ZnO-NWs/Metallic Glass Nanotube Hybrid Arrays: Fabrication and Material Characterization

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Abstract

In this work, we fabricated first-ever nanohybrid ZnO nanowires (ZnO-NWs)/Metallic Nanotube Arrays (MeNTA) structure for the large-scale fabrication of highly dense laterally and vertical aligned ZnO-NWs. To prepare heterogeneous surface MeNTA by using sputter-deposition of different metallic glass ($\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$), $\text{Cu}_{47}\text{Zr}_{42}\text{Al}_7\text{Ti}_4$, $\text{Pd}_{72}\text{Cu}_{12}\text{Si}_{16}$, $\text{W}_{50}\text{Ni}_{25}\text{B}_{25}$ and $\text{Ni}_{54}\text{B}_{0.3}\text{Si}_{36}\text{Cr}_{2.7}\text{Fe}_7$) over on contact-hole arrays created by a photoresist template with 650 nm height and various diameter (2, 10 and 20 μm). A ZnO seed layer is deposited by sputtering method on MeNTA to provide the nucleation sites to grow the nanowires inside the MeNTA. To perform the material analysis like surface morphology, crystal structural, and optical properties were characterized by using scanning electron microscopy (SEM), X-ray diffraction (XRD), and photoluminescence (PL), respectively. Our results confirm that, the nanowires are single crystal with hexagonal wurtzite structure presenting strong UV emissions can be used in optoelectronics, sensors, piezoelectric-nanogenerator, solar cells and battery applications in near future.

Introduction

ZnO-NWs are important n-type semiconductors with a wide bandgap of 3.37 eV, large surface-area-to-volume ratio, and high stability at room temperature due to high exaction energy (~ 60 meV).^{1, 2} The versatility of ZnO-NWs makes them ideal electrode for piezoelectric nanogenerator, solar cells, photodetectors, sensors, light-emitting diodes, photo catalysts, field emitter and energy harvesting applications.³⁻⁹ ZnO-NWs are biocompatibility, bio-safe non-toxicity, antibacterial, antimicrobial properties and physicochemical stability, for instance, ZnO-NWs coatings surface can also provide an excellent application for medical equipment and surgical tools.¹⁰⁻¹² Numerous methods have been developed to facilitate the fabrication of ZnO-NWs, including electro-chemical deposition,¹³ physical vapor deposition,¹⁴ pulsed laser deposition¹⁵, chemical vapor deposition,¹⁶ hydrothermal synthesis,^{17, 18} and vapor–liquid–solid (VLS) methods,¹⁹ using a variety of substrate materials (inorganic, organic, crystalline and amorphous). Nonetheless, the large-scale fabrication of ZnO-NWs is hindered by a number of factors.²⁰

Hydrothermal synthesis is a straight forward scalable approach, which can be performed under atmospheric pressure at low temperatures (<100 C) using a wide variety of substrates;²¹ however, it is inapplicable to bare silicon substrates due to high internal stress caused by lattice mismatch between ZnO-NWs and the substrate as well as a large difference in the coefficient of thermal expansion.^{21, 22} The sputter deposition of a ZnO seed layer on the surface of silicon substrate has been shown to reduce lattice mismatch and alignment the nanowires to improve array density.^{17, 23} A thin buffer layer on the surface of silicon has also been shown to overcome the effects of lattice mismatch, resulting in a sound electrical and thermal interface between the vertically-aligned ZnO-NWs and the substrate.²⁴ VLS and electron beam lithography techniques can be used to produce layer of metal catalytic particles, such as Au, Ni, Fe, Sn, Pt, to facilitate the growth of aligned ZnO-NWs; however, these methods require high growth temperatures, and the use of metallic particles places limitations on grain size and imposes difficulties in

removing contamination from unreacted catalyst material. Furthermore, some patterned growth strategies such as electron beam lithography is complex and expensive when operating at the micro-nanoscale, therefore as a result of those kinds of technique and material limitation, fabrication of large scale patterned ZnO-NWs is a big challenge for the construction of micro/nano scale devices for various application.^{24, 25}

