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## Research Article

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# Plastic deformation of synthetic quartz nanopillars by nanoindentation for multi-scale and multi-level security artefact metrics

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## Abstract

Individual authentication using artefact metrics has received increasing attention as a greater importance has been placed on the security of individual information. These artefact metrics must satisfy the requirements of individuality, measurement stability, durability, and clone resistance, in addition to possessing unique physical features. In this study, we proposed that nanostructures of synthetic quartz (SQ) deposited on an SQ plate may provide such sophisticated artefact metrics if morphological changes can be intentionally introduced into the SQ nanostructures at certain positions. We fabricated SQ nanopillars using a mass-production method (namely ultraviolet nanoimprint lithography) and investigated their mechanical deformation using nanoindentation with a spherical diamond tip through loading and unloading cycles. The SQ nanopillars with an aspect ratio of 1 (i.e. diameters  $D$  of 100 and 200 nm and heights  $H$  of 100 and 200 nm, respectively) could be plastically deformed without collapsing within a specified pillar-array format at programmed positions. The plastically deformed SQ nanopillar arrays demonstrated multi-scale (sub-millimetre, micrometre, and nanometre) and multi-level (shape, area, diameter, and height) individuality authentication and clone resistance capabilities. Because SQ is physically and chemically stable and durable, the individuality authentication will be a highly reliable media on Earth and in space.

## Introduction

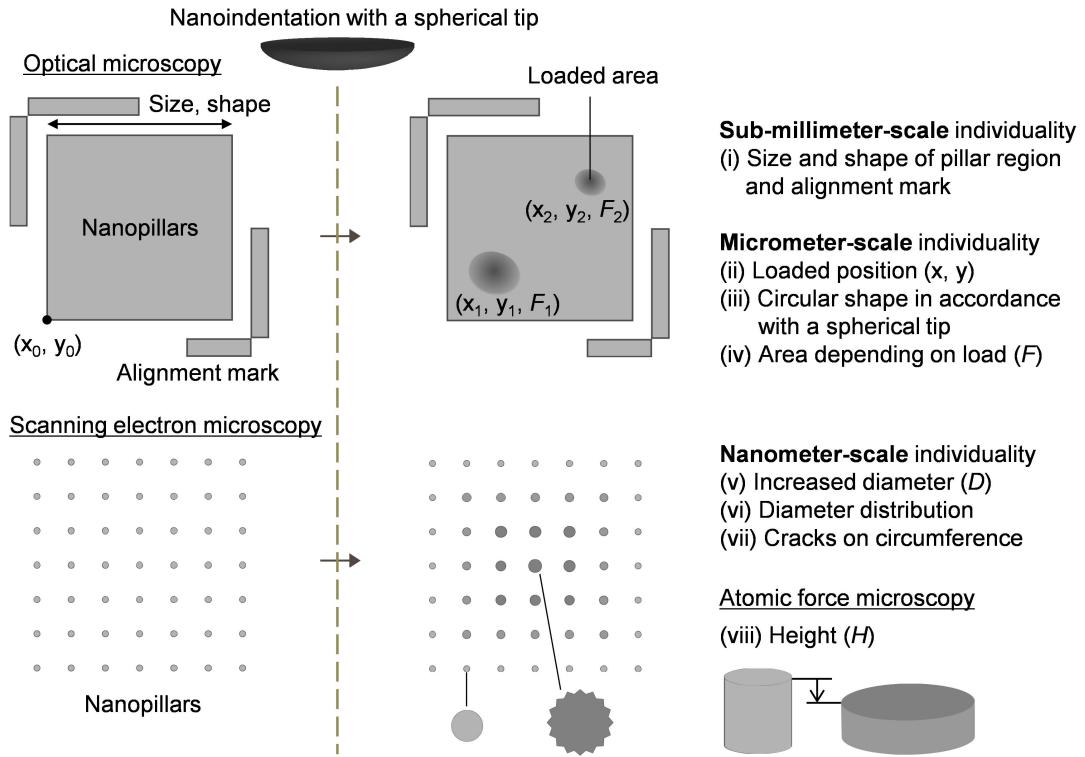
Individual authentication using artefact metrics has received increasing attention as a greater emphasis has been placed on the security of individual information.<sup>1</sup> Such artefact metrics utilise physical features that are unique to individual objects in terms of their optical, magnetic, electric, and/or mechanical properties. For example, ordinary paper has an identifiable surface consisting of microscopic and random patterns of microscale bundles of cellulose nanofibers.<sup>2</sup> Moreover, composite paper containing single-wall carbon nanotubes generates unique photoluminescence images.<sup>3</sup> Magnetic micro-fibres combined with organic polymer fibres demonstrate an inherent texture arising from their magnetic properties.<sup>4</sup> Integrated circuits with the delay variations of wires and transistors produce arbiter-based unclonable functions.<sup>5</sup> Randomly collapsed polymer resist nanostructures<sup>6</sup> and silicon random nanostructures<sup>7</sup> fabricated using lithographic methods can be identified optically. In addition to such unique physical features, the artefact metrics must satisfy the following requirements, namely individuality, measurement stability, durability, and clone resistance. Up to date, flammable organic artefact metrics have been mainly proposed.<sup>2-4,6</sup> Physically and chemically stable and durable artefact metrics should be made of an inflammable inorganic material like mineral sapphire and quartz, so that it can be a highly reliable media on Earth and in space for multi-level individual authentication.

Synthetic quartz (SQ), also known as synthetic fused silica, exhibits high stability and durability under ambient radiation, light exposure, temperature, and in the presence of chemical substances, including acids and organic liquids. SQ possesses a low thermal expansion coefficient and has been utilised as a reliable material in many fields. For example, SQ lenses are essential in optics in the visible frequency region.<sup>8</sup> In addition, SQ plates with selective metallisation are used as light-shielding and grey-scale photomasks in conventional and advanced photolithography.<sup>9</sup> SQ blocks are used as standard substances in nanoindentation tests.<sup>10</sup> The micro/nanostructures of such SQ materials may be fabricated using semiconductor fabrication technologies. These SQ microstructures may be utilised in macro-lens arrays.<sup>11-15</sup> SQ plates with structures that are smaller than visible wavelengths demonstrate unique optical functions in waveguide circuits,<sup>16</sup> photonic crystals,<sup>17,18</sup> and metlenses.<sup>19</sup> Plates with concave/convex nanometre-scale patterns can be fabricated from SQ using electron beam (e-beam) lithography and have

been used as templating moulds, which demonstrate high mechanical repeatability and light transparency in ultraviolet nanoimprint lithography for the mass production of semiconductor and optical devices.<sup>20-23</sup> Considering these findings, we proposed that the nanostructures of SQ plates may provide artefact metrics if morphological changes can be intentionally introduced into SQ nanostructures at specified locations.

