The 4th International scientific Conference on Nanotechnology& Advanced Materials &Their Applications (ICNAMA 2013)3-4 Nov, 2013

Spontaneous Formation of Micro- and Nano-Fibers on In-Y Thin Films

Dr.Ahmed M. H. Al-Ghaban
Materials Engineering Department, University of Technology/Baghdad
Email:ahmed_gadom@yahoo.com
T. Takahashi

ABSTRACT

Large amount of In-rich fibers are found on combinatorial deposited In-Y thin film. Sizes, morphologies, and distributions of fibers are most likely dependent on the film composition. Oxidation of the film seems to play an important role for the spontaneous formation of fibers. Demonstrate a potential application of combinatorial method to study fibers. Open a possibility for novel synthesis technique of one dimensional nanostructured materials. The results presented could be utilized as a new synthesis technique for one-dimensional nanostructured materials. The SEM results improve the direct and spontaneous formation of In micro-and nano-fibers.

التشكيل العفوي لالياف نانوية ومايكروية من الاغشية الرقيقة لنظام من الانديوم-ياتريوم

الخلاصة

كمية كبيرة من الالياف النانوية الغنية بالانديوم وجدت في اغشية رقيقة مرسبة اندماجيا لنظام الانديوم-ياتريوم. وجد ان حجم وطوبغرافية وتوزيع هذه الالياف يعتمد بصورة اساسية على التركيب الكيمياوي للغشاء المرسب. تعد اكسدة الغشاء من هذا النوع لاعب اساسي في تشكيل الالياف النانوية والمايكروية بشكل عفوي لهذا النظام. تم شرح الية خاصة لاعداد تطبيقات تلائم هذا النوع من تشكيل الالياف النانوية احادية الاتجاه وفتح افاق جديدة لانشاء تقنيات تكوينها ونموها. تعد هذه الدراسة رائدة في عرض الية الاستفادة من هذه التقنية لتشكيل الياف نانوية ومايكروية ذات اتجاه احادي النمو.نتائج المجهر الالكتروني الماسح اثبتت التكوين المباشر والعفوي لالياف الانديوم بهذا النظام.

INTRODUCTION

One-dimensional nanostructured materials also referred to as nanowires, nanorods, and nanowhiskers are known to exhibit unique physical and chemical properties compared to three-dimensional bulk materials. The attractive properties of nanowires provide many potential applications as novel functional nanodevices [1] [2]. While many different synthesis techniques for self-organized nanowires have been reported such as Vapor-Liquid-Solid (VLS) method [3], solution method [4] [5], laser

https://doi.org/10.30684/etj.32.4B.8
2412-0758/University of Technology-Iraq, Baghdad, Iraq

ablation [6] [7], and thermal evaporation [8] [9], the development of new synthesis concepts and techniques for nanowires with well-controlled morphology, growth rate, size, crystalline and chemistry is a challenging task. Nanowires are classified roughly into two groups based on their growth behavior. Firstly, wires growing from their tips, the wire forming species are supplied from vapor and/or liquid phase surrounding. One-dimensional growth in this case is most commonly facilitated through confinement by a liquid droplet. Most synthesis techniques reported so far utilizes this mechanism. Secondly, wires are also formed by growth from the roots. A well-known example is the spontaneous formation of soft metal (SM) whiskers such as Sn, Cd, and Zn used for electroplating materials for electronic components [10] to [12]. In this study large amount of In-rich fibers are found on combinatorially deposited In-Y thin film. Sizes, morphologies, and distributions of fibers are most likely dependent on the film composition. Oxidation of the film seems to play an important role for the spontaneous formation of fibers. Demonstrate a potential application of combinatorial method to study fibers. Open a possibility for novel synthesis technique of one dimensional nanostructured materials. The results presented could be utilized as a new synthesis technique for one-dimensional nanostructured materials.

