Pressure-Induced Structural Transformations in Si Nanocrystals: Surface and Shape Effects

Sarah H. Tolbert,[1] Amy B. Herhold,[1] Louis E. Brus,[2] and A. P. Alivisatos[1]
[1]*Department of Chemistry, University of California, Berkeley, California 94720*

and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
[2]*AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974*

(Received 26 May 1995)

The kinetics of solid-solid phase transitions are explored using pressure-induced structural transformations in Si nanocrystals. In agreement with the predictions of homogeneous deformation theories, large elevations in phase transition pressure are observed in nanocrystals as compared to bulk Si, and high pressure x-ray diffraction peak widths indicate an overall change in nanocrystal shape upon transformation. In addition, unlike the BC8 phase recovered in bulk Si, amorphous Si nanoclusters are obtained upon release of pressure, providing an example of kinetic size control over solid phases. [S0031-9007(96)00344-4]

PACS numbers: 64.70.Kb, 61.46.+w, 68.35.Rh, 81.30.–t

Recent progress in the preparation of finite-sized semiconductor crystallites has created an opportunity to better understand first order solid-solid phase transitions. Pressure-induced solid-solid phase transitions in extended semiconductors are generally highly hysteretic, are nucleated at defects, and typically involve multiple nucleations and domain fracture [1]. The space groups of the two phases frequently have a group-subgroup relationship [2]. This has led to the conclusion that these phase transitions must involve specific motions that carry the solid from one structure to another. Formally, this motion belongs to a specific irreducible representation of the higher symmetry group [2]. Convincing evidence for this model lies in the observation of soft modes, or vibrations of the crystal that tend towards lower frequency as the transition pressure is approached [3]. In this Letter, we demonstrate that studies of pressure-induced transformations in nanocrystals provide another route for observing the pathway of solid-solid phase transitions, as well as a means of explaining the hysteresis and fragmentation observed in bulk transformations.

Nanocrystals are smaller than the fragment domains that result when a single crystal undergoes a solid-solid phase transition. In addition, unlike bulk crystals, nanocrystals may be prepared with no interior defects, albeit with a large number of surface atoms. Nanocrystals of CdSe have been observed to transform from wurtzite to rocksalt structures as single domains, with only one nucleation event per crystallite [4]. Further, these CdSe studies [4] demonstrated that the smaller the nanocrystallite, the higher the transformation pressure. These observations led to a hypothesis, consistent with a homogeneous deformation mechanism for transition, in which the nanocrystals change shape upon structural transformation. If the nanocrystals have dominantly low index surfaces as synthesized in the low pressure phase, then the shape change must result in high index, high energy surfaces in the high pressure phase provided the temperature is low compared to the surface diffusion temperature. These newly created high energy surfaces destabilize the high pressure phase and, together with the absence of interior defect sites to initiate nucleation, explain the elevation in transformation pressure with the reduction of nanocrystal size.

The homogeneous deformation hypothesis therefore requires that nanocrystals change shape upon undergoing pressure-induced solid-solid transformations. Observing this change in shape, however, is not a simple matter [5]. At atmospheric pressure, the shape of a nanocrystal can readily be observed using transmission electron microscopy [6]. The pressure-induced transitions observed to date, although hysteretic, are reversible, so that back transformation prevents simple analysis of shape in recovered samples. The shape must therefore be determined at high pressure. In this Letter we demonstrate that x-ray diffraction linewidths can be used to observe the change in shape that occurs when Si nanocrystals are converted under pressure from the diamond to the primitive hexagonal structure.

Beyond access to the microscopic nature of phase transitions, another primary goal of nanocrystal research is the search for nonstandard bonding geometries in finite size. In very small clusters, these unusual geometries are sometimes found to be thermodynamically stable. In larger nanocrystals, however, the effect of size is not sufficient to stabilize these novel bonding geometries. In dynamic processes such as crystal growth and structural transformations, however, the possibility exists to use smaller variations in thermodynamic stability to trap *metastable* structures in larger crystallites. This effect is seen in the growth of kinetically trapped rocksalt phase CdS nanocrystals in a highly ionic polymer matrix [7]. In this work, we demonstrate the kinetic trapping of amorphous Si (*a*-Si) nanoclusters upon release of pressure from the β-Sn phase.