To achieve this use of SQ plates, we examined the indentation tests of solid materials at arbitrary positions via loading. In particular, nanoindentation with a Berkovich tip<sup>24</sup> is widely used to measure the Young's modulus of inorganic and organic substances, such as metals, oxides, nitrides, polymers, and biomaterials. The Young's modulus is determined via calculation from a load-displacement curve that is recorded using nanoindentation measurements upon loading and unloading until an arbitrary peak applied force is achieved, which is generally within the range of micro-Newtons to milli-Newtons.<sup>24</sup> Nanoindentation testing systems are typically equipped with a microscope to determine the position at which the probing tip is pressed downwards, as well as to observe and measure the indentation area optically. The Young's moduli of concave and convex regions of silicon (Si)<sup>25</sup> and polymer microstructures<sup>26</sup> have been investigated using nanoindentation with Berkovich diamond tips. The plastic deformation of polystyrene micro-pillars and lines have been similarly investigated using spherical tips.<sup>27,28</sup> By selecting adequate loading forces and positions, we determined that deformed shapes exhibiting fine patterns with a specified distribution may be achieved, which may be used to assign individuality and clone resistance to SQ nanostructures.

In this study, we fabricated SQ nanopillars using a mass-production method involving ultraviolet nanoimprint lithography and investigated their mechanical deformation via nanoindentation testing with a spherical diamond tip through cycles of loading and unloading. The changes in the mechanical shape of the SQ nanopillars with initial diameters of 100 and 200 nm and heights of 100 and 200 nm were studied in terms of their plastic deformation and failure. Additionally, the applicability of plastically deformed SQ nanopillars by nanoindentation is discussed for use in multi-scale and multi-level individuality authentication, as well as resistance, as illustrated in Figure 1.



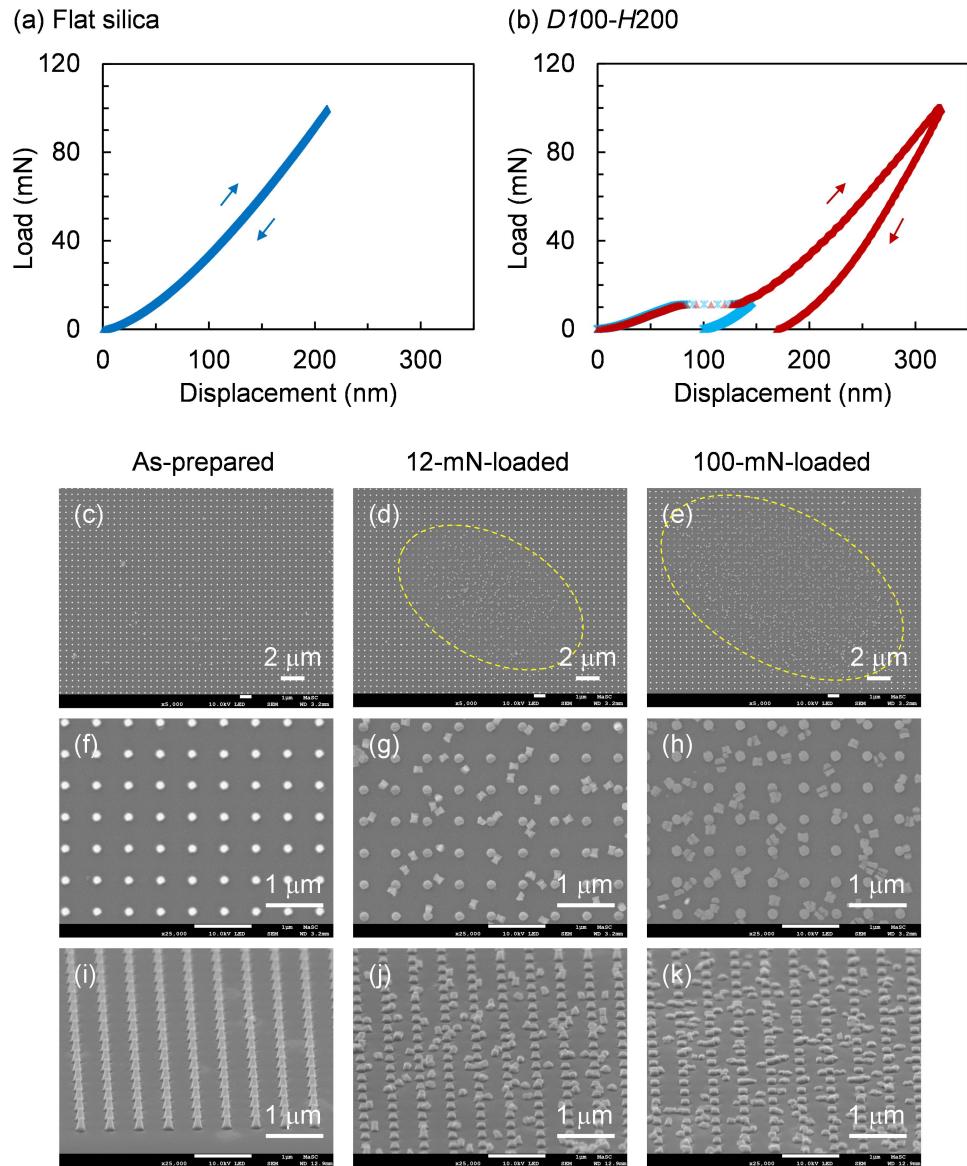
**Figure 1.** Multi-scale (sub-millimetre, micrometre, and nanometre) and multi-level (shape, area, diameter, and height) individuality authentication and clone resistance of long-term reliable synthetic quartz (SQ) nanopillars after plastic deformation by nanoindentation.

## Results

### Mechanical collapse and plastic deformation

First, we compared the morphological changes of a flat SQ plate and an SQ plate with SQ nanopillars of  $D100-H200$  (i.e. a diameter  $D$  of 100 nm and a height  $H$  of 200 nm) with an aspect ratio ( $H/D$ ) of 2 by nanoindentation testing with a spherical diamond tip. The SQ plate (Fig. 2a) with a thickness of 0.6 mm underwent elastic deformation without mechanical hysteresis between the loading and unloading curves until a peak load of 100 mN was achieved. This elastic deformation using a spherical diamond tip differed from a previously reported plastic deformation of an SQ plate with mechanical hysteresis using a Berkovich diamond tip with a sharpened three-sided pyramid shape<sup>21</sup>. The elastic deformation of the flat SQ plate enabled us to study the mechanical deformation of SQ nanopillars on the SQ plate, so that plastic deformation of the SQ nanopillars could be investigated. Figure 2b illustrates the load-displacement curves of the  $D100-H200$  SQ nanopillars measured using a spherical diamond tip. A loading/unloading hysteresis appeared in the load-displacement curve until a peak load of 100 mN was reached. During the progression to the peak load, a plateau region appeared at approximately 10 mN in the displacement range of 70–140 nm. To confirm the occurrence of mechanical hysteresis, the load-displacement curve was recorded until a peak load of 12 mN. The presence of the plateau region indicated the plastic deformation of the SQ nanopillars during the plateau region in the load-displacement curve.