EXPERIMENTAL PROCEDURE

Compositionally graded In-Y thin films were deposited using the combinatorial magnetron sputtering platform schematically shown in Figure (1). Two magnetron cathodes equipped with in and Y targets of 39 mm in diameter were placed facing the substrate at an angle of approximately 15° with respect to the substrate normal. The target-substrate distance was approximately 6 cm. The deposition chamber was evacuated prior to depositions to a base pressure of ~10^{-4} Pa using a turbo molecular pump. The In and Y targets were co-sputtered onto a standard 2 inch Si (100) substrate for 30 min at an Ar pressure of 0.35 Pa with DC powers of 25 W and 50 W, respectively. The depositions were carried out at room temperature, namely without intentional substrate heating.

Detailed surface investigations were carried out in a scanning electron microscope (SEM, JEOL JSM-6480) equipped with an energy dispersive X-ray analyzer (EDX, EDAX Genesis 2000). The investigations were focused on a film surface segment including compositions close to YIn_3 at which an appreciable amount of whiskers was observed. For the EDX analysis, In-L, Y-L, and O-K characteristic X-ray lines were used for the identification of In, Y, and O, respectively. In-Y compositions were quantified using the ZAF method. In addition to the morphological and compositional studies, structural analysis was performed by micro X-ray diffraction using a general area diffraction detector system (GADDS, Bruker D8) with a collimated X-ray beam (Cu-Kα) using a pin-hole collimator with 0.5 mm in diameter. The voltage and current settings were 40 kV and 40 mA, respectively. The incident angle of the X-ray beam was fixed at 15°.

RESULTS AND DISCUSSION

Exposure of the as-deposited films to atmosphere, In-whiskers were found to form spontaneously on certain film surface segments. Figure (2) shows a lab camera photograph of an In-Y film kept in atmosphere for 30 hours at room temperature. One can see a variation of film surface appearances along its composition gradient. As it will be shown below, this is primarily due to a variation of surface topographical features including different size and morphology of In-whisker formation.

Figure (3) shows a SEM micrograph obtained from a selected area of the film shown in Figure (2). After exposure of the film to atmosphere, whiskers are found to grow spontaneously on the film surface investigated. According to EDX measurements, no evidence for the presence of Y in the whiskers could be detected. The morphology, size, and population of In-whiskers appear to be largely dependent on the position along the In-Y concentration gradient, and hence on the as-deposited film composition. The In-whisker diameter observed ranges from ~0.2 µm to a few µm and occasionally even larger. It should be noted that such a small size of whiskers with the diameter of, in particular, < 1 µm is not common for typical spontaneous Sn-whiskers observed in plating. Generally speaking, thin In-whiskers with the diameter of < 1 µm with large population are observed at the film compositions close to stoichiometric YIn_3 while thicker whiskers with smaller population are primarily located at the In-rich side. When the Y composition is reduced to approximately 18 at.% (balance to 100 at.% is In), no whisker formation is observed, instead, hillock or nodule-like structures appear. Thus, an appreciable amount of spontaneous In-whiskering is confined to a narrowly concentration range of 18 to 25 at.%Y. To determine the cause for In-whisker formation, film cross-sections were studied. Fig. 4 provides cross-sectional SEM images obtained from a segment of a film exhibiting the growth of In-whiskers after exposure to atmosphere. The substrate was cleaved along the composition gradient. Figures (4b and c) display whiskers in the upper and lower region of the frame shown in Figure (4a), respectively. The growth of In-whiskers with the diameter of a few hundreds nanometers can be seen in Figure (4b). Figure (4c) shows cross-sectional as well as surface features of the In-Y film after In-whisker formation. In-whiskers are connected to the film surface at their roots. In addition, compared with a large tangle of In-whiskers seen from a top view Figure (4b), the actual population of roots at the film surface appears to be relatively small.

