

Probing the Electronic Density of States of Germanium Nanoparticles: A Method for Determining Atomic Structure

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ABSTRACT

We present first principles electronic structure calculations and photoemission measurements of the change in the valence band DOS of germanium as its dimensions are reduced from the bulk to the nanoscale. By comparing the calculated broadening of the s and s–p band peaks and the energy of surface dangling bonds to the measured DOS, we identify the most likely structure of these nanoparticles. We propose that, in contrast to recent interpretations, small 2–3 nm germanium nanoparticles prepared by gas-phase aggregation have a distorted diamond structure core due to effects of thermal reconstructions of the surface.

The past decade has witnessed dramatic progress in techniques for synthesizing and characterizing semiconductor quantum dots.¹ For II–VI quantum dots such as CdSe, colloidal chemistry approaches have clearly become the synthesis method of choice.^{2,3} For group IV quantum dots (Si and Ge), the lack of surface dipoles weakens the binding of surfactants to the nanoparticles during synthesis, making it difficult to control the growth process. Instead, a variety of alternative approaches have been proposed for synthesizing silicon and germanium quantum dots, including sonification of porous silicon,⁴ reduction of SiCl₄,⁵ inverse micelles techniques,⁶ high temperature and pressure reactions,^{7,8} and physical vapor deposition.⁹

A common challenge for all of these synthesis techniques is characterizing the structure of the resulting nanoparticles. These nanoparticles, which range in size from 1 to 5 nm, contain 50–5000 atoms and only 5–10 monolayers of material. Therefore, while the approximate size and shape of these particles can be estimated with TEM^{5,4}, STM,¹⁰ or AFM,⁹ it is difficult to directly observe the details of their atomic structure, particularly for the smallest 1–3 nm particles.

A common indirect approach for determining the atomic structure of nanoparticles is to compare their measured optical properties with those predicted by theoretical models

of nanoparticles with different sizes, structures, and chemistries. Recent advances in accurate, many-body electronic structure calculations, such as the quantum Monte Carlo (QMC)¹¹ approach, have enabled these techniques to make quantitative predictions of the effect of nanoparticle size,¹² structure,^{13,14} and chemistry¹⁵ on their optical properties. This in turn has provided insights into possible oxygen contamination of nanoparticles¹⁵ and reconstructions of their surfaces.¹⁶

In this paper, we examine an alternative approach for indirect characterization of the atomic structure of nanoparticles. We analyze the electronic density of states (DOS) in the valence band yielding insight into the bonding configuration of the investigated structures. As a test system, we choose to study germanium nanoparticles, synthesized using gas aggregation techniques.¹⁷ In addition to the technological importance of germanium nanoparticles, these nanoparticles are of interest as the structure of the nanoparticles is not fully resolved, and two different phases have been reported: Sato et al.¹⁸ used cluster beam techniques to synthesize particles in the 4–5 nm size range. By comparing the DOS of these clusters with theoretical predictions of the DOS of different structures of *bulk* germanium¹⁹ and early photoemission experiments on amorphous Ge,²⁰ they propose that Ge nanoclusters undergo a phase transition, such such clusters < 3 nm adopt the tetragonal ST-12 phase. In contrast, similar nanoparticles prepared by gas-phase aggregation¹⁷ have been analyzed with electron diffraction and appear to

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adopt the cubic (diamond) phase.¹⁷ Further, photoelectron spectroscopy (PES) measurements suggest a disordered surface region around a crystalline core of the nanoparticles.²² In addition, recent first-principles electronic structure calculations²³ predict the cubic phase to be the more stable phase.

To shed light on this controversy, we adopt a similar approach to the analysis of optical properties described above. First the valence band DOS of a set of germanium nanoparticles produced by physical vapor deposition is measured. Then a series of *ab initio* calculations are used to predict the DOS of model germanium nanoparticles with different sizes, structures, and surface terminations. By comparing these predicted DOS with the measured values, we propose the most likely structure of the experimental samples. It is found that the DOS contains distinct signatures indicating the crystal structure and degree of crystallinity of the nanoparticles and also the structure of the nanoparticle surfaces. Both the ST-12 structure and annealed diamond structure nanoparticles have broadened *s* and *s*-*p* bands compared to the ideal diamond structure. However, in contrast to previous interpretations,¹⁸ we propose that the measured DOS of small (2–3 nm) nanoparticles is most consistent with a thermally annealed cubic, diamond structure where the surface of the nanoparticles is reconstructed.