Metallic glasses (MGs) feature high yield strength, elastic strain, corrosion resistance, and magnetic permeability as well as good biocompatibility, temperature-independent electrical resistivity, and a large electrochemical surface area for catalytic reactions.²⁶⁻²⁸ The disordered atomic structure without grain boundaries and temperature-dependent mechanical behavior of bulk MGs (BMGs) facilitates their formation into structures of high geometric complexity from the nanometer scale to a few centimeters without appreciable plastic deformation.²⁹ Also, BMGs can be patterned at the micro/nano scales to form nanowires or nanotubes for a variety of applications. One study fabricated Pt-based bulk metallic glass (Pt-BMG) nanowires for use as a high surface area catalyst for methanol and ethanol oxidation with a highly resistant surface superior to that of carbon materials.³⁰ Nonetheless, BMGs tend to be brittle below the glass transition temperature.³¹ Thin-film metallic glass (TFMG) (also known as amorphous metallic alloys) are stable and non-brittle at room temperature, providing excellent ductility, good glass-forming ability, high fatigue strength, and biocompatible.³²⁻³⁵ Physical vapor deposition (radio-frequency magnetron sputtering) can be used to fabricate TFMG coatings in various thicknesses on a variety of substrate materials, including the polymer composites used in water, oil, and gas separation.^{36, 37} Pd-based TFMG coating on the silicon substrate (PdCuSi) and hybrid of TFMG with semiconductor material (ZnO-NWs, nanorod and nanotube) can also be used for the detection of hydrogen gas and UV photodetector.³⁸⁻⁴¹ Magnetron sputtering is a straight-forward approach to the deposition of TFMG over a patterned liftoff material to create a hybrid micro-nanoscale device with high chemical stability and excellent mechanical strength. This approach also provides excellent control over the diameter and length of free-standing metallic glass nanotubes heterostructures materials. Researchers have reported on $Zr_{55}Cu_{30}Al_{10}Ni_5$ metallic glass nanotube arrays.⁴² The patterning of multi component nanomaterial by controlling the shape and size can opens up the possibility forming of multifunctionality nanostructured materials for various application. For instance, MeNTA could be used as an artificial nano sucker device⁴³ and a biosensor detecting changes in the optical properties by filled with a specific antigen or target.⁴⁴ However, still, there is no further investigation a nanohybrid of 1D semiconductor metallic oxide (ZnO-NWs) within a high surface area of different kind MeNTA heterostructures materials.

This paper reports on a novel approach to the fabrication of a highly dense laterally and vertically aligned growth ZnO-NWs inside free standing MeNTA (ZnO-NWs/MeNTA) nanohybrid structure. For this Particular studies of nanohybrid ZnO-NWs/MeNTA, we used the RF magnetron sputtering technique to deposit Zr, Cu, Pd, W and Ni-based TFMG layers on a temple-assisted silicon substrate followed by a ZnO seed layer to provide the nucleation sites within the MeNTA. As the SEM image and XRD results confirmed that highly dense and crystalline lateral and vertical align of ZnO-NWs have been obtained in 10 and 20 diameter MeNTA. Also the MeNTA support templet was stable and not react with the solution

during the hydrothermal process. Moreover, this versatile method and techniques can be applied other one-dimensional nanostructure material. The high surface area of the integrating of dissimilar metals and ZnO nanowire in metallic glass provides different applications in near future.

Experimental Methods

One-side-polished single-crystal Si (100) wafers Hitachi (Japan) underwent cleaning sequentially using acetone, methanol, and chloroform (10 min each) sonication followed by drying under vacuum. The native oxide layer was removed via immersion in HF solution (50wt%) at room temperature for 5 min. The Si substrates were then oxidized via immersion in a mixture of H_2SO_4 and H_2O (2:1, mol %) for 5 min and subsequently rinsed with double distilled water. All chemicals and solvents were of reagent grade (Aldrich Chemical).⁴²

The basic strategy for the fabrication process of ZnO-NWs inside MeNTA is presented in Figure 1. In step **1**, a positive photoresist (thickness of 650 nm) was coated on the pretreated Si wafer. In step **2**, Lithography was used in the patterning of a contact-hole arrays with 2, 10 and 20 μm diameter on the photoresist after hard baking at 120 C for use as a template. In step **3**, RF magnetron sputtering system was used for the sputter-deposition of $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$, $\text{Cu}_{47}\text{Zr}_{42}\text{Al}_7\text{Ti}_4$, $\text{Pd}_{72}\text{Cu}_{12}\text{Si}_{16}$, $\text{W}_{50}\text{Ni}_{25}\text{B}_{25}$ and $\text{Ni}_{54}\text{B}_{0.3}\text{Si}_{36}\text{Cr}_{2.7}\text{Fe}_7$ TFMG coating over an as-prepared contact-hole photoresist template on the silicon substrates using an alloy target without substrate heating. The vertical distance between the substrate and target was maintained at 10 cm. Prior to deposition, the chamber was evacuated to a base pressure of 1.2×10^{-6} mTorr and introduction of argon gas to a working pressure of 3 mTorr. A Sputtering for a duration of seven minutes resulted in the formation of a Zr-MeNTA with a height of 650 nm and diameters of 2, 10, 20 μm . Cu-MeNTA, Pd-MeNTA, W-MeNTA, and Ni-MeNTA were also fabricated with a height of 650 nm and diameter of 20 μm .

In step 4, prior to the growth of ZnO-NWs, the ZnO seed layer was deposited by RF magnetron sputtering for 5-min at 100 W under argon ambient at 20 mTorr through on pre-coated TFMG followed by annealing at 80 C in furnace to improve the crystal film quality. In step **5**, the seed layer thin film Metallic glasses/photoresist/silicon wafer (TFMG/PR/Si) substrate were immersed in 20 mM equimolar solution of zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) in 100 mL deionized water at 90 C and aged for 3 hours the growth of nanowires. Note that the substrates floated in the growth solution upside down at the surface to promote uniform growth. In step **6**, the aged sample were removed from the solution then rinsed with DI water and dried at room temperature. In step **7**, the top metallic glass layer and ZnO-NWs on photoresist templates were removed via ultrasonic agitation using acetone for a period of 40 s to obtain a nicely nanohybrid ZnO NW/MeNTA.