The spontaneous growth mechanism of In-whiskers from YIn_3 thin films presented here are believed to be similar to the one proposed previously for rapid Sn-whisker formation from $RESn_3$ compounds [13], [14]. Namely, the growth of In-whiskers is driven by the preferential reaction of Y with atmosphere to form Y oxides and/or Y hydroxides. In the case of Y, the following reactions might occur upon exposure.

$$4YIn_3 + 3O_2 \rightarrow 2Y_2O_3 + 12In \qquad \ldots (1)$$

$$2YIn_3 + 6H_2O \rightarrow 2Y(OH)_3 + 6In + 3H_2. \qquad \ldots (2)$$

These reactions are energetically preferred because of the large exothermic standard enthalpies of formation for Y_2O_3 (-1919.4 kJ/mol [15]) and Y $(OH)_3$ (-1472.3 kJ/mol [16]) compared to that for YIn_3 (-41.8 kJ/mol [17]). While the formation of Y_2O_3 and/or Y (OH) 3 provides free in atoms, a large volume expansion occurs. Using molar volumes of In (1.57 x 10-5 m3/mol), YIn_3 (5.83 x 10-5 m3/mol [18]), Y_2O_3 (4.49 x 10-5 m3/mol [19]), and Y $(OH)_3$ (3.62 x 10-5 m3/mol [20]), one can estimate possible volume changes of +19.3% and +42.9% for the formation of Y_2O_3 and $Y(OH)_3$, respectively. These large expansive volume strain values cause compressive stresses in the film, which eventually act as the major driving force for In-whisker extrusion.

It is also interesting to notice in Figure (4c) that a layer of In is formed at the film-substrate interface.

In both cases, the oxygen content in the film increases as the exposure time is increased. On the other hand, the in content decreases as In-whiskers grow upon exposure. This indicates that the diffusion of in atoms to the roots of growing In-whiskers occurs upon exposure. Furthermore, as can be seen for 22 at. %Y, the nucleation and subsequent growth of In-whiskers seems to be correlated with the onset of the increase in oxygen content in the film. This supports the hypothesis that the formation of Y_2O_3 and/or Y $(OH)_3$ is involved for the growth of In-whiskers upon exposure of In-Y thin films.

One of the most interesting phenomena observed in the present In-Y thin film study is that the morphology and extrusion kinetics of In-whiskers are strongly affected by the chemical composition, even within the narrow composition range of 18 to 25 at.%Y. This range could be related to a possible homogeneity range for the formation of single phase Y1-xIn_3 with a Y deficiency. However, a more systematic study for the correlation between the composition, phase constitution, and morphology in as-deposited In-Y thin films is necessary for better understanding. As for the size of whiskers, Tu et al. have proposed that radius of Sn-whisker, R, is determined by a balance between surface energy per unit area, γ, and strain energy per unit volume, ε, as following [21], Thus,

$$R=2\gamma/\varepsilon \qquad \dots (3)$$

Qualitatively speaking, thin (thick) In-whiskers are expected to form when the strain energy, hence compressive stress, is large (small). It might be the case that the change in Y composition causes the change in reactivity between In-Y thin films and atmosphere, and hence the change in strain energy stored in the film. Lower strain energy should be associated with a lower Y content in the film simply because of the smaller volume of Y_2O_3 and/or Y $(OH)_3$ which could be formed. This is consistent with the here reported observation that thicker In-whiskers are formed at smaller Y concentrations than the nominal YIn3. It should also be pointed out that the In-whisker growth behavior may be influenced not only by the chemical composition, but also by the constitution and microstructure of the film. Sputtered thin films are known to exhibit quite different microstructural features compared to bulk materials [22]. For instance, the grain size of sputtered thin films is often in the range of 10-100 nm, which are one or two orders of magnitude smaller than those of typical bulk polycrystalline materials. Because of the large grain boundary density, the film reactivity to atmosphere is expected to be enhanced due to grain boundary diffusion as compared to bulk samples. The very large whisker growth rate, ~1500 Å/s, obtained in the present thin film study may be understood in terms of an accelerated reaction due to fine grain structures of the thin films.

