Raman scattering intensity. *In situ* Raman spectroscopy was performed under moderate and high laser power exposures and spectra were continuously collected at 1 s intervals. At low laser powers, the Raman scattering intensity was prohibitively low for *in situ* measurement. Therefore, reference spectra were collected for 1 s with moderate laser power, samples were then illuminated at reduced intensities for specific time intervals, and final spectra were collected for 1 s with moderate laser powers. Reference Raman spectra were also collected under nitrogen.

RESULTS AND DISCUSSION

Raman spectra of as-grown ^{74}Ge nanocrystals embedded in SiO₂ [Fig. 1(a)] exhibit the expected asymmetrically broadened line shape arising from phonon confinement. Figure 1(b) shows the Raman spectrum of exposed ^{74}Ge nanocrystals after 2 s of exposure to 488 nm laser radiation. The line shape of exposed nanocrystals exhibits a low frequency tail that was previously assigned to surface reconstruction-induced disordering and is manifested as an amorphous-like contribution to the overall scattering intensity [3]. The Raman spectrum of

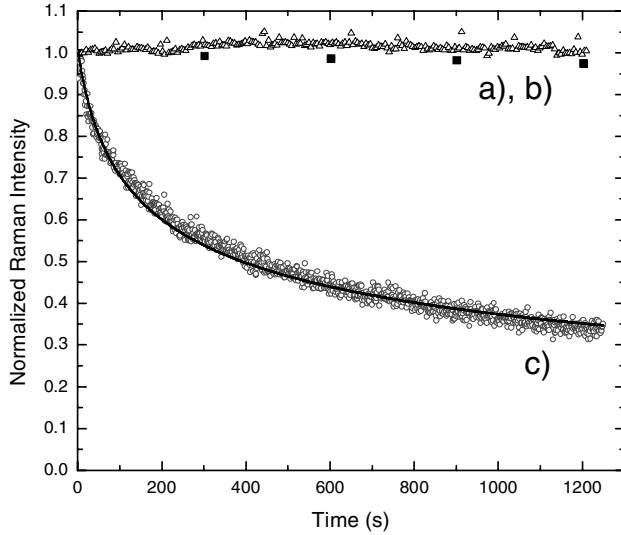


Fig. 2: The integrated Raman intensity from Ge nanocrystals as a function of time during continuous 488 nm laser illumination with a flux of 1.16×10^{21} photons $\text{cm}^{-2} \text{s}^{-1}$ a) under N_2 (Δ) and b) for intermittent laser exposure under air (\blacksquare). c) The normalized integrated Raman intensity of air-exposed Ge nanocrystals as a function of time during *in situ* Raman spectroscopy with 488 nm illumination and a flux of 1.16×10^{21} photons $\text{cm}^{-2} \text{s}^{-1}$ (\circ). The solid line shows the predictions of the photo-oxidation theory. All data points are normalized to the intensity of the $t = 1$ s laser exposure of each data series.

exposed Ge nanocrystals after 1250 s of 488 nm laser irradiation under air is shown in Fig. 1 (c). The overall scattering intensity decreases considerably during laser exposure and the fractional contribution of the amorphous-like component to the scattering intensity arising from the disordered shell is reduced, which is consistent with oxidation of the surfaces of nanocrystals.

The evolution of the integrated Raman intensity, normalized to the $t = 1$ s exposure, as a function of time for various experimental configurations is shown in Fig. 2. Under nitrogen, the Raman scattering intensity is stable with respect to time [Fig. 2(a)]. Furthermore, the scattering intensity is stable under intermittent laser exposure under air over a period of 20 min, indicating that hydrogen passivation stabilizes nanocrystals to oxidation at short times [Fig. 2(b)]. Continuous laser illumination under air, however, leads to a significant reduction of the scattering intensity over time [Fig. 2(c)]. The oxidation rate is the largest at short times, but decreases towards zero at the longest times. Because the Raman intensity is proportional to the total scattering volume, the evolution of the scattering peak gives a direct measure of the extent of oxidation in real time and may be used to analyze the kinetics of the oxidation process.