The surface morphology of the fabricated materials was characterized via scanning electron microscopy (SEM). Crystallographic structures were characterized using an X-ray diffractometer (XRD, Bruker D8 Discover) with monochromatic Cu Ka radiation at 40 kV and 200mA with a low glancing angle of 0.5. Elemental mapping of the materials was performed using field-emission Auger electron spectroscopy

(AES, JEOL JAMP 9510F) with an electron gun operated at 30 kV and beam current of 10 nA with the sample tilted at 30°. The photoluminescence (PL) spectra were obtained by using a He-Cd laser with a wave length of 325nm as an excitation source.

Results And Discussion

Figure 2. presents SEM images (40 tilt angle; various magnifications) of ZnO-NWs inner surface of freestanding metallic glass nanotube arrays. Note that the seed coating surface area of the metallic glass nanotubes acted as nuclei to promote a dense mass of laterally and vertically aligned grown ZnO-NWs. It also acted as a buffer layer to protect the nanowires from thermal shock and mechanical stress during the removal of photoresist under ultra-sonication. Figure 2 (a) and (d) shows a mass of non-aligned agglomerated ZnO-NWs growing laterally from the inside of the wall of a metallic glass nanotube as well as ZnO-NWs growing vertically from the bottom of the tube (height = 650 nm; diameter = 2 µm).

Figures 2 (b), (e) and (h) respectively present free-standing ZnO-NWs (height = 650 nm; diameter = 10 µm) at three magnifications. As shown in Figure. 2 (c), (f) and (i), the high mechanical strength and good adhesion characteristics of Zr-based TFMG also permit the fabrication of larger Zr-MeNTA (on the scale of 20 µm) with attached nanowires (height = 650 nm; diameter = 20 µm). The high surface to volume ratio of the ZnO-NWs and the specific metals used in the MeNTA are ideally suited to a wide range of bioengineering, catalysis, and sensor systems as well as converting motion to electricity. Figure. 2 (j) reveals the elemental mapping results obtained from the fabricated nanohybrid material of ZnO-NWs/Zr-MeNTA. the samples presented distinct signals indicative of Zr, Cu, Zn, and O but no signals of Ni or Al. We therefore disregard Ni and Al from subsequent analysis for brevity.

Figure. 3 (a-d) presents the morphology of a highly dense lateral and vertically of ZnO-NWs (height = 650 nm; diameter = 20 µm) respectively grown in Cu-MeNTA, Pd-MeNTA, W-MeNTA, and Ni-MeNTA. The outer surface area of the Pd-MeNTA wall can also provide different opportunity, for instance, hydrogen gas sensor due to the presence Pd metal in Pd₇₂ Cu₁₂ Si₁₆, similar opportunity like Pd thin film metallic glasses.⁴⁵ The SEM results demonstrate that the large surface area of the nanotubes greatly increased the seed area for the growth of NWs and corresponding NWs density. The high surface area of the MeNTA can provide a high quantity high surface volume ratio ZnO nanowire for an efficient photo catalyst, even compare to ZnO nanoparticles and bulk material, it had higher catalytic activity due to their high purity and crystallinity, therefore because of those different heterostructures, composites can be provided for catalysts or photo detection, sensors, and field emission applications.⁴⁶⁻⁴⁸ The mapping images clearly indicate an aspect of Zn and O present. The main constituent elements of these different MeNTA samples also had distinct indicative signals of Cu and Zr, Pd and Cu, W and Ni, and Ni and Si in Cu-MeNTA, Pd-MeNTA, W-MeNTA, and Ni-MeNTA respectively. But the minor elements did not show any major signals to the constituent sample, and were therefore omitted for brevity.

Figure 4 (a) represents XRD patterns of ZnO-NWs in samples with various size of Zr-MeNTA. The signal intensity of larger ZnO-NWs/Zr-MeNTA features (20 µm) was more intense than the smaller features,

indicating a higher density of NWs. all the samples revealed similar XRD patterns 34.42 (002). However, a weak diffraction peaks intensity is observed at a value of 34.42 and correspond to the (002) plane, due to much weaker signal arising from a non-promise lateral and vertical grown ZnO-NWs in 650 nm height with diameter of 2 μm Zr-MeNTA. This result is resembling with the SEM observation of the morphology. Figure 4(b) shows the XRD patterns of ZnO-NWs on the inner surface of the five ZnO seed coated MeNTA, as follows: 31.75 (100), 34.42 (002), 36.25 (101), 47.54 (102), 56.60 (110), 62.86 (103), and 67.96 (112). The strong diffraction peak of 34.42 correspondin to the (002) plane is indicative of hexagonal wurtzite structure (JCPDS Card No. 36-1451). This illustrates the preferential alignment of the nanowires along the c-axis indicating the high phase purity of the sample. Besides this, no other distinct peaks are detected, indicating the material is quite pure.

