

WS₂ nanotube formation by sulphurization: effect of precursor tungsten film thickness and stress

Sheung Mei Ng^a, Hon Fai Wong^a, Wang Cheung Wong^a, Choon Kiat Tan^a, Sin Yuk Choi^a, Chee Leung Mak^a, Gui Jun Li^a, Qing Chen Dong^{b*} and Chi Wah Leung^{a*}

^aDepartment of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

^bMOE Key Laboratory for Interface Science and Engineering in Advanced Materials and Research Center of Advanced Materials Science and Technology, Taiyuan University of Technology, 79 Yingze West Street, Taiyuan 030024, P.R. China

Email¹: dennis.leung@polyu.edu.hk

Phone/Fax: 852-27665670/852-23337629

Abstract

Transition metal dichalcogenides can exhibit as 2-dimensional layers, 1-dimensional nanotubes or 0-dimensional quantum dot structures. In general, dichalcogenide nanotubes are grown under stringent conditions, using high growth temperatures with tedious processes. Here, we report the controlled formation of tungsten disulphide (WS₂) nanostructures by manipulating the precursor film thickness, followed by a direct sulphurization process. WS₂ nanotubes were formed by ultra-thin tungsten precursor films, while particle-like WS₂ were obtained from thicker tungsten films under identical sulphurization conditions. To elucidate the origin of WS₂ nanostructure formation, micron-sized tungsten film tracks were prepared, and such patterned films were found to suppress the growth of WS₂ nanotubes. We attribute the suppression of nanotube formation to the relieving of film stress in patterned precursor films.

Keywords

Transition metal dichalcogenides, tungsten disulphide, nanotubes, patterning

1. Introduction

Two-dimensional layer materials possess attractive properties such as strong optical nonlinearities for optical storage [1-3], topological insulating behaviour [4] and thermoelectric properties [5], and

are being actively researched. In particular, transition metal dichalcogenides (TMD) with such layered structures are compounds of chemical formula MX_2 (M = metal, such as Mo, W, Ti; X = chalcogen, such as S, Se, Te), in which each layer consists of the metal atoms bound to the two chalcogen planes with strong covalent bond and only weak van der Waals' force between layers [6, 7].

For many of the layered MX_2 semiconductors, one of the remarkable properties is their gradual transition from being indirect bandgap material in the bulk form to direct bandgap ones upon thinning to single-atomic layers [8, 9]. This endues their potential for various optical [8, 10], electrical [11-13], and catalytic [14, 15] applications. Tungsten disulphide (WS_2) is a well-studied example, with the bandgap varying from 1.4 eV (indirect) in the bulk to ~ 1.95 eV (direct) in monolayers [8, 16]. Field-effect transistors have been fabricated with WS_2 sheets as the channel material [17].

Different routes were explored for the preparation of TMD such as mechanical and chemical exfoliation of bulk single crystals [9, 13, 18], physical vapour deposition (PVD) [19], chemical vapour deposition (CVD) and direct sulphurization [10, 20, 21]. Among these techniques, CVD and direct sulphurization are common methods used for the synthesis of single-crystal layered TMD, in which metal-containing precursors and chalcogens were introduced into a chamber for reaction under the flow of a carrier gas. Under extreme condition of high temperature and reduced atmosphere, polyhedral and cylindrical structures could be visualized [22].

Relatively little investigations have been made concerning the properties of layered TMD materials in tubular form. Multilayer WS_2 nanotube have been fabricated as transistors with high mobility up to $50 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [11]. There are also interests in using WS_2 nanotubes for catalytic reactions in hydrodesulphurization processes and photocatalysis, by forming heterogeneous catalysts between TMD and metal nanoparticles (such as Co or Pd) [23-25]. Finally, WS_2 nanotubes were also used for improving the properties of composites [26, 27]. By integrating WS_2 nanotubes into poly(methyl methacrylate) (PMMA), significant improvement in the thermal stability and elastic modulus of the polymer was observed, in addition to the shifting of the optical absorption band.

