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3D hierarchical architectures based on self-rolled-up silicon nitride membranes

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Abstract

This study presents the superior structural versatility of strained silicon nitride (SiN_x) membranes as a platform for three-dimensional (3D) hierarchical tubular architectures. The effects of compressive and tensile stressed SiN_x layer thickness on the self-rolled-up tube curvature, the sacrificial layer etching anisotropy on rolling direction and chirality, and stress engineering by localized thickness control or thermal treatment, are explored systematically. Using strained SiN_x membranes as an electrically insulating and optically transparent mechanical support, compact 3D hierarchical architectures involving carbon nanotube arrays and passive electronic components are demonstrated by releasing the functional structures deposited and patterned in 2D. These examples highlight the uniqueness of this platform that exploits 2D processing and self-assembly to achieve highly functional 3D structures.

 Online supplementary data available from stacks.iop.org/Nano/24/475301/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Strain-induced self-rolled-up membranes have attracted great interest since their emergence in 2000, fueled by their potential applications in optics, electronics, and biology [1–16]. Self-rolled-up tubes were first fabricated by Prinz *et al* by releasing a strained InAs/GaAs bilayer from a GaAs substrate using an AlAs sacrificial layer [13], wherein rolling is driven by a momentum generated between the oppositely strained InAs and GaAs layers. Since then, self-rolled-up tubes that are made of many different types of materials and precisely controlled 3D tubular architectures have been demonstrated through deposition by metalorganic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), plasma enhanced chemical vapor deposition (PECVD), etc. Examples include epitaxial single-crystal films (e.g. InGaAs/GaAs [1, 11, 13, 17, 18], InGaAsP/InGaAsP [9], Si–Ge/Si [12]), amorphous films (e.g. SiN_x/Cr [19] and SiO_x [4, 6, 15]), strained polymer bilayers [5], and hybrid

material systems [2, 10, 16, 19–21]. Various sacrificial layers have been successfully used for the formation of tubular structures, constrained only by the etching selectivity of the sacrificial layer to the strained thin film during the final release process. These include epitaxially deposited lattice-matched heterojunctions (e.g. AlGaAs for III–As system [1, 11, 13, 17, 18] and InGaAs for III–P system [9]), evaporated thin films (e.g. Ge/GeO_x [14, 22]), spun-on layers (e.g. photoresist [4, 6]), or simply commercial semiconductor substrates (e.g. Si [8, 12, 20]). Depending solely on the material system and desired tube dimensions, these films can be patterned into fully functional devices using conventional lithography before releasing and exhibit improved performance due to 3D physical, electronic, or electromagnetic confinement after releasing [1, 6, 7, 14, 23]. A clear advantage of self-rolled-up systems over other 3D patterned structures is the ability to fully functionalize the inner surface before rolling, allowing complex 3D devices to be fabricated with the precision of conventional lithography.

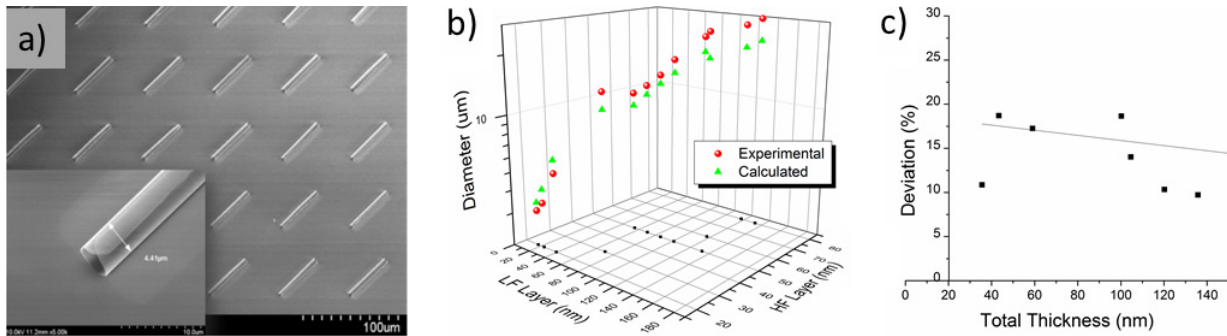


Figure 1. (a) Aligned array of 4.4 μm diameter tubes rolled from 39 nm LF and 20 nm HF SiN_x bilayers. Inset shows a single tube at high magnification. (b) 3D plot of tube diameter as a function of the compressive (LF) and tensile (HF) SiN_x membrane thicknesses (experimental: red spheres, calculated: green triangles). The planar projection of the plot (black squares) indicates the thickness combinations used for the diameter study. (c) Corresponding 2D plot of the calculated diameter deviation from the experimental value as a function of the total SiN_x membrane thickness.

This work focuses on silicon nitride (SiN_x) based self-rolled-up microtubes, which are attractive for photonic, electronic, and biological applications, because they are transparent under visible light, tunable in refractive index, non-toxic to biological systems, inexpensive to fabricate, and compatible with Si integrated circuits. Mei *et al* demonstrated SiN_x microtubes from a single-layer membrane deposited in a silane (SiH_4)/nitrogen (N_2)/helium (He) PECVD environment at high frequency (13.56 MHz) and high power (99 W) [6]. A strain gradient was created in the thin SiN_x film, when deposited on photoresist (PR) at 85 °C, which resulted in tubular structures upon PR removal. In this situation the microtube diameter can be predicted by the thermal expansion coefficient mismatch between the PR and SiN_x . By combining the compressive strain of thermally grown silicon dioxide and the tensile strain of PECVD silicon nitride, Seleznev *et al* fabricated an integrated-circuit-ready gas sensor using hybrid $\text{SiO}_2/\text{SiN}_x/\text{Ti}/\text{Au}$ tubular microheaters and microsensors [8]. The SiN_x film was deposited in their case under high frequency in an ammonia (NH_3)/silane (SiH_4) mixture, and microtubes were formed after etching the Si substrate using ammonium hydroxide.

