Stressed triangular lattices on microsized spherical surfaces and their defect management

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Triangular lattices were assembled on spherical surfaces and caps via thermal stress engineering on core/shell microstructures. The lattices on a complete spherical surface, when the total number is small, contain uniquely fivefold disclinations, whereas scars consisting of pentamer-heptamer chains emerged when more vertices are available (>360). Disclination-free pattern were obtained on caps, revealing the defect management strategy in nature. All the experimental observations can be explained by numerical studies to Thomson's problem [J. J. Thomson, Philos. Mag. **7**, 237 (1904)]. These results can help understand the various patterns assembled on curved surfaces, and be of essential importance for the en masse fabrication of nanostructures on pliable substrates. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2959822]

Stress developed in the various materials systems usually manifests negative effects. Macroscopically it is responsible for the fatigue of bridges, while at the microscopic scale it can change the migration of electrons in a semiconductor junction by a few orders of magnitude. However, stress also can be used for constructive purposes. Recently, stress engineering has proven to be a promising technique for the en masse fabrication of ordered micro- and nanostructures in large area. For instance, on a cracked template prepared "in a controlled manner" by developing stress in a bilayered structure, Fe-Ni-Co nanowires in 3 mm long has been grown.[1] By introducing controlled pinning to alter the buckling modes, various interesting ordered patterns were realized in thin Au films on compliant poly(dimethylsiloxane) substrate.[2,3] However, in these pioneering works, the patterns are exclusively stressed out in planar surfaces. Stress engineering on nonplanar surfaces for the assembly of ordered patterns would be of particular importance, for both academic and practical motivations. In fact, an orderly buckled substrate would be an applicable solution for making foldable electronic devices.[4] In recent years, we have succeeded in producing a series of Fibonacci spirals on conical support and triangulation patterns on spherical substrate.[5–7] The presence of defects (disclinations) in lattice patterns on a closed surface is compulsory, since the tessellation of a surface of genus g has to demonstrate the Euler–Poincaré characteristics $V+F-E=2-2g$, which degenerates to the Euler's rule $V+F-E=2$ for closed surfaces like a spherical surface ($g=0$). Therefore, the generation and arrangement of the disclinations have to be closely inspected. Moreover, noticing that in many practical situations the arena for packing is a curved surface of limited size (i.e.,$g=1$), defects in self-assembled patterns on such a curved surface are not compulsory but may be unavoidable. In this case, a proper management of the defects is necessary for an improved quality of the patterns.

In this letter, we are concerned with self-assembled patterns on microsized spherical surfaces and caps induced via thermal buckling, aiming at verifying the feasibility of third-route nanofabrication[1] on curved surfaces. The packing patterns of identical units on a spherical surface are typically triangular lattices with 12 fivefold disclinations, as was confirmed by theoretical works on the minimal energy configuration of identical charges on a conducting sphere,[8] known as the Thomson problem.[9] Numerical results concerning the Thomson problem and related issues often provoke disputes due to the intrinsic difficulty in finding the global minimum.[10] With regards to the true material systems, the exact pattern can hardly be predictable due to the sensitivity of imperfection for the buckling problem, therefore experimental study is still the primary route to reveal the actual patterns attainable.

The experimental setup and detailed processing parameters can be found in our previous publications.[6,7] In short, mixed powders of SiO and Ag_2O (here the mass ratio is fixed at 1:1) were coevaporated in a sealed chamber which was at first evacuated and then filled with a gas mixture of $90\%\,Ar+10\%\,H_2$ to a pressure of 3×10^4 Pa. A sapphire substrate was held at ~1.0 cm over the evaporating surface. By adjusting the composition of the precursor, stressed patterns of different vertex numbers and vertex separations can be obtained. Since only those core/shells that undergo buckling when they just arrive at the substrate can be later *ex situ* observed by a scanning electron microscope (SERION), therefore the critical parameter for a successful experiment is the cooling rate (at ~200 °C/min.). The stress developed by cooling in the time interval from the core/shell formation in vapor to its arrival at the substrate has to fall in a proper range: a too large stress will break the shell while a small stress suffices not to induce an observable buckling.