In this paper, we report the preparation of tungsten disulphide WS_2 nanostructures by direct sulphurization of tungsten (W) films. By simply controlling the precursor W film thickness, the resultant WS_2 nanostructure morphology was manipulated. Thin W films (with thickness between 0.5 and 1 nm) favoured the formation of nanotubes, while thicker W films (≥ 1 nm) induced the growth of particle-like WS_2 . To understand the origin of the WS_2 nanostructure formation, W films were prepatterned into micron-sized tracks; substrate patterning was reported previously for confining the locations for TMD growth, but not for changing the morphologies [28]. We

demonstrate that patterning of W films into micron-sized tracks suppresses the growth of nanotubes, and we attribute the effect to the relieving of stress in micron-sized track patterns. Our results provide a simple, easy and cost effective route to control the morphologies of WS₂ for different applications.

2. Experimental details

The growth of WS₂ nanotubes started with the deposition of W films on SiO₂/Si substrates, which were cleaned in an ultrasonic bath of acetone and ethanol for at least 15 minutes and dried with a nitrogen gas flow. After loading the substrates into the dc-magnetron sputtering chamber, the system was evacuated to a base pressure of 1×10^{-3} Pa or better. W films of nominal thicknesses ranging between 0.5 to 10 nm were then sputtered at 20 W with an Ar pressure of 0.2 Pa at room temperature.

W films were converted into WS₂ by a sulphurization process. W films were transferred to the centre of a quartz tube furnace, where a number of reaction parameters (such as sulphurization temperature and pressure) were controlled. Standard conditions used in this work, unless otherwise stated, involved the sulphurization of 0.5 nm W films at a temperature of 700 °C at 140 Pa under a 100-sccm Ar gas flow. Sulphur vapour was supplied by heating sulphur powder in a ceramic boat placed at the entrance of the quartz tube. Fig. 1 shows the schematic of the setup.

Surface morphology of WS₂ samples was characterized by scanning electron microscopy (SEM, JEOL-6335F) and transmission electron microscopy (TEM, JEOL JEM-2100F). For TEM observations, samples were transferred to copper grids, by spincoating PMMA as the protective layer and subsequently releasing the WS₂ layer from SiO₂ in 1 M NaOH at ~100 °C. Raman spectroscopy (Horiba Jovin-Yvon HR-800) with a 488-nm laser excitation source was used for chemical identification of the WS₂ formed.

The formation of nanotubes could be attributed to a number of possibilities and some of the potential factors had been examined. Firstly, roughness and grain size of precursor films were evaluated with atomic force microscopy (Veeco Nanoscope VIII) (AFM). To examine the effect of stress in precursor films on nanotube formation, photolithographic patterning was performed on 0.5 nm W films for defining tracks with widths between 10 and 55 μm. After curing the resist by exposure to UV light source under the photomask and subsequent soaking in the developer solution, patterns were transferred to the W films by placing the samples into a mixture of sodium phosphate and potassium phosphate buffer solution (pH = 7.0). The buffer solution is commonly used for the

dissolution of tungsten oxide [29], as oxidation naturally occurs on ultrathin sputtered W films to form WO_{3-x} once leaving the vacuum chamber.

3. Results and discussion

Effect of precursor film thickness

SEM images of WS_2 formed by sulphurizing W films with different thicknesses are presented in Fig. 2. W films with thicknesses 0.5 nm and 0.7 nm (Fig. 2 (a) and (b) respectively) give rise to wire-like structures upon sulphurization, while precursor W films of 1 nm to 10 nm (Fig. 2 (c) to (f)) yield rather clean surfaces. TEM observation of WS_2 formed from the 0.5 nm W film is shown in Fig.3. Images collected from different parts of the sample suggest that the wire-like structures observed in the SEM images (Fig. 2 (a)) are actually multiwalled WS_2 nanotubes, with thickness between 1 – 3 layers and tube diameter around 10 nm.

Raman spectra in Fig. 4 confirm the formation of WS_2 for all samples, based on the observation of characteristic E_{2g}^1 and A_{1g} vibration modes at $\sim 355\text{ cm}^{-1}$ and 418 cm^{-1} respectively [30]. A closer inspection of the spectra (Fig. 4 (b)) shows Raman shift ranging from 330 cm^{-1} to 440 cm^{-1} , indicating that WS_2 formed from W films of different thicknesses do not give identical peak frequency for the E_{2g}^1 and A_{1g} modes. The change of the peak frequencies and the peak separation as a function of precursor W film thicknesses is shown in Fig. 4 (c). The corresponding change in Raman shift is consistent with literature report, in which the A_{1g} mode (E_{2g}^1 mode) shows a redshift (a blueshift) with decreasing number of WS_2 layers [30]. The dotted line in Fig. 4 (c) indicates the critical W precursor film thickness, upon which morphology change of the resultant samples from nanotube structure to featureless surfaces occurred.

