

Evidence of an antisymmetry relation between a nanocavity and a nanoparticle: a novel nanosize effect

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 L253

(<http://iopscience.iop.org/0953-8984/15/17/101>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.119

The article was downloaded on 19/05/2010 at 08:46

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Evidence of an antisymmetry relation between a nanocavity and a nanoparticle: a novel nanosize effect

Xianfang Zhu¹

Department of Electronic Materials Engineering, Research School of Physical Science and Engineering, Australian National University, Canberra, ACT 0200, Australia
and
Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

E-mail: zhux@physast.uga.edu and xianfangzhu@hotmail.com

Received 14 February 2003

Published 22 April 2003

Online at stacks.iop.org/JPhysCM/15/L253

Abstract

A critical modelling of the nonequilibrium thermodynamic properties of nanocavities and nanoparticles is presented. We first correlate our newly observed experimental results about nanocavities in silicon that can shrink during energetic-beam irradiation with the available experimental phenomena of nanoparticle instabilities. Several new concepts, which challenge our current understanding of science, are put forward and a novel universal antisymmetry relationship between a nanoparticle and a nanocavity in condensed matter is revealed.

If a nanometre-sized particle (nanoparticle) in a vacuum is thought to be a cluster of atoms, a nanometre-sized cavity (nanocavity) in condensed matter can be considered as a cluster of vacancies. These two metastable condensed matter structures have an antisymmetry relation with respect to their mass and they can also demonstrate an antisymmetry relation with respect to other properties. For example, nanoparticles demonstrate an unusually low melt point [1–6], nanocavities in crystalline silicon (c-Si) intriguingly attract or getter loosely bonded or fast diffusion atoms [7–10] or mobile Si interstitials during ion implantation [11]. Although there is no full theoretical explanation, it is believed that the reason for these apparently diverse phenomena lies in their fundamental physics: a nanoparticle tends to dissociate and a nanocavity tends to shrink, both to an extent which is unpredictable from classical thermodynamic statistics theory. This is probably because both nanoparticles and nanocavities have a uniquely nanometre-curved surface-atom dangling-bond structure, which is believed

¹ Address for correspondence: Department of Physics and Astronomy, University of Georgia, Athens, GA 30602, USA.

to constitute the strikingly large driving force for such instabilities in nanostructures. This unique surface dangling-bond structure is believed to be fundamentally different from our current consideration of nanosize effects. There is a lot of evidence to show nanoparticle instability, but there is relatively little evidence to demonstrate nanocavity instability; although from the antisymmetry relationship in nanostructures as proposed above, many other novel properties of nanocavities can be predicted or designed. Recently, several experiments designed using the above principle showed that nanocavities in Si are indeed unstable and can shrink under irradiation from energetic beams [11–14]. However, neither a full understanding nor a correlation of the phenomena were achieved. In particular, a correlation of the above nanocavity instabilities with the well-known nanoparticle instabilities has never been explored and, therefore, the deep insight which such evidence for nanocavity instabilities would have provided has not been achieved either. In this letter, we describe, using critical modelling and comprehensive analysis, a further study of both the instabilities of nanoparticles and the instabilities of nanocavities. The study leads to two new concepts: (1) the nanometre-curved surface dangling-bond structure and (2) the antisymmetry relation between a nanoparticle and a nanocavity. The findings could offer an immediate prediction for fast sintering and superplasticity of nanoceramics. These findings are very meaningful for the future control of the fabrication of the next generation of nanoscale Si devices as well as for several other potential applications² [15] related to nanocavities in Si. The findings have similarly important implications for chemistry, biology, and medicine as demonstrated by emerging findings about nanocavities. In biology and medicine, in particular, there is widespread research interest in using nanocavity (shell-core) structures to design and build biological composites [16] and protein [17] structures at the molecular level and the concepts put forward in this letter will help this work. For example, a recent exciting science report [18] that man-made cells with nanocavities can capture and get rid of heavy poisonous elements (like Cd and Pb) in the human body implies a direct application of the principle given in this letter.

For the convenience of correlation with the well-known nanoparticle case and ensuing modelling, some key evidence relevant to this topic, concerning the nanocavity instabilities induced by energetic-beam irradiation in Si, that has appeared in recently published results [11–14] is first briefly summarized here.

