Glancing angle deposited Al-doped ZnO nanostructures with different structural and optical properties

A. Yildiz^{1,2*}, H. Cansizoglu¹, M. Turkoz^{1,3}, R. Abdulrahman¹, Alaa Al-Hilo¹, M.F. Cansizoglu¹, T. M. Demirkan¹, and T. Karabacak¹

¹ Department of Physics and Astronomy, University of Arkansas at Little Rock, Little Rock, Arkansas, 72204, USA

² Department of Energy Systems Engineering, Faculty of Engineering and Natural Sciences, Yildirim Beyazıt University, Ankara, Turkey

³ Department of Electrical- Electronic Engineering, Faculty of Engineering, University of Karabuk, Karabuk, Turkey

* Corresponding author: tel.: +90 312 324 15 55; fax: +90 312 324 15 05; e-mail address: yildizab@gmail.com

Abstract

Al-doped ZnO (AZO) nanostructure arrays with different shapes (tilted rods, vertical rods, spirals, and zigzags) were fabricated by utilizing glancing angle deposition (GLAD) technique in a DC sputter growth unit at room temperature. During GLAD, all the samples were tilted at an oblique angle of about 90° with respect to incoming flux direction. In order to vary the shapes of nanostructures, each sample was rotated at different speeds around the substrate normal axis. Rotation speed did not only affect the shape but also changed the microstructural

and optical properties of GLAD AZO nanostructures. The experimental results reveal that GLAD AZO nanostructures of different shapes each has unique morphological, crystal structure, mechanical, and optical properties determined by scanning electron microscopy , X-ray diffraction , transmission, and reflectance measurements. Vertical nanorods display the largest grain size, minimum strain, lowest defect density, and highest optical transmittance compared to the other shapes. Growth dynamics of GLAD has been discussed to explain the dependence of structural and optical properties of nanostructures on the substrate rotation speed.

Keywords

AZO nanostructures; nanostructure shape; glancing angle deposition; structural properties; optical properties

1. Introduction

Recent years have seen rapid progress in transparent conductive oxide (TCO) materials, especially for optoelectronics with indium tin oxide (ITO). The main technological interest in the ITO based devices lies in its very high transparency and low resistivity. Al-doped ZnO (AZO), which has similar properties with ITO, is expected to be an alternative to ITO due to its more advantages properties such as being a non-toxic, inexpensive, and abundant material [1]. Therefore, AZO is considered as a promising material to be used in a wide range of optoelectronic devices such as light emitting diodes (LED) and solar cells [2-3]. Most of these applications depend on the remarkable structural and optical properties of AZO. Recently, the low-dimensional AZO nanostructures have shown great potential for various nano-devices [4]. They also exhibit particularly interesting physical behaviors, which are different from those of their corresponding bulk counterparts. Although the effect of some parameters such as length, diameter, and aspect ratio of the ZnO nanostructures have been

considered by several researchers [5-7], the effect of shape in the AZO nanostructures has not been addressed yet. The major reason behind this gap in the literature is the difficulty of fabricating AZO nanostructure arrays in different shapes using common conventional techniques. Glancing angle deposition (GLAD) is a promising alternative nano fabrication method, which allows the growth of the nanostructures in different shapes [8]. During GLAD, the flux of the sputtered atoms come to the surface of the substrate at high angles (typically $>70^\circ$; in this study $\sim 90^\circ$). At initial stages, atoms form island-like structures on the substrate and shorter islands cannot capture enough flux, whereas longer islands get sufficient flux and continue to grow. This so-called “shadowing effect” results in the formation of isolated nanostructures through a physical self-assembly process (Details on the glancing angle deposition method can be found in [8, 9]). If no substrate rotation is used, longer islands tend to grow in the flux direction and form the tilted nanorods. If a discrete rotation (dr) is applied to the substrate azimuthally by 180° at a time, the tilted nanorods start to grow on top of the existing tilted rods in the opposite direction following the flux direction, resulting in zigzag shaped structures. If the substrate is rotated around its surface normal axis continuously, then the structures are forced to grow in lateral and vertical directions at different rates depending on the rotation speed. Although the flux comes at a certain direction at glancing angle, the rotation speed determines the direction and the rate of the flux locally on the substrate. For example, a relatively fast continuous rotation (cr) helps the structures grow in the vertical direction but with minimal rates in lateral directions. That results in the formation of vertical nanorods. On the other hand, a relatively slow cr allows the structures grow in both lateral and vertical directions leading to the formation of spiral shapes. The rotation speed not only determines the morphology of the structures, but can also affect the microstructural properties such as grain size and the strain in the structures. Moreover, the optical properties of the nanostructures vary due to the differences in microstructural properties and the light trapping

