# The influence of annealing conditions on the growth and structure of embedded Pt nanocrystals

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The growth and structure of Pt nanocrystals (NCs) formed by ion implantation in *a*-SiO<sub>2</sub> has been investigated as a function of the annealing conditions. Transmission electron microscopy and small-angle x-ray scattering measurements demonstrate that the annealing ambient has a significant influence on NC size. Samples annealed in either Ar, O<sub>2</sub>, or forming gas (95% N<sub>2</sub>: 5% H<sub>2</sub>) at temperatures ranging from 500 °C-1300 °C form spherical NCs with mean diameters ranging from 1–14 nm. For a given temperature, annealing in Ar yields the smallest NCs. O<sub>2</sub> and forming gas ambients produce NCs of comparable size though the latter induces H chemisorption at 1100 °C and above, as verified with x-ray absorption spectroscopy. This H intake is accompanied by a bond-length expansion and increased structural disorder in NCs of diameter >3 nm. © 2009 American Institute of Physics. [DOI: 10.1063/1.3079506]

### I. INTRODUCTION

Nanocrystals (NCs) have attracted considerable attention given their non-bulk-like characteristics stemming from finite-size, surface-, and/or quantum-related effects. For example, metallic NCs embedded in a dielectric matrix have potential applications in optical filters and switching devices due to their linear and nonlinear optical properties,<sup>1</sup> while Pt NCs on a supporting scaffold have been widely investigated for their important catalytic applications including the reduction in pollutant gases in automobile exhaust.<sup>2</sup> Ion implantation is one of many techniques used to form embedded NCs,<sup>3-7</sup> the primary advantage of which is an ability to control the depth and concentration of implanted atoms. Furthermore, the protection offered by the surrounding matrix enhances NC stability and durability.<sup>1</sup> Given that NC properties depend on size and structure,<sup>8</sup> it is important to understand the influence of the synthesis parameters on NC formation. In this report, we characterize Pt NCs formed in a-SiO<sub>2</sub> by ion implantation, focusing on the influence of the annealing conditions on NC size and structure. The size and shape of the particles were determined with small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) while extended x-ray absorption fine structure (EXAFS) spectroscopy was used to measure the NC structural parameters including the coordination number (CN), mean interatomic distance (bond length), variance [Debye-Waller (D-W) factor], and asymmetry [third cumulant  $(C_3)$ ] of the first nearest neighbor (NN) shell of atoms surrounding a Pt absorbing atom. Analysis of the x-ray absorption near-edge structure (XANES) was used to estimate the chemisorbed H content. This combination of four complementary analytical techniques (SAXS, TEM, EXAFS, and XANES) represents an effective and powerful means of characterizing nanoscale systems including embedded NCs.<sup>6,7,9–15</sup>

## **II. EXPERIMENTAL**

Amorphous SiO<sub>2</sub> (*a*-SiO<sub>2</sub>) layers (2  $\mu$ m thick) thermally grown on Si substrates were implanted at liquid nitrogen temperature with Pt ions. The energies and fluences are presented in Table I and varied between 3.4 and 5.6 MeV and  $1.8 \times 10^{16} - 3 \times 10^{17}$  cm<sup>-2</sup>, respectively, yielding peak atomic concentrations ranging from 0.3–9.0 at. %. After implantation, samples were annealed in Ar, O<sub>2</sub>, or forming gas (95% N<sub>2</sub>: 5% H<sub>2</sub>) for 1 hr at temperatures of 500 °C-1300 °C to promote NC nucleation and growth.

The NC size distribution was determined from transmission SAXS measurements performed at beamline 15ID-D of the Advanced Photon Source, USA, using an x-ray wavelength of 1.1 Å and a camera length of 1880 mm. The scattered intensity I(Q) was measured with a MAR-165 chargecoupled device (CCD) detector with a 5 s exposure time. SAXS samples were prepared with a procedure described elsewhere<sup>3</sup> wherein a hole is cored through the Si substrate below the *a*-SiO<sub>2</sub> layer to enable quantitative comparison between samples and avoid scattering contributions from the