- (1) Nanocavities created in crystalline Si by H implantation followed by annealing [9] have many dangling bonds on the surface of their inner wall. These dangling bonds give rise to extra high surface energy in the system, which constitutes a potential to drive the cavities to shrink and getter impurities in Si as mentioned before. However, without any external materials being gettering to the cavity sites or being subjected to any athermal activation, the so-created cavities in crystalline Si are quite stable and do not shrink at temperatures below 1000 °C.
- (2) If irradiated by self-ion beams at elevated temperatures, nanocavities in c-Si shrink by filling implanted atoms. This is called external shrinkage [19]. Specifically, it was found that if, during self-ion irradiation at temperatures of 300 °C or above, the Si surrounding the cavities is kept crystalline during the ion irradiation then the cavities behave as gettering sites for the implanted, mobile self-interstitials (self-gettering) [11]. Because the filling materials come only from an external source, this shrinkage is obviously slower. Alternatively, this process can be viewed as if the shrunk open volume diffuses as vacancies from the cavities out of the bulk sample into the surrounding space, where the implanted,

² The potential applications include (1) photoluminescence from porous Si induced via ion implantation (Zhu *et al.*, project under investigation), (2) gettering via nanocavities in Si [8], (3) smart-cut via nanocavities (see [15], also, Zhu *et al.*, unpublished work), and (4) low-*k* dielectric materials from nanocavities [20].

mobile self-interstitials serve as bridging carriers for the vacancies in the sample. The driving force for the external shrinkage is the cavity surface energy and it could also be affected by the ion cascade effect.

- (3) If the above ion-irradiation temperatures are at or below 100°C (down to the liquid nitrogen temperature), the instability of nanocavities is more pronounced and the nanocavities shrink much faster. In this case, it was found that the Si surrounding the cavities is preferentially amorphized and most of the shrunk volume of the cavities is believed to dissolve into the surrounding amorphized zone whereas the external shrinkage by self-gettering is believed to contribute less to the whole shrinkage. The former contribution is called internal (or intrinsic) shrinkage. The internal shrinkage process always accompanies the preferential amorphization because amorphization of a crystalline material has a positive activation volume [19]. It was observed that the amorphization of Si surrounding the cavities facilitates and speeds up the internal shrinkage. Hence, the internal shrinkage can be viewed as if the shrunk open volume diffuses from the cavities as vacancies into the a-Si surrounding the cavities or the atoms in the surrounding a-Si fill up the cavities. It will be seen in later modelling that in this way the amorphization (randomly arranged atoms) of Si surrounding the cavity makes a nanocavity closer to the antisymmetry relation with a nanoparticle as shown in figures 1 and 2 and therefore possibly also enhances the nanosize effect. The internal shrinkage is not only driven by the cavity surface energy but also by athermal activation of the energetic-beam irradiation [19]. The detailed relation of the internal shrinkage to the preferential amorphization and the athermal activation effect of the energetic beam are fully discussed in another paper [19]. Because of the observed, unpredictable, strong gettering ability of nanocavities in Si, a possible contribution to the ion-irradiation-induced shrinkage from gettering of the implanted atoms could not be excluded, even when an extremely thin cross-sectional transmission electron microscopy specimen was used in the *in situ* observation [14] where the projected range of the energetic ions is supposed to exceed the specimen thickness. Moreover, the ion-irradiation-induced athermal activation is complicated by the ion cascade effect. This creates problems when analysing the nanosize effect and also athermal activation effect during the ion-irradiation-induced internal shrinkage of the nanocavity.
- (4) To avoid the external gettering of implanted atoms and the ion cascade effect, a pure internal shrinkage of the same nanocavities in Si induced by energetic electron-beam irradiation was observed [21]. In this case, the predicated nanosize effect was detected and the real athermal activation effect on the shrinkage was also confirmed. Nevertheless, it is very surprising that the nanosize effect seems only to be operative within a certain size range. More specifically, the experiment showed that the shrinkage becomes much faster than predicted from classic theory when the cavity diameter is less than about 8 nm. However, the shrinkage slows down again and finally no detectable size change is observed once the cavity diameter shrinks to about 2 nm. Although passivation (or gettering) by local trace impurities in the very small cavities³ is inevitable and complicates the quantitative analysis, the experimental results definitely show that the nanosize effect is operative within a certain range when the cavities shrink to nanometre size.
- (5) It is also amazing that the shape of cavities always stays spherical during shrinkage either during ion irradiation or during electron-beam irradiation. This indicates that the surface energy must be unusually high so as to ensure a high surface mass diffusion under irradiation.

