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Insights into the Origins of Guided Micro-Trenches and Micro-Holes/Rings from Sn Segregation in Germanium-Tin Epilayers

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Abstract

We demonstrate the self-assembly synthesis of millimetre-long guided trenches and micro-holes/rings in the supersaturated GeSn epilayers through two approaches: epitaxial growth engineering and thermal annealing treatment. It reveals that the ordered trenches originate from a central nucleation point which typically accompanied by micro-hole/ring formation. These trenches are caused by the migration of Sn droplets on the film surface with the orientation dominantly along $\langle 100 \rangle$ or $\langle 110 \rangle$ axis, determined by the Sn-content of the epilayers and formation temperature. The holes/rings are postulated to be caused by the local droplet etching due to the development of Ge-Sn eutectic. The morphological and compositional evolution of the Sn-segregation is characterized by the combination of optical and electronic microscopy, spectroscopy, and atomic force microscope measurements. This work provides a comprehensive understanding of the mechanism for the Sn segregation in GeSn and suggests the new degree of freedom to the growth and engineering of droplet-assisted micro-structures.

1. Introduction

GeSn alloys are promising semiconductor materials for future optoelectronics, nanoelectronics, and energy harvesting due to their band gap tunability by Sn content and induced strain. Due to their high compatibility with Si-based devices¹⁻³, high-quality $\text{Ge}_{1-x}\text{Sn}_x$ crystalline has been realized on Si and Ge substrates using non-equilibrium growth techniques, including chemical vapor deposition (CVD)^{1, 4-7} and molecular beam epitaxy (MBE).⁸⁻¹⁰ However, Sn has low thermal solubility in Ge (less than 1% at Ge-Sn eutectic of 231°C), with the large lattice mismatch (17%) between α -Sn and Ge. These obstacles limit the introduction of high content of Sn in a Ge matrix. On top of that, GeSn films have poor thermal stability, particularly for films with high Sn content. As a result, the physicochemical, electrical, and optical properties of the GeSn films are highly susceptible to thermal-induced alternations during subsequent processing steps, causing undesired complexity in process designs.

The phase separation in the GeSn films caused by low thermal solubility has been observed not only during growth, but also during thermal treatments. Several studies have reported two main morphological evolutions for the phase separation process: the development of the densely-packed, isolated Sn-rich islands (droplets)¹¹⁻¹³, and the self-assembly of surface trenches caused by the movement of Sn droplets on surfaces.¹⁴⁻¹⁷ Despite the report of numerous studies in exploring the relationship between the Sn segregation and the heating temperature, strain relaxation and dislocation formation,⁹⁻¹⁴ the fundamental

1 mechanisms of the two abovementioned morphological evolutions remain
2 inconclusive. Among the GeSn research communities, much effort has been
3 focused on the growth of high quality GeSn.^{7, 10} Meanwhile, there has been
4 limited studies on the growth of GeSn layers with Sn segregation, where a
5 systematic explanation on the mechanism is called for.

6 On the other hand, the formation of metallic droplets can be used in
7 fabricating of micro and nano devices. Utilizing the migration feature and the
8 reservoir effect of the liquid droplet, versatile fabrication of miniaturized devices
9 can be achieved. For instance, metallic droplets serve as the catalysts at the heart
10 of the vapor–liquid–solid (VLS) mechanism, driving the growth of one-
11 dimensional semiconductor structures such as nanowire,¹⁸⁻¹⁹ nanotube,²⁰ and
12 nanosheet.²¹ Recently, the VLS growth is extended to novel solid –liquid–solid
13 (SLS) growth. Single-crystal in-plane Si nanowires were grown, embedded in
14 the metastable amorphous film by the self-running of the metal-droplets during
15 annealing.²²⁻²³ Apart from that, the metallic nano-droplets has become the key
16 approach for the growth techniques of various innovative compound
17 semiconductor nanostructures, such as nanoring by droplet epitaxy (DE), and
18 self-organized nanohole by the local droplet etching (LDE).²⁴⁻²⁵ In the case of
19 GeSn film, there has been reports showing that Sn wires,²⁶ Sn-rich nanocrystals²⁷
20 and in-plane GeSn nanowires²⁸⁻²⁹ can be synthesised from the migration or the
21 expansion of Sn droplets during the phase segregation.

1 In this work, self-assembled synthesis of millimetre-long guided trenches and
2 perfect micro-holes/rings were demonstrated from the supersaturated GeSn
3 epitaxial layers. The micro-holes/rings and trenches were observed from the as-
4 grown epitaxial and annealed GeSn films by carefully controlling the formation
5 of the Sn droplets/films. The obtained results shown that the migration of Sn
6 droplets only occurs in GeSn films >8% Sn content at a relatively low critical
7 annealing temperature. The orientation of the trenches is demonstrated to be
8 controllable, and the formation mechanism of the micro-holes and -rings is
9 proven to be similar to the DE and LDE of nanostructure. To the best of our
10 knowledge, this is the first report of micro-rings and holes in GeSn films. From
11 this work, our findings provide preliminary understanding on the growth of GeSn
12 layer with Sn segregation. This serves as a comprehensive foundation in possible
13 opportunities in the fabrication of micro-structured semiconductor films with
14 controllable morphology.