Tables 1 and 2 list the crystallite sizes of ZnO-NWs calculated using Equation 1. As shown in Table 1, there was almost no difference in the size of crystals in the smallest NWs (2 μm , 10 μm) and largest NWs (20 μm). The XRD results table 2 also indicate that the size of the crystals in the ZnO-NWs was nearly the same in all samples except the Pd-MeNTA, which might be due to a slightly thicker tube due to the high rate of Pd deposition. Crystal size (D) of ZnO-NWs was calculated from the FWHM of [002] diffraction peak using the Debye Scherrer equation, as follows:⁴⁹

$$D = \frac{0.9\lambda}{\beta \cos\theta} \dots\dots\dots (1)$$

where λ , θ , and β respectively indicate X-ray wavelength, Bragg diffraction angle, and FWHM.

Figure 5 (a) presents the photoluminescence (PL) spectra of as-fabricated ZnO-NWs grown in various types of metallic glass nanotube array. Measurements were obtained at room temperature using a He-Cd (Xe lamp) laser with a wavelength of 325 nm as an excitation source. All of the samples exhibited peaks in the ultraviolet (UV) region as follows: Zr-MeNTA (382 nm), Cu-MeNTA (395 nm), Pd-MeNTA (383 nm), W-MeNTA (389 nm), and Ni-MeNTA (394 nm). These results can be attributed to the near band edge emission associated with band-to-band excitonic recombination. We also observed weak broad emission peaks in the visible region incorporated as well as deep-level emissions (DLE) as follows: Zr-MeNTA (534 nm), Cu-MeNTA (534 nm), Pd-MeNTA (534 nm), W-MeNTA (520 nm), and Ni-MeNTA (523 nm). The weak broad emission band can be attributed to radiative recombination of photo generated holes with singly ionized oxygen vacancies or Zn interstitials with hydroxyl groups in the crystal lattice, which formed during the hydrothermal fabrication of ZnO-NWs.^{50, 46} Note that UV emission peak in W- MeNTA (at 389 nm) and Ni-MeNTA (at 394 nm) presented a redshift of more than 6 nm from the previously reported 383 nm for vertically-aligned ZnO nanowire array on a bi-axially textured Ni-W substrate.⁴⁸ This result is similar to the UV emission peak from Ni-doped ZnO-NWs.⁵¹ The near bandgap emission maximum of 395 nm in the Cu-MeNTA sample shows is somewhat red-shifted from the Cu-doped ZnO NW in comparison to the un doped structures (385 nm),⁵² 383 nm for ZnO NW in Pd-MeNTA and similar to Pd-nanoparticle-decorated ZnO-NWs and palladium-zinc oxide nanowire nanofiber 382 nm.^{47, 53} Table 3 lists

the defect density of the nanowires grown in the various types of MeNTA based on the ratio of NBE to DLE peak intensities (INBE/IDLE). Far more defects appeared in the Ni-MeNTA and W-MeNTA samples, compared to Zr-MeNTA, Pd-MeNTA, and Cu-MeNTA, due to the intense photoluminescence peak at 389 and 394 nm with a negligible deep band emission peak intensity ratio. Low defect density is crucial to the performance of UV photodetectors. However, the defect densities observed in a sample of ZnO-NWs/Zr-MeNTA, Pd-MeNTA, and Cu-MeNTA, can be beneficial for photocatalytic activity and gas sensor.^{54, 55} Figure 5(b) presents the schematic structure of nanohybrids ZnO-NWs/MeNTA and unusual growth of laterally and vertically alignment of ZnO-NWs inside the tube in the height of 650 nm with 2, 10, and 20 μm diameter. The wall thickness of the nanotube inside the photoresist the template is dependent on deposition time TFMG and ZnO seed coating. Figure 5b. (a-c) clearly shows the film of metallic glass, ZnO seed, and the grown NWs in the inner side and on the top part photoresist template. However, after ultra-sonication the top layer and photoresist template removed and only the inner side part of the nanowires is left. The schematic structure of laterally and vertically grown ZnO-NWs within the diameter of 2 μm ZnO side wall MeNTA all the NWs are mixed together and rather than growing perpendicular from the ZnO seed layer metallic glass surface. However, in diameter of 10 and 20 μm , a free vertically alignment ZnO-NWs density become increase beside to the mixed up of the lateral and vertical grown NWs and preferentially grow along a (002). XRD results also confirms that in 2 μm NWs/MeNTA have low intensity towards (002) orientation due to laterally grown and low density of vertically grown nanowires in small diameter. In case of 10 and 20 μm NWs/MeNTA the peak intensity (002) increased due to larger diameter and higher surface area to grow nanowires in vertically direction as shown in Figure 2.