Finally, as already mentioned above, the use of compositionally graded In-Y thin films enables the efficient investigation of interesting morphological In-whisker features. For instance, in Figure (5), a cross-sectional feature of a film exhibiting uniquely self-organized In-whiskers is presented. The thin In-whiskers with the diameter of ~0.2 μm are well-aligned, highly densely in a large area along the surface normal, and the length of each whisker is very similar and about 10 μm. This suggests that the whisker nucleate almost simultaneously. This type of whisker morphology may be useful for application such as gas sensors where a large surface to volume ratio is required.

CONCLUSIONS

In this work we have demonstrated the spontaneous formation of In-whiskers from YIn_3 thin films deposited by combinatorial magnetron sputtering. In-whiskers were found to be extruded spontaneously from the roots only upon exposure of the films to atmosphere, but not in vacuum. In-whisker growth is accompanied by an increase in oxygen content in the films. It is suggested that the In-whiskers are extruded from the film surface due to compressive stresses developed by preferential reactions of Y to form more stable compounds such as Y_2O_3.

We also found that the morphology and extrusion kinetics of In-whiskers were strongly dependent on the Y composition of as-deposited films. The diameter of the In-whiskers observed ranges from ~0.2 μm up to a few μm or even larger within a composition range between 18 and 25 at. % Y. Based on these data, the whisker morphology can be controlled through tuning the film composition. The results provide an alternative pathway towards the controlled growth of one-dimensional nanostructured materials.

REFERENCES

[1]. Lieber and Z. L. Wang, C. M. “Functional nanowires,” MRS Bull., vol. 32, pp. 99–108, 2007.

[2]. Xia,Y. P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, and H. Yan, “One-dimensional nanostructures: synthesis, characterization, and applications,” Adv. Mater., vol. 15, pp. 353–389, 2003.

[3]. Wagner and W. C. Ellis, R. S. “Vapor-liquid-solid mechanism of single crystal growth,” Appl. Phys. Lett., vol. 4, pp. 89–90, 1964.

[4]. Holmes, J. D. K. P. Johnston, R. C. Doty, and B. A. Korgel, “Control of thickness and orientation of solution-grown silicon nanowires,” Science, vol. 287, pp. 1471–1473, 2000.

[5]. Trentler, T. J. K. M. Hickman, S. C. Goel, A. M. Viano, P. C. Gibbons, and W. E. Buhro, “Solution-liquid-solid growth of crystalline III-V semiconductors: an analogy to vapor-liquid-solid growth,” Science, vol. 270, pp. 1791–1794, 1995.

[6]. Zhang, Y. F. Y. H. Tang, N. Wang, D. P. Yu, C. S. Lee, I. Bello, and S. T. Lee, “Silicon nanowires prepared by laser ablation at high temperature,” Appl. Phys. Lett., vol. 72, pp. 1835–1837, 1998.

[7]. Morales and C. M. Lieber, A. M. “A laser ablation method for the synthesis of crystalline semiconductor nanowires,” Science, vol. 279, pp. 208–211, 1998.

[8] B. D. Yao, Y. F. Chan, and N. Wang, “Formation of ZnO nanostructures by a simple way of thermal evaporation,” Appl. Phys. Lett., vol. 81, pp. 757–759, 2002.

[9]. Kong, Y. C. D. P. Yu, B. Zhang, W. Fang, and S. Q. Feng, ”Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach,” Appl. Phys. Lett., vol. 78, pp. 407–409, 2001.

[10]. Lindborg, U. “Model for spontaneous growth of zinc, cadmium and tin whiskers,” Acta Metall., vol. 24, pp. 181–186, 1976.

[11]. Lindborg, U. “Observations on the growth of whisker crystals from zinc electroplate,” Metall. Mater. Trans. A, vol. 6, pp. 1581–1586, 1975.