16 **2. Methods**

17 We conducted systematic growths and annealing experiments on the
18 metastable GeSn films, where the outcomes are discussed in Section 3.1 and 3.2.
19 The GeSn films were grown by reduced pressure chemical vapor deposition
20 (RPCVD) chamber (ASM E2000 reactor). Typically, GeSn films were grown on
21 850 nm-thick virtual Ge layers on 6" Si (100) substrate at growth temperatures
22 (T_G) range from 280 to 320°C. The flow rates of Ge_2H_6 and SnCl_4 range from

0.17-0.52 standard cubic centimeters per minute (sccm) and 60-80 sccm, respectively (series A, Table 1). The thickness of the obtained GeSn films ranges from 150 to 220 nm, with Sn content ranges from 3.3 to 11.5%. Subsequently, the GeSn wafers were diced into pieces (1.5 cm × 1.5 cm) and annealed using rapid thermal annealing (RTA) technique for 60 s at various annealing temperatures (T_A), ranging from 350 to 650 °C in nitrogen ambient (series B, Table 1). The growth and annealing parameters of the investigated samples in this study are listed in Table 1. The Sn segregation phenomenon could be visually distinguished from the colour of the film surface. The samples without obvious Sn segregation areas have shiny surface, visually distinguishable from the hazy or white-spotted precipitated samples. The experimental details and the subsequent characterization by X-ray diffraction (XRD), secondary ion mass spectrometry (SMIS), Raman spectroscopy, scanning electron microscopy (SEM), AFM, transmission electron microscopy (TEM) are described in the Supplementary Materials.

Table 1 Growth and annealing parameters of the investigated samples.

Sample	T_G (°C) ^a	T_A (°C) ^b	Sn(%) ^c	GeSn (004) ^{da}	SnCl ₄ (sccm)	Ge ₂ H ₆ (sccm)	Surface Colour
Series A							
A1	280	-	11.5	64.25	0.43	80	White spot
A2	290	-	10.0	64.55	0.43	80	Shining ^d
A3	290	-	10.2	64.54	0.52	80	White spot
A4	300	-	8	64.92	0.43	80	Shining ^d
A5	300	-	-	64.84	0.52	80	Shining ^d

A6	325	-	3.3	65.68	0.17	60	Shining ^d
A7	325	-	-	65.29	0.52	60	Hazy
Series B							
B1= A1	280	375-425	11.5	-	0.17	80	White spot
B2= A1	280	450	11.5	-	0.43	80	Hazy
B3= A2	290	375-550	10.0	-	0.43	80	White spot
B4= A4	300	300-650	8	-	0.43	80	Shining ^b

^a Growth temperature; ^b Annealing temperature; ^c XRD characterizing of the GeSn peak in the no white spot area; ^d The sample without obvious Sn segregation area.

3. Results & Discussion

Figure 1. Morphology of the guided micro-trenches and micro-hole/rings on the as-grown $\text{Ge}_{0.898}\text{Sn}_{0.102}$ sample (A3). (a) The photograph of the corresponding 6-inch GeSn samples show the millimetre-sized white spots. (b) Optical microscope image of the white spot which shows the divergent trenches from a

1 central perfectly round micro-ring. Inset shows a micro-hole from another white
2 spot observed in (a). (c) Histogram of the size of the micro-holes and -circles.
3 (d)-(f) SEM-EDS mapping of the Ge and Sn elements for the micro-trenches. (g)-
4 (i) AFM images of micro-rings and -trenches.

5
6 **3.1 Growth experiments.** For the growth experiments (series A), squarish white
7 Sn- segregation spots in millimetre size appeared on the GeSn surface when the
8 growth temperature is lower than 290 °C, with slight overflow of SnCl₄ supply
9 (Figure 1a). Here, the SnCl₄ overflow is defined as the flow rate where Sn content
10 in the GeSn epilayers is saturated (no significant increase) and the Sn segregation
11 occurs. As presented in Table 1, with the same Ge₂H₆ flow rate of 80 sccm and
12 fixed growth temperature of 290 °C, the Sn segregation spots appeared with
13 increasing SnCl₄ flow rate from 0.43 to 0.52 sccm (A2 to A3). At the same time,
14 with fixed Ge₂H₆ and SnCl₄ flow rates, the Sn segregation spots appear with
15 decreasing the growth temperature (A4, A2 to A1; A5 to A3). From the left shift
16 of the position of the (004) peak of GeSn in 2 θ - Ω scan (Table 1), it could be
17 deduced that the Sn-content increases slightly with the SnCl₄ flow rate, and
18 significantly increases with the reduction of growth temperature. The optical
19 microscope images, energy-dispersive X-ray spectroscopy (EDS) analysis, AFM
20 of the grown GeSn samples were shown in Figure 1, and in supporting
21 information Figures S1-3 and S7-8. From the optical microscope images in
22 Figure 1b and S1, it can be clearly observed that these white spots consist of