WS_2 nanostructures can be distinguished from single crystal WS_2 flakes by Raman spectroscopy: it was suggested that single crystals of WS_2 give rise to a single peak of A_{1g} vibrational mode, while nanostructures of WS_2 would result in the distortion or even splitting of the peak [31]. In our case, the morphology of WS_2 changes from nanotubes to particles with increasing W film thickness, and both structures would be expected to split the A_{1g} mode in the Raman spectrum. For more definitive determination of the Raman response of nanotubes and nanostructures, localized Raman investigations (by tip-enhanced Raman spectroscopy, for example) would be needed.

The appearance of nanotubes has been attributed to high temperature processing conditions, which induces thermal stress and trigger bending and faceting [22]. Although the sulphurization

temperature (700 °C) used in this work was not as high as reported values (1000 °C in [22]), the intrinsic film stress due to the sputtering process and volume expansion during the conversion to WS₂ also favoured the formation of nanotubes by delaminating or buckling from the W-SiO_x surface. Therefore, nanotubes appeared on WS₂ prepared from 0.5 nm and 0.7 nm W films, and 0.7 nm W films showed less nanotubes formation as compared to 0.5 nm ones.

For thicker W films (≥ 1 nm), the reaction rate for WS₂ formation may vary significantly with position over the W film. At the locations where unreacted W are present, the strong W-W bonding between surface atoms and underlying atoms would not favour the buckling of WS₂ from W, and localized crumpling of WS₂ flakes from W could lead to formation of particle-like surfaces.

When the precursor film thickness is varied, a number of possibilities can result in the formation of nanotubes, such as the film roughness, grain size of films, releasing of film stress, among many others. Yet we attributed the formation of nanotubes in ultra-thin W films to the intrinsic stress developed during the sputtering process for the following reasons. Firstly, the increase in sputtered film thickness is expected to promote film roughness and grain size. The root mean square roughness of the precursor W films with different thicknesses was measured with AFM, the results of which are summarized in Figure 5. In our case, the variation of film thickness from 0.5 to 10 nm did not induce significant change in the roughness value. Besides, there were no significant morphological variations among films with different thicknesses, and they exhibited similar grain sizes. We therefore conclude that such a minimal change of film roughness and grain size would not be related to the nanotube formation process.

Film stress naturally occurs during the film deposition process. Such intrinsic stress can be released by the recrystallization process, when the samples are annealed at elevated temperatures (\sim half of melting point). Such annealing process can be deployed in principle to illustrate the influence of film stress on nanotube formation. However, W has such a high melting point (\sim 3400 °C) that renders this approach impractical. In addition, our WS₂ were synthesized under relatively high temperature of 700°C at 140 Pa. This means that even higher temperature would be needed for stress relaxation. As high vacuum and high substrate temperatures would induce diffusion of W into SiO₂/Si, this would potentially damage the as-grown WS₂. We therefore adopted the strategy of patterning the W precursor films for controlling the film stress and investigate its influence on the WS₂ nanotube formation.

Effect of patterning precursor films into tracks

Patterning of films have been demonstrated to release film stress and prevent film cracking without elevating the sample temperature [32]. In addition, by patterning only W precursor films of the same thickness, the intrinsic film properties such as roughness, grain size and interfacial qualities would be identical.

In this work, film stress was engineered by patterning the 0.5 nm W films into tracks ranging from 10 to 55 μm by photolithography. It was found that patterning of W films into micron-sized strips can suppress the formation of nanotubes (Fig. 6). WS_2 formed on 10 μm and 30 μm tracks did not show any nanotubes, while that of 55 μm showed some nanotubes. Raman spectra in Fig. 7 (a) and (b) indicate that the tracks are indeed WS_2 . Fig. 7 (c) presents the peak frequencies of the two vibrational modes as a function of the W track widths, and no significant changes due to the patterning process can be detected. Raman mapping was performed on those tracks (boxed region in Fig. 7(d)). Characteristic WS_2 vibrational modes of E_{2g}^1 and A_{1g} (Fig. 7 (e) and (f)) indicate that WS_2 are formed as tracks on top of the Si substrate, and Fig. 7 (g) targets at Si vibrational mode.