High pressure x-ray diffraction and optical absorption were used to examine the phase stability of SiO_2 coated Si nanocrystals [8]. This covalent semiconductor was chosen because it contrasts well with previous high pressure studies on ionic semiconductor nanocrystals [4,9]. The lack of ionic stabilization in Si results in an extremely rich phase diagram: Bulk Si has been observed in as many as 11 different solid structures between atmospheric pressure and 45 GPa. Extensive theoretical and experimental work has gone into understanding the many stable phases of bulk Si. Bulk Si transforms from the diamond structure to the β-Sn phase at approximately 11 GPa [10,11]. The β-Sn phase undergoes a transformation to the closely related *Imma* structure at 13 GPa [12]. The *Imma* phase then converts to a primitive hexagonal (PH) structure near 16 GPa [11–13]. By 40 GPa, bulk Si is found in a hexagonal close packed structure (HCP) [13]. Upon partial release of pressure from 40 GPa, the PH and β-Sn phases are again observed [11]. Bulk Si does not, however, transform back to the diamond phase upon full release of pressure. Instead, a number of metastable crystalline [14] and amorphous [15] phases are observed. The most common of these, known as BC8, is a slightly distorted tetrahedral structure [16] and is preceded by the more distorted R8 phase [17].

The nanocrystal samples used in these experiments consist of diamond phase Si crystallites coated with an approximately 15 Å thick layer of SiO_2 [8]. The nanocrystals were synthesized by gas pyrolysis [8] of Si_2H_6 and O_2, and characterized using transmission electron microscopy (TEM), electron diffraction, x-ray diffraction, luminescence, and optical absorption. Nanocrystal sizes ranged from 100 to 500 Å in diameter with size dispersions varying from 20% for small samples to 35% for larger samples. Samples were observed to be highly crystalline, both by TEM and by agreement of TEM sizes and sizes calculated from x-ray diffraction peak widths.

High pressure experiments were carried out using piston-cylinder style diamond anvil cells; pressures were determined using standard ruby fluorescence techniques. The Si nanocrystal samples were dissolved in ethylene glycol (EG). Under pressure, EG forms a glass which deforms in a quasihydrostatic manner up to about 10 GPa. Above this pressure, EG will support significant pressure gradients. High pressure optical absorption data were obtained using a scanning Cary model 118 UV–visible spectrometer. High pressure x-ray diffraction experiments were carried out on at the Standford Synchrotron Radiation Laboratory (SSRL). Monochromatic 20 KeV x rays were utilized in an angle dispersive geometry. Diffraction peak widths were deconvoluted for both the instrument function and broadening due to pressure gradients; a Gaussian distribution of pressures around the measured pressures was assumed. Pressure broadening was found to change the peak widths by less than 20%. Domain sizes were calculated from the peak widths using the Scherrer formula.

Like bulk Si, Si nanocrystals are indirect gap semiconductors. Optical absorption thus shows only a featureless rising edge in the diamond phase [18]. Despite the lack of discrete features, the onset of structural transformation can be easily seen in the absorption spectra as a large increase in optical density (O.D.) [19] and the loss of the $\sqrt{\text{O.D.}}$ versus energy dependence in the spectrum. Figure 1(a) shows the change in absorbance observed in 96 Å diameter crystallites. These hysteresis data are constructed by integration of the absorption intensity between 1.95 and 2.05 eV. Similar results are obtained by integration at any other comparable visible wavelengths. The upstroke semiconductor-to-metal transformation in Fig. 1(a) appears at approximately 22 GPa, in sharp contrast to the bulk Si diamond to β-Sn transition which takes place around 11 GPa [10,11]. Also, in contrast to bulk Si, nanocrystals appear to recover to a semiconducting phase, while the metastable BC8 phase most commonly observed in recovered bulk Si is a semimetal [16].

Since optical absorption cannot distinguish the many metallic high pressure phases of Si, diffraction experiments are required to determine the actual structures involved. High pressure x-ray diffraction powder patterns obtained on 492 Å Si nanocrystals are presented in Fig. 1(b). Nanocrystals are initially in the diamond phase [20] (circled 1) and are seen to be stable to well above the bulk Si diamond to β-Sn phase transition pressure of 11 GPa [10,11]. With application of sufficient pressure, however, the system can be converted to the PH structure [13] (2). Upon partial release of pressure, an *Imma* phase is observed (3) as well as a β-Sn phase (not shown) [12]. Upon full release of pressure, instead of recovering the metastable BC8 phase [16] observed in bulk silicon, the sample appears to form *a*-Si (4).