Unlike SiN_x films deposited under high frequency (HF) at 13.56 MHz, films deposited under low frequency (LF) at 380 kHz are naturally compressively strained. Thus, oppositely strained bilayer (LF/HF) deposition can be achieved using a single tool. Unique to SiN_x deposited through PECVD using ammonia/silane mixtures [24], the gas ratio of NH_3/SiH_4 can be adjusted to obtain a high amount of amine fragments in the film, which can result in large amounts of compressive strain and yield smaller diameter microtubes. Additionally, it provides an opportunity to augment the thin film properties after deposition. Specifically, rapid thermal annealing (RTA) allows control over film thickness, composition, and strain through ammonia outdiffusion after microtube formation.

In this paper, we report a systematic study of the fabrication of a myriad of rolled-up 3D SiN_x based architectures by utilizing the tunability of SiN_x film stress via PECVD deposition parameters under high and low frequency in an ammonia (NH_3)/silane (SiH_4)/nitrogen (N_2)

system. We explore the effect of various sacrificial layers on the self-rolling behavior to realize 360° control of rolling direction and chirality, despite the isotropic strain in the SiN_x bilayer. We thereafter demonstrate that SiN_x microtubes can be used as a 3D mechanical support for coaxial metallic structures, carbon nanotube arrays, and other functional components.

2. Results and discussion

2.1. Control of SiN_x tube diameter

Similar to single-crystal strained films (e.g. InGaAs/GaAs), SiN_x tubes of different diameters can be fabricated by varying the thickness or strain of the compressive and tensile components [17]. Figure 1(a) shows an ordered array of rolled-up SiN_x microtubes with an outer diameter of 4.4 μm , formed spontaneously by releasing a 39 nm thick LF (compressive)/20 nm thick HF (tensile) SiN_x bilayer deposited on a Si(111) substrate.

Figure 1(b) summarizes the experimentally measured microtube diameters as a function of LF and HF thicknesses in a 3D plot, with projection (black squares) indicating the thickness combinations used in the diameter study. As expected, the microtube diameter increases with the total thickness of the film, however it can be seen that the contribution from the LF (compressive) and HF (tensile) film thicknesses are not equal. Specifically, a disproportional diameter increase can be seen between the combinations (nm LF/nm HF) 117/60 and 117/80, respectively exhibiting diameters of 25.4 μm and 25.5 μm , compared to 117/80 and 133/80, showing an increase from 25.5 μm to 28 μm . Adapting the classical stress model for bimetallic thermostat deflection [25], the strain-induced self-rolled-up SiN_x bilayer tube diameter D , in nm, can be expressed as:

$$D = \frac{E_1^2 t_1^4 + E_2^2 t_2^4 + 4E_1 E_2 (t_1^3 t_2 + t_1 t_2^3) + 6E_1 E_2 (t_1 t_2)^2}{3|\Delta\varepsilon|(1+\nu)E_1 E_2 (t_1 + t_2)(t_1 t_2)} \quad (1)$$

where subscripts 1 and 2 represent LF and HF layers, respectively, $\Delta\varepsilon$ is the strain difference between LF and HF

layers, t is thickness in nanometers of the individual layers (t), and ν is Poisson's ratio.

For the samples reported in figure 1, the residual stress, σ , in the films was measured using a FSM 500TC metrology tool to be -1168 and 406.95 MPa for the compressive and tensile strained SiN_x films, respectively. The Young's modulus, E , of the SiN_x films is proportional to the film density, which is sensitive to the deposition plasma frequency and power [26, 27]. The LF compressive film exhibits a higher Young's modulus than its HF counterpart, reported to be around 180 GPa and 170 GPa, respectively [27]. $\Delta\varepsilon$ is calculated by $\sigma_{(\text{LF})}/E_{(\text{LF})} - \sigma_{(\text{HF})}/E_{(\text{HF})}$. The diameters, using ν of 0.25 [28], are then calculated using equation (1) above. Good agreement has been found between the experimental and calculated diameters, as shown in figures 1(b) and (c). The stronger dependence of tube diameter on the compressive (LF) film thickness relative to the tensile (HF) film thickness is a result of the relatively larger Young's modulus. An overall trend of decreasing deviation with increasing total thickness between the calculated and experimental values can be seen from the linear fit shown in figure 1(c). However, a more detailed investigation will be necessary to understand and correct the deviation over a wide thickness range including much thinner films, comprising the accurate measurement of Young's modulus, additional surface stress correction [29], and the effect of substrate or sacrificial layer surface roughness.

2.2. 360° control of rolling direction and chirality

SiN_x films deposited by PECVD differ fundamentally from epitaxial films, in that internal strain is developed not by crystal lattice mismatch, but by density differences and thermal mismatch during deposition, which can be tuned by deposition conditions. In the case of cubic single crystals such as Si or GaAs, the Young's modulus along $\langle 110 \rangle$ is larger than that along $\langle 100 \rangle$; therefore, self-rolling occurs spontaneously along the softer $\langle 100 \rangle$ direction [17, 18]. In contrast, for amorphous films including SiN_x , the mechanical properties are isotropic in the thin film plane; thus their rolling direction is determined by the sacrificial layer's etching behavior, isotropic or anisotropic.