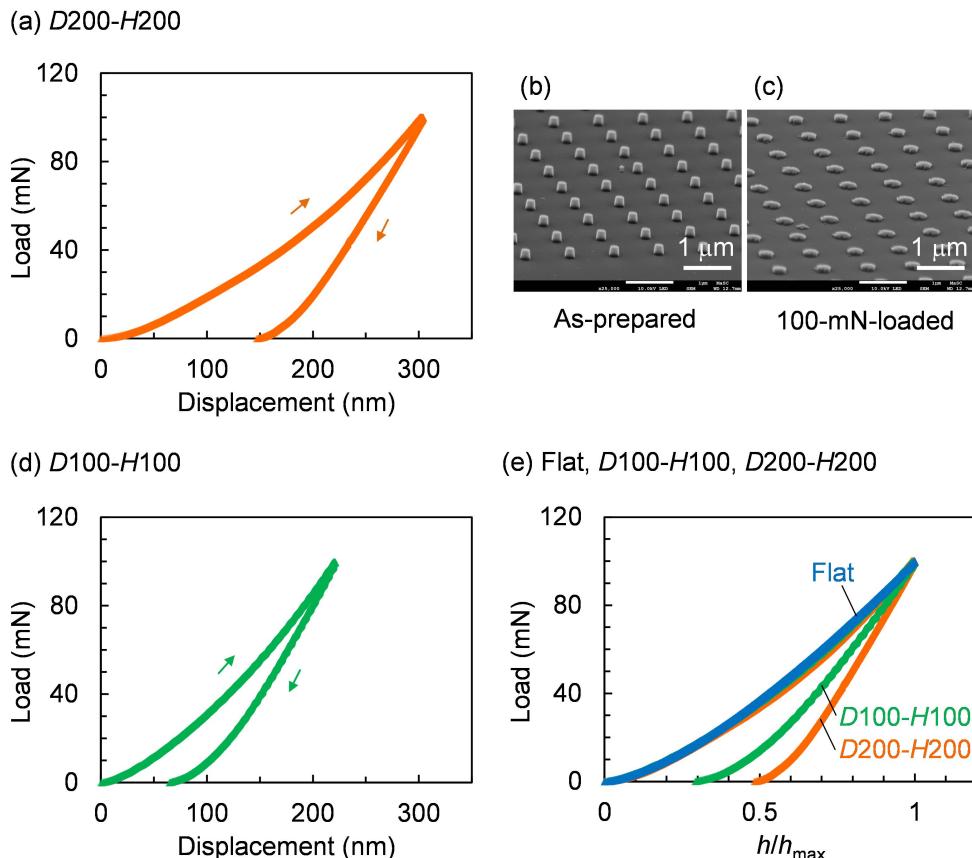
To identify the plastic deformation of the *D*100-*H*200 SQ nanopillars, we compared the field emission scanning electron microscopy (FE-SEM) images of the as-prepared SQ nanopillars before (Figs. 2c, 2f, and 2i) and after loading until peak loads of 12 mN (Figs. 2d, 2g, and 2j) and 100 mN (Figs. 2e, 2h, and 2k). As depicted in Figs. 2d and 2e, the low magnification surface images confirmed the presence of a discernible elliptical shape at the probed position upon indentation testing. The elliptical shape and the direction of its long axis, which were in accordance with the shape of the spherical probing tip, could also be visualised by optical microscopy (Fig. S1, Supporting Information). A comparison between Figs. 2d and 2e revealed that the area of the elliptical shape generated at a peak force of 100 mN was larger than that generated at a peak force of 12 mN. Therefore, the area of the elliptical shape depended not only on the shape of the spherical probing tip but also on the applied peak load. This area enlarged as the applied peak load was increased. The high magnification surface images (Figs. 2f–h) and tilted images (Figs. 2i–k) confirmed that the *D*100-*H*200 SQ nanopillars collapsed in the plateau region at approximately 10 mN, and fractures were randomly distributed. Interestingly, the peak load of 12 mN caused the *D*100-*H*200 SQ nanopillars to fracture in the in-plane direction parallel to the SQ substrate surface and near the middle of the height of the nanopillars. Tilted FE-SEM images revealed that the pillar height of  $207 \pm 5$  nm decreased to  $90 \pm 8$  nm after applying a peak load of 12 mN. The elliptical-shape area, wherein approximately 480 SQ nanopillars were fractured, was  $16 \times 10 \mu\text{m}^2$ . Because the 480 SQ nanopillars had an approximate contact area of  $160 \mu\text{m}^2$ , the peak load of 12 mN corresponded to a pressure of 75 MPa. Applying a peak load of 100 mN not only caused fracturing but also resulted in the plastic deformation of the broken nanopillars remaining on the substrate surface, and fractured pieces were distributed across the substrate surface, as depicted in Figs. 2h and 2k. Several fractured pieces were split in half in the out-of-plane direction along the pillar height. The FE-SEM observations demonstrated that the *D*100-*H*200 SQ nanopillars with an aspect ratio of 2 were fractured near the centre of the pillar height at 12 mN. Subsequently, the residues on the SQ substrate surface caused plastic deformation at 100 mN.



**Figure 2.** (a, b) Load-displacement curves of SQ with (a) a flat surface and (b) D100-H200 nanopillars measured by nanoindentation. (c–h) Surface and (i–k) tilted SEM images of the (c, f, i) as-prepared D100-H100 SQ nanopillars and those after deformation by nanoindentation until a peak load of (d, g, j) 12 mN and (e, h, k) 100 mN.

### Plastic deformation of low-aspect-ratio nanopillars

Figures 3a and 3d depict the load-displacement curves of the *D*200-*H*200 and *D*100-*H*100 SQ nanopillars with a low *H/D* value of 1 measured at a peak load of 100 mN. The *D*200-*H*200 SQ nanopillars demonstrated a larger loading/unloading hysteresis of 150 nm than the *D*100-*H*100 SQ nanopillars with a hysteresis of 70 nm. The absence of a plateau region on loading in these load-displacement curves indicated the occurrence of the plastic deformation of the *D*200-*H*200 and *D*100-*H*100 SQ nanopillars. To confirm this plastic deformation, we compared the FE-SEM images of the as-prepared *D*200-*H*200 SQ nanopillars (Fig. 3b) and those after mechanical deformation at a peak load of 100 mN (Fig. 3c). No fractures were observed to occur in the *D*200-*H*200 SQ nanopillars after undergoing mechanical deformation. The initial diameter of 200 nm was enlarged concomitantly with the decrease in the initial height of 200 nm. As depicted in Figs. 3b and 3c, the loading process until 100 mN caused the plastic deformation of the *D*100-*H*100 nanopillars, wherein the initial diameter enlarged and fractures were not observed. It was confirmed that nanoindentation with a spherical tip of the *D*100-*H*100 and *D*200-*H*200 SQ nanopillars with an aspect ratio of 1 resulted in plastic deformation without fractures.



**Figure 3.** Load-displacement curves of the (a) *D*200-*H*200 and (d) *D*100-*H*100 SQ nanopillar surfaces. (b, c) Tilted SEM images of the (b) as-prepared *D*200-*H*200 SQ nanopillars and (c) the pillars after deformation at a peak load of 100 mN. (e) Relationship between the normalised displacements ( $h/h_{max}$ ) and loads measured for SQ with a flat surface, as well as with the *D*100-*H*100 and *D*200-*H*200 nanopillars.