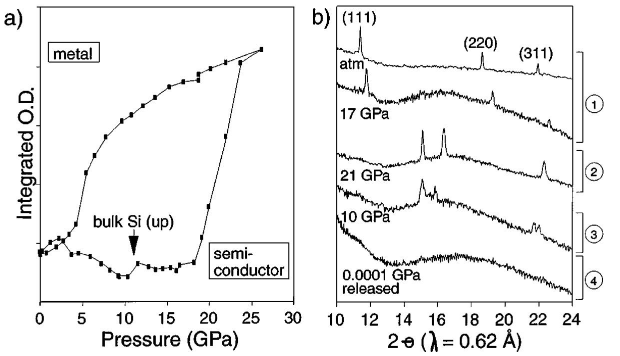

FIG. 1. (a) Phase behavior for 9.6 nm diameter Si crystallites coated with SiO_2 measured by optical absorption. The metal-semiconductor transition is seen at about 22 GPa (upstroke) and 5 GPa (release). The arrow marks the bulk Si diamond to β-Sn transition pressure. (b) High pressure x-ray diffraction data obtained on 49 nm diameter Si nanocrystals coated with SiO_2. Circled numbers are explained in the text.

A striking feature of the high pressure behavior observed in Si nanocrystals is the extreme elevation in upstroke phase transformation pressure observed in crystallites as large as 500 Å in diameter. These nanocrystals contain $\sim 10^6$ atoms per crystallite, so the vast majority of atoms are in an almost completely bulklike interior environment. A possible origin for this elevation in transition pressure is a low density of defect nucleation sites for transformation in nanocrystals resulting from the crystalline nature of the Si lattice and the high quality Si/SiO$_2$ interface [21,22]. This hypothesis requires further testing, since it appears that in CdSe and CdS nanocrystals, which also show a substantial elevation in transition pressure, the surface acts as a nucleation site [23]. Insight gained from studies on CdSe and CdS nanocrystals can thus be used to postulate that high pressure phases are destabilized because the surface structure is disrupted upon structural transformation [4]. It is highly unlikely that the stable Si/Si/O$_2$ interface can survive intact when the interior Si atoms, but not the exterior SiO$_2$ atoms, undergo a phase transition. This results in the destruction of the low energy Si/SiO$_2$ interface upon structural transition. Large changes in surface energy result in significant elevations in transformation pressure, even for big crystallites. Analogous results have been observed in GaAs/AlAs superlattices. [24]. Future experiments that include the influence of different surfaces and different thicknesses of oxide will be required to fully determine the origin of the phase transition elevation.

Because of the symmetry of the structures involved, Si nanocrystals can be used to seek evidence for a path driven change in the shape of a nanocrystal upon transformation, providing direct confirmation of the homogeneous deformation theory of phase transitions in solids [3]. Propagating atoms of a diamond phase crystallite along the proposed transition path produces a crystallite with a long axis in the (001) direction, and shorter axes in the plane of the degenerate (100) and (010) directions [25,26]. By examining the widths of the (100) and (001) diffraction peaks, evidence for overall changes in nanocrystal shape upon transformation can be obtained [27].

Figure 2 shows an enlargement of the Si nanocrystal PH diffraction pattern at 21 GPa. The peak widths in the (100) and (001) directions are clearly different. When deconvoluted for the instrument function and pressure gradients and averaged over multiple diffraction patterns between 20 and 30 GPa, these peak widths correspond to domain sizes of 549 ± 68 Å in the (001) direction and 267 ± 10 Å in the (100) direction. This results in an aspect ratio of 2.1 ± 0.3, in good agreement with a value of ~1.9 expected from the change in unit cell shape along the most probable transition path [25,26]. The domain size in the (101) direction is in reasonable agreement with the geometric average of these two domains. These results strongly suggest an overall change in nanocrystal shape upon transformation. Note that the alternative explanation, that the nanocrystals fragment upon transformation, can be ruled out from the data: At 17 GPa, a pressure where the nanocrystals are still clearly in the diamond phase, some broadening of the diffraction peaks in comparison to atmospheric pressure is seen due to pressure inhomogeneity and strain. While the peak widths in the PH (100) direction are significantly broader than the 17 GPa diamond phase lines, the peak widths in the PH (001) direction are actually narrower than the 17 GPa diamond phase lines. This effect cannot result from fragmentation. The difference in peak widths thus provides direct evidence for an overall change in nanocrystal shape. The results are a confirmation of the homogeneous deformation theory of phase transformations.