Conclusions

This paper presents a novel approach to the large-scale fabrication of nanohybrid structure of ZnO-NWs inside MeNTA on a silicon substrate. The novel nanohybrid materials (ZnO-NWs/MeNTA) were successfully fabricated by a hydrothermal synthesis method of ZnO-NWs in a template-assisted ZnO seeded pre-deposited of $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$, $\text{Cu}_{47}\text{Zr}_{42}\text{Al}_7\text{Ti}_4$, $\text{Pd}_{72}\text{Cu}_{12}\text{Si}_{16}$, $\text{W}_{50}\text{Ni}_{25}\text{B}_{25}$ and $\text{Ni}_{54}\text{B}_{0.3}\text{Si}_{36}\text{Cr}_{2.7}\text{Fe}_7$ films by sputtering. The template was then removed after successful growth of ZnO-NWs to enable fabricating a dense lateral and vertical aligned grown ZnO-NWs inside MeNTA. Integrating the high thermal and mechanical stability of the ZnO seed layer with the high strength and ductility properties of metallic glass maintain the as-grown ZnO-NWs at MeNTA during removal of the photoresist template under ultrasonic vibration and mechanical failures due to external stress. The resulting ZnO-NWs in all samples exhibited good crystal quality and strong UV emissions.

Declarations

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Competing interests

The authors declare no competing financial interests.

Authors' contributions

J.P.C. conceived the research. G.S.W., T.Y.C., K.W.T., C.J.Y. and C.J. conducted the experiments. J.P.C., P.S., and B.R.H. analyzed the results. G.S.W., P.S., B.R.H., and J.P.C. prepared the manuscript. All authors reviewed the manuscript.

References

- (1) Liu, J.; Xie, S.; Chen, Y.; Wang, X.; Cheng, H.; Liu, F.; Yang, J. J. N. r. I. Homoepitaxial regrowth habits of ZnO nanowire arrays. *Nanoscale Res. Lett.* **2011**, 6, 619.
- (2) Ren, Y.; Yuan, Z.; Fan, J.; Huang, W.; Shuai, C. J. A. P. A. Annealing temperature-dependent morphology, structure, and optical properties of well-aligned ZnO nanowire arrays. *APPL PHYS A-MATER* **2018**, 124(9), 655.
- (3) Cheng, C.; Lei, M.; Feng, L.; Wong, T. L.; Ho, K. M.; Fung, K. K.; Loy, M. M.; Yu, D.; Wang, N. J. A. N. High-quality ZnO nanowire arrays directly fabricated from photoresists. *Phys. Chem.* **2009**, 3, 53-58.
- (4) Ahmad, R.; Majhi, S. M.; Zhang, X.; Swager, T. M.; Salama, K. N. J. A. i. c.; science, i., Recent progress and perspectives of gas sensors based on vertically oriented ZnO nanomaterials. *Adv. Colloid Interface Sci*, **2019**, 270, 1-27.
- (5) Muchuweni, E.; Sathiaraj, T.; Nyakoty, H. J. M. S. i. S. P. Low temperature synthesis of ZnO nanowires on GAZO thin films annealed at different temperatures for solar cell application. *Mater Sci Semicond Process* **2017**, 68, 80-86.
- (6) Campos, A. C.; Paes, S. C.; Correa, B. S.; Cabrera-Pasca, G. A.; Costa, M. S.; Costa, C. S.; Otubo, L.; Carbonari, A. W. Growth of Long ZnO Nanowires with High Density on the ZnO Surface for Gas Sensors. *ACS Applied Nano Materials* **2020**, 3 (1), 175-185.
- (7) Qin, Y.; Yang, R.; Wang, Z. L. J. T. J. o. P. C. C. Growth of horizonatal ZnO nanowire arrays on any substrate. *J. Phys. Chem. C* **2008**, 112, 18734-18736.
- (8) Consonni, V.; Briscoe, J.; Kärber, E.; Li, X.; Cossuet, T. J. N. ZnO nanowires for solar cells: a comprehensive review. *Nanotechnology* **2019**, 30, 36.