SiN_x microtubes arrays can readily be rolled-up along the long (a) and short (b) edges of a radially distributed rectangular pad array (figure 2). The sacrificial layer in this case is 80 nm thick polycrystalline Ge film deposited by electron beam evaporation, which can be readily etched isotropically using $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ at elevated temperatures (~ 80 – 120°C). The microtube arrays in figures 2(a) and (b) are fabricated from the same 16 nm LF/20 nm HF bilayer patterned into identical rectangular pads, but with etching windows opened in orthogonal directions. Clearly, the rolling direction is determined by the membrane release direction, demonstrating the controllability of rolling amorphous membranes using isotropic sacrificial layers such as polycrystalline Ge. This is in clear contrast to releasing strained single-crystal InGaAs/GaAs membranes, where the rectangular pads in the radial pattern rolled-up from the $\langle 100 \rangle$

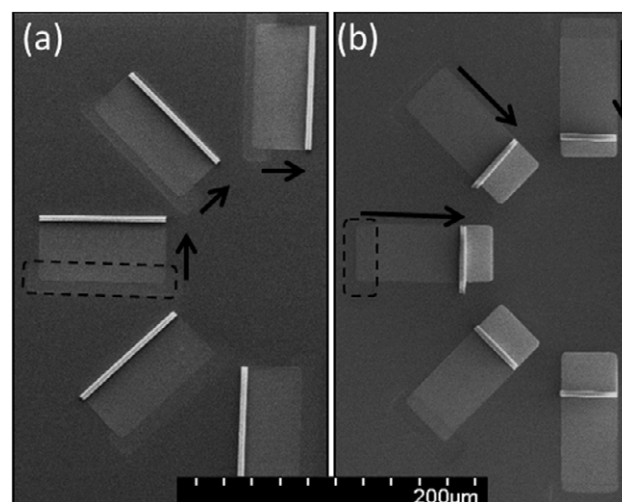


Figure 2. Control of rolling direction: SEM images of microtubes rolled-up rectangular-shaped SiN_x thin film membranes (16 nm LF/20 nm HF) oriented in a radially distributed pattern (only half the wheels are shown). The etching window (outlined by dashed lines) is opened by optical lithography and dry etched to expose the sacrificial layer sidewall along either the long edge (a) or short edge (b) of each rectangular pad. The arrows indicate the pads' rolling directions, which originates from the etch window and proceeds forward.

direction irrespective of the orientation of the etching window, due to the anisotropic mechanical properties of the cubic crystal thin film [18].

It is worth mentioning that substrate surfaces with irregular morphology (such as indentations or protrusion) do not seem to prohibit the formation of microtubes when SiN_x films are deposited conformally, but rather result in imprinted surface abnormalities complementary to the sacrificial layer's surface topography. Examples are provided in figure S1 of the supplemental information (available at stacks.iop.org/Nano/24/475301/mmedia).

On the other hand, using single-crystal silicon substrates allows us to exploit the etch selectivity of crystal planes through KOH or NH_4OH etches, forcing SiN_x films to roll preferentially in the $\langle 110 \rangle$ direction irrespective of the patterned membrane orientation. We have observed, as shown in figure S2 of the supplemental information (available at stacks.iop.org/Nano/24/475301/mmedia), that arrays of rectangular-shaped SiN_x bilayers deposited on Si(111) substrates maintain near-perfect spatial order when fully released and rolled into microtubes, whereas those fabricated on Si(100) substrates are more disordered and randomly dispersed on the substrate. This is because KOH etching of Si(111) proceeds along the lateral direction (the fast etching (110) plane) preferentially, while hardly any etching takes place in the surface normal direction (the slow etching (111) plane). For (100) substrates, vertical ($\langle 100 \rangle$) and lateral ($\langle 110 \rangle$) etching proceed at nearly equal rates, resulting SiN_x microtubes suspended far above the substrate which lose alignment when fully released.

Chiral structures can also be achieved via anisotropic etching of single-crystal sacrificial layer/substrates. We have

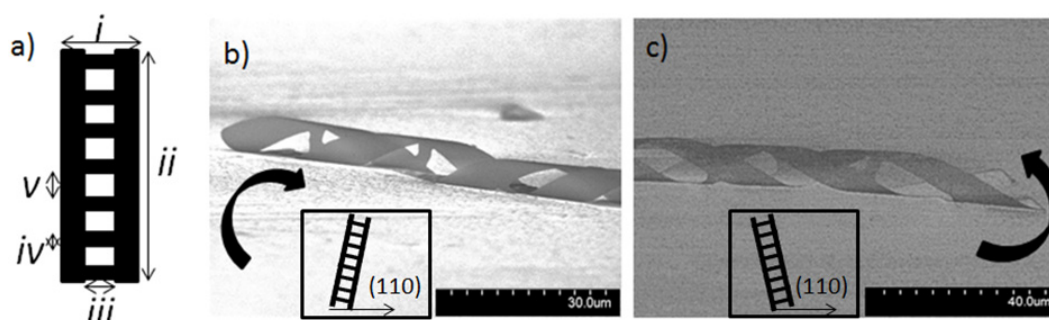


Figure 3. Scheme (a) of the ladder-shaped SiN_x membrane geometry where all parameters $i-v$ are defined as labeled; and tilted SEM images of rolled-up helices having left-handed (b) and right-handed (c) chirality. Dimensions $i-v$ are 20, 204, 6, 3, and 20 μm for (b) and (c), with rotation angles of -15° and $+15^\circ$ from the (110) plane, respectively.

observed that ladder-shaped SiN_x membranes with high aspect ratios can be guided into helical structures with the desired chirality within a range of misalignment angles. Specifically, by orienting a high aspect ratio rectangular pad 10° – 15° off the (110) plane on a Si(111) substrate, chirality with a predictable rotation angle and turn-to-turn pitch can be obtained.