³ The gettering ability is supposed to increase dramatically with decreasing size of the nanocavities.

- (6) Another relevant piece of evidence concerns the observed liquid-like structure and wetting ability of the preferentially amorphized Si surrounding the cavities during irradiation. The strong wetting ability suggests that a so-created a-Si zone contains a very high concentration of vacancies (or dangling bonds). It also further supports the proposed mechanism that the vacancies are emitted from the cavities during internal shrinkage.

It is widely accepted that both the nanosize effect and the quantum size effect⁴ occur when the size confining a condensed matter system is so small that it becomes comparable to the lattice distance. The current nanosize effect on nanostructure thermodynamic instabilities is generally explained by a contribution from a high ratio of disordered surface atoms whereas the quantum size effect is expected when an electron energy level is quantized. This is normally referred to as the nanoparticle case. Nevertheless, from the above explanation, the observed striking shrinkage of nanocavities, the corresponding intriguing preferential amorphization, the arrestingly strong gettering ability of nanocavities, and, in particular, the directly observed nanosize effect on nanocavity internal shrinkage are all hardly expected. To explore this new nanosize effect, it would be interesting to look at the internal shrinkage process of a nanocavity in another way, as shown in figure 1 and then antisymmetrically correlate it to the case of a nanoparticle. A nanocavity can be construed as a cluster of many vacancies and its shrinkage can be thought of as the diffusion of vacancies out of the cavity into the a-Si matrix surrounding the cavity. In contrast, a free nanoparticle is a cluster of many atoms and its dissociation is a process of diffusion of the atoms out of the particle and evaporation into space. Figure 1 schematically illustrates how a nanoparticle and a nanocavity might behave under external excitation, i.e. dissociation of a nanoparticle and shrinkage of a nanocavity. In detail, when being subject to external excitation such as heating or any energetic-beam irradiation, a nanocavity (a cluster of randomly distributed vacancies) would shrink or condense by emitting vacancies out of the cavity into its surrounding matrix which would consist of random distributed atoms (amorphous structure); a nanoparticle (a cluster of random distributed atoms or an amorphous structure) would dissociate or evaporate by emitting atoms out of the particle into its surrounding free space (randomly distributed vacancies). It is experimentally well-known that when particle size is reduced to the nanometre range its melting point and evaporation point drop with size faster than predicted by classical thermodynamics [3]. In this context, it may be possible to assert that the shrinkage of nanocavities may occur in a similar way. Such phenomena cannot be simply ascribed to the larger contribution of the surface atoms or a quantum size effect in terms of modification to the electron energy band structure. Although a detailed theoretical explanation is impossible at this stage, the surface bonding arrangements will be explored in the discussion below. Let us consider the nanoparticle case first. The surface atomic arrangement of a nanoparticle is shown schematically in figure 2. When a particle size (r) becomes comparable to the lattice constant (d) or the dangling-bond length, the angle (θ) associated with the negative curvature of a nanoparticle surface will be appreciable. This would cause a substantial change to the bonding structure of the surface atoms on the nanoparticle. Thus, an additional tensile stress would build-up on the nanoparticle surface and effectively increase the surface

⁴ Here, for the first time the nanosize effect is clarified into two fundamentally different aspects. That is, the nanometre-curved surface-atom dangling-bond structure effect and the quantum-size confinement effect. Although the quantum size confinement effect causes the quantization of electron energy level, which lays the base for the development of quantum-sized optoelectronic materials, this letter mainly focuses on the nanometre-curved surface-atom dangling-bond structure effect (including its consequent distortion of local lattice and symmetry), which are responsible for the thermodynamic instability of a nanostructure.