mechanisms of the nanostructures in different shapes. An understanding of the effect of the rotation speed or namely the shape on nanostructures can provide an essential input for optimization of solar cell and LED performance [10, 11]. Therefore, it is of crucial importance to investigate how the morphological, microstructural, and optical properties of GLAD AZO nanostructures are influenced by changing the shape of structures.

In this study, AZO nanostructure arrays in different shapes such as tilted rods, spirals, zigzags and vertical rods were deposited by GLAD technique. Structural and optical properties of AZO nanostructures were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), and ultra violet – visible – near infrared (UV-Vis-NIR) spectroscopy. Measurements reveal that the vertical nanorods show enhanced crystal structure and transmit light more effectively than the nanostructures in other shapes. We also compared optical and structural properties of AZO nanostructures with a thin film control sample. Our results can provide valuable information for the practical fabrication of AZO nanostructure based devices and can be applied to other TCOs as well.

2. Experimental

The AZO thin film (TF) and nanostructures were deposited by DC sputtering on Si and glass substrates in the same deposition system. The ZnO-Al (2 wt.%) target (Kurt Lesker) was utilized as the source material. Samples were attached to a substrate modulator with tilt and rotation control at a distance ~ 18 cm away from the AZO target. All of the samples were deposited at room temperature under 6×10^{-6} mbar base pressure with a DC power of 110 W. Argon (working gas) pressure was 3.5×10^{-3} mbar. The weight loadings (i.e. material amount, mass loading) of all the nanostructured and TF coatings were kept similar and set to ~ 0.2 - 0.3 mg/cm² range, which was measured by a quartz crystal microbalance (QCM) method. QCM crystals were placed on the substrate holder near the samples and mass loading values were

measured by comparing the QCM frequencies before and after deposition. The deposition times for the TF and the GLAD nanostructures were 46 min and 120 min, respectively. The nanostructures were deposited under similar experimental conditions except the rotation speed. The incidence angle of the flux was set at about $\sim 90^\circ$ for all of the nanostructures, whereas the rotation speeds were 0, 0.2 (*cr*), 1/40 (*cr*) and 1/60 (*dr*) rotation per minute (rpm) for the tilted, vertical, spiral and zigzag structures, respectively.

θ - 2θ scan X-ray diffraction (XRD) patterns for each shape of the nanostructures were gained with Rigaku MiniFlex 600 with a step size of 0.01° and using $1.54 \text{ \AA}$ wavelength. The morphological characterization of the samples were done by scanning electron microscopy (SEM, JEOL 7000F). The layer porosity (includes microstructural pores and gaps between nanostructures) of the nanostructures and the density of the film were calculated with the help of measuring the mass with QCM and calculating the volume with the layer thickness information from SEM images. The total optical reflection and transmission profiles of the samples were obtained by UV-vis-NIR spectroscopy measurements by utilizing an integrating sphere (Shimadzu UV-3600). The light source was incident at a normal angle and near-normal angle of 8° on the samples for transmittance and reflectance measurements, respectively.