TABLE I. S	Summary of	f Pt in	nplantation	parameters.
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Partial implanted fluence according to beam energy (cm <sup>-2</sup> )						
Total fluence (cm <sup>-2</sup> )	3.4 MeV	4.5 MeV	5.6 MeV	at. %		
$1.8 \times 10^{16}$	$0.5 \times 10^{16}$	$0.6 \times 10^{16}$	$0.7 \times 10^{16}$	0.3		
$5.6 \times 10^{16}$	$1.5 \times 10^{16}$	$1.8 \times 10^{16}$	$2.3 \times 10^{16}$	0.9		
$1.0 \times 10^{17}$		$1.0 \times 10^{17}$		3.0		
$3.0 \times 10^{17}$		$3.0 \times 10^{17}$		9.0		

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substrate. Analysis of the SAXS spectra was based on a maximum-entropy method with the assumption of spherical NCs (Ref. 16) (confirmed by TEM). The latter measurements were performed with a Phillips CM300 microscope operating at 300 kV, using samples prepared in a cross-section geometry by the small-angle cleavage technique.<sup>17</sup> For reliable statistics, a minimum of 2000 particles were measured with TEM for comparative determinations of the size distribution.

EXAFS and XANES measurements were carried out at beamline 20-B of the Photon Factory, Japan, in fluorescence mode at the Pt  $L_3$  edge (11 564 eV). The sample temperature was maintained at  $12 \pm 1$  K to minimize thermal vibrations and data were collected using a Ge  $6 \times 6$  pixel array detector with the Si (111) monochromator detuned by 50% for harmonic rejection. Samples were prepared by removing the Si substrate below the a-SiO<sub>2</sub> layer using a combination of mechanical grinding and selective wet chemical etching in KOH solution.<sup>18</sup> A Pt foil (200 nm thick) was used as a crystalline standard and a Pt reference was measured simultaneously in transmission mode for energy calibration. The XANES spectra were aligned with respect to the absorption edge of the Pt foil. The pre-edge region between 150 and 30 eV was used for the background removal and the amplitude of the spectra was then normalized to the smoothly varying EXAFS background at >150 eV above the edge. EXAFS data were analyzed with the ATHENA (Ref. 19) and ARTEMIS (Ref. 19) programs, interfaces for the IFEFFIT (Ref. 20) code. Following background removal, spectra were Fourier transformed over a photoelectron wave number (k) range of 4.9-14.6 Å<sup>-1</sup>. Structural parameters were extracted from the first NN shell isolated by inverse Fourier, transforming over a non-phase-corrected radial distance (R) range of 1.7–3.1 Å. Theoretical standards generated by the FEFF8 code<sup>21</sup> were fitted to the experimental spectra. The amplitude reduction factor  $(S_0^2)$  and energy shift parameter  $(\Delta E_0)$  were determined from the Pt foil and thereafter fixed for all samples.

## **III. RESULTS AND DISCUSSION**

#### A. NC growth

Figure 1 shows TEM micrographs of samples implanted with  $1 \times 10^{17}$  cm<sup>-2</sup> and annealed in forming gas at (a) 1100 °C, (b) 1200 °C, and (c) 1300 °C. The NCs are spherical in shape, justifying our use of a spherical model for the SAXS data analysis. (No definitive evidence of large scale faceting was apparent consistent with the amorphous nature of the matrix. Should a small degree of faceting be present, we anticipate a negligible influence on the SAXS data analysis.) The largest average particle sizes are observed in samples annealed at the highest temperatures. The diffraction pattern for Pt NCs annealed at 1100 °C [Fig. 1(d)] demonstrates the NCs retain the face-centered cubic (FCC) structure characteristic of bulk Pt, while the high resolution image of Fig. 1(e) shows the NCs are single crystalline.

Figure 2 presents x-ray scattering intensities I(Q) as a function of the scattering vector Q (left panels) for samples implanted with  $1 \times 10^{17}$  cm<sup>-2</sup> and annealed in Ar, O<sub>2</sub>, or forming gas, as well as the scattering contribution of an unimplanted *a*-SiO<sub>2</sub> layer. The shift of the peak to lower Q is



FIG. 1. TEM micrographs of Pt NCs in SiO<sub>2</sub> for an implantation fluence of  $1 \times 10^{17}$  cm<sup>-2</sup> and annealing in forming gas at (a) 1100 °C, (b) 1200 °C, and (c) 1300 °C. (d) Selected area diffraction pattern and (e) high resolution image of an individual NC.