1 divergent trenches with a micro-ring/hole in the centre. The statistical counts
2 from optical microscope images show that more than 30% of the trenches
3 have >1 mm length. By counting more than 40 white spots, it is found that the
4 number of micro-holes or micro-rings are equal (close to 20). Most of the micro-
5 rings' diameter ranges from 50 to 350 μm , while the diameter of micro-holes is
6 less than 30 μm (Figure 1c). It should be noted that an intermediate shape
7 between the ring and hole with a diameter of 60 μm was also observed (Figure
8 S1d). These micro-rings/holes are in perfect circular shape (Figure 1b). Aside
9 from micro-rings and holes, the trenches exhibit highly ordered pattern with
10 dominant orientation along $\langle 110 \rangle$ axis at the initial stage of the formation, which
11 subsequently changed to $\langle 100 \rangle$ axis at the later stage (Figure 1b). A large Sn
12 droplet (diameter of >10 μm) with the Sn content of ~97.8% (Figure 1d-f and
13 Figure S7) was observed on the tip of the trenches, which can be postulated as
14 the product of segregation and movement of the Sn droplets. Besides the
15 abovementioned morphological observations, reciprocal space mapping (RSM)
16 of the GeSn samples (S2-S3) displays the no-white-spot areas. The no-white-spot
17 areas have a high Sn content of ~10.2%, in contrast to the low Sn content of a
18 ~2.5% on the white-spot area. The distinguishable contrast between no-white-
19 spot areas and white-spot area suggests the presence of Sn segregation.³⁰ On the
20 other hand, the immobile Sn-rich droplets appear at >300°C growth temperature
21 with the overflow of the SnCl_4 flow rate (A6 and A7). For these samples, the Sn-

1 contents of GeSn layers are less than 8% and the surfaces is hazy with high-
2 density Sn-droplets.

3 AFM analysis shows that the micro-rings have the >200 nm depth, where the
4 sidewalls of the micro-rings increases to 200 nm at the ring edges (Figure 1g and
5 i, line 1). At the same time, some particles are observed in the middle region of
6 the ring with 300 nm height, higher than the original film surface. The difference
7 in height indicates that the lost material in the ring has migrated to the edge and
8 the middle regions of the ring during growth process. Similar changes are also
9 observed at the height curve across the trenches (Figure 1h and i, line 2). For the
10 development of the trenches, several reports proposed that the free moving Sn-
11 droplets originate from the directional flow of Ge pushed out from the eutectic
12 liquid Sn droplets.^{14, 26} The recent *in-situ* experiment under SEM and optical
13 microscope also provide evidence of the formation of the trenches during the
14 annealing of the GeSn layers.¹⁴⁻¹⁵ To reduce the Gibbs free energy, the Sn-
15 droplets migrate toward the supersaturated and strained GeSn epilayers and leave
16 the strain-free and stable Ge (or low Sn-content GeSn) layer behind (details in
17 Section 3.3). The Sn-droplets and low Sn-content trenches in GeSn can also be
18 further verified from the EDS mapping of Ge and Sn element in Figure 1e and f.
19 The self-running of Sn droplets is similar to the growth of the lateral Si NWs by
20 the SLS method, where the In droplets move on unstable Si amorphous film
21 during the annealing, resulting in the stable single-crystal Si nanowires.²³ The
22 morphology of the micro-rings and micro-holes could be supported by the fact

that the formation of nano-holes and -rings from droplet-assisted DE and LDE (See details in Section 3.5).²⁴ For the droplet-assisted formation of nano-ring, an abruptly raised height at the edge of nano-rings also was observed, which is attributed to the crystalline at the perimeter of the nano-droplet.²⁴

Figure 2. Morphology of the micro-trenches on the annealed GeSn samples with Sn content of 8 to 11.5 % at different annealing temperatures. (a) Photograph; (b) spot density and percentage of total spot area on the whole GeSn surface; (c) growth rate of the spot/trenches. (d)-(e) AFM images of the Ge_{0.90}Sn_{0.10} samples after annealing at 400 and 550 °C and (f) Ge_{0.885}Sn_{0.115} sample after annealing at 375°C. (g)-(i) The corresponding optical microscopy pictures and schematic model of the direction of the trenches in (d)-(f).