3. Results and Discussion

3.1. Morphological Properties and Crystallinity of AZO nanostructures

Fig. 1 shows the top-view and cross-sectional SEM images of AZO TF and GLAD nanostructures. As seen in Fig. 1, AZO nanostructures have significantly different shapes. This variety can be understood from the growth dynamics of GLAD and influence of rotation speed on the nanostructure shape that was explained above. Fig. 1 reveals that modifying the flux direction and rate locally by adjusting the rotation speed has a strong impact on the

morphologies of GLAD AZO nanostructures. Surface of the TF looks relatively smooth and thickness of the film is measured $\sim 460 \pm 7.0$ nm from cross sectional SEM images (Fig. 1a and 1f). Tilted nanorods (Fig. 1b and 1g) have grown toward the incoming flux direction (i.e. atoms coming from the left corner in Fig. 1g). In the case of the vertical nanostructure arrays, most of the AZO nanorods are well-aligned, densely packed and have very narrow diameters (Fig. 1c and 1h). The large diameter and well-separated nanostructures are observed in the case of spiral nanostructure arrays (Fig. 1d and 1i). The isolated nanostructures having large separations between each other are also obtained for zigzag nanostructures (Fig. 1e and 1j).

The AZO nanostructure arrays deposited in different shapes exhibit obvious differences in diameter, length and density. The length and the diameter of the nanostructures are in the ranges of ~ 550 - 1000 nm and ~ 90 - 190 nm, respectively (Table 1). For instance, the length of the vertical nanostructures is ~ 550 nm with diameter of ~ 90 nm, whereas zigzags with length (i.e., nominal thickness) of ~ 1000 nm and diameter of ~ 190 nm are observed. Normalized layer density (w.r.t. AZO theoretical bulk density) within the coatings' nominal thickness ranges between 48.8 ± 3.5 - 78.1 ± 4.8 % for AZO nanostructures, which are lower than the density of TF with 95.7 ± 5 % (Table 1), which is due to the isolated geometry of GLAD nanostructures. SEM results of Fig. 1 also show that tilted nanostructure arrays (layer density is 48.8 ± 3.5) are considerably more separated than the nanostructures with other shapes. On the other hand, the nanostructure arrays with spiral shapes have the smallest gaps. Although the top view SEM image of spirals suggests the formation of well separated structures, cross sectional SEM image reveals that they have two different growth stages, such that they grow very dense at initial times and then start getting isolated from each other. However, the first layer is still dominant in the overall layer and results in a relatively high film density value for the spirals. Density of a GLAD film has been shown to be mainly

dependent on deposition angle rather than the rotation speed of substrate by the growth simulations [12]. However, differences in the layer densities of our GLAD AZO nanostructures show that the rotation speed can also have a notable effect on film density along with different crystalline and morphological properties. Similarly, GLAD Si nanostructures of different shapes (pillars, oblique, helix), which were produced by different substrate rotation speeds at constant deposition angle of 83° , were also reported to have different film densities. Change in the layer densities of our GLAD AZO nanostructures may be explained by a competitive growth dynamics of different crystalline orientations/phases [13-16]. Although the same deposition angle is expected to provide a same deposition rate (average number of particles coming to the substrate in time), rotation speed can influence the growth rate at a local point. If the vertical growth rate of a particular orientation/phase is favorable in tilted structures, another one might be more dominant in spirals. For example, at initial stages, randomly oriented islands can grow together leading to a denser first layer as we observe in our results. This can be followed by a preferential growth of islands with crystal orientations that can follow the obliquely incident flux leading to tilted columns with a tilted crystallographic texture [16]. However, in the case of GLAD spiral or vertical structures, substrate rotation can disrupt the growth of such crystal orientations of tilted columns, and promote the ones that can accommodate substrate rotation and display a higher vertical growth rate compared to the former ones. Preferential growth of certain crystal orientations depending on the rotation speed can also affect the crystallite/grain sizes in lateral direction, which can results in structures of different diameters as we observe in GLAD AZO by different rotation speeds (shapes). On the other hand, this potential growth mechanism needs a further study, which beyond the scope of this work.