indicative of NC growth with increasing annealing temperature. The corresponding size distributions recovered from the fit to the SAXS data (using the maximum-entropy method) are displayed in the right panels. (Note the different horizontal scales in the size distributions.) Mean diameters are listed in Table II which also includes the maximum and standard deviation from a Gaussian fit to the distributions. Though the latter may not always be most accurately described by a Gaussian,<sup>12</sup> the standard deviation is indicative of the extent of NC size variation in a given sample. As shown in Fig. 2, the NCs increase in size with increasing annealing temperature for all ambients, though at a given temperature annealing in Ar yields significantly smaller NCs than annealing in either O<sub>2</sub> or forming gas. Though these two ambients produce NCs of similar sizes, differences are apparent in the growth rates as a function of temperature.

Figure 3 shows an Arrhenius plot of the squared mean NC radius for samples annealed in Ar, O<sub>2</sub>, or forming gas. Activation energies  $(E_{act})$  for Pt NC growth were  $0.83 \pm 0.10$ and  $1.34 \pm 0.05$  eV for annealing in Ar and O<sub>2</sub>, respectively. Two distinct temperature regimes for NC growth are apparent for annealing in forming gas at temperatures <900 °C,  $E_{\text{act}} = 0.09 \pm 0.01 \text{ eV}$ , while beyond 900 °C,  $E_{\text{act}}$ =1.93  $\pm$  0.33 eV. Similar observations have been reported for other metals<sup>22,23</sup> where the sluggish and effectively temperature independent increase in NC size at low temperatures was attributed to a growth mechanism governed by irradiation-induced disorder. The different activation energies suggest differences in the interaction of the annealing ambient with the matrix and/or Pt atoms. For example, annealing in  $O_2$  may enhance Pt atomic transport in *a*-SiO<sub>2</sub> in a manner analogous to the observed for Au (Ref. 23), in contrast to annealing in inert Ar where no thermodynamic



FIG. 2. (Color online) Measured SAXS intensity I(Q) as a function of the scattering vector Q (left) and respective diameter distributions (right) for samples implanted with  $1 \times 10^{17}$  cm<sup>-2</sup> and annealed in either Ar, O<sub>2</sub>, or forming gas at the temperatures indicated in each panel. The scattering contribution of a blank SiO<sub>2</sub> is also plotted for comparison on the left panels. Note the different horizontal scales on the diameter distribution plots.

interactions are anticipated. Annealing Au NCs in a  $H_2$ -containing ambient (Ar:  $H_2$ ) (Ref. 23) yielded no significant differences in contrast to our observations for Pt NCs which—when annealed in forming gas—exhibit a much higher activation energy for temperatures beyond 900 °C.

The influence of this H chemisorption on the electronic and structural properties of Pt NCs is discussed in Secs. III B and III C.

Figure 4 compares the size distributions determined from SAXS and TEM for samples implanted with different

TABLE II. Mean NC diameter  $\mathbf{D}_{mean}$  obtained from SAXS measurements. Peak is the peak of each distribution determined from a Gaussian fit to the experimental distributions, with standard deviation  $\boldsymbol{\sigma}$ .

	Argon			Oxygen			Forming Gas		
Annealing Temp.	<b>D</b> <sub>mean</sub> (nm)	Peak (nm)	$\boldsymbol{\sigma}$ (nm)	<b>D</b> <sub>mean</sub> (nm)	Peak (nm)	<b>σ</b> (nm)	<b>D</b> <sub>mean</sub> (nm)	Peak (nm)	$\boldsymbol{\sigma}$ (nm)
500 °C							1.2	1.2	0.1
800 °C	1.1	1.0	0.1	1.1	1.1	0.2	1.4	1.2	0.1
900 °C	1.6	1.7	0.3						
1000 °C	1.8	1.4	0.2	2.9	2.7	0.5	2.7	2.4	0.4
1100 °C	2.8	2.7	0.4	4.7	4.6	1.1	3.5	3.1	0.5
1200 °C	4.0	3.4	0.6	7.7	7.5	1.6	7.4	6.1	1.3
1300 °C				10.1	10.0	2.2	13.9	12.3	2.9



FIG. 3. (Color online) Arrhenius plot of the squared mean NC radius ( $R^2$ ) as a function of the inverse temperature ( $k_B$  is the Boltzmann constant; T is the annealing temperature). The lines are linear fits to the experimental data.