1

2 **3.2 Annealing experiments.** To further investigate these self-assembled micro-
3 ring/holes and trenches, the as-grown GeSn (with Sn content of 3.3 to 11.5%)
4 films without the white spot areas were annealed at temperatures of 350–650 °C
5 for 60 s (series B, Table 1). Figure 2a and Figure S5 show the optical microscope
6 images and photographs. For samples with Sn contents of 3.3 and 8%, the surface
7 of the samples remains shiny after the annealing. From the Figure S5a, it is
8 observed that for $\text{Ge}_{0.92}\text{Sn}_{0.08}$ samples, the Sn segregation was hardly observed
9 until the annealing temperature increased to 650 °C, where sparse and immovable
10 Sn-rich droplets appeared. However, for the GeSn samples with the higher Sn
11 content ($\text{Ge}_{0.9}\text{Sn}_{0.1}$ and $\text{Ge}_{0.885}\text{Sn}_{0.115}$), Sn segregation happens at around 400 and
12 375 °C, along with the trenches and mobile Sn droplets. As shown in Figure 2a,
13 the Sn segregation area (white spot) could be visually observed. Similar to the
14 as-grown samples, these trenches originate from the central position of the white
15 spots and Sn-segregation phenomenon was not observed beside these spot zones
16 (Figure S5 and S6). We also noticed that the entire surfaces of $\text{Ge}_{0.885}\text{Sn}_{0.115}$
17 samples are hazy with high-density of Sn-droplets when the annealing
18 temperature is larger than 450 °C (Figure 2a).

19 Based on the above experiments, it can be concluded that the migration of Sn
20 droplets occurs in the GeSn films with Sn content of >8% from a relatively low
21 critical annealing temperature, while the immovable Sn-rich islands mostly
22 appear in the GeSn films with low Sn content at higher annealing temperature.

1 The similar observations have been reported, such as the trenches occurs in the
2 Sn-content of 10% (250 °C,¹⁴ 450 °C³¹), 12% (460 °C),³² 17% (300 °C)²⁶ and the
3 immovable Sn-droplets in 5.4 % (600 °C),³³ 6.5 % (650 °C),¹³ and 7.8 % (620 °C)
4 ¹¹ GeSn epilayers. From the thermodynamic point of view, the migration of the
5 droplets requires large Gibbs free energy change between the supersaturated
6 GeSn film and crystalline stable Ge (or low-content GeSn). The Gibbs free
7 energy change for Sn segregation can be written as^{17, 26}

$$8 \quad \Delta G = -(\Delta G_V + \Delta G_S) + \Delta G_{in} \quad (1)$$

9 where ΔG_V is the reduction of the free energy from the high supersaturation GeSn
10 to Ge (or low-content GeSn) and Sn droplet, which is determined by the mixing
11 enthalpy and entropy. ΔG_S is the changes of strain energy from compressive
12 GeSn films to strain free-Ge (or low-content GeSn). ΔG_{in} is the changes of the
13 interfacial energy from Ge/GeSn interface and a non-equilibrium GeSn surface
14 to the equilibrium Ge surface and the Sn droplet surface (including the liquid–
15 vapor and liquid–solid surface). From a thermodynamic point of view, the initial
16 nucleation of Sn droplets will be near the defects or dislocations, as it will reduce
17 the Sn droplet surface energy (ΔG_{in}). Base on the calculation from Yu *et al.*,³⁴
18 the Gibbs free energy of the strained-GeSn for the Sn-content of 0, 3, 8, 10, and
19 11.5% at 400 °C has an energy of 0, 1, 6, 9, and 12 meV. Thus, due to the high
20 Sn content (10-11.5%) in this work, the ΔG_V and ΔG_S are enough to drive the
21 movement of Sn droplets. This also explains the occurrence of more Sn
22 segregation with white spots when the growth temperature decreases from 300

1 to 280°C (Part 3.1), which can be attributed to the Sn content that exceeds the
2 threshold value of 8% (bigger Gibbs free energy gap). We notice that our
3 obtained results are slightly different from the recent MBE growth experiment
4 from Wang *et al.*¹⁷ where the density of white-spots increases when the growth
5 temperature increases from 155 to 175 °C. This result is due to the constant of
6 Sn-content of the GeSn films at 20% during growth while the increase of the
7 substrate temperature increases the migration of Sn atoms.

8 The effect of Sn-content and temperature on the formation of the white-
9 spots/trenches could be assessed by analysing the density (quantity) and the total
10 area of the white spot in the samples at different annealing temperature with
11 varying Sn-content samples. As no Sn-segregation is found beyond the white-
12 spot region and Sn trenches all originate from the central position, the density of
13 spots should reflect the nucleation density of the white spots. As shown in Figure
14 2b, the spot density and total area increases with the annealing temperature and
15 the Ge_{0.885}Sn_{0.115} sample presents the spot density 10-100 times higher than that
16 of the Ge_{0.9}Sn_{0.1} sample at the similar temperature. It shows Ge_{0.885}Sn_{0.115} sample
17 has higher temperature sensitivity with the higher density and total spot area
18 increases rapidly with temperature range of 420-440 °C. For the high Sn-content
19 layer, more significant Sn segregation occurs on the epilayers' surface and with
20 lower critical temperature. The Sn segregation is not solely due to the high
21 supersaturation (larger Gibbs free energy gap between GeSn and Ge) as
22 discussed above. The high-density non-equilibrium defects in GeSn, such as the