The spherical topology of the core/shell microstructures constitutes a strong constraint on the stressed patterns. Figure 1(a) displays a nearly spherical core/shell with a radius $R\approx2.02$ μm. On this microstructure, a stressed pattern of 40 vertices is found to fall in the category of triangular tessellation of a closed surface. The mean distance between the neighboring vertices a is about 1.15 μm. For an estimation of the total number of vertices, the equation $n=(8\pi/\sqrt{3})(R/a)^2$ can be used.[10–12] Remarkably, 12 pentam-

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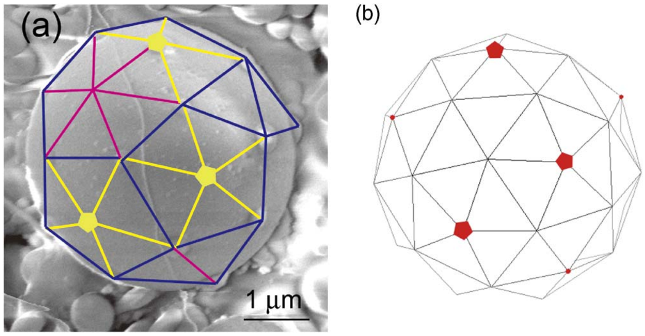

FIG. 1. (Color online) (a) Stressed triangular pattern of 40 vertices on the surface of a nearly spherical Ag core/SiO_x microstructure showing proximate fivefold disclinations. $R\approx 2.02$ μm, $a\approx 1.15$ μm. (b) Voronoi representation of numerical solutions to the Thomson's problem of N=40 [courtesy of Bowick (Ref. 14)].

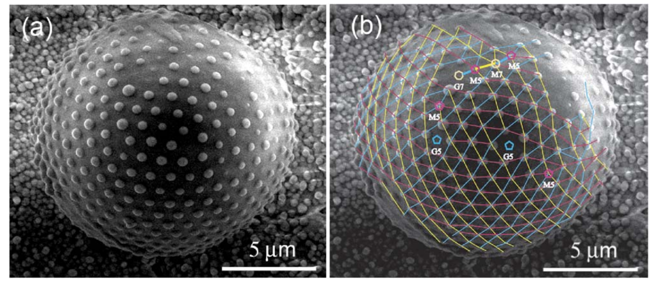

FIG. 2. (Color online) (a) Stressed pattern on a spherical surface with $R\approx 7.0$ μm and $a\approx 1.0$ μm. The number of vertices amounts to about 600. (b) Voronoi representation of the same stressed pattern with defects highlighted. M5: pentamer, M7: heptamer, G5: pentagon, and G7: heptagon. Note that the excessive fivefold and sevenfold disclinations make their presence in chain.

ers have to make their presence in the pattern to meet the Euler's rule, thus they are intrinsic to the two-dimensional (2D) crystal on a closed surface. In the stressed pattern shown in Fig. 1(a), three pentamers are visible to the readers, and they are found to share either an edge or a vertex point, which is compulsive due to the small total number of vertices. This close proximity of disclinations has been also verified in small carbon fullerenes (from C_{50} downward), which helps to overthrow the hasty isolated-pentagon principle for the construction of fullerene cages.[13] In the stressed lattices containing a moderate total number of vertices (around 200), pentamers stay separated and they are the unique defect of the pattern.[7]