fluences and annealed in forming gas at 1100 °C for 1 hr. In contrast to other metals,<sup>6,7</sup> the implantation fluence does not significantly affect mean Pt NC size—samples with concentration maxima ranging from 0.3–9.0 at. % exhibit mean NC diameters varying from only 3.4–2.9 nm. Lower fluences yield larger NCs as a result of the disorder-mediated nucleation of Pt NCs, as described previously.<sup>4</sup> Similarly, the broad size distributions characteristic of metallic NCs produced by ion implantation<sup>24</sup> are not observed. For example, annealing in Ar (Fig. 2) at temperatures of 1100 °C–1200 °C yields mean NC diameters that vary from 2.8–4.0 nm with standard deviations of less than 15%.



FIG. 4. (Color online) Diameter distributions obtained from SAXS and TEM measurements for samples implanted with different fluences (as indicated in each panel) and annealed at 1100  $^{\circ}$ C.



FIG. 5. (Color online) Normalized XANES spectra for the  $L_3$  edges of the Pt foil and the NC samples annealed in either Ar,  $O_2$ , or forming gas, at different temperatures, as indicated on the graphs. All spectra were energy calibrated relative to a Pt reference measured simultaneously to the samples.

Given that NC properties are dependent on size, a narrow size distribution is beneficial for technological applications.

#### **B. H chemisorption**

Figure 5 shows Pt  $L_3$  near-edge absorption spectra for samples annealed in Ar, O<sub>2</sub>, or forming gas. The difference in energy between the inflection points of the absorption edges ( $E_i$ ) for NC samples and the crystalline foil is shown in Fig. 6 as a function of NC size. Annealing in Ar or O<sub>2</sub> ambients yields similar results in both Figs. 5 and 6. For NCs with mean diameter <2.0 nm,  $E_i$  is shifted to higher ener-



FIG. 6. (Color online) Difference between  $E_i$  of the NC samples and the Pt foil as a function of NC diameter, being  $E_i$  the inflection point of the Pt  $L_3$  edge.

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FIG. 7. (Color online) Normalized XANES spectrum for the  $L_3$  edge of the Pt foil fitted with a Lorentzian superimposed on an arc tangent curve (A + B). The individual curves are also shown (A: arc tangent and B: Lorentzian).

gies (0.5-1.5 eV) relative to the crystalline foil as a result of finite-size-related perturbations to the electronic properties of Pt NCs.<sup>9</sup> This shift decreases with increasing diameter as the NCs become more bulklike and is negligible beyond 4.0 nm. In contrast, samples annealed in forming gas exhibit the largest shift (1.5-2.0 eV) for the biggest NCs.

The prominent peak immediately beyond the absorption edge is commonly termed the "white line" and—for the Pt  $L_3$  absorption edge—is the result of an electronic transition from an occupied  $2p_{3/2}$  core level to an unoccupied *d* state of the absorbing atom.<sup>25</sup> For Au, the *d* states are completely filled and a significant white line is not observed. Upon H chemisorption by Pt atoms, bonding and antibonding states form and are localized closer to H and Pt atoms, respectively.<sup>26</sup> These unoccupied antibonding states can also accommodate an electronic transition from the  $2p_{3/2}$  core level and, as a consequence, the intensity of the white line increases proportionally with the amount of H chemisorbed. The finite-size-related perturbations referred to above also yield an increase in white line intensity for nonhydrogenated NCs <3.0 nm in diameter.<sup>9</sup>

For our analysis, XANES spectra were fitted with a Lorentzian superimposed on an arc tangent: the former representing transitions to bound states and the latter representing transitions to the continuum. Figure 7 is a representative example, showing the two contributions (and their sum) for a Pt foil. Transitions to the continuum were considered equal for all samples. Fitting was performed by aligning the inflec-



FIG. 8. (Color online) Normalized XANES spectra for the Pt  $L_3$  edges of samples implanted with  $1 \times 10^{17}$  cm<sup>-2</sup> and annealed in forming gas at the temperatures shown in the graph. The dotted lines represent the fitting to the data. Spectra vertically offset for clarity.