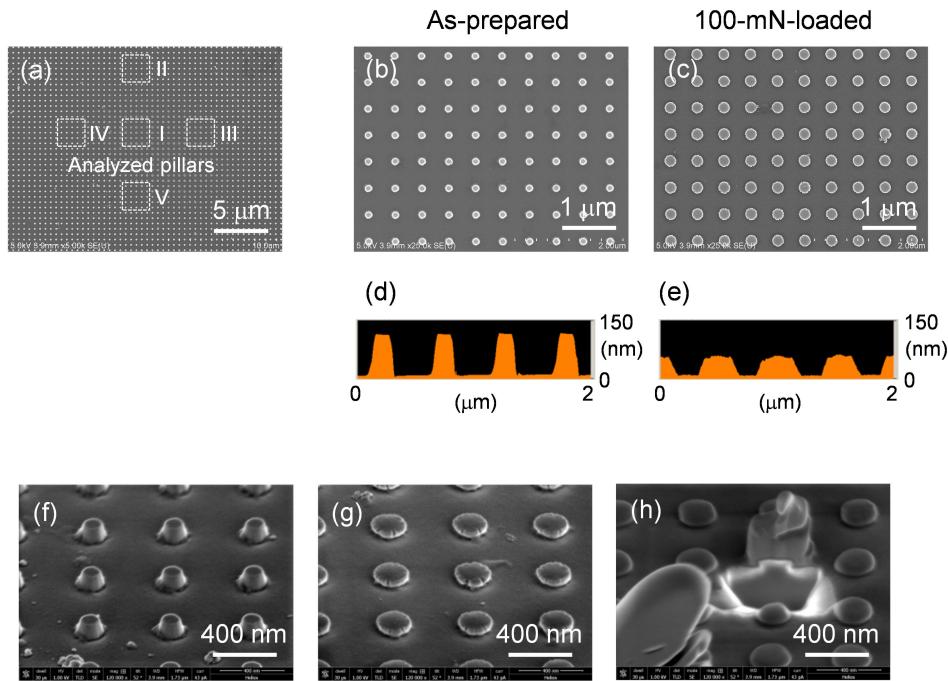
To investigate the differences between the plastic deformations of the *D*100-*H*100 and *D*200-*H*200 SQ nanopillars, the load-displacement curves were compared in detail. The maximum displacement ( $h_{\max}$ ) values at a peak load of 100 mN were 220 nm for *D*100-*H*100 and 300 nm for *D*200-*H*200. The values of  $h_{\max}$  were larger than the respective pillar heights. This indicates that until the load reached the peak load, the nanoindentation induced the plastic deformation of the SQ nanopillars together with the elastic deformation of the underlying SQ plate surface. The displacement values after the unloading reached 0 mN were 70 nm for *D*100-*H*100 and 150 nm for *D*200-*H*200. Figure 3e depicts the load-displacement curves replotted as a function of  $h/h_{\max}$  to normalise the practical displacement ( $h$ ) with the maximum displacement ( $h_{\max}$ ). Until the peak load was reached, the load-displacement curves of the *D*100-*H*100 and *D*200-*H*200 SQ nanopillars were almost identical to that of the flat SQ plate without nanopillars. After unloading, the *D*200-*H*200 SQ nanopillars exhibited a higher  $h_{\max}$  value than that of the *D*100-*H*100 SQ nanopillars. This finding suggests that the *D*200-*H*200 SQ nanopillars induced larger plastic deformation than that of the *D*100-*H*100 SQ nanopillars regardless of the same aspect ratio of 1.

Based on the contrasting brightness of the transformed the *D*100-*H*100 SQ nanopillars, FE-SEM imaging revealed an elliptical indentation shape with long- and short-axis lengths of 17 and 10  $\mu\text{m}$ , respectively, which were discernible at the position at which the spherical diamond tip was pressed, as depicted in Fig. 4a. The elliptical indentation shape had an approximate area of  $170 \mu\text{m}^2$ , which was reflected by the individual shape of the spherical tip. A morphological analysis of 25 transformed SQ pillars present in five square regions labelled I to V within the elliptical indentation shape was conducted in terms of their average diameter ( $D_{\text{ave}}$ ), maximum diameter ( $D_{\max}$ ), and minimum diameter ( $D_{\min}$ ) determined via FE-SEM, and the results are summarized in Table 1. The average diameters of the transformed SQ nanopillars were 179 (region I), 127 (region II), 143 (region III), 114 (region IV), and 130 (region V) nm.

To clarify the shape changes in the *D*100-*H*100 SQ nanopillars achieved by loading until 100 mN, the diameter and height were determined by FE-SEM and atomic force microscopy (AFM) and compared before and after loading. Before nanoindentation, the *D*100-*H*100 SQ nanopillars had an average top diameter of  $105 \pm 3$  nm (Fig. 4b) and height of 105 nm (Fig. 4d) with a truncated cone shape, as illustrated in the tilted FE-SEM image (Fig. 4f). Nanoindentation until a peak load of 100 mN transformed the truncated cone shapes to mushroom-like shapes, as depicted in Fig. 4g. The transformed *D*100-*H*100 SQ nanopillars had an average diameter of  $228 \pm 13$  nm (Fig. 4c) and height of 50 nm (Fig. 4e). The transformed *D*100-*H*100 SQ nanopillars had a diameter and height that were approximately two times larger and half that of the *D*100-*H*100 SQ nanopillars before nanoindentation, respectively. The increase in diameter and decrease in height observed for the transformed SQ nanopillars suggest that the loading by nanoindentation caused the transformation of the truncated cone-shaped SQ nanopillars to mushroom-shaped SQ nanopillars via plastic deformation as the sidewalls of the SQ nanopillars spread to periphery spaces. As depicted in Fig. 4g, random radial cracks were generated along the circumferences of the transformed mushroom-like SQ nanopillars. The focused ion beam (FIB)-SEM cross-sectional image (Fig. 4h) confirmed that the transformed SQ nanopillars possessed a mushroom shape.

The plastic deformation of the *D*100-*H*100 SQ nanopillars from the truncated cones occurred without collapse and was similar to that of the *D*200-*H*200 SQ nanopillars (Fig. 3c). The FIB-SEM image of the mushroom-like *D*100-*H*100 SQ nanopillars after nanoindentation revealed that the bottom sections were barely transformed, whereas the middle and top sections were enlarged and spread to periphery spaces during the plastic deformation. The plastic deformation induced by increasing the load until 100 mN is considered in the following discussion. The spherical diamond tip pressed the tops of the SQ

nanopillars inwards. The middles of the SQ nanopillars preferentially spread to their periphery spaces as the load was increased. The bottoms were barely affected owing to the presence of the underlying SQ substrate. As depicted in Fig. 3e, the D200-H200 SQ nanopillars exhibited a larger deformation ratio ( $h/h_{\max}$ ) of 0.49 than that of the D100-H100 SQ nanopillars ( $h/h_{\max} = 0.28$ ) after unloading. This indicates that the peak load of 100 mN caused the tops of the D100-H100 SQ nanopillars to be displaced by approximately 220 nm due to the transformation of the SQ nanopillars together with the underlying substrate. The surface position of the underlying elastic substrate was recovered to its initial position by unloading; however, the initial 100-nm height of the nanopillars decreased by approximately 40 nm to a residual height of 60 nm due to plastic deformation (Figs. 3d, 4e). Considering the D200-H200 SQ nanopillars, the initial nanopillar height of 200 nm decreased by 150 nm to a residual height of 50 nm (Fig. 3a). Therefore, the D200-H200 SQ nanopillars exhibited a larger plastic deformation than that of the D100-H100 SQ nanopillars, although they possessed the same aspect ratio of 1. The load-displacement curve measured for the D200-H100 SQ nanopillars was almost consistent with that measured for the D100-H100 SQ nanopillars. Considering the D200-H100 SQ nanopillars, a residual height of 60 nm remained after unloading (Fig. S2, Supporting Information). These findings revealed that the residual heights obtained after plastic deformation were independent of the aspect ratio of the height to the diameter and were dependent on the height of the nanopillars. The nearly constant residual layer thicknesses of approximately 50–60 nm strongly suggested the presence of a region that is difficult to transform near the bottom of the SQ nanopillars.