1 vacancies from the low-temperature growth and the dislocation from the large
2 lattice and thermal mismatch, also plays a major role in Sn segregation.²⁶ These
3 defects not only reduce the activation energy barrier of the nucleation of the Sn-
4 droplets, but also act as the Sn motion route which aggravates the Sn migration.
5 It should be pointed out that the previous work which suggests this nucleation Sn
6 island are based on liquid films, where the nucleation sites are possibly located
7 on the nonequilibrium defects²⁶. For the partially-relaxed GeSn layer, a recent
8 study via atom probe tomography has shown that the formation and propagation
9 of dislocations facilitates the Sn transport toward the surface through pipe
10 diffusion.³⁵ From TEM image of the GeSn investigated in this study, it also
11 clearly shows that high-density dislocations are clustered near the droplets (see
12 Figure 6 e). The temperature dependence on spot density and the total area also
13 suggests that the Sn-segregation is thermally activated. Fundamentally, Sn atoms
14 require sufficient energy to escape from bulk Ge atoms (with the bond energy of
15 Ge-Sn $\sim 230 \text{ kJ mol}^{-1}$)³⁶ and overcome both energy barrier (nucleation of Sn
16 nucleus) and kinetic barriers (diffusion of the Sn atoms to nucleus) for Sn
17 segregation. This escape energy can be sourced from externally-applied thermal
18 energy, which explains the thermally-activated characteristics of Sn segregation
19 phenomenon.

20 With prolonged annealing time after nucleation, the Sn islands migrate
21 while forming the trenches, with a moving grain boundary or grain-growth front
22 as shown in Figure 2d-i and S5. By measuring the size of the spot areas, the

1 average growth rate of the trenches/spots on $\text{Ge}_{0.9}\text{Sn}_{0.1}$ samples increases from
2 11.8 to 42.5 $\mu\text{m/s}$ when the temperature changes from 400 to 500 $^{\circ}\text{C}$; meanwhile,
3 the growth rate of the $\text{Ge}_{0.885}\text{Sn}_{0.115}$ samples slightly decreases from 9.3 to 8.2
4 $\mu\text{m/s}$ as temperature increases from 385 to 435 $^{\circ}\text{C}$ (Figure 2c). The activation
5 energy for the etching rate of the trenches of the $\text{Ge}_{0.9}\text{Sn}_{0.1}$ sample was calculated
6 to be ~ 0.4 eV using the Arrhenius equation. Eng *et al.* suggested this activation
7 energy reflects the thermal stability of the GeSn films.¹⁵ A higher activation
8 energy of ~ 1.4 eV was found on (111) surface compared to ~ 1.1 eV on the (001)
9 surface with the same Sn-content of 8%.¹⁵ The higher activation energy can be
10 attributed to high-stability (111) surface.¹⁵ As compared to the work reported by
11 Eng *et al.*, the activation energy of $\text{Ge}_{0.9}\text{Sn}_{0.1}$ sample in our work is about a
12 quarter, indicating lower stability of the $\text{Ge}_{0.9}\text{Sn}_{0.1}$ due to the higher Sn-content.
13 Nevertheless, it is challenging to assess the growth activation energy of the
14 $\text{Ge}_{0.885}\text{Sn}_{0.115}$ sample due to the decrease of the spot size when the annealing
15 temperature increases. We attribute the decrease of the etching rate for
16 $\text{Ge}_{0.885}\text{Sn}_{0.115}$ samples to the increase of the white spot density, which hamper the
17 movement of the Sn droplets when two nearby areas meet (Figure S1).

18 AFM was used to analyse the direction of the trenches on annealed GeSn film.
19 For the $\text{Ge}_{0.9}\text{Sn}_{0.1}$ film, the trenches are propagated along with four $\langle 100 \rangle$
20 directions under the annealing temperature of 400 $^{\circ}\text{C}$ (Figure 2d), while the
21 propagations occur along four $\langle 110 \rangle$ directions under 550 $^{\circ}\text{C}$ annealing
22 temperature (Figure 2e). For the $\langle 110 \rangle$ direction trenches, the wire-like Sn

1 droplets assemble on the tip of the trenches, developing to the $\{110\}$ etching
2 plane (Figure 2h). The $\langle 100 \rangle$ direction trenches (2g) were developed by two
3 etching planes which are close to the $\{110\}$ plane. On the other hand, for the
4 $\text{Ge}_{0.885}\text{Sn}_{0.115}$ samples, the growth directions are uniform and without a fixed
5 etching plane (Figure 2f and i). As mentioned earlier, the trenches in the as-grown
6 sample are propagated along $\langle 110 \rangle$ at the initial stage of the GeSn growth, where
7 their orientation is shifted to $\langle 100 \rangle$ at the later stage of the growth. It is expected
8 that these kinks may be caused by the sudden change of growth conditions, such
9 as change in temperature, which causes abrupt termination of the GeSn growth.
10 At the same time, the annealing experiments above shows that low temperature
11 promotes the growth along $\langle 100 \rangle$ direction. The $\{110\}$ planes are the lowest
12 surface energy facets along the zone axis of $\langle 001 \rangle$ for Ge.³⁷ Thus, as similar to
13 the VLS nanowire growth and dendrite cell growth,³⁸⁻³⁹ the anisotropy of the
14 solid-liquid interfacial energy may play a crucial role to determines the direction
15 of the trenches. For the GeSn film with the high Sn-content, the small surface
16 energy difference between the $\{110\}$ and other planes and the large etching rate
17 might result in the disordered trenches. These results indicate the available
18 pathways to control growth directions of the trenches, like the adjustment of the
19 orientation of the nanowires.