tion points of the arc tangent and experimental data. The fits for samples annealed in forming gas are shown in Fig. 8. The area encompassed by the Lorentzian was considered proportional to the number of d electron vacancies.<sup>27,28</sup> For NCs >3.0 nm (where finite-size-related perturbations are negligible), the difference between the area of the Lorentzian and that of the foil is indicative of the amount of H chemisorbed (where each Pt-H bond generates one extra d electron vacancy in the Pt atom<sup>26</sup>). Fitting results are listed in Table III and are plotted in Fig. 9 as a function of NC size. For NCs <3.0 nm in diameter, results are independent of ambient and dominated by finite-size effects. For larger particles, annealing in Ar or O<sub>2</sub> yields near bulklike behavior, while annealing in forming gas results in a significant increase in white line area as consistent with H chemisorption. For such samples, the shift in  $E_i$  apparent in Fig. 6 results from broadening of the white line. Our results are consistent with previous studies for supported Pt NCs where both the energy of the  $L_3$  edge and white line intensity were influenced by H chemisorption.<sup>29–31</sup>

Following Kubota and co-workers,<sup>32,33</sup> quantification of the H content from XANES analysis would necessitate an

TABLE III. Results obtained by fitting a Lorentzian curve to the white line of the XANES spectra for each annealing environment at different temperatures. Area Lor. is the area of Lorentzian and  $N_{\text{NC-foil}}$  is the difference between the area of the Lorentzian fit to the NC and the Pt foil, shown in percentage relative to the area for the Pt foil.

	Argon		Ox	kygen	Forming Gas	
Annealing Temp.	Area Lor.	N <sub>NC-foil</sub> (%)	Area Lor.	N <sub>NC-foil</sub> (%)	Area Lor.	N <sub>NC-foil</sub> (%)
500 °C					8.7	$18.8 \pm 0.8$
800 °C	8.5	$16.6 \pm 0.6$	8.5	$16.5 \pm 3.3$	8.1	$4.0\pm7.1$
900 °C	8.8	$20.7 \pm 4.3$	7.8	$6.8 \pm 1.0$		
1000 °C	7.6	$3.7 \pm 0.6$	7.3	$-0.4 \pm 0.4$	7.4	$1.1 \pm 1.2$
1100 °C	7.1	$-2.1 \pm 1.5$	7.2	$-1.2 \pm 1.3$	8.0	$9.3 \pm 0.6$
1200 °C	7.4	$0.4 \pm 0.4$	6.9	$-5.2 \pm 0.5$	8.1	$11.5 \pm 0.8$
1300 °C			6.9	$-4.7\pm0.2$	9.2	$26.1\pm2.2$



FIG. 9. (Color online) Area of the Lorentzian fitted to the XANES data (white line peak) as a function of NC diameter.

appropriate calibration curve; at present lacking for our materials system (though under development). Nonetheless, our qualitative findings demonstrate the applicability of this form of XANES analysis to the study of H chemisorption in Pt NCs and, as shown below, are invaluable for the interpretation of the EXAFS results presented in Sec. III C.

## C. NC structure

Figure 10 shows  $k^2$ -weighted EXAFS spectra and the corresponding non-phase-corrected Fourier transforms (FTs) for samples implanted with  $1 \times 10^{17}$  cm<sup>-2</sup> and annealed in Ar or forming gas at temperatures ranging from

500 °C-1300 °C. (Similar results were apparent for Ar and O<sub>2</sub> ambients and thus only the former is shown.) Refined fitting parameters for the first NN shell are listed in Table IV. Scattering contributions from the first four NN shells are apparent in the FTs for annealing temperatures >1000 °C; the fitting parameters for which were consistent with the FCC structure. For an Ar (and  $O_2$ ) ambient, the decrease in amplitude of the first NN peak is the result of the decrease in NC size at lower annealing temperatures as apparent from both TEM and SAXS (Figs. 1 and 2, respectively). The increase in surface-to-volume ratio with decreasing NC size yields a decrease in average CN (due to undercoordinated surface atoms) and an increase in structural disorder (due to relaxed/reconstructed surface atoms) both of which contribute to this decrease in amplitude. For samples annealed in forming gas, the largest NCs  $(1300 \ ^{\circ}C)$  yield an amplitude less than that of smaller sized NCs (1000  $^{\circ}C-1200 ^{\circ}C$ ).