- (9) Leontie, L.; Sprincean, V.; Untila, D.; Spalatu, N.; Caraman, I.; Cojocaru, A.; Şuşu, O.; Lupan, O.; Evtodiev, I.; Vataavu, E. J. T. S. F. Synthesis and optical properties of Ga₂O₃ nanowires grown on GaS substrate. *Thin Solid Film* **2019**, 689, 137502.
- (10) Li, Z.; Yang, R.; Yu, M.; Bai, F.; Li, C.; Wang, Z. L. J. T. J. o. P. C. C. Cellular level biocompatibility and biosafety of ZnO nanowires. *J. Phys. Chem. C* **2008**, 112, 20114-20117.
- (11) Singh, A.; Singh, S. J. B. o. M. S. ZnO nanowire-coated hydrophobic surfaces for various biomedical applications. *Bull. Mat. Sci.* **2018**, 41, 94.
- (12) Zhou, J.; Xu, N. S.; Wang, Z. L. J. A. M. Dissolving behavior and stability of ZnO wires in biofluids: a study on biodegradability and biocompatibility of ZnO nanostructures. *Adv. Mater.* **2006**, 18, 2432-2435.
- (13) Zheng, M. J.; Zhang, L. D.; Li, G. H.; Shen, W. Z. Fabrication and optical properties of large-scale uniform zinc oxide nanowire arrays by one-step electrochemical deposition technique. *Chem. Phys. Lett.* **2002**, 363 (1), 123-128.
- (14) Jeong, J. S.; Lee, J. Y. Investigation of initial growth of ZnO nanowires and their growth mechanism. *Nanotechnology* **2010**, 21 (47).
- (15) Son, H. J.; Jeon, K. A.; Kim, C. E.; Kim, J. H.; Yoo, K. H.; Lee, S. Y. Synthesis of ZnO nanowires by pulsed laser deposition in furnace. *Appl. Surf. Sci.* **2007**, 253, 7848-7850.
- (16) Choi, J.; Ji, H.; Tambunan, O. T.; Hwang, I. S.; Woo, H. S.; Lee, J. H.; Lee, B. W.; Liu, C.; Rhee, S. J.; Jung, C. U.; Kim, G. T. Brush-Shaped ZnO Heteronanorods Synthesized Using Thermal-Assisted Pulsed Laser Deposition. *ACS APPL MATER INTER* **2011**, 3, 4682-4688.
- (17) Muchuweni, E.; Sathiaraj, T. S.; Nyakoty, H. Low temperature synthesis of ZnO nanowires on GAZO thin films annealed at different temperatures for solar cell application. *Mater Sci Semicond Process* **2017**, 68, 80-86.
- (18) Muchuweni, E.; Sathiaraj, T. S.; Nyakoty, H. Effect of annealing on the microstructural, optical and electrical properties of ZnO nanowires by hydrothermal synthesis for transparent electrode fabrication. *MAT SCI ENG B-ADV* **2018**, 227, 68-73.
- (19) Tai, G. A.; Liu, J. S. ZnO nanowire arrays: controllable preparation and effect of annealing temperature on optical properties. *Mater. Res. Innov.* **2014**, 18(1), 20-26.
- (20) Qin, Y.; Yang, R.; Wang, Z. L. Growth of Horizontal ZnO Nanowire Arrays on Any Substrate. *J PHYS CHEM C* **2008**, 112(48), 18734-18736.
- (21) Muchuweni, E.; Sathiaraj, T. S.; Nyakoty, H. Hydrothermal synthesis of ZnO nanowires on rf sputtered Ga and Al co-doped ZnO thin films for solar cell application. *J ALLOY COMPD* **2017**, 721, 45-54.

- (22) Tam, N. D.; Singh, K.; Meyyappan, M.; Oye, M. M. Vertical ZnO nanowire growth on metal substrates. *Nanotechnology* **2012**, 23 (19), 5.
- (23) Bahramian, R.; Moshaii, A.; Eshghi, H. Effect of seeding modification of substrate on the growth and UV detection properties of ZnO nanowires. *Mater. Lett.* **2016**, 179, 222-225.
- (24) Ngo-Duc, T.; Singh, K.; Meyyappan, M.; Oye, M. M. Vertical ZnO nanowire growth on metal substrates. *Nanotechnology* **2012**, 23 (19), 194015.
- (25) Fan, H. J.; Lee, W.; Scholz, R.; Dadgar, A.; Krost, A.; Nielsch, K.; Zacharias, M. Arrays of vertically aligned and hexagonally arranged ZnO nanowires: a new template-directed approach. *Nanotechnology* **2005**, 16 (6), 913-917.
- (26) Zong, H.; Geng, C.; Kang, C.; Cao, G.; Li, L.; Zhang, B.; Li, M. Excellent near-infrared transmission of Zr-based thin film metallic glasses. *Results Phys.* 2018, 10, 612-615.
- (27) Yiu, P.; Diyatmika, W.; Bonninghoff, N.; Lu, Y. C.; Lai, B. Z.; Chu, J. P. Thin film metallic glasses: Properties, applications and future. *J. Appl. Phys.* **2020**, 127(3), 16.
- (28) Chen, W. T.; Manivannan, K.; Yu, C. C.; Chu, J. P.; Chen, J. K. Fabrication of an artificial nanosucker device with a large area nanotube array of metallic glass. *Nanoscale* **2018**, 10 (3), 1366-1375.
- (29) Kumar, G.; Tang, H. X.; Schroers, J. J. N. Nanomoulding with amorphous metals. *Nature*, **2009**, 457(7231), 868-872.
- (30) Carmo, M.; Sekol, R. C.; Ding, S.; Kumar, G.; Schroers, J.; Taylor, A. D. Bulk Metallic Glass Nanowire Architecture for Electrochemical Applications. *ACS Nano* **2011**, 5(4), 2979-2983.
- (31) Song, S.; Bei, H.; Wadsworth, J.; Nieh, T.-G. J. I. Flow serration in a Zr-based bulk metallic glass in compression at low strain rates. *Intermetallics* **2008**, 16(6), 813-818.
- (32) Yu, C.-C.; Lee, C.; Chu, J. P.; Greene, J.; Liaw, P. K. J. A. M., Fracture-resistant thin-film metallic glass: Ultra-high plasticity at room temperature. *APL Mater* **2016**, 4 (11), 116101.
- (33) Schuh, C. A.; Hufnagel, T. C.; Ramamurty, U. Mechanical behavior of amorphous alloys. *Acta Mater.* **2007**, 55 (12), 4067-4109.
- (34) Kaushik, N.; Sharma, P.; Ahadian, S.; Khademhosseini, A.; Takahashi, M.; Makino, A.; Tanaka, S.; Esashi, M. J. J. o. B. M. R. P. B. A. B. Metallic glass thin films for potential biomedical applications. *Int. J. Biomed. Res.* **2014**, 102 (7), 1544-1552.
- (35) Yiu, P.; Diyatmika, W.; Bönninghoff, N.; Lu, Y.-C.; Lai, B.-Z.; Chu, J. P. J. J. o. A. P. Thin film metallic glasses: Properties, applications and future. *J. Appl. Phys.* 2020, 127 (3), 030901.