Figure 3. Morphology of the micro-rings on the annealed $\text{Ge}_{0.9}\text{Sn}_{0.1}$ sample at 400 °C. (a)-(e) Optical microscopy, (f)-(g) AFM of the micro-ring from (e); and (h)-(k) SEM-EDS mapping measurements of the micro-rings with Si, Ge and Sn elements from (c).

3.3 Detailed characterization of micro-holes and -rings. Figure 3 shows the morphology of the micro-rings on the annealed GeSn sample. Similar to the as-grown GeSn (Figure 1), micro-rings/holes appear at the centre of the white spot on annealed GeSn film ($\text{Ge}_{0.9}\text{Sn}_{0.1}$) with diverging trenches (Figure 3). One of the differences observed in annealed GeSn samples from the as-grown samples is that some white spots do not have a micro-rings/holes in their central region (Figure S5) on the annealed samples. These results suggest possible correlations between the rings/holes and trenches. To further investigate the origin of micro-

rings/holes, the morphology, structure, and element distribution of these structures after annealing are studied and discussed in the followings.

As shown in Figure 3a-e, the circles/holes from the annealed samples have similar features with the as-grown samples in terms of the shape, the size, and the cross-sectional structure. Figure 3f-g shows the AFM analysis of a micro-ring from the centre of the white spot in Figure 3e. The step height curve suggests the presence of particles in the ring and the migration of the substance from the ring to the external region. The element around the rings were analysed by SEM-EDS. As shown in Figure 3h-k, external region of the ring is mainly Ge (low Sn content) with some Sn-rich particles. On the other hand, we also found that the ditch in the rings is Si while the particles in the rings/holes are the low Sn-content GeSn. Additional EDS mapping and point analysis of the as-grown and annealed GeSn samples also present similar results (S6-S8, supplementary information).

Figure 4. Raman analysis of the micro-ring and trenches on the annealing $\text{Ge}_{0.900}\text{Sn}_{0.100}$ film. (a) and (b) Intensity mapping of the micro-ring with the wavelength around $270\text{-}305\text{ cm}^{-1}$ and $520\text{-}522\text{ cm}^{-1}$. (c) Intensity mapping of the tip of trench with the wavelength around $270\text{-}305\text{ cm}^{-1}$. (d) Raman spectra correspond to regions labelled by 1, 2, 3 in (c).

To further understand the structural properties of the investigated GeSn samples, we performed Raman mapping on the micro-rings and trenches. The Raman intensity maps of Ge-Ge ($270\text{-}305\text{ cm}^{-1}$) and Si ($520\text{-}522\text{ cm}^{-1}$) bands show obvious inhomogeneous distribution of Raman intensities in Figure 4a and b, respectively. Within the ring region, a high intensity band of $\sim 520\text{ cm}^{-1}$ is observed, indicating the high abundance of silicon element; whereas the external region of the ring shows high intensity of Ge-Ge band, indicating high abundance of germanium element. The observed inhomogeneous distribution of Ge-Ge band intensity around the ring can be attributed to the presence of various Sn-content due to the Sn-segregation. As shown in Figure 4c, the Raman intensity of the Ge-Ge band is high on the trench while weak or no intensity is observed outside the trench region or on the Sn-droplets. The Raman spectra of different three zones in Figure 4c are shown in Figure 4d, where Zone 1, 2, and 3 represents out of spot area, Sn droplet, and in spot area, respectively. Based on the peak position of the Ge-Ge band in point 1 (290.3 cm^{-1}) and 3 (296.8 cm^{-1}) and the equation of $\Delta\omega = -83.11x - 374.53\varepsilon$ ($\Delta\omega$, x , and ε are the Raman spectral shift compared to the

1 bulk Ge at 300.4 cm^{-1} , Sn content, and strain, respectively),⁴⁰ the Sn content
2 on/out of the trench was calculated to be around 9% and 4%. Here, the
3 compressive strain of -0.7%, -0.12% for the position at the Sn stable zone and
4 trench zone was obtained via XRD-RSM (S2 and S3). The Raman results is
5 consistent with the extracted Sn contents of around 10% and 2.5% by RSM.