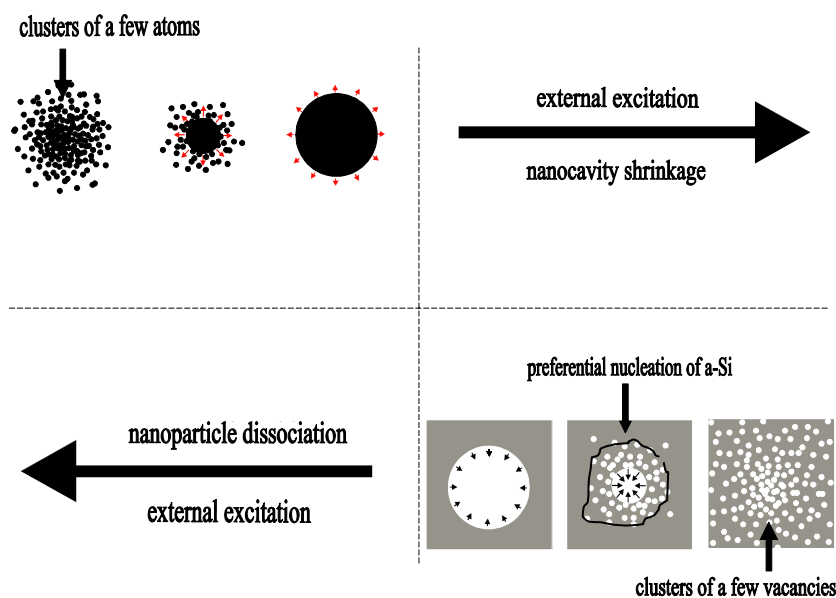


Figure 1. Schematic illustration of the antisymmetry relation between a nanocavity and a nanoparticle.

(This figure is in colour only in the electronic version)

energy. Another important observation is that the ‘Debye temperature’⁵ [22] of a nanoparticle is lower than that of bulk material. Consequently, it can be further inferred that because of the surface tensile stress, the vibration frequency of the surface dangling bonds would be decreased and thus the Debye temperature of a nanoparticle would be lower and cause the nanoparticle to melt. The additional surface energy caused by the negatively curved dangling-bond structure constitutes the driving force for the nanoparticle to dissociate or melt. However, if a nanoparticle is of the size of a cluster of several atoms, the tensile stress may vanish and such a cluster would be stable until the ambient temperature is further increased.

Turning now to the nanocavity case, a schematic diagram of the nanocavity case is also shown in figure 2. When the size (r) of a cavity approaches the lattice constant or the dangling-bond length (d), the angle (θ) related to the positive curvature would be considerable. Thus, a compressive stress would be expected to build up on the surface of the inner wall of a nanocavity. This compressive stress may provide an additional surface energy to drive the nanocavity to shrink. Or, in other words, the compressive stress would possibly lead to a speeding up of the vibration of the dangling bonds on the nanocavity surface and thus may increase the Debye temperature of a region surrounding the nanocavity and induce the nanocavity to condense and get other atoms. However, if a nanocavity is reduced to the size of a cluster of several vacancies, this compressive stress may vanish and hence a small vacancy cluster may be

⁵ ‘Debye temperature’ here is not a clear concept as exactly defined in the case of a crystalline solid. As a particle reaches nanosize, most of the atoms in it will deviate from their equilibrium positions (amorphous or gas-like) and will lose translational symmetry. It is hard to define the concept of lattice in such a structure. The case is the same when referring to the Debye temperature of the inner wall of a nanocavity in this letter. Therefore, the concept of Debye temperature in a nanostructure or in an amorphous structure cannot be defined in the strict sense. It will be seen that all the other traditional concepts in science are always challenged when they are borrowed to account for non-equilibrium, amorphous, or nonlinear phenomena.

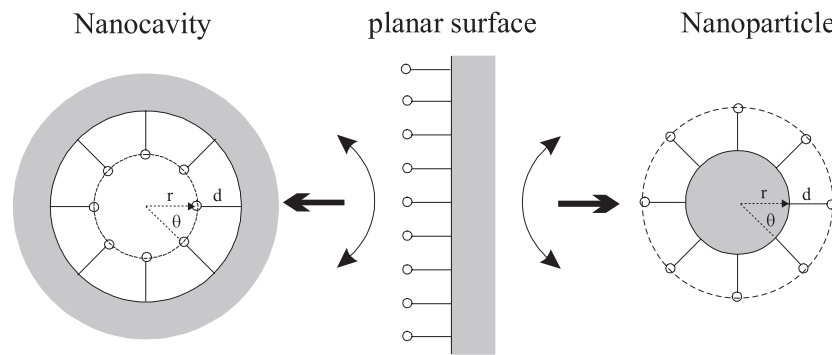


Figure 2. Schematic diagrams showing the concepts of positive curvature of a nanocavity and negative curvature of a nanoparticle and the related surface atomic arrangements.

expected to be relatively stable. Indeed, clusters of three vacancies or dangling bonds in a-Si are predicted from computer modelling [23] to be very stable. The above modelling of a nanocavity instability is consistent with the kinetic features of nanocavity shrinkage under electron-beam irradiation as observed in the *in situ* experiments and therefore can offer a very good explanation of the novel nanosize effect on the shrinkage of nanocavities [21].