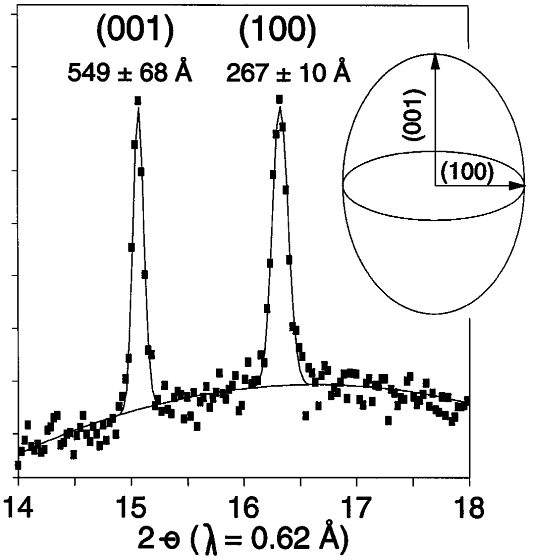

FIG. 2. Expanded view of Fig. 1(b) (circled 2) shows that the (001) and (100) diffraction peak widths differ. The difference in domain size is due to a shape change in the crystallites.

Another observation of interest is the recovery of *a*-Si upon release of pressure in nanocrystals, in contrast to the recovery of the metastable BC8 phase in bulk Si. Amorphous Si is a metastable phase of Si which can be kinetically trapped upon release of high pressure under certain circumstances [15]. Under the conditions of this experiment, *a*-Si is not kinetically favored in the bulk. A wide variety of experimental and theoretical work, however, has suggested that *a*-Si is more stable than diamond phase Si in very small size nanoclusters (below ~30 Å in diameter) [28]. This result is reasonable as long range bonding is not required to stabilize the amorphous phase. While *a*-Si is not predicted to be thermodynamically stable in larger sizes, it is likely that some stabilization of the amorphous phase persists even for 500 Å nanocrystals. These ideas can be combined to explain the experimental result. The amorphous phase, while not the thermodynamic ground state, is stabilized in finite size, and, as a result, the barrier for the β-Sn to *a*-Si reaction is reduced in comparison to the β-Sn to BC8 reaction channel. An additional kinetic factor favoring the dynamic formation of *a*-Si in finite size systems can also be found: As the β-Sn to a-Si transition is diffusive (that is, it has no symmetry prescribed transition path), no change in the nanocrystal shape is required upon transition, and thus there are no symmetry dictated changes in the surface structure. All of this points to an important idea in nanocrystal studies: While "novel" bonding geometries do not generally appear to be thermodynamically stable in large crystallites, it is possible to use kinetics in combination with the slightly altered stability of higher lying states to trap metastable structures. This general phenomenon is worth further exploration.

In summary, high pressure optical absorption and x-ray diffraction studies show large elevations in the semiconductor-to-metal structural transformation in SiO_2 coated Si nanocrystals. The elevation can be attributed to the absence of available nucleation sites and to the destruction of the low energy Si/SiO_2 interface at the structural transformation. Recovery of a-Si clusters upon release of pressure shows further how the observed phase stability in nanocrystals can be controlled by kinetics: Formation of a-Si clusters is demonstrated to be a kinetically, rather than a thermodynamically, controlled process. Finally, overall changes in the shape of a nanocrystal upon transformation are observed by x-ray diffraction in Si crystallites. These changes, induced by the motion of interior atoms along a transition path, are the root of kinetic control of phase stability in nanometer scale systems. Further, the observed changes in nanocrystal shape provide direct evidence that homogeneous deformations play a role in phase transitions in semiconductors [29].

The authors would like to thank Christopher Johnson for his help with this research effort, Benjamin Schwartz for a critical reading of the manuscript, and David Schiferl for the use of his diffraction cell. This work was supported by the Department of Energy (DOE) under Contract DE-AC0376SF00098. X-ray diffraction experiments were performed using the facilities of the University of California–LLNL PRT at SSRL, which is operated by the DOE, Division of Chemical Sciences.

---

[1] R.E. Hanneman, M.D. Banus, and H.C. Gatos, J. Phys. Chem. Solids **25**, 293 (1964); U.C. Venkateswaran, L.J. Cui, B.A. Weinstein, and F.A. Chambers, Phys. Rev. B **45**, 9237 (1992).

[2] F. Falk, J. Phys. (Paris), (Colloq.) **43**, C4-3 (1982), and references therein.

[3] D.J. Chadi and R.M. Martin, Solid State Commun. **19**, 643 (1976); B.A. Weinstein, in *High Pressure Science and Technology,* edited by K.D. Timmerhaus and M.S. Barber (Plenum, New York, 1979), Vol. 1 p. 141; S.-K. Chan, Mater. Sci. Forum **56-58**, 101 (1990); T.P. Dougherty *et al.,* Science **258**, 770 (1992).