6 The elemental distribution and crystal structure of the micro-circle from the
7 annealing $\text{Ge}_{0.9}\text{Sn}_{0.1}$ sample at $400\text{ }^{\circ}\text{C}$ was also analysed using the transmission
8 electron microscope (TEM). The cross-section TEM sample (Figure 5b) was
9 prepared by piecing the GeSn film across the ring using the SEM-focused ion
10 beam (FIB, Figure 5a). The EDS chemical mappings at the external, internal and
11 central of the ring with the distribution of O (purple), Ge (yellow), Si (green) and
12 Sn (blue), is presented in Figure 5c-i. The presence of O element can be
13 postulated as the residual oxygen in the RTA system and the atmospheric contact
14 after GeSn growth. The elemental map of Si and the cross-section TEM images
15 (Figure 5b) clearly reveal that the Ge layer were fully etched in the ring. Apart
16 from that, it was observed that a thin SiO_x layer was grown under the ring which
17 was halted at the edge of the Ge/Si interface (Figure 5c and d). Note that the O
18 element is also concentrated on the surface of GeSn layer and Sn droplet (Figure
19 5c). The element distribution of the Ge and Sn indicates the presence of GeSn
20 layer with a low Sn content (2-6 %) embedded with some Sn droplets which
21 cover the underline Ge layer and Ge particle (Figure 5e-i). It is also observed that
22 the height of the Ge layer near the edge of the ring is around 200 nm higher than

1 the as-grown Ge layer (Figure 5g). EDS line scans along the red lines marked in
2 Figure 5 g and i also clearly show the GeSn and Ge layer, O-rich Sn droplet and
3 SiO_x layer.

4 Similar to the droplet-assisted formation of nano-hole/ring, we propose the
5 following mechanisms on the formation of the micro-rings on the annealed
6 samples: 1), the O-rich Sn liquid dissolves the GeSn and Ge film along the ring.
7 2), a thin SiO_x layer grows on the silicon surface after the O-rich Sn droplet
8 contacted the silicon. 3), the Ge particle grows subsequently on the SiO_x layer
9 due to the over-saturated Ge in the Sn droplets. 4), after the migration of the Sn-
10 droplet outside the ring, the top GeSn film is transformed into the low Sn-content
11 GeSn film and with some small Sn droplets (Figure 5f-g). Some residual Sn
12 atoms cover the Ge particle and formed GeSn shell on the Ge particle (Figure 5i-
13 h). For as-grown samples (A1 and A3), the formation of the micro-rings is similar
14 except for the SiO_x layer as minimal oxygen content is present in the RPCVD
15 chamber during the epitaxial growth.

Figure 5. STEM-EDS analysis of the element distribution of micro-ring on the annealing $\text{Ge}_{0.90}\text{Sn}_{0.10}$ epilayer. (a) and (b) Representative SEM and HAADF-STEM images of the observed area. (c)-(i) EDS chemical mappings on different zones of the ring showing the distribution of O (purple), Ge (yellow), Si (green) and Sn (blue) at the external (c-e) internal (f-g) and central (h-i) zone. (j) and (k) EDS line scan along the red arrows marked in (f) and (h).

Figure 6. TEM crystal structure and dislocation analysis of the micro-rings on the annealed $\text{Ge}_{0.90}\text{Sn}_{0.10}$ epilayer. (a) The bright-field (BF) mode image of the particle; (b)-(c) the observed area and corresponding SAED pattern; (d) HRTEM and FFT images of a grain in (a); (e) and (f) BF and HRTEM images of the GeSn/Ge layer near the ring; The corresponding FET image is inside (f).

The bright-field (BF) mode image and selected area electron diffraction (SAED) pattern (Figure 6a and b-c) indicate polycrystalline characteristics of Ge particles with several grains. This is due to the non-epitaxial and multiple nucleation of the Ge on the SiO_x layer. The HRTEM image and corresponding Fast Fourier Transform (FFT) image in Figure 6d shows one of the grains is single crystalline. However, at the edge of the ring, the re-crystallized Ge crystal is a single crystal due to the homogeneity epitaxy (shaded area in red in Figure 6e and S11). We also noticed that the surface GeSn layer is single crystal without

obvious stacking and twin defect (Figure 6f). However, from the BF image (Figure 6e), significant amount of misfit dislocations and threading dislocations are on the GeSn layer. In the case of as-grown GeSn samples, the dislocations are mainly the misfit dislocations at the GeSn/Ge interface (Figure S10). We suggest that the threading dislocations in GeSn epilayer is mainly caused by the process of Sn segregation which destructs the original crystal structure.

3.4 Proposed formation process of the micro-structures. We have discussed the formation of immobile Sn-rich droplets which occurs specifically on the low Sn-content samples (<8%) at high annealing temperature (Process I, Figure 7). For the high Sn-content layer, the Sn aggregation (with micro-trenches) occurs at relatively low annealing/growth temperature with a movement mode due to their high supersaturation.