Fig. 2 presents the XRD patterns of the AZO nanostructures of different shapes and conventional flat AZO TF. Also, the inset of Fig. 2 represents an enlarged region of XRD

patterns for the (002) plane. Approximate peak positions in the XRD patterns are found to be consistent with the previous reports [5-7]. The structural parameters such as peak position and full-width-half-maximum (FWHM) of XRD pattern for each shape of the nanostructure arrays are summarized in Table 1. Note that FWHM of the instrument is 0.093° . The most intense peak corresponds to the diffraction from (002) plane, indicating that the samples have a preferential [002] orientation along the normal direction of the substrate surface. However, weak (100) and (101) diffraction peaks are also observed for the zigzags, which suggests a polycrystalline structure. Sharp (002) XRD peaks with narrow FWHM can imply that c-axes of the samples are well oriented along the normal direction of the substrate surface. However, the intensity of (002) diffraction peak does not increase as the FWHM decreases among the samples, denoting a complex relationship. This might be due to tilted texture observed in some GLAD nanostructures where crystal planes tend to follow the flux direction [17-19]. As can be seen in Table 1 and Fig. 2, the lowest FWHM value (0.111°) belongs to the vertical nanorods suggesting a longer range crystal order, which will be discussed in more detail below.

3.2. Estimation of grain sizes and strains

Fig. 3 includes the grain size values of different GLAD AZO nanostructures estimated by the analysis of (002) FWHM data using Scherrer's formula ($D = \frac{0.9\lambda}{\beta \cos \theta}$) [20]. Here D is the grain size, λ is the X-ray wavelength (0.1541 nm), θ is the Bragg angle, and β is the instrumental corrected FWHM. $\beta = [\beta_{\text{measured}}^2 - \beta_{\text{instrumental}}^2]^{1/2}$, where β_{measured} is the FWHM of the AZO (0 0 2) diffraction peak measured from the samples, and $\beta_{\text{instrumental}}$ is the instrumental FWHM of the diffraction peak from a standard silicon sample [21]. As expected, the grain size increases with decreasing FWHM. It is estimated as 34.03 nm for the TF. On the other hand, the grain sizes for the nanostructures are found to be greater than the grain

sizes of the TF. They vary between 47.36 to 78.21 nm, depending on the shape of the nanostructures. The highest grain size belongs to the vertical nanorods, which indicates a better crystalline structure.

All the samples show a shift in their 2θ (002) peak position with respect to the equilibrium 34.467° value of the bulk ZnO (JCPDS file No. 75-1526). This shift indicates the existence of strain incorporated in the coatings. The lattice constants are given by the equation

$$\left(\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \right) \quad [22],$$

where a and c are the lattice constants, and d_{hkl} is the crystalline plane distance. This equation gives the lattice constant $c = 2 d_{hkl}$ for the (0 0 2) diffraction peak. Now, the strain ε along the c -axis can be determined by using formula

$$\left(\varepsilon = \frac{c - c_0}{c_0} \times 100 \right) \quad [23],$$

where c_0 (0.52069 nm) is the unstrained lattice parameter of ZnO.

Strain values calculated from the (002) XRD peak positions are shown in Fig. 3 for different AZO structures. Positive strain values in our notation correspond to compressive stress, while negative values are for tensile stress. It is well known for sputter deposited thin films that, due to a “ion peening” effect, films quickly develop a residual compressive stress (i.e. shift to smaller 2θ values in XRD) that might eventually result in buckling and delamination of the film from the substrate [24-26]. However, it has been also demonstrated that when the grain sizes are small enough, such as at early stages of the sputter deposition, film can develop a tensile stress due to the atom-to-atom attraction forces at the grain boundaries [21]. As can be seen from Fig. 3, conventional AZO film has a notable compressive strain, which is consistent with the relatively thick sputter deposited films reported in the literature [21,23]. It also indicates that the grain size of the AZO thin film has developed sufficient large values to eliminate the tensile stress contribution from grain boundaries. On the other hand, GLAD AZO nanostructures of different shapes have a quite different behavior. Although, zigzag and spring shapes have larger grain sizes compared to that of thin film, they show a notable tensile