[12]. Key, P. L. “Surface morphology of whisker crystals of tin, zinc and cadmium,” Proc. 20th Electronic Components Conference, pp. 155–160, 1970.

[13]. Chuang and S. F. Yen, T. H. “Abnormal growth of thin whiskers in a Sn3Ag0.5Cu0.5Ce solder ball grid array package,” *J. Electron. Mater.*, vol. 35, pp. 1621–1627, 2006.

[14]. Dudek and N. Chawla, M. A. “Mechanisms for Sn whisker growth in rare earth-containing Pb-free solders,” *Acta Mater.*, vol. 57 pp. 4588–4599, 2009.

[15]. Lavut and N. V. Chelovskaya, E. G. “Enthalpy of formation of diyttrium trioxide,” J. Chem. Thermodyn., vol. 22, pp. 817–820, 1990.

[16]. Diakonov, I. I. K. V. Ragnarsdottir, and B. R. Tagirov, “Standard thermodynamic properties and heat capacity equations of rare earth hydroxides: II. Ce(III)-, Pr-, Sm-, Eu(III)-, Gd-, Tb-, Dy-, Ho-, Er-, Tm-, Yb-, and Y-hydroxides. Comparison of thermochemical and solubility data,” *Chem. Geol.*, vol. 151, pp. 327–347, 1998.

[17]. Palenzona and S. Cirafici, A. “Thermodynamic properties of Y, Th, and U, MX3 compounds with IIIA and IVA elements,” Thermochim. Acta, vol. 13, pp. 357–360, 1975.

[18]. K. H. J. Buschow, H. W. de Wijn, and A. M. van Diepen, “Magnetic susceptibilities of rare-earth-indium compounds: RIn3,” *J. Chem. Phys.*, vol. 50, pp. 137–141, 1969.

[19] L. Smrcok, “Rietveld refinement of Y2O3 using the Pearson VII profile shape function,” Cryst. Res. Technol., vol. 24, pp. 607–611, 1989.

[20] G. W. Beall, W. O. Milligan, and H. A. Wolcott, “Structural trends in the lanthanide trihydroxides,” J. Inorg. Nucl. Chem., vol. 39, pp. 65–70, 1977.

[21] K. N. Tu, C. Chen, and A. T. Wu, “Stress analysis of spontaneous Sn whisker growth,” J. Mater. Sci.: Mater. Electron., vol. 18, pp. 269–281, 2007.

[22] J. A. Thornton, “High rate thick film growth,” Annu. Rev. Mater. Sci., vol. 7, pp. 239–260, 1977.

Figure (1) The combinatorial magnetron sputtering platform of In-Y thin films.