- (36) Kassa, S. T.; Hu, C.-C.; Liao, Y.-C.; Chen, J.-K.; Chu, J. P. Thin film metallic glass as an effective coating for enhancing oil/water separation of electrospun polyacrylonitrile membrane. *Surf. Coat. Technol.* **2019**, 368, 33-41.
- (37) Gizaw, E. T.; Yeh, H.-H.; Chu, J. P.; Hu, C.-C. J. S.; Technology, P. Fabrication and characterization of nitrogen selective thin-film metallic glass/polyacrylonitrile composite membrane for gas separation. *Sep. Purif. Technol.* 2020, 237, 116340.
- (38) Yamazaki, H.; Hayashi, Y.; Masunishi, K.; Ono, D.; Ikehashi, T. J. E.; Japan, C. i., A review of capacitive MEMS hydrogen sensor using Pd-based metallic glass with fast response and low power consumption. *Electron Comm Jpn.* **2019**, 102 (3), 70-77.
- (39) Huang, B.-R.; Chu, J. P.; Hsu, C.-L.; Chen, Y.-S.; Chang, C.-H. J. A. a. m.; interfaces, Few-layer thin-film metallic glass-enhanced optical properties of ZnO nanostructures. *ACS Appl. Mater.* **2017**, 9 (45), 39475-39483.
- (40) Huang, B. R.; Chu, J. P.; Saravanan, A.; Yenesew, M. M.; Bönninghoff, N.; Chang, C. H. J. C. A. E. J. High-Performance Sensor Based on Thin-Film Metallic Glass/Ultra-nanocrystalline Diamond/ZnO Nanorod Heterostructures for Detection of Hydrogen Gas at Room Temperature. Chang, *Chem. Eur. J.* **2019**, 25 (44), 10385-10393.
- (41) Huang, B.-R.; Chu, J. P.; Hsu, C.-L.; Greene, J. E.; Chen, Y.-S.; Chang, C.-H. J. J. o. M. C. C., Improving the optical and crystal properties of ZnO nanotubes via a metallic glass quantum dot underlayer. Chang, *J. Mater. Chem. C*, **2019**, 7 (17), 5163-5171.
- (42) Chen, J.-K.; Chen, W.-T.; Cheng, C.-C.; Yu, C.-C.; Chu, J. P. J. M. T., Metallic glass nanotube arrays: Preparation and surface characterizations. *Materials Today* **2018**, 21 (2), 178-185.
- (43) Chen, W.-T.; Manivannan, K.; Yu, C.-C.; Chu, J. P.; Chen, J.-K. J. N., Fabrication of an artificial nanosucker device with a large area nanotube array of metallic glass. *Nanoscale* **2018**, 10 (3), 1366-1375.
- (44) Chen, W.-T.; Li, S.-S.; Chu, J. P.; Feng, K. C.; Chen, J.-K. J. B.; Bioelectronics, Fabrication of ordered metallic glass nanotube arrays for label-free biosensing with diffractive reflectance. *Biosens. Bioelectron.*, **2018**, 102, 129-135.
- (45) She, X.; Shen, Y.; Wang, J.; Jin, C. J. L. S.; Applications, Pd films on soft substrates: a visual, high-contrast and low-cost optical hydrogen sensor. *Light Sci. Appl.* **2019**, 8 (1), 1-10.
- (46) Xu, S.; Wang, Z. L. J. N. R. One-dimensional ZnO nanostructures: solution growth and functional properties. *Nano Res.* **2011**, 4 (11), 1013-1098.
- (47) Bera, A.; Basak, D. J. N. Pd-nanoparticle-decorated ZnO nanowires: ultraviolet photosensitivity and photoluminescence properties. *Nanotechnology* **2011**, 22 (26), 265501.

(48) Chhikara, D.; Srivatsa, K.; Kumar, M. S.; Singh, P.; Das, S.; Panwar, O. J. A. M. Growth and field emission properties of vertically-aligned ZnO nanowire array on biaxially textured Ni-W substrate by thermal evaporation. *Adv. Mater* **2015**, 862-866.