**Figure 4.** (a–c) Surface SEM images and (d, e) AFM height profiles of the (b, d) as-prepared D100-H100 SQ nanopillars and (a, c, e) the pillars after deformation at a peak load of 100 mN. (f, g, h) Tilted SEM images of the (f) as-prepared D100-H100 SQ nanopillars, and (g) those after deformation and (h) after deformation and exposure to an FIB to observe the cross-sectional image of a deformed SQ nanopillar.

**Table 1.** Analysed regions I-V (Fig. 4a) and characterised diameters ( $D_{\text{ave}}$ ,  $D_{\text{max}}$ , and  $D_{\text{min}}$ ) after the deformation of the *D*100-*H*100 SQ nanopillars.

Region	I	II	III	IV	V
$D_{\text{ave}}$	179	127	143	114	130
$D_{\text{max}}$	188	136	158	134	138
$D_{\text{min}}$	172	118	128	100	120

## Discussion

In this section, multi-scale individuality and clone resistance for artefact metrics is discussed based on the plastic deformation of SQ nanopillars. SQ, which is also known as synthetic fused silica, is an exceptionally reliable material considering its chemical and physical stability. As illustrated in Fig. 1, SQ nanopillar arrays on an SQ substrate demonstrate multi-scale individualities at (i) sub-millimetre-, (ii)–(iv) micrometre-, and (v)–(vii) nanometre-scales. The divisions noted in roman numerals are used to discuss the various properties of these nanopillars. At the sub-millimetre scale, (i) the sizes and shapes of the nanopillar arrays and the positioning alignment marks are discernible using optical microscopy in addition to FE-SEM. (ii) The loaded positions (x, y), (iii) ellipsoidal indentation shape in accordance with the shape of the spherical diamond tip used for nanoindentation, and (iv) indentation area depending on the load  $F$  can be recognised at the micrometre-scale using FE-SEM. At the nanometre-scale, (v) the diameter  $D$  and (vi) diameter distribution within the indentation, as well as (vii) the numbers of cracks on the circumferences of the mushroom-like nanopillars can be discerned using FE-SEM. Additionally, (viii) the heights  $H$  of the initial and transformed nanopillars can be measured using AFM.

In terms of (i), the sizes and shapes of the nanopillar arrays, as well as the positioning alignment marks, are freely designed and fabricated using e-beam and nanoimprint lithography to achieve array sizes of  $100 \times 100 \mu\text{m}^2$  and alignment-mark bar sizes of  $10 \mu\text{m}$  in width and  $50$  or  $100 \mu\text{m}$  in length in this study (Fig. S3h, Supporting Information). The loaded position (ii) is freely determined using an indentation testing apparatus. Because the spherical diamond tip has an ellipsoidal shape, the ellipsoidal indentation shape (iii) formed on the pillar array reflects this spherical diamond shape and can be analysed using the long- and short-axis lengths and directions. An increase in the peak load  $F$  causes the ellipsoidal indentation area (iv) to become enlarged. The plastic deformation of the *D*100-*H*100 SQ nanopillars with an identical diameter and height resulted in the increase in their diameters (v) and decrease in their heights (viii) with specific distributions (vi) within the indentation. The *D*100-*H*100 SQ nanopillars with an initial truncated cone structure were transformed into mushroom-like structures with cracks (vii) around their spheres. The numbers and positions of these cracks differed among the deformed SQ nanopillars, as depicted in Fig. 4g. Therefore, SQ nanopillars with aspect ratios of approximately 1 could be deformed plastically without failure using nanoindentation with a spherical diamond tip. The plastically deformed SQ nanopillars can provide multi-scale and multi-level individualities and clone resistances for artefact metrics. However, considering SQ nanopillars with a high aspect ratio, such as the *D*100-*H*200 SQ nanopillars, it is difficult to certify their individualities because fractures generated by

collapse would not be present during use, and would prevent the analysis of the diameters of the transformed SQ nanopillars in a specified area using software. The generated fractures reduce the accuracy of individuality authentication for clone resistance. Because SQ can endure strong deep ultraviolet light and radiation exposure, as well as heat treatment above 1000 °C and chemical treatments with strong acids and common solvents, SQ nanopillars on SQ substrates can be considered to be a highly reliable media for multi-level individual authentication for artefact metrics both on Earth and in space.

In this study, we described multi-scale and multi-level individuality authentication and clone resistance for artefact metrics using SQ nanopillars deformed by nanoindentation. The SQ nanopillars were fabricated using ultraviolet nanoimprint lithography, which is an industrially acceptable process that may be conducted at a high throughput and low cost. The SQ imprint moulds were precisely prepared using e-beam lithography. By using a nanoindenter with a spherical diamond tip, SQ nanopillars demonstrated the ability to be deformed plastically without collapsing in a certain pillar-array structure at programmed positions. Mushroom-like SQ nanopillars with peripheral cracks were deformed from SQ nanopillars with a truncated cone structure, and they appeared to possess shapes akin to an island in the ocean. The scale is 1/10<sup>12</sup>. A pillar-top area of approximately 100 × 100 nm<sup>2</sup> in a pillar-array area of 100 × 100 μm<sup>2</sup> just corresponds to the island area of Guam (5.5 × 10<sup>2</sup> km<sup>2</sup>) in comparison with the surface area of the Earth (5.1 × 10<sup>8</sup> km<sup>2</sup>). Scanning using FE-SEM and AFM resembles observation using an artificial satellite. The pillar-top area was transformed via nanoindentation with a spherical diamond tip. To identify the shapes of the individual SQ nanopillars and their assemblages, multi-scale observations and multi-level measurement methods, including optical microscopy, FE-SEM, and AFM, are required, as were conducted in this study. Because SQ is physically and chemically stable, in addition to being a durable material, individuality authentication using plastically deformed SQ nanopillars is expected to be feasible both on Earth and in space.

## Methods

**Fabrication of nanopillars.** SQ nanopillars with diameters (*D*) of 100 and 200 nm and heights (*H*) of 100 and 200 nm, abbreviated as *D*100-*H*100, *D*100-*H*200, *D*200-*H*100, and *D*200-*H*200, were fabricated using mass-replicable ultraviolet nanoimprint lithography (UV-NIL). Silica imprint moulds with square-grid hole arrays were prepared by e-beam lithography according to our previous reports.<sup>29,30</sup> An 80-nm-thick film of a positive-tone resist was prepared by spincoating ZEP520A (ZEON) onto a silica substrate (Shin-Etsu) with dimensions of 20 × 20 × 0.5 mm<sup>3</sup> and annealing at 180 °C for 10 min. The top-coating of a conductive organic layer of ESPACER (Showa Denko) was then conducted at a spinning speed of 2000 rpm for 60 s, followed by annealing at 70 °C for 3 min in ambient air.