To measure the valence band DOS synchrotron-radiation-based PES up to 14 eV binding energy was performed. The experiments were carried out at the high-flux, high-resolution undulator beamline 8.0 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.²⁴ For photoelectron detection the ellipsoidal mirror analyzer endstation was used. The joint resolution of the beamline and detector is estimated to be 0.3–0.4 eV. The incoming photon flux was measured with a highly transmissive (>90%) gold grid, and all spectra were normalized with respect to this flux. For the photoemission experiments, a photon energy of $h\nu = 200$ eV was chosen.

The nanocrystals were synthesized in a gas-aggregation type source, which is described in detail in ref 17. The particles were condensed out of the gas phase in a helium buffer gas atmosphere and subsequently deposited *in situ* at the synchrotron facility. Their average size can be tuned from 1 nm to more than 5 nm and they exhibit a narrow size distribution of 20% fwhm. Structural analysis of nanoparticles 4–5 nm in size revealed a bulk-like cubic (diamond) phase,¹⁷ and early photoemission experiments show a distribution of Ge3d surface core-level shifts²² indicating a reconstructed surface of these nanocrystals.

For the PES measurements, carefully outgassed, native-oxygen-passivated silicon wafers were used as substrates. Multiple monolayers of nanocrystals were deposited to obtain a complete coverage of the substrate as monitored by Si2p core level photoemission. The resulting films consisted of individual nanocrystals on top of each other as evidenced by atomic force microscopy.²² To avoid oxidation of the nanocrystal sample from residual gas, the residual gas pressure was kept on the order of 10^{-9} Torr in the synthesis chamber and 10^{-10} Torr in the detector chamber. Analysis

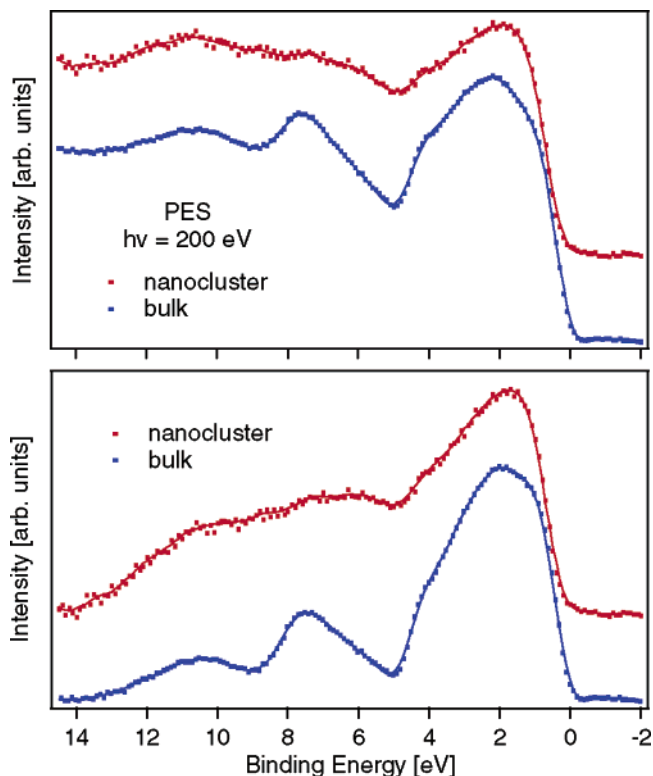


Figure 1. PES valence band spectra (top) and secondary electron background corrected data (bottom) for a bulk crystal and 3.3 nm nanocluster sample. The spectra were acquired with a photon energy of $h\nu = 200$ eV.

of the Ge3d core level photoemission showed the samples to be contamination free.