Figure 3(a) shows the design of ladder-shaped rectangular strips of a SiN_x membrane with a total width of i and length of ii . The ladder rung dimensions are given by a width of iii , height of iv , and spacing between ladder steps of v . As in the case of microtubes, the curvature of the rolled-up helical structures are determined by the embedded strain, but the amount of overlap or spacing from turn-to-turn (pitch) and chirality are determined by the ladder geometry and degree of rotation off of the fastest etch plane. This architecture simulates the DNA-like double helix structure, where ladder rungs are analogous to DNA base pairs. Shown in figures 3(b) and (c) are two rolled-up membranes demonstrating a double helix with complementary rotations (left-hand for 3(b) and right-hand for 3(c)). This has been achieved by orienting the strips ($i = 20 \mu\text{m}$, $ii = 204 \mu\text{m}$, $iii = 6 \mu\text{m}$, $iv = 3 \mu\text{m}$, and $v = 20 \mu\text{m}$) by 15° relative to (110) facets to the left or right, as illustrated in the figure insets. To explore the geometry effects of chirality controllability, ladder structures were patterned with varying pad aspect ratios and ‘base pair’ dimensions over a parameter space detailed in table S3 in the supplemental information (available at stacks.iop.org/Nano/24/475301/mmedia), while film thickness was held constant at 55 nm LF/20 nm HF. We found that all pads oriented at an angle 15° clockwise, relative to (110) facets, (figure 3(b)) experienced etching first on the bottom left and top right corners, resulting in left-hand chiral double helices, and vice versa for counterclockwise rotation (figure 3(c)). High uniformity of the chiral structure formation was found in ladders with offset angles of 15° , high aspect ratios ($ii/i \geq 10 \mu\text{m}$), and large rung spacings ($v \geq 15 \mu\text{m}$). Note that long pads suffer from the isotropic nature of the strained SiN_x bilayer, expanding in both dimensions and creating periodic wrinkling prior to release.

As expected, ladders oriented perpendicular to the (110) plane experienced nearly symmetric etching and, with the exception of the highest aspect ratio pad, rolled into tubes

exhibiting no chirality. In this case the areas near the rungs are the slowest etching ones, and thus the last points of contact before full release of the thin film resulting in symmetric rolling. Chiral uniformity among different aspect ratio ladders decreases when the offset angle deviates from 15° . Beyond a $\pm 3^\circ$ tolerance, the aspect ratio becomes the dominant chirality control factor. Owing primarily to a greater torque before full release, high aspect ratio (long and narrow) ladders are more likely to form a double helix, whereas shorter, wider pads more often exhibited no chirality. In SiGe/Si/Cr trilayers reported previously, the chirality direction was predicted based on sacrificial layer asymmetry for pad widths up to 1 μm [20, 30]. In comparison, the ladder structures explored here have total pad widths greater than 1 μm , periodic spacing between ladder rungs, and are made of an amorphous thin film. Longer pads with larger rung spacings ($v \geq 15 \mu\text{m}$) are most consistent with predictions [20] for obtaining helices from a single high aspect ratio rectangular pad, due to the high aspect ratio between ladder rungs. Short, wide ladders suffer from buckling ladder rungs, inducing an additional strain vector and reducing the overall torque. Because of this, random rolling behavior was observed in ladders having a low aspect ratio ($ii/i \leq 8 \mu\text{m}$) and long rungs ($iii \geq 7 \mu\text{m}$) with narrow spacing ($v \leq 6 \mu\text{m}$) over all offset angles. Additionally, at offset angles less than 10° , low aspect ratio ladders exhibited no chirality, while higher aspect ratio ladders at the same offset angle rolled normally. The formation of DNA-like helical structures, enabled by the amorphous SiN_x membranes through anisotropic release, could lead to unique Janus architectures if functional structures or materials can be patterned in 2D before release. The effect of aspect ratio, offset angles, and ladder rung spacing on chirality reported here provides basic boundary conditions for fabricating such chiral structures. Future studies will include systematic modeling to establish the relationship between mechanical torque due to ladder rung spacing and chirality as a function of geometry.

2.3. Structural hierarchy by local stress control

Local curvature modulation in the rolled-up structures due to thickness or stress variation can also be used to create unique

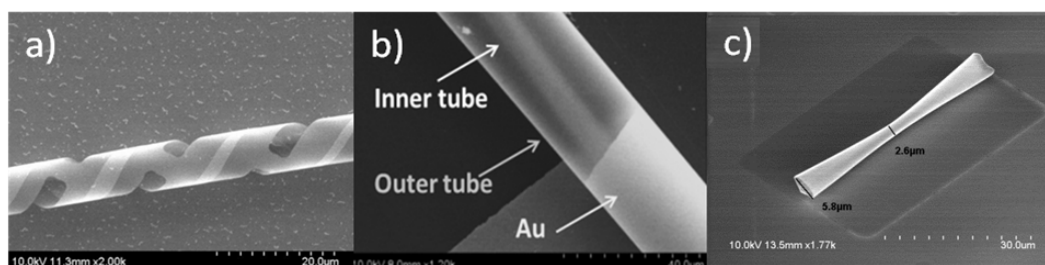


Figure 4. (a) Local thickness variations in chiral tubes induced by angular alignment variations relative to the (110) etch plane on a Si(111) substrate. (b) Coaxial tube arrays due to addition of compressively strained Au (70 nm) onto a 16 nm LF/20 nm HF SiN_x bilayer. (c) Local diameter variations (5.8–2.6 μm) in 50 μm long single-roll microtubes subjected to a post-rolling anneal at 600 °C for 60 s.