[4] S.H. Tolbert and A.P. Alivisatos, Science **265**, 373 (1994); S.H. Tolbert and A.P. Alivisatos, J. Chem. Phys. **102**, 4642 (1995).

[5] Observation of macroscopic changes in crystal shape upon structural transformation have been made in some temperature induced transformation molecular crystals: W.L. Fraser and S.W. Kennedy, Acta Crystallog. Sect. B **28**, 3101 (1972); S.W. Kennedy, J.H. Patterson, R.P. Chaplin, and A.L. Mackay, J. Solid State Chem. **10**, 102 (1974).

[6] J.J. Shiang, A.V. Kadavanich, R.K. Grubbs, and A.P. Alivisatos, J. Phys. Chem. **99**, 17 417 (1995).

[7] J. Lin, E. Cates, and P.A. Bianconi, J. Am. Chem. Soc. **116**, 4738 (1994).

[8] K.A. Littau, P.J. Szajowski, A.J. Muller, A.R. Kortan, and L.E. Brus, J. Phys. Chem. **97**, 1224 (1993); W.L. Wilson, P.F. Szajowski, and L.E. Brus, Science **262**, 1242 (1993).

[9] A.P. Alivisatos, T.D. Harris, L.E. Brus, and A. Jayaraman, J. Chem. Phys. **89**, 5979 (1988); X.S. Zhao, J. Schroeder, P.D. Persans, and T.G. Bilodeau, Phys. Rev. B **43**, 12 580 (1991); M. Haase and A.P. Alivisatos, J. Phys. Chem. **96**, 6756 (1992).

[10] J.C. Jamieson, Science **139**, 762 (1993).

[11] J.Z. Hu and I.L. Spain, Solid State Commun. **51**, 263 (1984).

[12] M.I. McMahon and R.J. Nelmes, Phys. Rev. B **47**, 8337 (1993); M.I. McMahon, R.J. Nelmes, N.G. Wright, and D.R. Allan, Phys. Rev. B **50**, 739 (1994).

[13] H. Olijnyk, S.K. Sikka, and W.B. Holzapfel, Phys. Lett. **103A**, 137 (1984).

[14] Y.-X. Zhao, F. Buehler, F.R. Sites, and I.L. Spain, Solid State Commun. **59**, 679 (1986).

[15] M. Imai, K. Yaoita, Y. Katayama, J.-Q. Chen, and K. Tsuji, J. Non-Cryst. Solids **150**, 49 (1992).

[16] R.H. Wentorf and J.S. Kasper, Science **139**, 338 (1963); F.P. Bundy, J. Chem. Phys. **41**, 3809 (1964).

[17] J. Crain *et al.*, Phys. Rev. B **50**, 13 043 (1994).

[18] S.H. Tolbert, A.B. Herhold, C.S. Johnson, and A.P. Alivisatos, Phys. Rev. Lett. **73**, 3266 (1994).

[19] B. Welber, C.K. Kim, M. Cardona, and S. Rodriguez, Solid State Commun. **17**, 1021 (1975).

[20] JCPDS-ICDD powder pattern card #27-1402, (c) 1989.

[21] E. Yablonovitch, Science **246**, 347 (1989).

[22] K. Mizushima, S. Yip, and E. Kaxiras, Phys. Rev. B **50**, 14 952 (1994).

[23] S.H. Tolbert, Ph.D. Thesis, UC Berkeley, 1995.

[24] L.J. Cui, U.D. Venkateswaran, B.A. Weinstein, and F.A. Chambers, Phys. Rev. B **45**, 9248 (1992).

[25] The (100) diffraction peak actually averages over two unequal orthorhombic axes in the plane perpendicular to the (001) direction.

[26] M.T. Yin and M.L. Cohen, Phys. Rev. B **26**, 5668 (1982); R.J. Needs and R.M. Martin, Phys. Rev. B **30**, 5390 (1984); K.J. Chang and M.L. Cohen, Phys. Rev. B **31**, 7819 (1985); S.P. Lewis and M.L. Cohen, Phys. Rev. B **48**, 16 144 (1993).

[27] A. Guinier, *X-Ray Diffraction in Crystal* (Freeman, San Francisco, 1963), p. 137.

[28] S. Veprek, Z. Iqbal, and F.-A. Sarott, Philos. Mag. **45**, 137 (1982); U. Röthlisberger, W. Andreoni, and M. Parrinello, Phys. Rev. Lett. **72**, 665 (1994).

[29] See also L.E. Brus, J.A.W. Harkless, and F.H. Stillinger (to be published).