The valence band PES data for a 3 nm nanocrystal sample and a bulk-crystal reference are shown in the top panel of Figure 1. The spectra were acquired with a photon energy of $h\nu = 200$ eV. In the bulk spectrum the *s*, *s*-*p*, and *p* bands, well described in the literature,^{20,25} can be identified. In the nanocrystal spectrum, however, the *s* and *s*-*p* bands are strongly broadened and merged into one large feature. Additionally, the *p* band is shifted toward lower binding energies. To make the experimental data comparable to the theoretical DOS predictions, the spectra have to be corrected for inelastically scattered electrons. The loss spectrum was approximated by a function with magnitude at each point proportional to the spectrum area at lower binding energy. The background corrected data is shown in the bottom panel of Figure 1.

Our theoretical calculations were performed using the local density approximation (LDA) to density functional theory.²⁶ The atomic cores are represented by norm conserving, Hamann pseudopotentials, and the electronic states are expanded in plane waves with an 11Ry cutoff. This approach has previously been demonstrated to accurately predict the structures of both bulk²⁷ and nanoscale²³ germanium systems. To calculate the DOS for each nanoparticle, the LDA energies of all the occupied electronic states were calculated and then the resulting energy spectrum was Gaussian broadened by 0.4 eV to produce spectra equivalent to the measured spectra. This LDA approach to calculating the DOS

Table 1. Structures of the Calculated Germanium Nanoparticles

sample	composition	core structure	surface structure
A	Ge ₂₁₁ H ₁₄₀	crystalline diamond	H terminated
B	Ge ₂₁₁	crystalline diamond	dangling bonds
C	Ge ₂₁₁	MD relaxed diamond	MD relaxed
D	Ge ₁₄₅ H ₁₀₈	crystalline ST-12	H terminated
E	Ge ₁₄₅	MD relaxed ST-12	MD relaxed

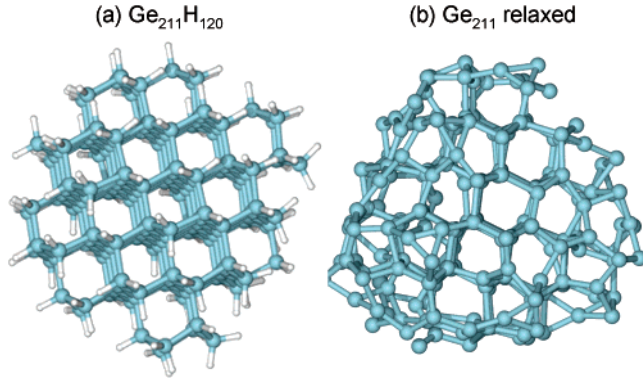


Figure 2. Atomic structures of (a) sample A, Ge₂₁₁H₁₄₀ with a diamond structure core and (b) sample D, Ge₂₁₁ with an MD relaxed structure.

has previously been demonstrated to accurately predict the DOS of bulk semiconductor materials, but to our knowledge these are the first predictions for experimentally realizable nanoparticle systems.

A series of different nanoparticle structures were calculated to examine the effect of different nanoparticle core and surface structures on the DOS. These structures are summarized in Table 1. The reference sample, A, is Ge₂₁₁H₁₄₀. This is a 2 nm germanium quantum dot, with a crystalline diamond structure and a surface fully terminated with hydrogen atoms to remove surface dangling bonds and reconstructions. In sample B, Ge₂₁₁, the surface hydrogen atoms are removed, while freezing the Ge core, to examine the effect of imperfect surface passivation on the DOS. To examine the effect on the DOS of a noncrystalline core, a series of molecular dynamics (MD) simulations were then performed. In sample C the germanium atoms were heated to 1000 K for 1 ps and then cooled to 300 K for a further 2 ps, allowing all the atoms to adopt a thermally equilibrated structure. Finally, to compare the DOS of nanoparticles with a diamond structure core to those with the ST-12 structure, sample D uses the ST-12 Ge₁₄₅H₁₀₈ nanoparticle studied in ref 23 and sample E uses the same MD process applied to sample C to remove the hydrogen atoms and thermally equilibrate this structure.