Electron beam drawing was conducted using an ELS-G125S writer (Elionix) at an acceleration voltage of 130 kV and a beam current of 100 pA. Square-grid hole arrays (with a pitch of 500 nm for *D*100 and 1000 nm for *D*200) and micrometre-scale bars (with a width of 10 μm and a length of 50 or 100 μm) were drawn on separated areas of 100 × 100 μm<sup>2</sup> grids and around the corners of each hole-array area, respectively. The micron-bars were used as indicators that were discernible using an ENT-2100-equiped optical microscope (Elionix). Resist masks were prepared by rinsing with ultrapure water (18.2 MΩ·cm), immersion in a ZED-N50 developer (ZEON), and rinsing with a ZMD-B solvent (ZEON). The silica surfaces were excavated via electron cyclotron resonance (ECR) etching using an EIS-200ER etcher (Elionix) with C<sub>3</sub>F<sub>8</sub> gas for 90 s. The residual resist materials were removed by exposure to vacuum UV light using an UEM20-172 Xe excimer lamp (Ushio). Silica imprint moulds separated into 10 × 10 mm<sup>2</sup> were cleaned by immersion in sulfuric acid and rinsed using ultrapure water and UV/ozone exposure for

20 s using a UVE-110-1H cleaner (Sen Light) before use. The mould surfaces were modified with an antisticking molecular layer formed using tridecafluoro-1,1,2,2-tetrahydrooctyltrimethoxysilane (FAS13) by chemical vapour surface modification at 150 °C for 1 h.<sup>31-33</sup>

UV-NIL was performed as illustrated in Fig. S3 (Supporting Information). A UV-curable resin of NL-KK1<sup>34,35</sup> was diluted with 1-methoxy-2-propanol and spincoated onto a 4-inch SQ wafer (Shin-Etsu) with a 10-nm-thick CrN hard mask and annealed at 50 °C for 2 min. The modified silica imprint mould and resin-coated SQ wafer were set as a superstrate and substrate, respectively, in an ImpFlex Essential nanoimprint stepper (Sanmei). UV nanoimprinting used for copying the pillar resist patterns was conducted under the following conditions: an applied pressure of 1.0 MPa, 365-nm light intensity at 100 mW cm<sup>-2</sup>, and an exposure duration of 20 s. The UV exposure was conducted using an L11921-400 UV-LED (Hamamatsu Photonics). Subsequent three-type dry etching for the selective removal of the residual resist layer, CrN hard mask, and silica was performed. Anisotropic oxygen reactive ion etching (O<sub>2</sub> RIE) was conducted using a lab-made apparatus<sup>35</sup> to remove the residual resist layer (conditions: an oxygen-gas mass flow rate of 10 sccm, chamber pressure of 0.5 Pa, and radio frequency bias power of 20 W). Argon ion beam milling using a 20IBE-C apparatus (Hakuto) was then conducted to remove the CrN hard mask (conditions: a beam bias of 600 V, beam current of 400 mA, acceleration voltage of 200 V, and milling duration for 0.5 min). Finally, ECR etching in the same manner as described for the preparation of the silica imprint moulds was used to remove the residual silica. SQ nanopillars with heights of 100 and 200 nm were prepared via ECR etching for 90 and 180 s, respectively. The SQ wafer was diced into plates (15 × 15 mm<sup>2</sup>), and plates with nanopillar surfaces were fabricated using stripping masks via exposure to vacuum UV light and immersion in a Cr etchant. Surface cleaning was then conducted by immersion in sulfuric acid and rinsing with ultrapure water (18.2 MΩ·cm).

**Mechanical deformation and shape characterisation of nanopillars.** Nanoindentation using an ENT-2100 nanoindenter (Elionix) with a spherical diamond tip (radius of curvature: 200 μm) was performed for the evaluation of the mechanical strength and location-selective mechanical deformation of the nanopillars. SQ plates with nanopillars were fixed on an automated XY stage using a Crystalbond 509 adhesive (Aremco Products). The positions required to conduct the nanoindentation process were confirmed by optical microscope observations of the micron-bars and nanopillar areas, and the XY stage was operated using a PC. Load-displacement curves were collected until a peak load of either 12 or 100 mN was recorded at a rate of 5 mN s<sup>-1</sup> with an interval of 5 s at the peak load.

Sub-millimetre- and micrometre-scale individuality authentications were performed via reflection-mode optical microscopy using a BX51 microscope (Olympus) with a charge coupled device (CCD) camera. Nanometre-scale individuality authentications were performed via FE-SEM using an S-4800 (Hitachi High-Technologies) and JSM-7800F (JEOL), as well as AFM using an S-image (Hitachi High-Tech Science) with an OMCL-AC200TS-R3 silicon cantilever (Olympus). The optical microscopy and FE-SEM images were analysed using WinRoof software (Mitani). The diameters and heights of the as-prepared and mechanically deformed nanopillars were determined from the FE-SEM observations of the normal surfaces at an angle of 0° and the inclined surfaces at 70°, respectively. Pt-Pd was deposited onto the SQ surfaces for 20 s using an E-1010 ion sputtering apparatus (Hitachi High-Technologies) prior to the FE-SEM observations. A cross-sectional SQ nanopillar was prepared by exposure to a focused ion beam using a Helios NanoLab 600i FIB/SEM (FEI) and the electron beam deposition of Pt into the system prior to SEM observations at a tilt angle of 52°.

## Data availability

All data generated or analysed during this study are included in this published article (and its Supplementary Information files).

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## Author contributions

S. I. and T. O. conducted the experiments. S. I. performed the figure generation. S. I., M. A., H. Y., and M. N. conceived the experiments. S. I. and M. N. wrote the main manuscript. All authors contributed to the discussion and analysis of the presented results. All authors reviewed the manuscript.

## Additional Information

**Supplementary information** accompanies this paper at <http://www.nature.com/srep>

## Competing interests

The authors declare no competing interests.

## Figure legends

**Figure 1.** Multi-scale (sub-millimetre, micrometre, and nanometre) and multi-level (shape, area, diameter, and height) individuality authentication and clone resistance of long-term reliable synthetic quartz (SQ) nanopillars plastically deformed by nanoindentation.