3D hierarchical architectures. This can be achieved through either pre-rolling fabrication steps or a post-rolling thermal processing. Thickness variation can be created in high aspect ratio pads by forcing a membrane to overlap itself as it is released from the substrate. As seen in figure 4(a), a high aspect ratio ladder ($i = 17 \mu\text{m}$, $ii = 451 \mu\text{m}$, $iii = 5 \mu\text{m}$, $iv = 3 \mu\text{m}$, and $v = 25 \mu\text{m}$) is patterned onto a 39 nm LF/20 nm HF SiN_x bilayer and offset at 10° to the left, relative to the (110) facet, to achieve an overlapping chiral structure, improving rigidity. In addition, the turn-to-turn overlap distance can be modulated within the same microtube (overlap is seen as bright areas in SEM). This can be useful in achieving large bandwidth RF components, as each overlapping area has a different capacitance and inductance [14]. Strain gradients resulting from additional thin films can also be used as a pre-rolling curvature modulation technique. Materials with different internal stress or thickness will result in a diameter change and can be used, as seen in figure 4(b), to achieve coaxial and triaxial architectures.

By patterning a second level stress material (e.g. Au) in selected areas on strained SiN_x membranes, the curvature of the rolled-up SiN_x structures can be changed locally. Figure 4(b) shows a coaxial tube structure, where the inner tube (smaller diameter) consists of a 39 nm LF/20 nm HF SiN_x film and the outer tube (larger diameter) consists of an additional 70 nm thick Au film on the lower end (bright opaque area) while the upper end is the same SiN_x film as the inner tube (transparent). This was achieved by carefully placing the Au layer right after the SiN_x membrane finishes its first turn with a diameter of $\sim 7 \mu\text{m}$. When the second turn encounters the Au + SiN_x film (with a total thickness of 129 nm), the reduced torque causes the diameter to increase to $\sim 28 \mu\text{m}$, creating a gap between the first and second turn. Similarly, a third level stress layer can be patterned at locations after the second turn to induce a gap between the second and third turn; and so on so forth. These gaps can be engineered by simply changing the thicknesses of the additional layers, allowing coaxial and triaxial microtubes on the same substrate. Note that the additional layer (Au in this case) can be continuous or discrete. In the latter case, the width and spacing of the Au pads are important when designing coaxial microtubes. If the Au pads are separated too far apart, the microtube can tear or collapse instead of assuming the same diameter as areas with the Au pads, owing to the difference between relaxed diameters. Detailed design,

simulation, and fabrication of local stress control using patterned conductive strips for passive electronic components will be reported separately.

In addition, curvature variations can be engineered through post-rolling thermal processing when SiN_x film is deposited using a SiH₄ and NH₃ mixture. The detailed chemistry of the SiN_x formation process can be found in section 4. The SiN_x microtube diameter can be reduced when subjected to thermal annealing at a temperature above the deposition temperature (300 °C), as a result of NH₃ outdiffusion. Shown in figure 4(c), a 60 s anneal at 600 °C in N₂ atmosphere results in as much as a 2× reduction in diameter at the center of the microtube relative to the ends, resulting in a graduated cone architecture. The as-rolled-up tube diameter and length were 4.2 and 50 μm, respectively. We believe the uneven reduction in diameter along the tube is a result of a local thermal gradient along the microtube axis, where heat is trapped in the center and more dissipation occurs at the ends. Depending on the length of the tube and local thermal engineering, various unique structures can be created using this mechanism. Locally constrained microtubes can be useful as low-pass filters in microfluidic channels, where the channel radius has a large impact on the inertia and friction experienced by the fluid.

2.4. 3D hierarchical architectures by heterogeneous integration

By using SiN_x strained bilayers as a vehicle to roll-up other materials, multi-turn tubular architectures consisting of metals, semiconductors, dielectrics, or polymers can be produced. Depending on the amount of additional stress introduced upon the bilayer, the rolled-up hybrid tube can have a larger or smaller diameter than the bilayer itself. Chrome (Cr) and nickel (Ni), with well characterized strain at nearly every deposition rate and thickness [31], can be used to provide greater tensile stress than the HF SiN_x layer. For example, a 9% diameter reduction is seen from a hybrid microtube consisting of 16 nm LF SiN_x/20 nm HF SiN_x/5 nm Cr compared to the 16 nm LF/20 nm HF SiN_x bilayer alone. Cr can also be deposited such that it replaces the HF SiN_x layer to provide the tensile strain.

Shown in figure 5(a) is a rolled-up metal-SiN_x hybrid structure that consists of a stack metal layer (5 nm Ni/60 nm Au/5 nm Ni) patterned into parallel square turning meander