The simulated atomic structures of samples A and C are shown in Figures 2a and 2b, respectively. Figure 2b shows that heating the nanoparticle to 1000 K has two effects: (i) it anneals the surface structure, introducing reconstructions that remove the dangling bonds present in sample B. (ii) It thermally disorders the core of the nanoparticle about the original diamond crystal structure. Analysis of the structures

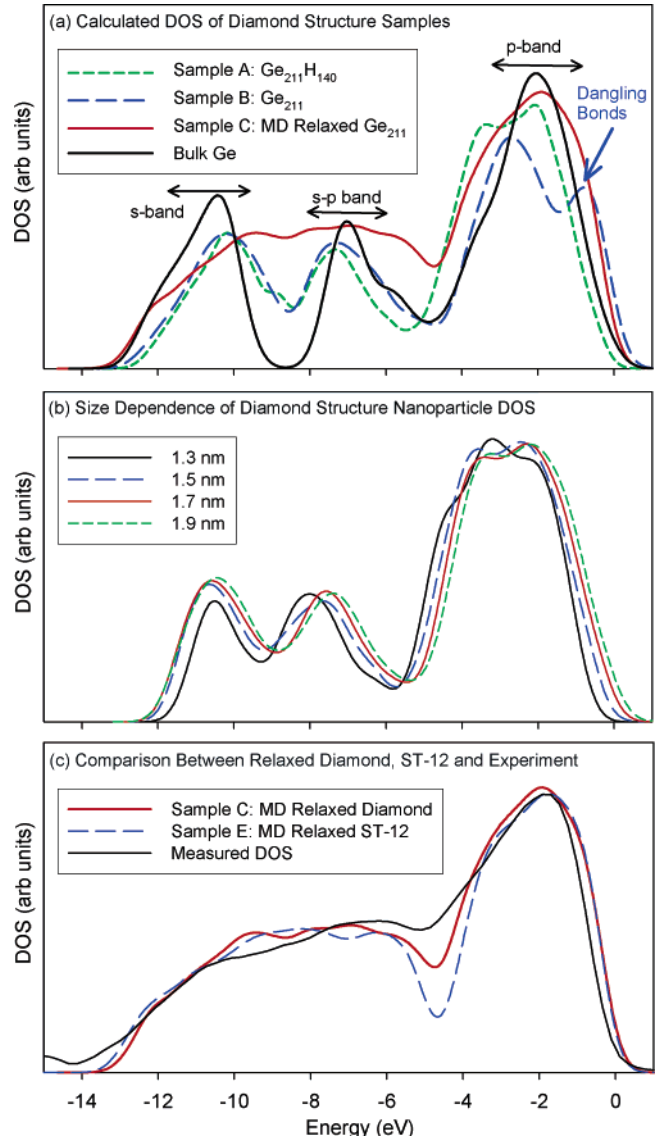


Figure 3. (a) Predicted electronic DOS of the germanium nanoclusters listed in Table 1, (b) calculated size dependence of the DOS for diamond structure nanoparticles, and (c) comparison of calculated diamond and ST-12 DOS with the measured DOS.

of samples A and C shows that the MD simulation disorders the Ge–Ge bond lengths such that the RMS distribution of bond lengths increases from 0.08 Å in sample A to 0.4 Å in sample D. The distribution of Ge–Ge bond angles is also significantly broadened, increasing the RMS deviation from 109.4° from 2° in sample A to 24° in sample C.

To examine the effects of size distribution on the DOS of the nanoparticles, we performed a series of DOS calculations for both hydrogen terminated, crystalline diamond (similar to sample A) and ST-12 (similar to sample D) nanoparticles with stoichiometries Ge₂₈H₃₆, Ge₄₅H₄₈, Ge₈₁H₇₆, Ge₁₁₁H₈₈, and Ge₁₄₅H₁₀₈ which range in size from 0.5 to 2.0 nm.