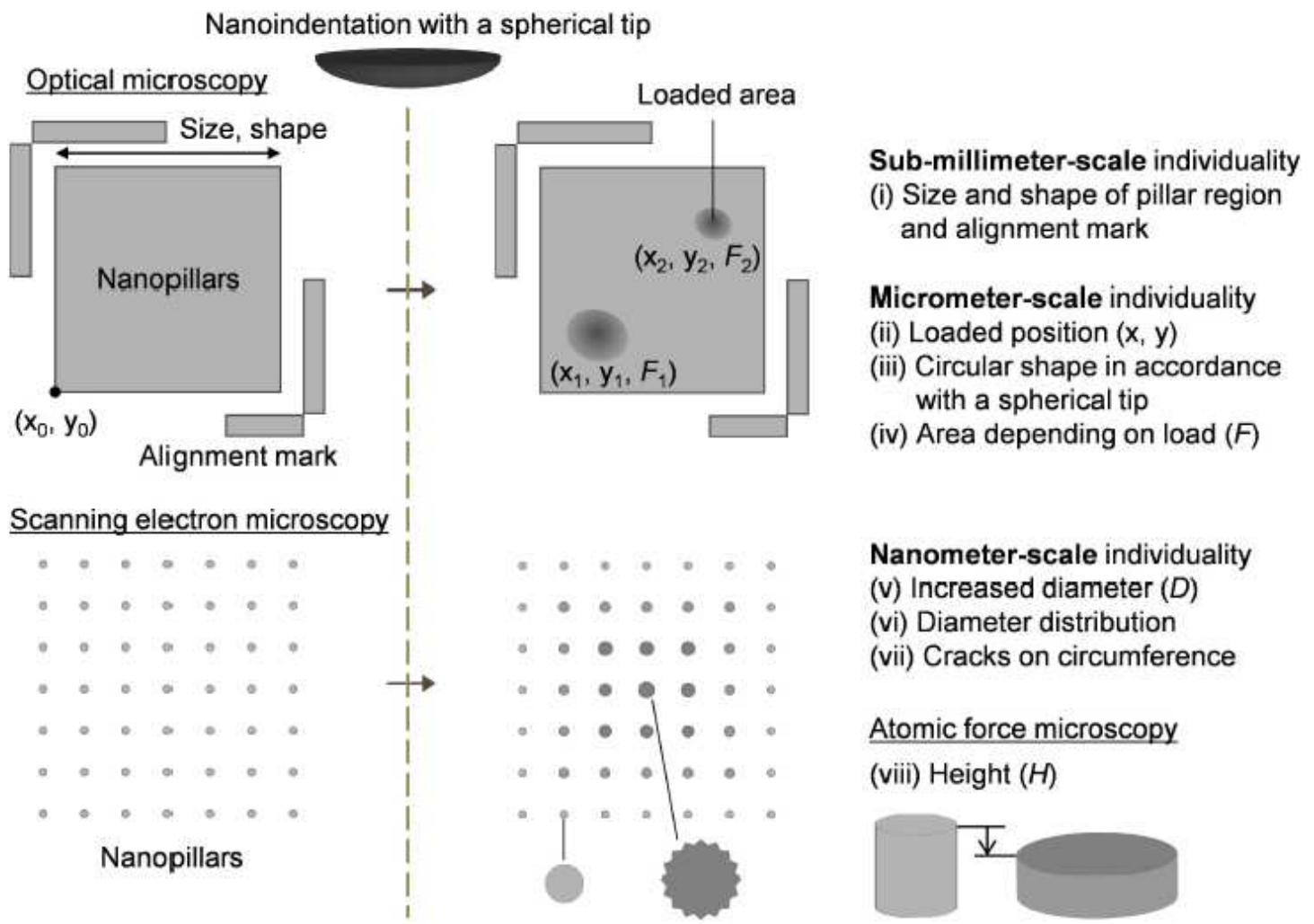
**Figure 2.** (a, b) Load-displacement curves of SQ with (a) a flat surface and (b) D100-H200 nanopillars measured by nanoindentation. (c–h) Surface and (i–k) tilted SEM images of the (c, f, i) as-prepared D100-H100 SQ nanopillars and those after deformation by nanoindentation until a peak load of (d, g, j) 12 mN and (e, h, k) 100 mN.

**Figure 3.** Load-displacement curves of the (a) D200-H200 and (d) D100-H100 SQ nanopillar surfaces. (b, c) Tilted SEM images of the (b) as-prepared D200-H200 SQ nanopillars and (c) the pillars after deformation at a peak load of 100 mN. (e) Relationship between the normalised displacements ( $h/h_{\max}$ ) and loads measured for SQ with a flat surface, as well as with the D100-H100 and D200-H200 nanopillars.

**Figure 4.** (a–c) Surface SEM images and (d, e) AFM height profiles of the (b, d) as-prepared D100-H100 SQ nanopillars and (a, c, e) the pillars after deformation at a peak load of 100 mN. (f, g, h) Tilted SEM images of the (f) as-prepared D100-H100 SQ nanopillars, and (g) those after deformation and (h) after deformation and exposure to an FIB to observe the cross-sectional image of a deformed SQ nanopillar.

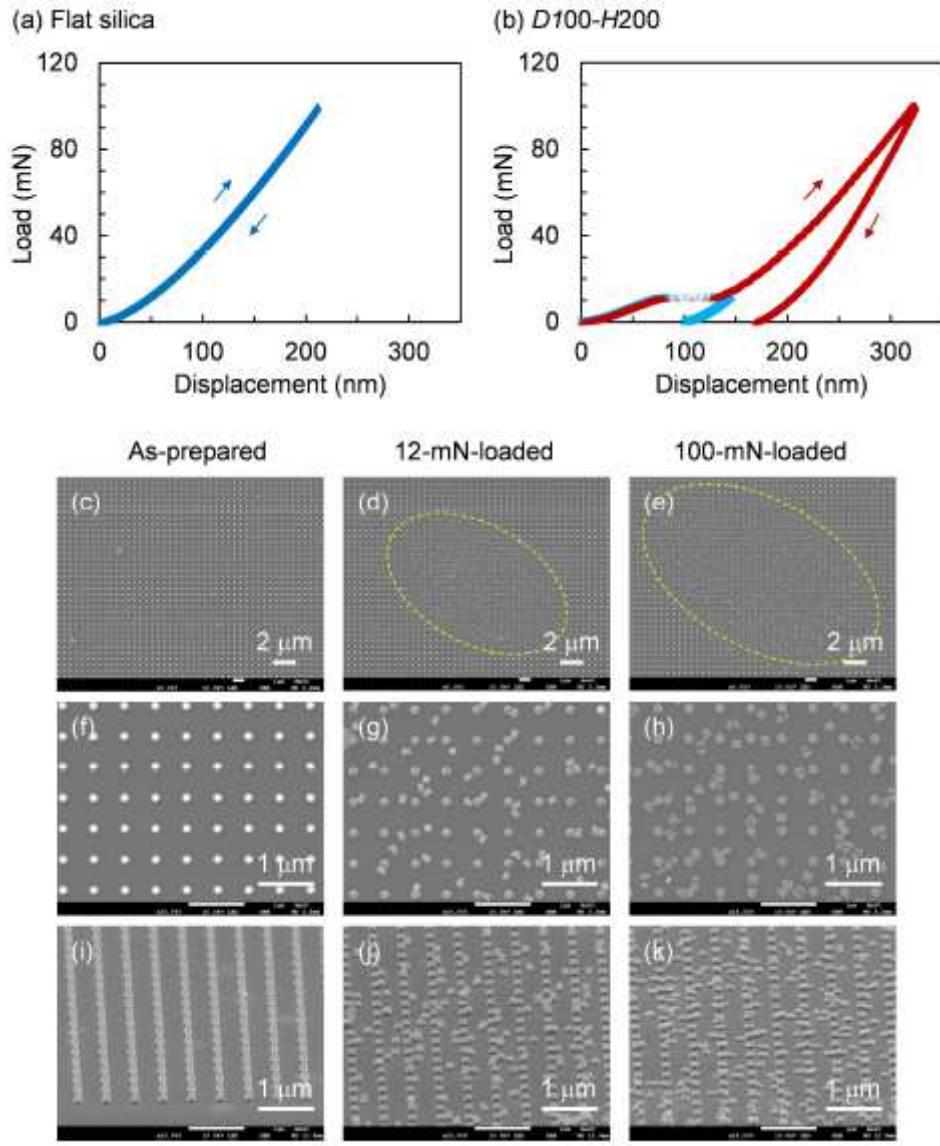
**Table 1.** Analysed regions I–V (Fig. 4a) and characterised diameters ( $D_{\text{ave}}$ ,  $D_{\max}$ , and  $D_{\min}$ ) after the deformation of the D100-H100 SQ nanopillars.