In a real experiment, because of the inevitable passivation (gettering) effect of trace impurities on the surface of a nanocavity and the corresponding reduction in the surface energy, the above theoretical starting and ending sizes for the nanosize operation range should be larger than the experimentally observed ones. Thus, it is still difficult to quantitatively correlate the observed experimental nanosize data at this stage with the model prediction. It would be similar for the nanoparticle case because there is always inevitably more or less passivation to nanoparticle surface dangling bonds by strong bonding atoms, such as H passivation from trace water molecules in the atmosphere.

It should also be pointed out that the above instability analysis is only applicable to nanostructures with dangling bonds on their surface and therefore is not applicable to nanostructures without surface dangling bonds such as nanotubes or the C_{60} fullerene structure. The latter nanostructures can be very stable because the atoms on their surface are fully coordinated. However, the nanosize curvature analysis is still applicable to guide our fabrication and processing mechanisms for fullerene and nanotubes. For example, for fabrication, it can be predicted that a nanotube always tends to preferentially (non-uniformly) nucleate on a catalyst nanoparticle to avoid the higher energy barrier for the formation of a highly nanosize-curved cap and then it can easily grow indefinitely in the tube axis direction. For processing, it can be predicted that a nanotube should be more stable than C_{60} fullerene because the latter structure is, on average, more curved than the former. Thus, it would be possible to purify nanotubes from a fullerene and nanotube mixture by preferentially removing the fullerene.

In addition to the above two kinds of nanosize effect, two extreme situations can be predicted as schematically shown in figure 3 for the interaction of a nanocavity and a nanoparticle, which is not only fundamentally important but also technically meaningful for future device fabrication. The first case is that where a nanoparticle floats in a nanocavity when it loses weight in space. The other is where a nanoparticle rests on the surface of a nanocavity with its weight. Because the Debye temperature of the nanoparticle is lower than and the Debye temperature of the nanocavity is higher than that of the bulk material, a nanoparticle is 'hotter' than a nanocavity if the nanoparticle floats inside the nanocavity. Similarly, the

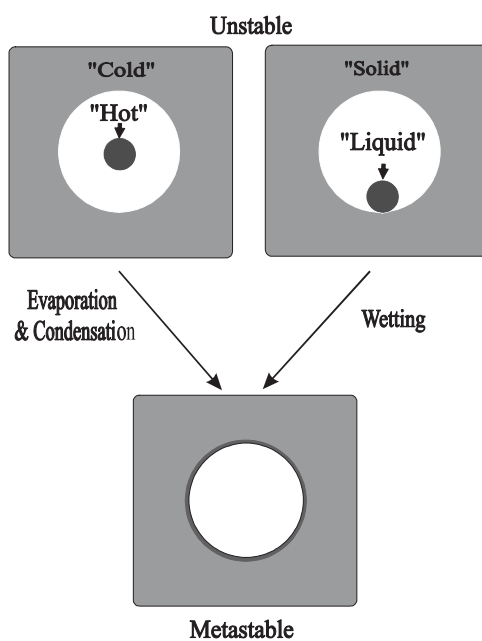


Figure 3. Schematic illustration of the interaction between a nanocavity and a nanoparticle.

nanoparticle behaves like a 'liquid' if the nanoparticle rests on the surface of the nanocavity. Thus, in the former case, the particle is 'hot' enough to evaporate and the cavity surface is 'cold' enough for the evaporated atoms to condense on it. In the latter case, the particle behaves much more like a 'liquid' and then the 'liquid' wets the cold surface of the cavity. Although direct experimental evidence for these predictions is necessary, they have already been supported by the observation that the nanocavity keeps its spherical shape during its ion-beam-induced shrinkage [14] and electron-beam-induced shrinkage [21] and by the previous observations of gettering by decorating the cavity surface with uniform layers of Au and other metals [8] and [10]. The 'contact epitaxy' [24] observed in Ag nanoparticles supported by a Cu planar surface also implies a similar tendency.