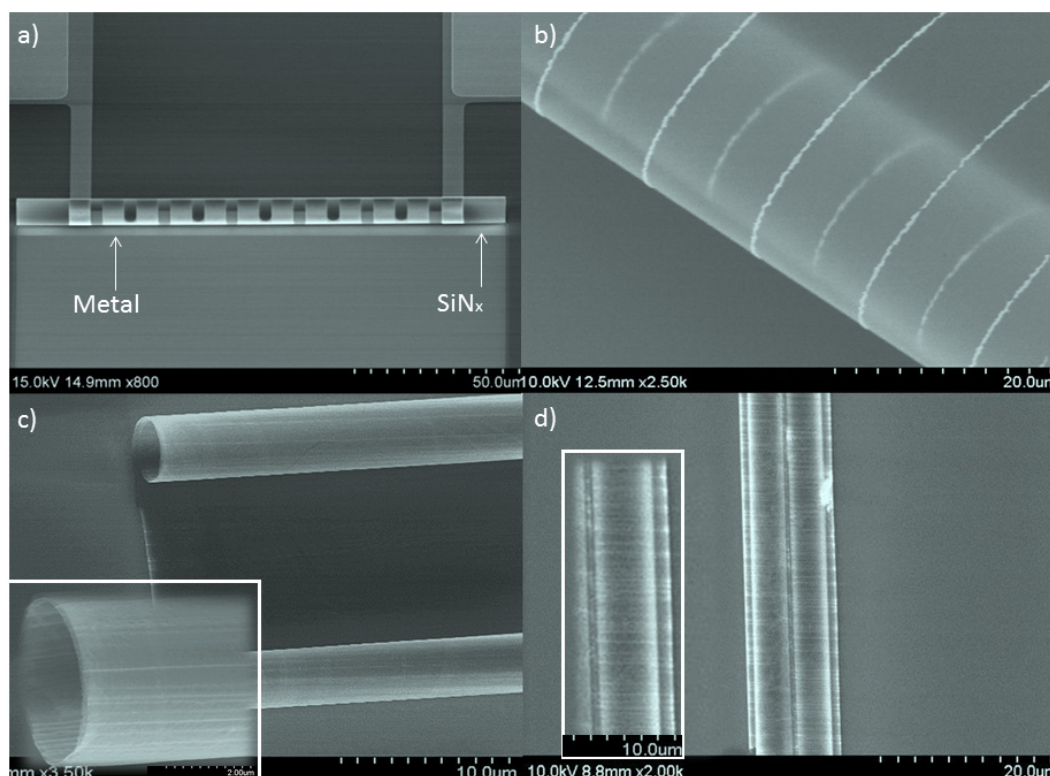


Figure 5. SEM images of silicon nitride based hierarchical hybrid tubes. (a) An inductor design consisting of four turns of 5 nm Ni/60 nm Au/5 nm Ni square wave pattern, rolled-up by a 36 nm strained SiN_x bilayer. (b) 16 nm LF SiN_x/20 nm HF SiN_x/7 nm Cr (exposed)/70 nm Au quadlayer rolled downward due to local stress from chromium oxide, (c) carbon nanotube (CNT) arrays aligned along the axial direction within a rolled-up SiN_x microtube (inset: zoomed-in image of the microtube end, showing CNTs as high contrast lines), and (d) CNT arrays aligned along the radial direction within a rolled-up SiN_x microtube (inset: zoomed-in image of the microtube midsection, showing the gap between microtube rotations).

strips on a strained SiN_x bilayer, yielding a radial superlattice of (SiN_x/metal)_n. The rolling direction is from the bottom up, as indicated by the arrows. The number of windings in this case is four and the inner diameter is 8 μm. This structure can function as a compact inductor with the strained SiN_x film not only serving as the vehicle to reduce the footprint, but also as the insulation between turns of metal. The metal strip in each winding (radial direction) carries current flowing in the same direction, thus more windings are required to achieve higher inductance. More metal strips along the tube axis will also lead to higher inductance, but since adjacent strips carry opposite current they have to be spaced far apart in order to minimize canceling inductance. The detailed theory of the rolled-up inductor design, targeting miniaturization and performance enhancement, can be found in [14] and electrical performance will be reported separately. Any conductive thin film can be patterned and rolled-up in similar fashion to form metallic windings, provided the material resists the sacrificial layer etchant and there is sufficient net strain embedded in the hybrid thin film. The rolling direction can even be dynamically changed if the net strain direction reverses during the rolling process. Shown in figure 5(b) is a scroll of parallel thin (broken) Au lines rolled downward instead of up. This was realized by subjecting a quadlayer, consisting of 16 nm thick LF SiN_x, 20 nm thick HF SiN_x, 7 nm thick Cr thin film, and 70 nm thick and 1 μm wide Au lines, to a RCA

SC1 solution (5-DI:1–30% H₂O₂:1–30% NH₄OH) at 75 °C to etch a germanium sacrificial layer. Initially, the released membrane experienced a torque that rolls the membrane upward. As etching proceeded, Cr was rapidly oxidized when encountering the SC1 solution, resulting in the formation of a compressively strained chromium oxide (CrO₂) layer. The torque from the oxidized chrome resulted in unrolling followed by downward rolling, yielding the image shown in figure 5(b). Note that the rapid oxidation and expansion of the underlying Cr layer has also caused partial delamination of the Au lines, resulting in broken and thinner lines as shown. Downward rolling can also be readily achieved by reversing the strain direction of the SiN_x bilayer. However, patterning Cr in selected areas allows dynamic upwards rolling and downwards rolling triggered during releasing.

Figures 5(c) and (d) show rolled-up CNT structures where a 16 nm LF/20 nm HF SiN_x bilayer is used as a vehicle to roll-up aligned CNT arrays, with CNTs aligned along the axial and radial directions, respectively. Aligned CNTs grown from Fe catalyst lines (5 Å thick, 10 μm wide, 100 μm pitch) were first transferred (including Fe) to the strained SiN_x bilayer with an average density of 5 CNTs μm^{−1}. The SiN_x/CNTs hybrid membrane is then released and rolled-up from both sides of the pad when the Ge sacrificial layer is removed in H₂O₂. This yields a 4 μm diameter final structure having a radial superlattice of (SiN_x/CNT)_n, where

n is the number of windings, and effectively increases the density of CNTs by n times. As expected, CNTs have no measurable influence on the local strain and do not change the diameter of the SiN_x microtubes relative to the bilayer alone. Note that the outer edges of the microtubes in figure 5(d) appear to have gaps, which result from the decreased torque experienced in the area surrounding the now oxidized Fe catalyst strip (10 μ m wide). Similar to the coaxial tube in figure 4(b), the compressively strained strip forces the microtube diameter to increase by ~ 2 μ m, so that a 1 μ m gap is created between turns. However, the SiN_x/CNTs membrane retracts back to the original curvature after passing the Fe strip (100 μ m pitch), resulting in a gap approximately every eight turns. The hierarchical structure created this way can serve as a platform for high density and small footprint CNT based devices. Additionally, this hybrid membrane can provide a mechanism to incorporate CNTs into 3D structures for mechanical reinforcement, taking advantage of the high tensile strength of CNTs and decreasing the probability of SiN_x membrane shearing, discussed previously.