Given the identical film thickness and sulphurization conditions were used for preparing WS_2 samples, the change of morphology is solely attributed to the patterning of the continuous W film into tracks. Photolithographic patterning of W films relieves the stress of the films. As a result nanotube formation is not favoured (10 μm in Fig. 6 (a-b) and 30 μm in Fig. 6 (c-d)). When the track-width is increased to 55 μm , nanotubes start to emerge again.

To form nanotube structures from plain films, an important requirement is the onset of curvature (in form of buckling, wrinkling, or delamination) from the flat substrate surface for the curling up of materials. Whether this occurs depends on the initial stress in the films, as well as the critical loading that the film can withstand before it starts to curl up. The critical load for buckling P_{cr} is related to the track width L in the form $P_{cr} \propto \frac{1}{L^2}$ [33]. A small L implies that larger P_{cr} will be needed to induce buckling and forming nanotubes. When the track width increases from 10 up to 55 μm , the critical loading decreases around 30 times. Therefore nanotubes started to form in wider tracks (Fig. 6 (f)). One should also note that the residual stress in patterned films is also reduced with decreasing width of the tracks [34]; on the other hand, given the small thickness of the starting W film used as compared with the patterned track width in this work, the stress modulation effect is not expected to be the contributing factor for the onset of film curvature .

4. Conclusion

In summary, we reported the synthesis of WS₂ by direct sulphurization of sputtered tungsten films. Two approaches have been demonstrated for controlling the nanostructure evolution of the fabricated WS₂. Ultra-thin tungsten films favoured the growth of WS₂ nanotubes, while thicker ones yielded particles-like structure. In addition, patterning with micron-sized tracks suppressed the nanotube growth. We attributed the suppression of nanotube formation in patterned tracks to the reduced tendency of stress relieving by the samples. With these simple means, the formation of WS₂ nanostructures can be controlled.

Acknowledgements

This work is supported by Hong Kong Polytechnic University (Grant codes: 1-ZE14/ G-UA5G/ G-YBJ1). The experiments were conducted at the Hong Kong Polytechnic University Research Facility in Materials Characterization and Device Fabrication (UMF) -Centre for Electron Microscopy. We acknowledge the use of the facilities and engineering supported by Dr. Wei Lu. Q. Dong thanks the financial support from the National Natural Science Foundation of China (Grant No.: 61307030), Program for the Outstanding Innovative Teams of Higher Learning Institutions of Shanxi (OIT), the Natural Science Foundation for Young Scientists of Shanxi Province, China (Grant No.: 2014021019-2).