Figure 11 shows the CN (from EXAFS) as a function of NC size (from SAXS). For comparison, the size-dependent average CN for spherical FCC particles calculated from<sup>34</sup>

$$CN_{NC} = 12(1 - 3R_{NN}/2D)$$
(1)

is also included, where  $R_{\rm NN}$  is the NN distance and D is the NC diameter. Experiment and theory agree well with the exception of the large NCs annealed in forming gas. For such samples, H chemisorption not only reduces the CN but—as



FIG. 10. (Color online)  $k^2$  weighted (top graphs) and the respective Fourier-transformed (nonphase corrected) EXAFS spectra (bottom graphs) of the Pt foil and Pt NCs implanted with  $1 \times 10^{17}$  cm<sup>-2</sup> and annealed in Ar or forming gas at the temperatures shown in the graphs. Spectra in the top graphs have been vertically offset for clarity.

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TABLE IV. Structural parameters obtained from first NN shell EXAFS analysis. CN=coordination number, D-W factor=Debye-Waller factor, and  $C_3=third$  cumulant.

Sample		CN (atoms)	Bond length (Å)	D-W factor (Å <sup>2</sup> )	$\begin{array}{c} C_{3} \\ (10^{-5} \text{ Å}^{3}) \end{array}$
Pt foil		12	$2.759\pm0.001$	$0.0017 \pm 0.0001$	$-2 \pm 1$
Argon	1200 °C 1100 °C 1000 °C 900 °C 800 °C	$11.5 \pm 0.7 \\ 9.8 \pm 0.5 \\ 8.8 \pm 0.7 \\ 6.6 \pm 0.6 \\ 6.2 \pm 0.4$	$2.745 \pm 0.003 2.747 \pm 0.003 2.742 \pm 0.005 2.741 \pm 0.006 2.728 \pm 0.004$	$\begin{array}{c} 0.0023 \pm 0.0002 \\ 0.0031 \pm 0.0002 \\ 0.0041 \pm 0.0003 \\ 0.0055 \pm 0.0005 \\ 0.0067 \pm 0.0004 \end{array}$	$-4 \pm 3$ $5 \pm 3$ $8 \pm 5$ $29 \pm 7$ $17 \pm 5$
Oxygen	1300 °C 1200 °C 1100 °C 1000 °C 900 °C 800 °C	$12.3 \pm 1.1 \\ 12.0 \pm 0.9 \\ 11.9 \pm 0.7 \\ 10.9 \pm 1.4 \\ 7.4 \pm 0.5 \\ 5.2 \pm 0.9$	$\begin{array}{c} 2.753 \pm 0.005 \\ 2.750 \pm 0.004 \\ 2.751 \pm 0.003 \\ 2.743 \pm 0.008 \\ 2.739 \pm 0.004 \\ 2.723 \pm 0.011 \end{array}$	$\begin{array}{c} 0.0013 \pm 0.0003 \\ 0.0015 \pm 0.0003 \\ 0.0017 \pm 0.0002 \\ 0.0029 \pm 0.0005 \\ 0.0049 \pm 0.0003a \\ 0.0054 \pm 0.0008 \end{array}$	$ \begin{array}{c} -5 \pm 5 \\ -5 \pm 4 \\ 0 \pm 3 \\ 1 \pm 3 \\ 12 \pm 5 \\ 14 \pm 13 \end{array} $
Forming Gas	1300 °C 1200 °C 1100 °C 1000 °C 800 °C 500 °C	$9.5 \pm 2.1 \\ 10.1 \pm 1.0 \\ 10.4 \pm 0.5 \\ 9.1 \pm 0.5 \\ 7.3 \pm 1.4 \\ 6.4 \pm 1.7 \\ \end{cases}$	$\begin{array}{c} 2.801 \pm 0.013 \\ 2.777 \pm 0.006 \\ 2.765 \pm 0.003 \\ 2.755 \pm 0.003 \\ 2.709 \pm 0.012 \\ 2.687 \pm 0.017 \end{array}$	$\begin{array}{c} 0.0034 \pm 0.0009 \\ 0.0021 \pm 0.0004 \\ 0.0025 \pm 0.0002 \\ 0.0028 \pm 0.0002 \\ 0.0086 \pm 0.0012 \\ 0.0093 \pm 0.0020 \end{array}$	$14 \pm 14 \\ 7 \pm 5 \\ 6 \pm 3 \\ 5 \pm 3 \\ 38 \pm 17 \\ 35 \pm 31$

shown in Fig. 12—also increases the D-W factor (circled). Clearly H chemisorption induces considerable structural perturbations in the Pt NCs. The general increase in structural disorder with decreasing NC size apparent in Fig. 12 is the result of the greater fraction of (relaxed/reconstructed) surface atoms (mentioned above) and the associated broadening of the bond-length distribution.<sup>9</sup> Note that the increase in D-W factor is linear with inverse diameter or, equivalently, the surface-to-volume ratio.