# Figures



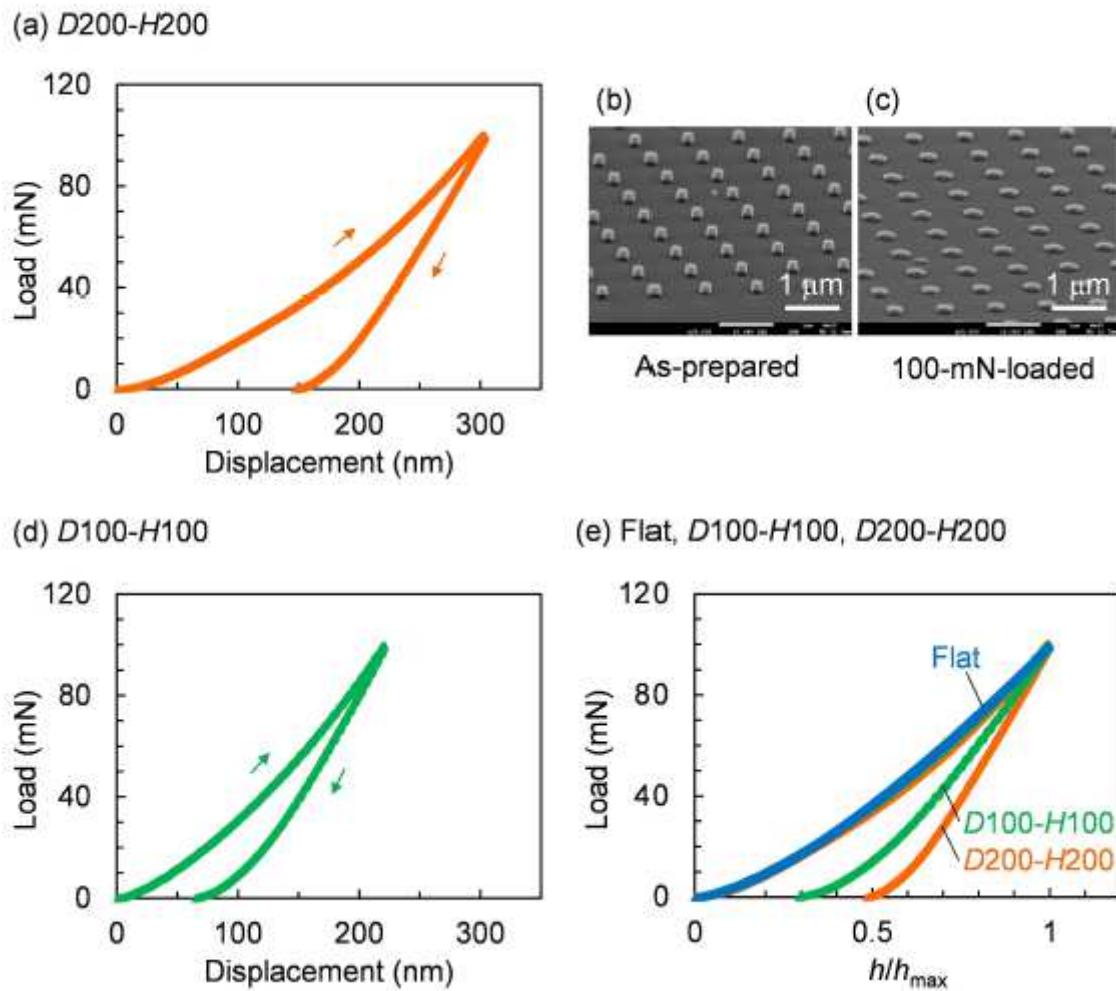
**Figure 1**

Multi-scale (sub-millimetre, micrometre, and nanometre) and multi-level (shape, area, diameter, and height) individuality authentication and clone resistance of long-term reliable synthetic quartz (SQ) nanopillars plastically deformed by nanoindentation.



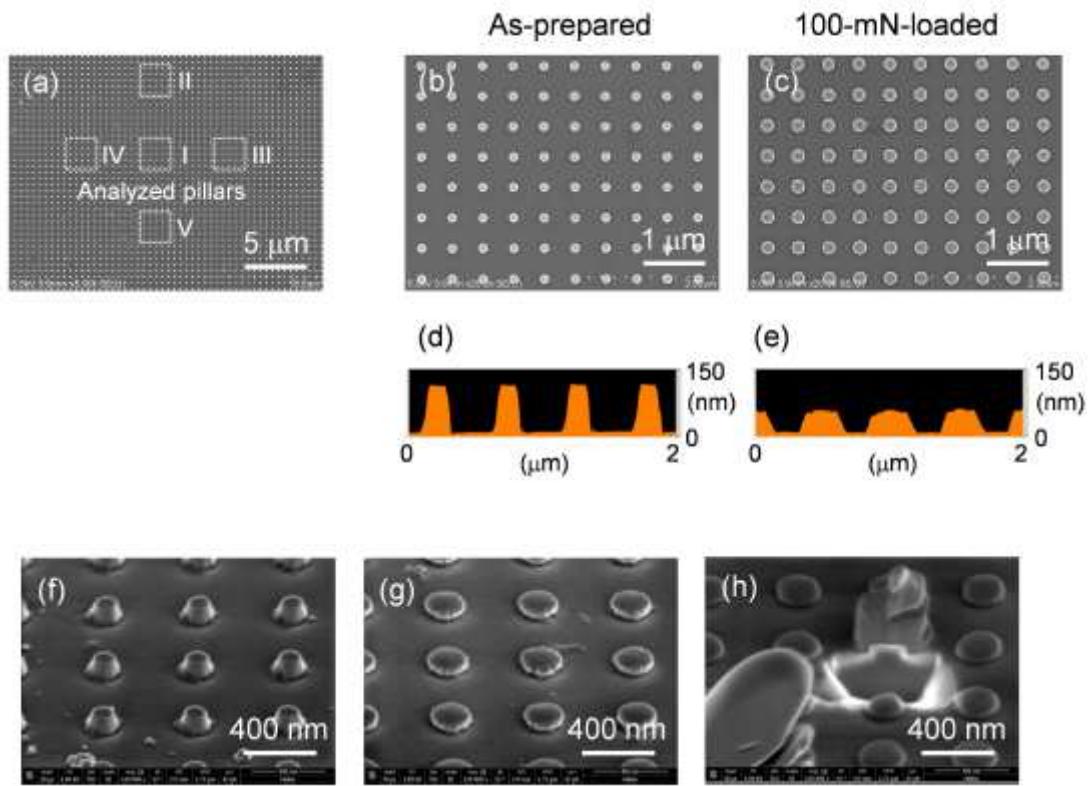
**Figure 2**

(a, b) Load-displacement curves of SQ with (a) a flat surface and (b) D100-H200 nanopillars measured by nanoindentation. (c–h) Surface and (i–k) tilted SEM images of the (c, f, i) as-prepared D100-H100 SQ nanopillars and those after deformation by nanoindentation until a peak load of (d, g, j) 12 mN and (e, h, k) 100 mN.



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**Figure 4**

(a–c) Surface SEM images and (d, e) AFM height profiles of the (b, d) as-prepared D100-H100 SQ nanopillars and (a, c, e) the pillars after deformation at a peak load of 100 mN. (f, g, h) Tilted SEM images of the (f) as-prepared D100-H100 SQ nanopillars, and (g) those after deformation and (h) after deformation and exposure to an FIB to observe the cross-sectional image of a deformed SQ nanopillar.