Reference

- [1] S. Fujimori, S. Yagi, H. Yamazaki, N. Funakoshi, Crystallization process of Sb-Te alloy films for optical storage, *J. Appl. Phys.* 64 (1988) 1000-1004.
- [2] S. Liu, J. Wei, F. Gan, Nonlinear absorption of Sb-based phase change materials due to the weakening of the resonant bond, *Appl. Phys. Lett.* 100 (2012) 111903.
- [3] J. Wei, S. Liu, Y. Geng, Y. Wang, X. Li, Y. Wu, A. Dun, Nano-optical information storage induced by the nonlinear saturable absorption effect, *Nanoscale* 3 (2011) 3233-3237.
- [4] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, S.-C. Zhang, Topological insulators in Bi_2Se_3 , Bi_2Te_3 and Sb_2Te_3 with a single Dirac cone on the surface, *Nature Phys.* 5 (2009) 438-442.
- [5] D.A. Wright, Thermoelectric Properties of Bismuth Telluride and its Alloys, *Nature* 181 (1958) 834.
- [6] L. Rapoport, Y. Bilik, Y. Feldman, M. Homyonfer, S.R. Cohen, R. Tenne, Hollow nanoparticles of WS_2 as potential solid-state lubricants, *Nature* 387 (1997) 791-793.
- [7] J.L. Verble, T.J. Wietling, P.R. Reed, Rigid-layer lattice vibrations and van der waals bonding in hexagonal MoS_2 , *Solid State Commun.* 11 (1972) 941-944.
- [8] H.R. Gutiérrez, N. Perea-López, A.L. Elías, A. Berkdemir, B. Wang, R. Lv, F. López-Urías, V.H. Crespi, H. Terrones, M. Terrones, Extraordinary Room-Temperature Photoluminescence in Triangular WS_2 Monolayers, *Nano Lett.* 13 (2013) 3447-3454.
- [9] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, F. Wang, Emerging Photoluminescence in Monolayer MoS_2 , *Nano Lett.* 10 (2010) 1271-1275.
- [10] C. Cong, J. Shang, X. Wu, B. Cao, N. Peimyoo, C. Qiu, L. Sun, T. Yu, Synthesis and Optical Properties of Large-Area Single-Crystalline 2D Semiconductor WS_2 Monolayer from Chemical Vapor Deposition, *Adv. Opt. Mater.* 2 (2014) 131-136.
- [11] R. Levi, O. Bitton, G. Leitus, R. Tenne, E. Joselevich, Field-Effect Transistors Based on WS_2 Nanotubes with High Current-Carrying Capacity, *Nano Lett.* 13 (2013) 3736-3741.
- [12] S. Najmaei, M. Amani, M.L. Chin, Z. Liu, A.G. Birdwell, T.P. O'Regan, P.M. Ajayan, M. Dubey, J. Lou, Electrical Transport Properties of Polycrystalline Monolayer Molybdenum Disulfide, *ACS Nano* 8 (2014) 7930-7937.
- [13] N. Huo, S. Yang, Z. Wei, S.-S. Li, J.-B. Xia, J. Li, Photoresponsive and Gas Sensing Field-Effect Transistors based on Multilayer WS_2 Nanoflakes, *Sci. Rep.* 4 (2014) 5209.
- [14] J. Lin, Z. Peng, G. Wang, D. Zakhidov, E. Larios, M.J. Yacaman, J.M. Tour, Enhanced Electrocatalysis for Hydrogen Evolution Reactions from WS_2 Nanoribbons, *Adv. Energy Mater.* 4 (2014) 10301875.
- [15] Y. Zhang, Q. Ji, G.-F. Han, J. Ju, J. Shi, D. Ma, J. Sun, Y. Zhang, M. Li, X.-Y. Lang, Y. Zhang, Z. Liu, Dendritic, Transferable, Strictly Monolayer MoS_2 Flakes Synthesized on SrTiO_3 Single Crystals for Efficient Electrocatalytic Applications, *ACS Nano* 8 (2014) 8617-8624.
- [16] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, Electronics and optoelectronics of two-dimensional transition metal dichalcogenides, *Nature Nanotechnol.* 7 (2012) 699-712.
- [17] M.W. Iqbal, M.Z. Iqbal, K.M. Farooq, M.A. Shehzad, Y. Seo, J.H. Park, C. Hwang, J. Eom, High-mobility and air-stable single-layer WS_2 field-effect transistors sandwiched between chemical vapor deposition-grown hexagonal BN films, *Sci. Rep.* 5 (2015) 10699.
- [18] X. Mao, Y. Xu, Q. Xue, W. Wang, D. Gao, Ferromagnetism in exfoliated tungsten disulfide nanosheets, *Nanoscale Res. Lett.* 8 (2013) 430.
- [19] T.A.J. Loh, D.H.C. Chua, Growth Mechanism of Pulsed Laser Fabricated Few-Layer MoS_2 on Metal Substrates, *ACS Appl. Mater. Interfaces* 6 (2014) 15966-15971.
- [20] A.L. Elías, N. Perea-López, A. Castro-Beltrán, A. Berkdemir, R. Lv, S. Feng, A.D. Long, T. Hayashi, Y.A. Kim, M. Endo, H.R. Gutiérrez, N.R. Pradhan, L. Balicas, T.E. Mallouk, F. López-Urías, H. Terrones, M. Terrones, Controlled Synthesis and Transfer of Large-Area WS_2 Sheets: From Single Layer to Few Layers, *ACS Nano* 7 (2013) 5235-5242.