Thus, during growth or annealing, the Sn-nucleus (droplet or film) could be easily-developed on the high Sn-content epilayer, especially near the locations of defects.²⁶ After the nucleation process, the nearby Sn atoms diffuse to the Sn-nucleus and develop to be a large Sn film. Attributing to the anisotropy nature of the single crystal GeSn, the round shape of the micro-holes/rings also implies that the liquid films might be a circle with several tens of micrometres in diameter (Process II and III, Figure 7). If the liquid Sn film has a diameter of <30 μm , it may fully etch the bottom GeSn and Ge epilayer (case II, figure 7) before the formation of the trenches. Tonkikh *et al.*, found that the formation of large Sn-

1 rich GeSn areas across the Ge film only occurs when the annealing temperature
2 is less than 400 °C.²⁷ They suggested the formation of the liquid phase may occur
3 via the creation of a Ge-Sn eutectic, promoting the etching of the top Ge layer.
4 Thus, similar to the formation of nanohole by local Ga/Al droplet etching,²⁴ the
5 micro-holes are likely to be the creation of a Ge-Sn eutectic island which etches
6 the underneath Ge film (case IV_a, figure 7). On the other hand, for the annealed
7 samples, there are some white spots without a micro-rings/holes in their central
8 (Figure S5). This always occurs at the high annealing temperature or when the
9 Sn content of the GeSn sample is 11.5% (case IV_b, figure 7). We suggest that the
10 phenomenon may be attributed to the increase of the mobility of the Sn droplets
11 on the film surface, where the short residence time of the liquid island weakens
12 the etching of the underneath Ge film.

13 If the size of the film island is larger than 50 μm, the etching only occurs
14 along the perimeter of the film island, which leads to the ring morphology (case
15 III and IV_c, figure 7). This micro-circle is similar to the formation of the nano-
16 circle using the droplet epitaxy method. On (001) oriented substrates, the
17 crystalline GaAs first appeared as a ring along the perimeter of the nano-droplet
18 (the triple point).²⁴ The perimeter of the droplet, where the intersection of the
19 crystal with the droplet surface establishes a three-phase-line, can act as a
20 preferential incorporation or nucleation which serves as an initial place for
21 crystallization. For our case, similar etching occurs along with the crystallization
22 of Ge at the edge of the holes/circles, which acts as a nucleation seed for further

1 crystallization and etching toward the central of the ring. In conjunction to the
 2 observed intermediate state between the rings and holes as discuss earlier, the
 3 explanation of the micro-hole/rings using the concept of the droplet etching
 4 should be feasible. The concept of thermal etching without the assistance of
 5 liquid droplet could not explain the round shape of the circle/ring due to the
 6 anisotropy of the single crystal GeSn and Ge. However, to fully study the
 7 formation of the micro-holes/circles, the in-situ observation under the SEM or
 8 optical microscope should be conducted in the future.

9

10 **Figure 7.** Propose the formation process of the droplets, trenches, holes and rings
 11 on a GeSn film: I), Immobile Sn-rich droplets developed on the low Sn-content
 12 GeSn film (<8%) in high growth/annealing temperature; II) and III), liquid films
 13 developed on the high Sn-content GeSn film at low growth/annealing

1 temperature. IV) Sn liquid assisted etching resulting in the micro-holes, -rings
2 and trenches.

4 **4. Conclusions**

5 In conclusion, the self-assembly of micro-rings/holes and ordered trenches
6 on metastable GeSn epilayers were presented via epitaxial growth and thermal
7 annealing. Ordered trenches are observed to originate from a nucleation point
8 which accompanied by a micro-hole or micro-ring. From the morphological
9 observations, the ordered trenches are postulated to be caused by the migration
10 of Sn islands on the surface to reduce the Gibbs free energy of the supersaturated
11 and strain GeSn epilayers. The direction of the trenches is found to be determined
12 by the growth condition, the annealing temperature and the Sn contents of the
13 GeSn epilayers. Due to the lowest surface energy along the zone axis of $\langle 001 \rangle$,
14 the etching plane of the $\langle 110 \rangle$ and $\langle 100 \rangle$ axis trenches both are $\{110\}$ planes.
15 Most of the micro-rings and holes present with the perfect circle morphology has
16 diameters of less than 30 μm and large than 50 μm , respectively. The formation
17 micro-holes/circles can be attributed from the droplet etching due to the
18 development of Ge-Sn eutectic. Our studies not only provide an insight into
19 controlled growth of GeSn films at a uniform composition and along with a
20 comprehensive investigation of their thermal stability, but also provide the means
21 to control the direction of the self-running droplets, adding another degree of
22 freedom to the growth and design of droplet-assisted micro- and nanostructures.

Supporting Information:

The supporting information is available free of charge via the internet at <http://pubs.acs.org>.

(1) Materials and Methods. (2) Representative morphology data of the micro-rings and -trenches on the as-grown $\text{Ge}_{0.898}\text{Sn}_{0.102}$ epilayer obtained from optical microscope and AFM. (3) XRD data. (4) SIMS data of the as-grown $\text{Ge}_{0.90}\text{Sn}_{0.10}$ epilayer before annealing. (5) The additional optical microscope images and AFM mappings for GeSn epilayers shown in Figure 2. (6) Complete SEM-EDS analysis. (7) Complete TEM analysis. (PDF)

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Conflicts of interest

There are no conflicts to declare.

Author Contributions

Chuan Seng Tan and Shaoteng Wu designed the experiments. Lin Zhang and Shaoteng Wu grown the samples. Shaoteng Wu and Bongkwon Son, Qimiao Chen, Lim Yu Dian and Hao Zhou performed the characterizations. Shaoteng Wu, Bongkwon Son, Lim Yu Dian and Lin Zhang wrote the manuscript.

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