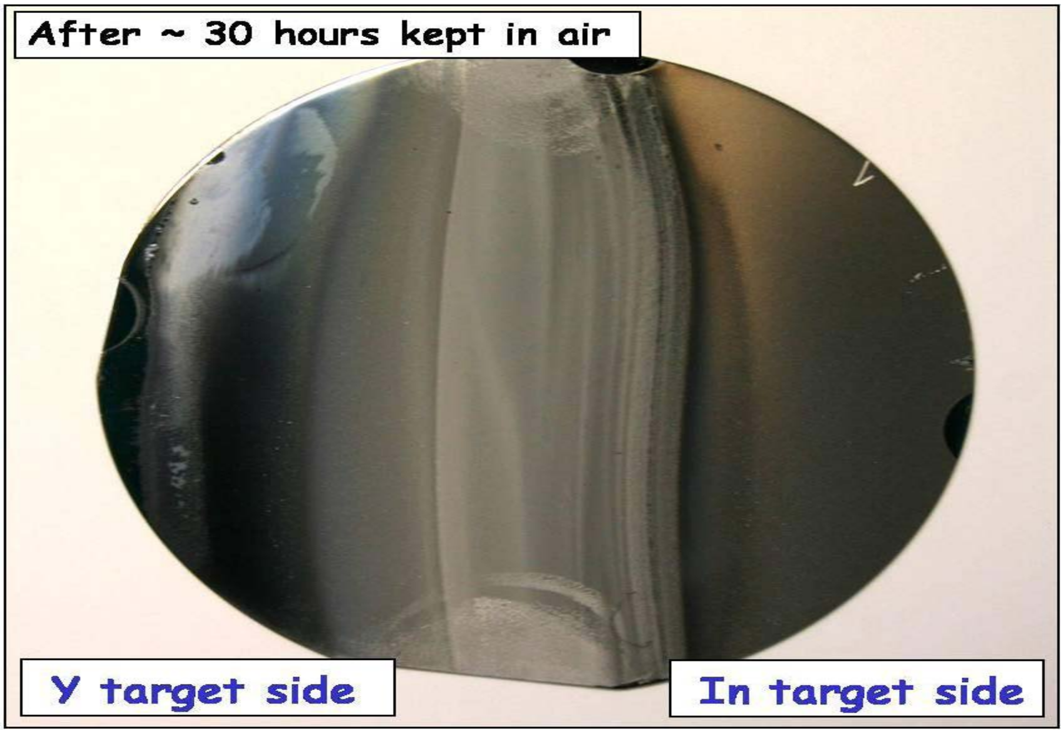

Figure (2) The as-deposited combinatorially sputtered In-Y thin films.

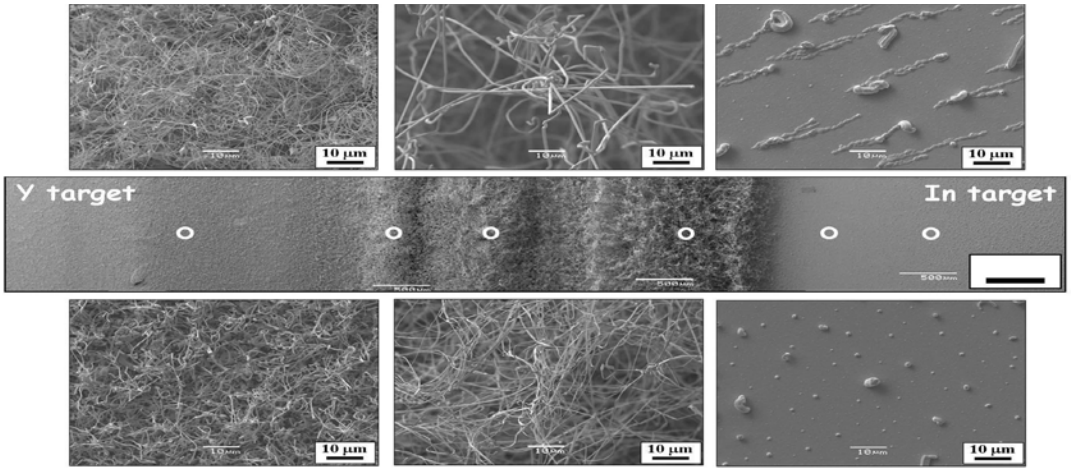

Figure (3) (SEM of Y-In surface after exposure in air).