- [21] J.-G. Song, J. Park, W. Lee, T. Choi, H. Jung, C.W. Lee, S.-H. Hwang, J.M. Myoung, J.-H. Jung, S.-H. Kim, C. Lansalot-Matras, H. Kim, Layer-Controlled, Wafer-Scale, and Conformal Synthesis of Tungsten Disulfide Nanosheets Using Atomic Layer Deposition, *ACS Nano* 7 (2013) 11333-11340.
- [22] R. Tenne, L. Margulis, M. Genut, G. Hodes, Polyhedral and cylindrical structures of tungsten disulphide, *Nature* 360 (1992) 444-446.
- [23] B. Višić, H. Cohen, R. Popovitz-Biro, R. Tenne, V.I. Sokolov, N.V. Abramova, A.G. Buyanovskaya, S.L. Dzvонkovskii, L.O. L., Direct Synthesis of Palladium Catalyst on Supporting WS₂ Nanotubes and its Reactivity in Cross-Coupling Reactions, *Chem. Asian J.* 10 (2015) 2234-2239.
- [24] Y. Tsverin, R. Popovitz-Biro, Y. Feldman, R. Tenne, M.R. Komarneni, Z. Yu, A. Chakradhar, A. Sand, U. Burghaus, Synthesis and characterization of WS₂ nanotube supported cobalt catalyst for hydrodesulfurization, *Mater. Res. Bull.* 47 (2012) 1653-1660.
- [25] Y. Tsverin, T. Livneh, R. Rosentsveig, A. Zak, I. Pinkas, R. Tenne, Photocatalysis with hybrid Co-coated WS₂ nanotubes, *Nanomater. Energy* 2 (2013) 25-34.
- [26] C.S. Reddy, A. Zak, E. Zussman, WS₂ nanotubes embedded in PMMA nanofibers as energy absorptive material, *J. Mater. Chem.* 21 (2011) 16086-16093.
- [27] W. Zhang, S. Ge, Y. Wang, M.H. Rafailovich, O. Dhez, D.A. Winesett, H. Ade, K.V.P.M. Shafi, A. Ulman, R. Popovitz-Biro, R. Tenne, J. Sokolov, Use of functionalized WS₂ nanotubes to produce new polystyrene/polymethylmethacrylate nanocomposites, *Polymer* 44 (2009) 2109-2115.
- [28] S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B.I. Yakobson, J.-C. Idrobo, P.M. Ajayan, J. Lou, Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers, *Nature Mater.* 12 (2013) 754-759.
- [29] J. Oh, C.V. Thompson, Selective Barrier Perforation in Porous Alumina Anodized on Substrates, *Adv. Mater.* 20 (2008) 1368-1372.
- [30] A. Berkdemir, H.R. Gutierrez, A.R. Botello-Mendez, N. Perea-Lopez, A.L. Elias, C.-I. Chia, B. Wang, V.H. Crespi, F. Lopez-Urias, J.-C. Charlier, H. Terrones, M. Terrones, Identification of individual and few layers of WS₂ using Raman Spectroscopy, *Sci. Rep.* 3 (2013) 1755.
- [31] M. Krause, M. Viršek, M. Remškar, N. Salacan, N. Fleischer, L. Chen, P. Hatto, A. Kolitsch, W. Möller, Diameter and Morphology Dependent Raman Signatures of WS₂ Nanostructures, *Chem. Phys. Chem.* 10 (2009) 2221-2225.
- [32] K. Zhang, C. Rossi, C. Tenailleau, P. Alphonse, J.-Y. Chane-Ching, Synthesis of large-area and aligned copper oxide nanowires from copper thin film on silicon substrate, *Nanotechnology* 18 (2007) 275607.
- [33] A.C. Ugural, S.K. Fenster, *Advanced Mechanics of Materials and Applied Elasticity*, Pearson Education, Inc., 2012.
- [34] A. Wikström, P. Gudmundson, S. Suresh, Thermoelastic analysis of periodic thin lines deposited on a substrate, *J. Mech. Phys. Solids* 47 (1999) 1113-1130.