Laser heating of the nanocrystals was considered as a possible source of the enhanced oxidation rate under visible laser irradiation. The temperature of the nanocrystals was determined by comparison of the anti-Stokes and Stokes scattering intensities. Anti-Stokes and Stokes spectra, shown in Fig. 3, were collected under dry nitrogen to ensure intensity stability over time. The temperature of illuminated nanocrystals is 306 K, indicating that sample heating is negligible and that the significant oxidation rate enhancement is not due to a local laser-induced temperature increase. Therefore, the reduction of the Raman scattering intensity under room temperature illumination is assigned to a photo-oxidation process.

The extent of oxidation varies almost linearly with the logarithm of the laser power, as shown in Fig. 4. Since laser heating of the nanocrystals is negligible, the dependence of oxidation extent on laser power indicates that the process is not diffusion rate limited. For the case of the most highly-oxidized nanocrystals, the total remaining Ge volume is approximately 0.3 of the starting volume, which corresponds to formation of a 1 nm thick oxide shell surrounding the crystalline Ge core.

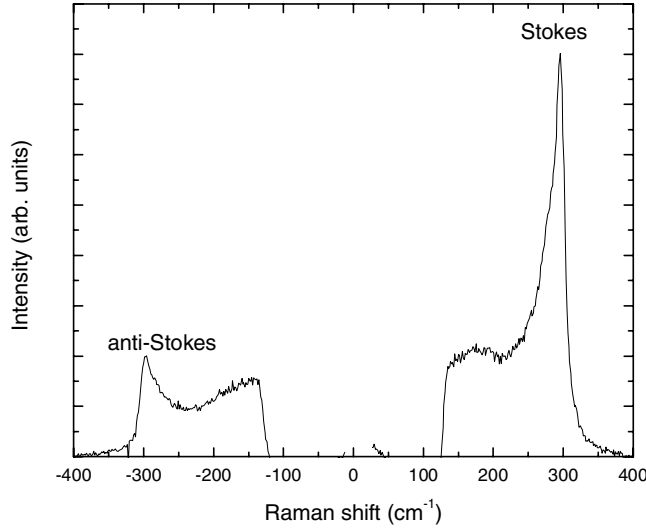


Fig. 3: Stokes and anti-Stokes spectra from exposed Ge nanocrystals under N₂ obtained using the 488 nm line of an Ar laser with a flux of 1.16×10^{21} photons $\text{cm}^{-2} \text{s}^{-1}$. The corresponding temperature of illuminated nanocrystals is 306 K, indicating that laser heating is negligible and is not responsible for the observed oxidation rate enhancement.

To describe the kinetics of visible light photo-oxidation, an electron-active oxidation model is invoked. This model was first qualitatively proposed by Young to describe visible light photo-oxidation of Si [4], and is based on a tunneling mechanism originally proposed by Mott [5]. According to this oxidation mechanism, above bandgap light excites carriers inside Ge nanocrystals, thereby enhancing the tunneling probability of electrons through the growing oxide shell to molecular oxygen at the surface [4]. When an electron with energy greater than 1 eV interacts with molecular oxygen, dissociation to a neutral oxygen atom and a negatively charged oxygen ion, both of which are more mobile than molecular oxygen, can occur [4]. The rate limiting step for photo-oxidation is the tunneling of electrons through the oxide for molecular oxygen dissociation. We note that the maximum oxide shell thickness under the present conditions, and thus the maximum oxidant diffusion length, is 1 nm (corresponding to consumption of 70 % of the total Ge volume). Within this model, we find that the time dependent nanocrystal radius is given by:

$$\frac{dr}{dt} = -\frac{1}{3} r \eta I \alpha v \exp\left(\frac{-2\sqrt{2m^*U(r)}}{\hbar} (R_0 - r)\right) \quad (1)$$

where I is the incident photon flux, α is the nanocrystal absorption coefficient, v is the Ge volume consumed per oxidation event, m^* is the electron effective mass, $U(r)$ is the tunneling barrier, and R_0 is the average initial nanocrystal radius. The factor η accounts for the rapid thermalization of excited carriers to lower energy states which significantly reduces the tunneling probability. The size dependent tunneling barrier, $U(r)$, is a function of the valence band alignment between Ge and GeO₂, which itself is a function of particle size due to quantum confinement effects. A bulk valence band offset of 2 eV, consistent with recent experimental measurements [6], is used along with the size dependent valence band positions calculated by Niquet and co-workers [7].