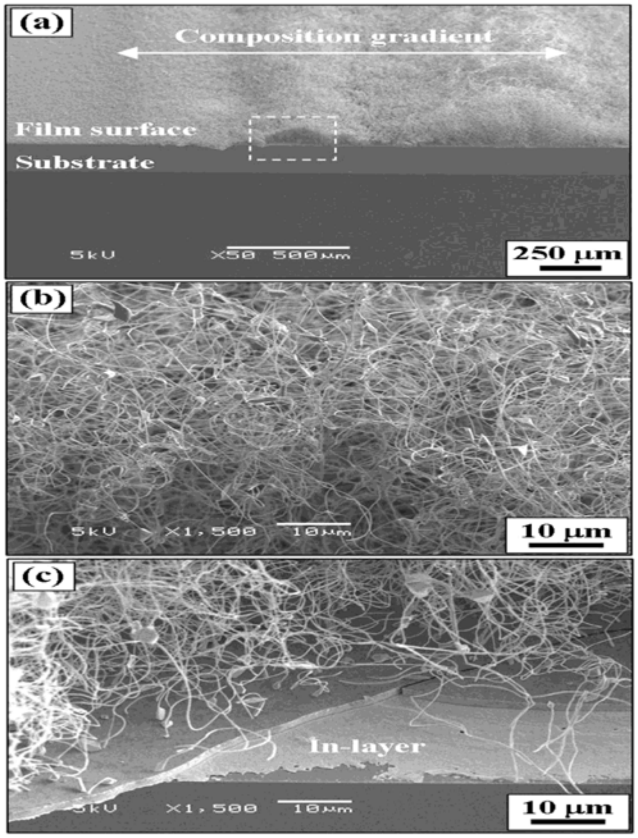

Figure (4) (SEM micrographs showing cross-sectional features of a film with composition gradient: (a) low magnification image (left side corresponds to In-rich. area, high magnification images of a top (b), and a bottom (c) part of In-whiskers grown. The micrographs were taken after one month exposure to atmosphere).

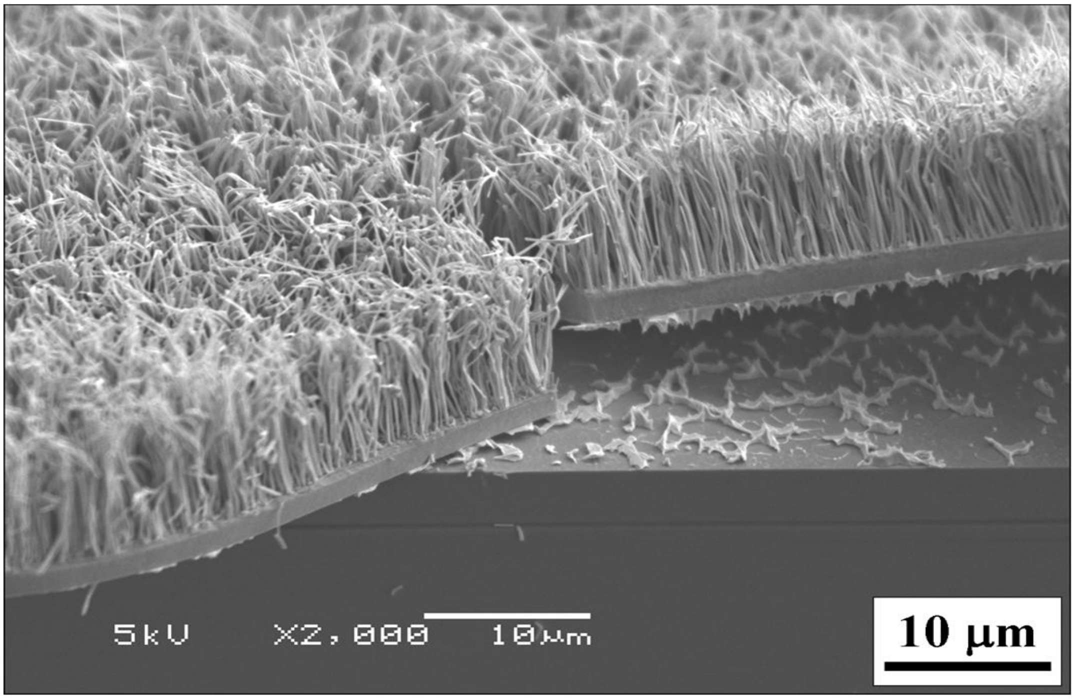

Figure (5) (SEM micrograph of uniform, dense In-whisker structure forming on a film surface. This micrograph was taken after three days exposure).