Triangular tessellation on spherical surfaces occurs in a variety of distinct occasions, well-known examples include those of holes in a radiolarian, of charges beneath the skin of a helium liquid drop, and so forth. The prototypical model for the tessellation of a spherical surface is the Thomson's problem,[9] i.e., to find the distribution of N identical charges that minimizes the Coulomb energy $E=\Sigma_{i\neq j}^{N}(1/|r_i-r_j|)$. By comparing with the simulation result to the Thomson's problem,[14] Fig. 1(b) plotting the case $N=40$, we see that the numerical simulation fits our stressed pattern very well. Excellent agreement was also verified for the cases $N=46$ and 140.[7] This strongly suggests that the stressed patterns on a spherical surface can be equally modeled with mutually repulsive charges, though the interactions involved may differ a lot. In fact, the energy analysis of the buckled surface does support this analogue. For the one-dimensional undulation of a planar surface, the total free energy change is the sum of the capillary energy $\propto 1/\lambda^2$ (relatively smaller for our system since almost no area expansion in the surface) and the elastic energy change $\propto 1/\lambda$, where λ is the wavelength or separation of the adjacent stress concentration points.[15] Extending the analysis to 2D buckling in a closed surface will bring the total free energy change approximated into a term $\propto 1/\lambda^s$, where the parameter $s>1.0$ due to the curvy nature of the surface. This is in analogy with the generalized Riesz problem, i.e., particles mutually interacting via the potential $E=\Sigma_{i\neq j}^{m}(1/|r_i-r_j|^s)(s\geq 1.0)$, with the Thomson problem being its particular case. Studies on the generalized Riesz problem support the robustness of the least energy configuration against the varied interactions, particularly when the number of particles is small (<500).

For the stressed patterns on a closed surface, though 12 pentamers suffice to satisfy the Euler's rule, more disclinations may be needed to reach a least energy configuration, this is the case when the vortex number becomes large. By introducing an equal number of additional pentamers and heptamers, some intuitionally inconceivable configurations can be realized to accommodate more stress. Moreover, these additional disclinations prefer to condensate into clusters or form pentamer-heptamer grain boundary scars.[11] Figure 2 shows the stressed pattern on a core/shell structure with $R\approx 7.0$ μm, which consists of roughly 600 vertices. The mean distance between neighboring vertices is $a\approx 1.0$ μm. In addition to the separate fivefold disclinations (pentagons and pentamers are denoted as G5 and M5, respectively), also sevenfold disclinations are present (denoted as G7 and M7 for heptagons and heptamers). The pentagon (heptagon) at the place of the pentamer (heptamer) does not alter the topological character in the sense that they contribute an equal disclination, yet the appearance of the polygonal disclinations in the stressed patterns is a surprise. In the numerical simulation for Thomson's problem with particle numbers up to tens of thousand, no such polygoncal disclinations have ever been reported. The appearance of pentagons/heptagons in the stressed patterns is a feint, the centers of the pentagons/heptagons do correspond to a stressed site, but only less effectively decorated by the preferential growth. In the subsequent discussion, we will only mention the pentamers and heptamers.

As revealed by numerical studies that additional defects tend to aggregate in line,[16,17] chains of adjacent pentamer-heptamer can be observed on the stressed patterns of a large number of vertices. The number of vertices for the pattern in Fig. 2 is over 600, far exceeding the critical number set by Bausch *et al.*[10] Figure 3 shows a stressed pattern on a heavily stressed core/shell structure with a radius $R\approx 7$ μm and a mean distance $a\approx 1.2$ μm for vertices. Though partial blistering off of the shell occurred due to the extremely large stress required to form such a pattern, yet there are only $\sim$400 vertices since the SiO_2 layer for this core/shell is a little thicker. The presence of grain boundary scar strongly depends on the level of the stress. In Fig. 3 two grain boundary scars can be clearly identified. However, no face-dual polyhedron with square faces, predicted by Ref. 17, has been found.

The disclinations in the close-packing patterns on a spherical surface, intrinsic may they be, are unwelcome for practical usage, especially when regularity of the pattern is of

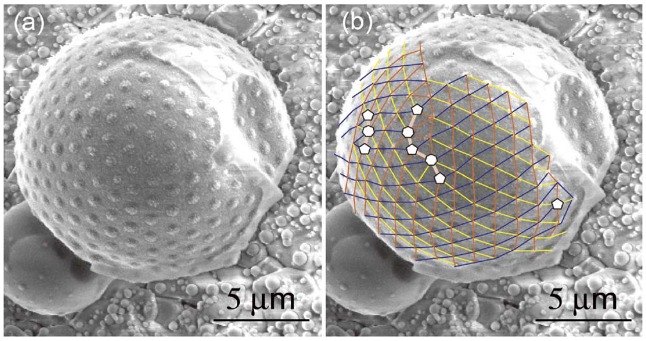

FIG. 3. (Color online) Grain boundary scars in the stressed pattern on a core/shell structure with $R \approx 7.0$ μm and $a \approx 1.2$ μm. The number of vertices totals roughly 400. Pentamers and heptamers are accentuated with white polygons at the centers (right).