The antisymmetry relation shown in figure 1 is only an ideal model which, for a solid case, explains two extremes: a solid nanosphere of totally randomly arranged atoms in completely empty space and a totally empty nanocavity in a solid matrix of totally randomly arranged atoms, which are shown by positions 1 and 1' in figure 4 respectively. Between these two ends, there are still many varieties of paired structures for such an antisymmetry relation for the solid case. For example, in a sequence from the extreme end to the centre of the antisymmetry axis, figure 4 lists a few more typical antisymmetrical structures: a solid nanosphere in gas (position 1b) versus a gas nanosphere in a solid (position 1b'), a solid nanosphere in liquid (position 1a) versus a liquid nanosphere in a solid (position 1a'), and a 'cold' (or with a higher Debye temperature) solid nanosphere structure embedded in a 'hot' (or with a lower Debye temperature) solid matrix versus a 'hot' (or with a lower Debye temperature) solid nanosphere structure embedded in a 'cold' (or with a higher Debye temperature) solid matrix (not listed but should be located between positions 1a and 1a' in figure 4), and finally at the centre of the antisymmetry axis, the antisymmetric difference vanishes and the particle, the cavity, and the two matrixes surrounding the particle and the cavity are all of the same structure and properties and they all lose their identities and overlap with each other and all are viewed as an indefinitely

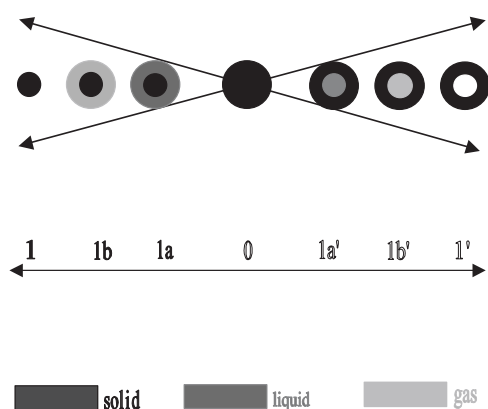


Figure 4. Schematic illustration for the extended antisymmetry relation between a solid nanosphere in vacuum (position 1) and a nanosphere vacuum cavity in a solid (position 1'): a solid nanosphere in liquid (position 1a) and a solid nanosphere in gas (position 1b) respectively versus a liquid nanosphere in a solid (position 1a') and a gas nanosphere in a solid (position 1b'). The antisymmetry centre is at position 0, where a solid nanosphere is embedded in an identical solid matrix. The arrows show the directions in which interaction among atoms or molecules becomes weaker whereas the antisymmetry relation and the instability (dissociation or shrinkage) of nanospheres are intensified.

large, bulk, uniform and stable structure. Therefore, the closer to the antisymmetry centre, the weaker the antisymmetry relation, and the more stable the structures. Also the closer to the centre, the shapes of the embedded sphere phase would no longer necessarily be kept spherical. This is because the driving force for them to approach their equilibrium states (spherical particle and cavity) is reduced, depending on the passivation or bond structure coordination degree (or coherence) of their surface dangling bonds by atoms or molecules from the gas, liquid, and solid matrix. In addition, any structure constraint from a matrix such as a crystalline structure matrix would also place more structure arrangement requirement on the embedded particle or cavity and thus would also change their interface structure, properties, and shapes. The long distance diffusion required to kinetically achieve their final equilibrium states would also be more difficult to realize in these cases. Therefore, the embedded sphere phase would be metastabilized as many kinds of structures, configurations, and morphologies.