In Figure 3a we compare the LDA calculated valence electronic DOS for the 2 nm diamond structure, germanium nanoparticle samples A, B, and C shown in Table 1, and bulk germanium.²¹ As expected, bulk germanium exhibits the most distinct features in the DOS, with clearly identifiable s, s–p, and p bands, similar to previous reports in the

literature.²⁰ In the DOS of the perfectly crystalline, hydrogen passivated sample *A*, each of these three bands is also present, with each peak broadened due to the finite size of the cluster. The DOS for sample *B* without passivation shows these same three peaks and an additional higher energy peak above the top of the valence band (see arrow in Figure 3a). By analyzing the location of the states responsible for this peak, it is identified as a band of dangling bond states on the surface of the cluster. Annealing the cluster to produce sample *C* removes these dangling bond states and further broadens the three features. In sample *C* the p-band peak is still clearly distinguishable, but the s and s-p band peaks have almost merged into a single peak.

Figure 3b shows the calculated size dependence of the DOS for hydrogen terminated, diamond structure nanoparticles. It shows that for nanoparticles ranging in size from 1.3 to 2.0 nm the s, s-p, and p peaks are clearly defined and exhibit relatively small size dependent shifts. A similar insensitivity to size is observed for ST-12 structure nanoparticles. This confirms that the signature broadening of the s and s-p bands observed in our measured DOS and calculated DOS for sample *C* is predominantly a result of structural disorder and surface reconstruction and not a simple finite size effect.

In Figure 3c we compare our measured, background corrected DOS with the predicted DOS for samples *C* and *E* (MD relaxed diamond structure and ST-12 structure). We observe that the DOS of both the relaxed diamond and ST-12 structures have s and s-p bands that are significantly broadened with respect to the bulk and hydrogen terminated diamond structure clusters. Both of these calculated DOS closely match our measured DOS, with sample *C* showing the closest agreement.

The additional DOS that leads to the broadening and merging of the s and s-p bands in bulk Ge samples has previously been attributed to the five-membered rings of Ge atoms found in the ST-12 phase, compared to the purely six-membered rings of atoms in the cubic (diamond) phase.¹⁹ In earlier photoemission studies on Ge nanocluster films, produced by means of the cluster beam technique,¹⁸ a similar change in the DOS was observed, and based on these theoretical predictions the particles were interpreted to exhibit the ST-12 phase.²⁸ Here we present an alternative interpretation of the experimental data in which the broadening of the s and s-p bands are assigned to states resulting from surface reconstructions including odd-membered rings of atoms as well as distortions of bond lengths and angles in the core of the nanoparticles. This interpretation is consistent with previous investigations showing that bond length distortions affect the DOS in the lower part of the valence band²⁹ and broadening the distribution of bond angles shifts the p band to lower binding energies.^{19,29} This interpretation of these nanoparticles as diamond structure cores with reconstructed surfaces is consistent with our electron diffraction measurements of slightly larger (4–5 nm) nanoparticles which appear to adopt the cubic (diamond) phase.¹⁷

In conclusion, we present the first predictions and experimental data of the change in the DOS of germanium as its

dimensions are reduced from the bulk to the nanoscale. By calculating the DOS of Ge nanoparticles with a range of structures we identify the signatures in the DOS of surface dangling bonds, surface reconstructions, and distortions of the core structure. The calculated broadening of the s and s-p band peaks and the shift of the p band are consistent with our measured DOS for 3 nm germanium nanoparticle samples. These results are also consistent with recent TEM measurements of larger (4–5 nm) germanium nanoparticles, which clearly demonstrate fringes matching a diamond structure core and recent predictions that the diamond structure is the lowest energy core structure for germanium nanoparticles.²³ We therefore conclude that the most likely structure of small 2–3 nm germanium nanoparticles is a distorted diamond structure core and a reconstructed surface.

We find that comparing measured DOS spectra with theoretical predictions provides an alternative technique for indirectly determining the structure of nanoparticles that is complementary to both existing direct measurements such as TEM and AFM and to comparisons of optical properties with theoretical predictions.

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