3. Conclusion

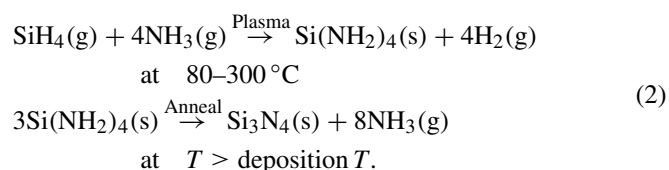
In this study, strained SiN_x membranes have been demonstrated as a versatile platform to achieve unique rolled-up 3D hierarchical structures. The control of compressive and tensile strain in low frequency and high frequency plasma CVD enables monolithic control of the diameter of rolled-up tube arrays. Additional strained layers enable the control of upwards and downwards rolling, as well as the dynamic nature of certain material combinations. The amorphous nature of the film allows 360° control of the rolling direction by lithographical patterning. Combined with the sacrificial layer etching orientation dependence, helical structures with defined chirality are realized. Local stress control allows the creation of hierarchical structures, including coaxial tubes with controlled gap between turns or a lateral gradient of curvature. Rolling-up functional materials, including metal lines and CNTs arrays, using strained SiN_x membranes as a vehicle, presents a pathway to create complex 3D architectures that can potentially lead to advanced functionalities that are otherwise out of reach. Essentially, the processing method demonstrated in this study, in which 3D architectures are fabricated simply by releasing strained 2D hybrid membranes, represents a new design and fabrication paradigm that processes like 2D and functions like 3D.

4. Methods

4.1. Growth and characterization of silicon nitride thin films

A STS mixed frequency nitride PECVD system was used for the deposition of SiN_x thin films. Depending on deposition parameters such as pressure, gas flow ratio and rate, substrate temperature, and RF power and frequency, SiN_x films deposited using a NH₃/SiH₄/N₂ gas mixture can show a range of densities from 2 to 2.5 mg cm⁻³ and refractive

indices from 1.8 to 2.35 [32]. Stress embedded within the film is directly related to density and refractive index, and thus can also be varied widely depending on deposition parameters. The overall reaction for SiN_x films deposited using an NH₃/SiH₄/N₂ plasma [24] is:



Compared to other CVD processes, using a NH₃/SiH₄/N₂ PECVD allows lower processing temperatures and creates an amine-rich membrane. Because of this, the film thickness, geometry, and diameter can be drastically altered after rolling via a high temperature RTA, due to outdiffusion of embedded hydrogen and ammonia within the SiN_x film, as shown in equation (2). (See figure 3(c) and related discussions.)

Both tensile and compressive, as well as zero (compensated), stress can be produced in the film, depending primarily on the operating plasma frequency. Compressive stress is generated at high power and low frequency (LF), whereas tensile stress dominates at high frequency (HF). Low pressure promotes compressive stress by providing a longer mean-free-path for the radicals in the plasma, allowing more to reach the surface for a denser, and thus more compressively strained film [27]. In this study, compressive SiN_x was deposited at 60 W, 380 kHz, 550 mTorr, and 240 °C, resulting in -1168 MPa of residual compressive stress, as measured using a FSM 500TC. In comparison, tensile SiN_x was deposited at 20 W, 13.56 MHz, 900 mTorr, and the same temperature, resulting in $+406.95$ MPa of residual tensile stress. SiH₄, NH₃, and N₂ flow rates and ratios widely affect the embedded strain of the film, as reported in [32]. For this study, 40.0 sccm of SiH₄ and 20 sccm of NH₃ (SiH₄/NH₃ ratio of 2) was used to create the compressively strained SiN_x film, in addition to the parameters previously outlined. Likewise, in addition to the higher frequency and pressure, 40.0 sccm of SiH₄ and 55.0 sccm of NH₃ (ratio of 0.72) was used to create the tensile layers used in this study. N₂ flow was kept constant at 1960 sccm. Further details of the deposition conditions can be found in section S3 of the supplemental information (available at stacks.iop.org/Nano/24/475301/mmedia).

4.2. Fabrication process of rolled-up silicon nitride microtubes

The process flow for fabricating rolled-up SiN_x microtubes is shown in figure 6.

Using process parameters previously discussed, a strained SiN_x bilayer film was deposited using the low (compressive strain) and high (tensile strain) frequency conditions sequentially 6(b), on the sacrificial layer and substrate 6(a). Photolithography was then carried out to define the dimension of the membrane 6(c), followed by dry etching 6(d) through the SiN_x bilayer and beyond the sacrificial layer using Freon 14 (CF₄) reactive ion etching (RIE). This