In conclusion, nanoclusters of atoms (or of vacancies) can provide a bridge between isolated atoms (or isolated vacancies) and bulk materials (or empty space). Bulk materials, empty space, isolated atoms, and isolated vacancies in condensed matter can all be accounted for with our current scientific understanding. However, nanoparticles or nanocavities in a certain size range can display unusual physical and chemical behaviour. That is, there is an intriguing antisymmetry relation between a nanoparticle and a nanocavity: a nanoparticle tends to dissociate but a nanocavity tends to shrink to an extent which does not seem predictable from our current understanding of science. The dissociation tendency of a nanoparticle becomes stronger when the ambient temperature is elevated whereas the shrinkage tendency of a nanocavity becomes stronger at lowered ambient temperature. The observed nanosize effect for each case seems to be attributable not only to one simple argument of a large contribution from surface atoms but also to the nanosized-curvature effects. The effects seem only to be operative within a certain nanosize range. Thus, the intrinsic driving force for both the instability of a nanoparticle and that of a nanocavity is probably from a complicated interplay between the geometric and electronic structure of atoms restricted by nanosized,

negative curvature in the surface of a nanoparticle or by nanosized, positive curvature in the surface of a nanocavity. Interestingly, in a structural sense, a preferential amorphization of Si surrounding a nanocavity (i.e. the surrounding atoms becoming more randomly arranged than those in the crystal) makes a nanocavity closer to the antisymmetry relation with a nanoparticle surrounded by free space, which could be roughly viewed as being surrounded by randomly arranged vacancies. Therefore the preferential amorphization would enhance the nanosize effect and thus facilitate the shrinkage of the cavity as observed. The above antisymmetry relation presents a challenge for current science.

The author would like to express sincere appreciation for critical discussions and full support from Professor Jim Williams and Dr Mark Ridgway in Electronic Materials Engineering at the Australian National University. Critical discussions and continuous support and encouragement from Professors R Averback, K C Hsieh, K Kim, and Ian Robertson in the Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign and Professor Z G Wang from the Institute of Semiconductors, Academia Sinica are also especially acknowledged.

References

- [1] Lai S L, Guo J Y, Petrova V, Ramanath G and Allen L H 1996 *Phys. Rev. Lett.* **77** 99
- [2] Schmidt M *et al* 1997 *Phys. Rev. Lett.* **79** 99
- [3] Schmidt M, Kusche R, Issendorff V B and Heberland H 1998 *Nature* **393** 238
- [4] Bertsch G 1997 *Science* **277** 1619
- [5] Wales D J and Berry R S 1990 *J. Chem. Phys.* **92** 4473
- [6] Berry R S 1990 *Sci. Am.* **263** 50
- [7] Ascheron C E, Petravic M and Williams J S 1994 (*Advanced Materials '93, IV/Laser and Ion Beam Modification of Materials*) ed I Yamada *et al* Trans. Mater. Res. Soc. Japan **17** 377
- [8] Myers S M, Follstaedt D and Bishop D M 1994 *Mater. Res. Soc. Symp. Proc.* **316** 33
- [9] Wong-Leung J, Ascheron C E, Petravic M, Elliman R G and Williams J S 1995 *Appl. Phys. Lett.* **66** 1231
- [10] Wong-Leung J, Nygren E and Williams J S 1995 *Appl. Phys. Lett.* **67** 416
- [11] Williams J S, Zhu X F, Ridgway M C, Conway M J, Williams B C, Fortuna F, Ruault M-O and Bernas H 2000 *Appl. Phys. Lett.* **77** 4280
- [12] Zhu X F, Williams J S, Llewellyn D J and McCallum J C 1999 *Appl. Phys. Lett.* **74** 2313
- [13] Zhu X F, Williams J S and McCallum J C 1999 *Mater. Res. Soc. Symp. Proc.* **540** 127
- [14] Zhu X F *et al* 2001 *Appl. Phys. Lett.* **79** 3416
- [15] Yun C H *et al* 1998 *Appl. Phys. Lett.* **73** 2772
- [16] Kurth D G, Lerthmann P, Volkmer D, Müller A and Schwahn D 2000 *J. Chem. Soc., Dalton Trans.* **98** 3989
- [17] Gu L, Cheley S and Bayley H 2001 *Science* **291** 636
- [18] Hsieh Kuang-Chien 2002 private communications
- [19] Zhu X F 2000 *PhD Thesis* Australian National University
- [20] Cheung N W 2000 private communication
- [21] Zhu X F *et al* to be published
- [22] Zhu X F *et al* 1999 *Appl. Phys. Lett.* **75** 136
- [23] Chaudhari P, Spaepen F and Steinhardt P J 1983 *Glass Metals II* ed H Beck and H-J Güntherodt (Berlin: Springer) ch 5
- [24] Yeadon M, Ghaly M, Yang J C, Averback R S and Gibson J M 1998 *Appl. Phys. Lett.* **73** 3208