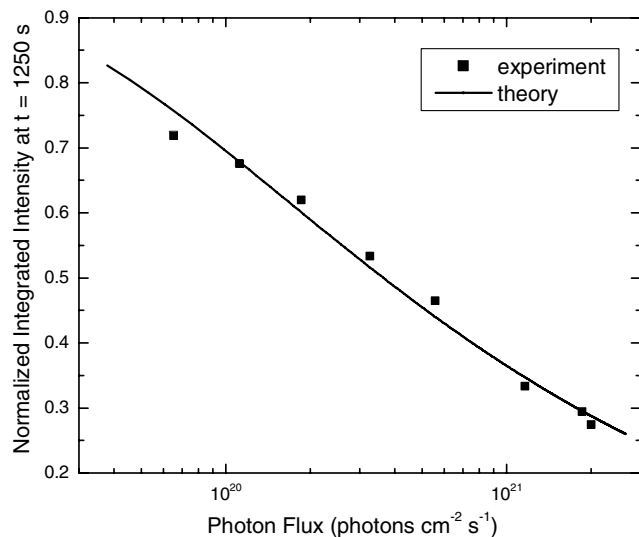


Fig. 4: Normalized integrated Raman intensity from Ge nanocrystals as a function of photon flux after 1250 s of 488 nm laser illumination under air (data points). The solid line shows the calculated values according to the theory presented in the text.

All physical parameters are known, with the exception of the thermalization efficiency factor, η , and the nanocrystal absorption coefficient, α . The product of these terms is thus used for fitting the experimental data. The solid lines in Figs. 2 & 4 give the fit of the electron active photo-oxidation model and both show excellent agreement to the experimental observations.

CONCLUSION

The kinetics of photo-oxidation of Ge nanocrystals under visible laser illumination were observed by *in situ* Raman spectroscopy. Both the time-resolved data and the effect of power on extent of oxidation are well-described using an electron active oxidation mechanism in which the rate limiting step is the tunneling of photo-excited carriers through the forming oxide skin followed by molecular oxygen dissociation and rapid atomic and/or ionic oxygen diffusion to the nanocrystal core. Preliminary experimental results indicate that the rate of photo-oxidations is strongly sensitive to the excitation energy, with higher energy excitation leading to more rapid oxidation. Future work will be dedicated to fully characterizing the influence of *both* excitation energy *and* excitation power on photo-oxidation and comparing the results to the predictions of the proposed theoretical model.

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REFERENCES

- [1] G. Ledoux, J. Gong and F. Huisken, *Appl. Phys. Lett.* **79**, 4028 (2001).

- [2] K. C. Scheer, R. A. Rao, R. Muralidhar, S. Bagchi, J. Conner, L. Lozano, C. Perez, M. Sadd and B. E. W. Jr., *J. Appl. Phys.* **93**, 5637 (2003).
- [3] I. D. Sharp, Q. Xu, C. Y. Liao, D. O. Yi, J. W. Beeman, Z. Liliental-Weber, K. M. Yu, D. N. Zakharov, J. W. A. III, D. C. Chrzan and E. E. Haller, *J. Appl. Phys.* **97**, 124316 (2005).
- [4] E. M. Young, *Appl. Phys. A* **47**, 259 (1988).
- [5] N. F. Mott, *Trans. Faraday Soc.* **35**, 1175 (1939).
- [6] V. V. Afanas'ev and A. Stesmans, *Appl. Phys. Lett.* **84**, 2319 (2004).
- [7] Y. M. Niquet, G. Allan, C. Delerue and M. Lannoo, *Appl. Phys. Lett.* **77**, 1182 (2000).