concern. This is particularly the case when dealing with the arrays of optical sensors, or with foldable electronic devices, where disclinations are evidently unfavorable. Note that a bounded curved surface can be covered by purely hexagons, it is thus possible to achieve an acceptable regularity in places not in the very proximity to the boundary.

In this work, we show that disclination-free triangular lattices on curved surface could be achieved. On the core/shell structure that a hole is pierced in the shell (in the case of thinner shell, due to gravity or unfavorable contact to the substrate), the shell will recede towards the opposite end of the droplet due to draining effect. If thermal buckling occurs at this critical moment, a stressed pattern is then formed on the spherical cap. Figure 4(a) shows a spherical cap roughly half the area of a complete spherical surface, which was covered by a nearly perfect triangular lattice [Fig. 4(b)]. No disclination can be identified.

It has been proven by Axel Thue in 1892 that triangular lattice is the close packing for nonoverlapping diskcs of equal size in the plane. Moreover, this close packing is robust against the concrete interactions among the packing units, this is why it is observed in many enormously differing systems such as the beehive, the 2D electron gas (Wigner lattice), etc. This is to say that many phenomena in the physical world can be understood from the point of views of close packing of mutually repulsive units. Evidently in an open, curved surface, the existence of a free boundary provides a route for stress relaxation. The packing can be as perfectly triangular as possible in the central region of the support that the stress, and also the defects, will be left to the boundary. We speculate that this provides a flexible strategy to adjust the varying stress level on hand in different developmental phases for patterns in life.

The stressed patterns are a global feature of the support, it responses immediately to the geometry variation of the supporting surfaces. We noted in our previous study that on conical supports the stressed patterns reproduce the magic Fibonacci spirals. Therefore, it reminds us of the importance of simultaneous control of the geometry of the support and the stress accumulated therein in doing self-assembly via stress engineering. The current results are still at the explanatory stage for the understanding of stressed phenomena, further theoretical and experimental works are desirable to elucidate many essentials questions such as the dependence of the total number of stressed vertices upon the stress available and the support geometry, the location of the defects, and the length and number of the pentamer-heptamer chains, etc.

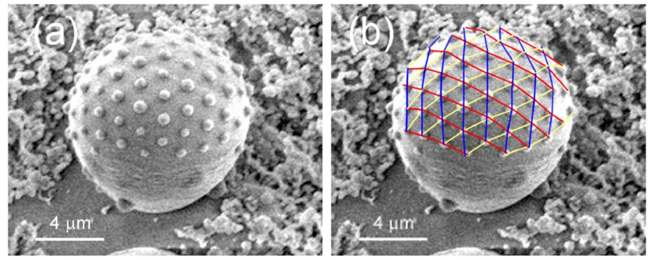

FIG. 4. (Color online) Disclination-free triangular stressed lattice on a spherical cap of SiO_2 supported by Ag core.

In summary, stressed patterns showing different packing features were produced via stress engineering on spherical Ag core/SiO_2 shell microstructures. The features can be well explained in analogy with the Thomson problem. Depending on the total stress energy, a definite number of most stressed vertices are produced which are arranged in a way both to meet the topological requirement and to seek for the least energy configuration. In the case of small vertices number, a regular triangular tessellation with simply 12 fivefold disclinations is generated, whereas grain boundary scars of adjacent pentamer-heptamer disclinations are provoked on large and heavily stressed supports where the number of vertices is generally large. A nearly perfect triangular lattice can be obtained by piercing the primary spherical surface immediately followed by the thermal stress process. These results can produce analogous solution to the similar packing problems, and provide effective fabrication route and defect management strategy for the en masse production of self-assembled structures on curved surfaces.

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