EXAFS measurements of the difference in Pt-Pt bond length of the foil and NC samples at a temperature of ~12 K ( $R_{bulk}$ - $R_{NC}$ ) is plotted in Fig. 13 as a function of the inverse diameter. For samples annealed in Ar or O<sub>2</sub>, a bondlength contraction is observed; the magnitude of which increases as NC size decreases and is the result of capillary pressure.<sup>35,36</sup> Using a simple liquid-drop model, as we previously demonstrated for Au (Ref. 7) and Cu NCs,<sup>37</sup> the surface tension  $\gamma$  can be calculated from<sup>38</sup>



where *K* is the bulk compressibility. Using  $K_{Pt}$ =4.34 × 10<sup>-3</sup> GPa<sup>-1</sup> (Ref. 39) yields  $\gamma$ =1.7±0.4 and 2.2±0.1 J/m<sup>2</sup> for annealing in Ar and O<sub>2</sub>, respectively, consistent with that reported for bulk Pt [2.6–3.5 J/m<sup>2</sup> (Ref. 38)] but less than that determined from high energy electron diffraction of Pt NCs (3.7–10.6 nm) formed by vacuum evaporation on C grids (3.37–3.89 J/m<sup>2</sup>).<sup>38</sup> As noted previously, a slight degree of NC faceting is not expected to significantly perturb our results.

Annealing in forming gas yields a significantly greater value of surface tension  $(8.6 \pm 0.5 \text{ J/m}^2)$  and a bond-length expansion for the larger NCs where an appreciable H content was measurable with XANES. A bond-length expansion has also been reported in small Pt clusters subsequent to H chemisorption and attributed to a H-induced decrease in electron density between Pt atoms.<sup>29,40,41</sup> H atoms were bound at the Pt cluster surface for temperatures up to



FIG. 11. (Color online) First NN shell CNs determined by EXAFS analysis for Pt NC samples annealed in Ar,  $O_2$ , or forming gas as a function of mean NC diameter recovered from SAXS analysis (symbols). The solid line represents the values calculated for an FCC spherical particle.



FIG. 12. (Color online) D-W factor as a function of the inverse NC diameter for samples annealed in Ar,  $O_2$ , or forming gas (symbols). The solid lines are linear fits to the experimental values.

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FIG. 13. (Color online) Difference between the bond length of Pt foil and NCs  $(R_{\text{bulk}}-R_{\text{NC}})$ , as a function of the inverse NC diameter for samples annealed in Ar, O2, or forming gas. The solid lines are linear fits to the experimental values.

500 °C.<sup>29,40,41</sup> For the much increased annealing temperatures used herein ( $\leq 1300$  °C), the H content may not be confined to the NC surface but is potentially distributed over the NC volume.

## **IV. CONCLUSIONS**

In summary, we have characterized Pt NCs formed in a-SiO<sub>2</sub> by ion implantation and thermal annealing. TEM and SAXS measurements demonstrated that the NC size is strongly dependent on both annealing temperature and ambient. In contrast, the implantation fluence had a much smaller effect with lower fluences actually yielding larger sizes as attributed to a defect-mediated nucleation process. Compared to other metallic NCs produced under similar conditions, Pt NCs are smaller and exhibit very narrow size distributions.

XANES measurements demonstrated the presence of Pt-H bonding in NCs annealed in forming gas at high temperatures. In large NCs (>3.0 nm), H chemisorption induced a bond-length expansion, a decrease in Pt CN, and an increase in structural disorder as apparent with EXAFS. The surface tension for such hydrogenated Pt NCs was strikingly different than that of bulk material and NCs annealed in Ar or O<sub>2</sub>. Clearly H chemisorptions yields significant structural perturbations in Pt NCs.

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