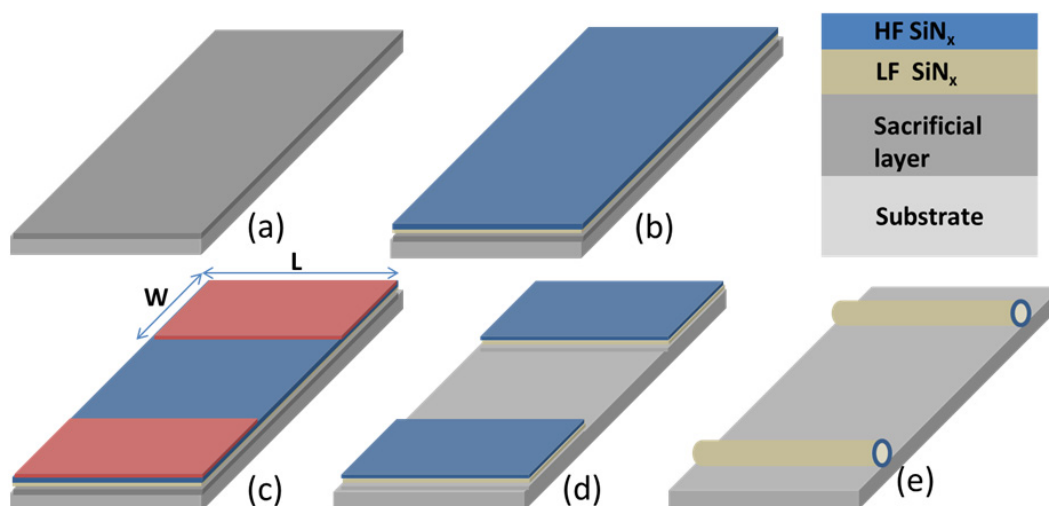


Figure 6. Schematic illustration of process flow of the fabrication of silicon nitride tubes. (a) Clean substrate and deposit sacrificial layer (e.g. Ge on glass), (b) deposit low frequency (LF, compressive) and high frequency (HF, tensile) strained silicon nitride film, (c) define pads lithographically using photoresist (red colored), (d) dry etch through the stack into the sacrificial layer using CF_4 , and (e) etch the sacrificial layer to release the strained membrane to enable self-rolling. The color denotation is illustrated on the upper right.

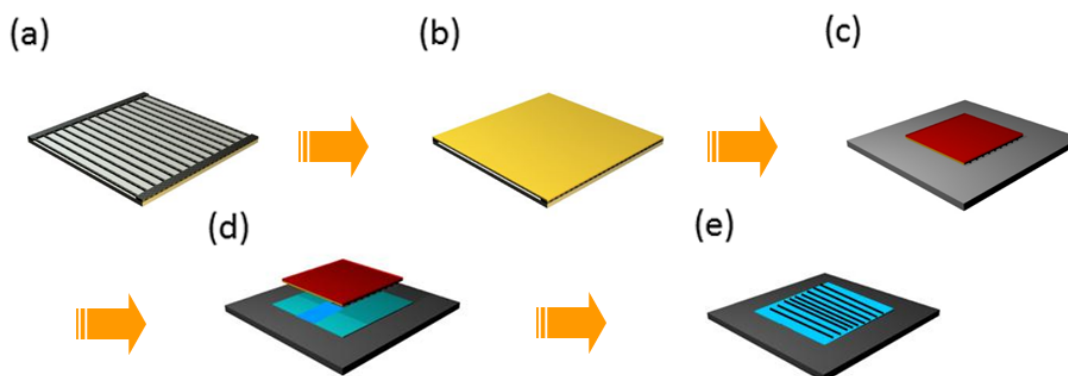


Figure 7. Schematic of CNT polymer transfer onto the SiN_x bilayer. (a) Grow aligned CNTs on quartz, (b) drop-cast polymer (gold) and anneal at 65°C , (c) attach thermal tape (red) and cut away edges, (d) transfer CNT + PVA + tape onto the SiN_x substrate (blue), remove thermal tape by heating at 90°C , (e) and remove polymer using DI.

is to ensure exposure of the sacrificial layer sidewalls to the etchant, leading to uniform lateral etching, membrane release, and rolling 6(e). Depending on the dimension of the pad defined in step 6(c), the released SiN_x membrane rolls-up spontaneously along the long side (L) or short side (W) during the sacrificial layer etch. Our dimensions remained within a L/W ratio of 2.5–8 (7.7–26.5 for chirality experiments) and a T/W ratio of 0.0036–0.01 (0.0034–0.01 for chirality experiments). These values were predicted from data points which satisfy geometric conditions for rolling single-crystal strained membranes from their long side or corners, respectively [33].

Various substrates including crystalline $\text{Si}(100)$, $\text{Si}(111)$, and glass were used for this study. Different sacrificial layers were explored to release the strained SiN_x films, including crystalline silicon, amorphous a-Si, Ge, GeO_2 , and aluminum (Al); various material combinations allowing high etch selectivity between sacrificial layer and strained SiN_x film. For single-crystal Si, the crystal orientation dependent anisotropic etching effect can be readily used to release silicon nitride films directly from $\text{Si}(100)$ and (111) substrates

into ordered microtube arrays. Typically, 45% potassium hydroxide (KOH) solution heated to 47°C is used, yielding a typical lateral etch rate of 380 nm min^{-1} . The MOS compatible ammonium hydroxide (NH_4OH) can also be used for such etching [7]. In the case of evaporated Ge sacrificial layers, a 30% H_2O_2 solution heated to 70°C was used to etch at a rate of 480 nm min^{-1} . Alternatively, germanium oxide can be used as a sacrificial layer, either directly deposited or by oxidizing evaporated Ge, achieving a lateral etch rate of 840 nm min^{-1} in room temperature DI water. Although processing with germanium oxide has more restraints, it is advantageous in situations that prohibit the use of stronger etchants.

The process of transferring the CNT array from its native growth substrate onto the silicon nitride bilayer film was developed to be compatible with the SiN_x bilayer and is illustrated in figure 7. CNT hybrid microtubes were transferred over to glass slides having a Ge/LF SiN_x /HF SiN_x stack, defined via RIE, and wet etched using H_2O_2 , releasing the microtube. (See figure 5 and related discussions.) Details of the growth method for CNT arrays can be found

in [34]. Briefly, 0.5 nm thick Fe catalyst lines were deposited on quartz substrates and growth was done at 925 °C under 20 sccm of Ar and 20 sccm of H₂, bubbled through chilled ethanol, yielding aligned CNT densities of typically 5 μm^{-1} (7(a)). SWNTs are successively encapsulated in PVA (polyvinyl alcohol) and annealed at 65 °C for 1 h. Thermal tape is placed over the hardened PVA and edges are cut away, as seen in figures 7(b) and (c). The resulting film is transferred via thermal release tape and, once transferred onto the receiving substrate, is heated by the receiving substrate (90 °C) to allow removal of the tape (7(d)). Finally, the PVA is washed away with water, leaving pristine, perfectly aligned CNTs.

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