(49) Shrama, S. K.; Saurakhiya, N.; Barthwal, S.; Kumar, R.; Sharma, A. J. N. r. I. Tuning of structural, optical, and magnetic properties of ultrathin and thin ZnO nanowire arrays for nano device applications. *Nanoscale* **2014**,9 (1), 1-17.

(50) Djurišić, A. B.; Choy, W. C.; Roy, V. A. L.; Leung, Y. H.; Kwong, C. Y.; Cheah, K. W.; Gundu Rao, T.; Chan, W. K.; Fei Lui, H.; Surya, C. J. A. F. M. Photoluminescence and electron paramagnetic resonance of ZnO tetrapod structures. *Adv.* **2004**,14 (9), 856-864.

(51) He, J. H.; Lao, C. S.; Chen, L. J.; Davidovic, D.; Wang, Z. L. J. J. o. t. A. C. S., Large-scale Ni-doped ZnO nanowire arrays and electrical and optical properties. *Chem.Soc.* **2005**, 127, 16376-16377.

(52) Robak, E.; Coy, E.; Kotkowiak, M.; Jurga, S.; Załęski, K.; Drozdowski, H. J. N. The effect of Cu doping on the mechanical and optical properties of zinc oxide nanowires synthesized by hydrothermal route. *Nanotechnology* **2016**,27(17), 175706.

(53) Choi, J.; Chan, S.; Joo, H.; Yang, H.; Ko, F. K. J. W. r. Three-dimensional (3D) palladium-zinc oxide nanowire nanofiber as photo-catalyst for water treatment. *Water Res.* **2016**,101, 362-369.

(54) Ahn, M.-W.; Park, K.-S.; Heo, J.-H.; Park, J.-G.; Kim, D.-W.; Choi, K. J.; Lee, J.-H.; Hong, S.-H. J. A. p. I. Gas sensing properties of defect-controlled ZnO-nanowire gas sensor. *Int. J. Appl. Phys.* **2008**, 93, 263103.

(55) Kuo, T.-J.; Lin, C.-N.; Kuo, C.-L.; Huang, M. H. J. C. o. M. Growth of ultralong ZnO nanowires on silicon substrates by vapor transport and their use as recyclable photocatalysts. *Chem. Mater.* **2007**, 19, 5143-5147

Tables

Table 1. ZnO NW crystallite size at different diameter of metallic glass nanotube substrate

ZnO NW/MeNTA	Radian	X = 2θ	degree	Crystal size (nm)
650 nm H/1.5 μm D	0.0035	34.494	17.247	39.62
650 nm H/10 μm D	0.00357	34.487	17.243	38.84
650 nm H/20 μm D	0.0035	34.505	17.252	40.1

Table.2. Crystal size in ZnO-NWs grown on various metallic glass nanotubes

ZnO NW/MeNTA	Radian	X = 2 θ	degree	Crystallite size (nm)
Zr-MeNTA	0.003455	34.505	17.252	40.1
Cu-MeNTA	0.003354	34.498	17.249	41.4
Pd-MeNTA	0.003084	34.489	17.245	44.9
W-MeNTA	0.003312	34.493	17.246	41.8
Ni-MeNTA	0.003498	34.487	17.243	39.6

Table 3. UV-vis broadband emissions and defect density of the ZnO-NWs in various metallic glass nano tube array.

ZnO NW/MeNTA	Near band-edge (NBE) nm	Deep-level-emission (DLE) nm	Ratio of NBE to DLE peak intensity (I_{NBE}/I_{DLE})
Zr-MeNTA	382	534	4.4
Cu-MeNTA	395	534	5.08
Pd-MeNTA	383	534	5.23
W-MeNTA	389	520	9.71
Ni-MeNTA	394	523	10.6

Figures

Figure 1

Schematic representation of the fabrication process of ZnO-NWs in ZnO seed coated MeNTA using contacted-hole photoresist template.

Figure 2

SEM images of (a), (d) and (g) ZnO-NWs grown in a height of 650 nm with a diameter of 2 μm, (b), (e) and (h) 650 nm in height with a diameter of 10 μm, (c), (f) and (i) 650 nm in height with a diameter of 20 μm and (j) elemental maps.

Figure 3

SEM images and elemental mapping of ZnO-NWs (height = 650 nm; diameter = 20 μm): (a) Cu-MeNTA; (b) Pd-MeNTA; (c) W-MeNTA; and (d) Ni-MeNTA, respectively.

Figure 4

(a) XRD patterns of ZnO-NWs of various diameter grown in Zr-MeNTA. (b) XRD patterns of ZnO NW grown in different metallic glass nanotube arrays.

Figure 5

(a) Emission spectra of ZnO-NWs using incident Xe lamp (325 nm) at room temperature (b) Schematic structure of nanohybrids ZnO-NWs/MeNTA and laterally and vertically alignment of ZnO-NWs in the height of 650 nm with 2, 10, and 20 μm diameter.