strain. This might originate from the increased number of void-defects within the grains of those nanostructures. During GLAD, nanostructure growth tends to follow the incoming flux direction. Therefore, as the substrate goes through discrete (zigzags) or slow rotation (spirals), newly arriving atoms may not uniformly coat the crystal planes that try to follow the flux direction through twisting their orientations. This disruptive growth dynamics can lead to the formation of large amount of voids among the rotating/twisting crystal planes of GLAD nanostructures at discrete or slow substrate rotation speeds. These voids can generate a tensile stress that overcomes the compressive stress component during sputter growth [25, 27]. As can be seen from Fig. 3, spirals have a higher tensile strain compared to that of zigzag structures that is consistent with the proposed crystal growth dynamics described above. Number of disruptions in zig-zag growth is only four times (4 “zigs” and “zags”, see Fig. 1), while on the other hand it is numerous at each step of the continuous rotation of spirals. Moreover, we suddenly see a compressive strain for tilted and vertical nanorods that have larger grain sizes compared to other samples (Fig. 3). This can be also understood through the similar growth mechanism. In tilted nanorods, substrate is kept stationary that provides an enhanced crystal growth without the disruption of substrate rotation, which leads to the formation larger grains with reduced void-defects. The compressive stress is lower in tilted nanorods due to the large gaps among them that release the intrinsic stress on the coating [27]. The other limit is the fast substrate rotation that also leads to the growth of large grains with little compressive stress. Fast rotation speeds results in denser nanorods compared to those of tilted ones that reduce the gaps among them. This minimizes the lateral growth rods due to the preferential growth on tops versus on the sidewalls because of the shadowing effect of GLAD. This process leads to an effective vertical growth of nanorods that can allow uninterrupted growth of crystal planes along the rod axis, which gives much larger grain sizes. The gaps among the nanorods also relax the compressive stress. Overall, fast rotation speeds during

GLAD provides a nanostructured AZO coating with large grain sizes with minimal defects and stress [28].

3.3. Optical Measurements

Fig.4 shows optical transmission, reflection and absorption profiles of AZO TF and nanostructures of this study. Fig. 4 a) depicts the optical transmittance spectra of the samples that were normalized to their respective mass loadings. The average normalized transmittance in the visible region are about 71% , 77%, 69%, 55%, and 11% for the TF, vertical nanorods, tilted nanorods, spirals, and zigzags, respectively. The reflection profiles in Fig. 4 b) reveal that all of the nanostructures reflect light much lower than their thin film analog. The AZO film reflect 15 % of light in average throughout the spectrum whereas the vertical, tilted and spiral AZO nanorods reflect around 7.5 % of total light. On the other hand, the zigzag structures reflect extremely low (around ~2 %) throughout the spectrum. As can be seen in Fig. 4 c), AZO film absorbs less light than all of the nanostructures in the UV region of the spectrum, likely due to its high reflectivity arisen from its relatively smooth surface. On the other hand, vertical rods absorb the least and zigzags absorb the most among all, especially in the visible spectrum. In order to better understand the trend in optical measurements, we consider that two competing factors of layer porosity and crystal quality can affect the optical properties of AZO nanostructures. The AZO films with high crystal quality (fewer defects) would be expected to have higher transmittance due to a wide band gap expected for AZO. On the other hand, well-separated nanostructures can result in light scattering in the nanostructure layer and trap the light; thus they can introduce a light trapping property and increase light absorption. The increase in porosity of AZO nanostructures has already been reported to result in a decrease in the transmission with an increase of the GLAD angle from 0 to 45 in another study [28]. A further increase resulted in an increase in transmittance with

porosity [28]. On the other hand, improving crystal quality with increasing grain size and decreasing strain can enhance the transmittance of ZnO nanostructures [29].

As seen from Table 1, the TF is denser compared to nanostructures, as expected; however, it has the highest strain value with the lowest grain size, which is indicating a relatively low quality crystal structure (i.e. more defects). Therefore, transmittance behavior of the TF can qualitatively be explained by taking into account its dense structure rather than its crystal quality. This implies that a high transmittance of the TF is related to avoiding light trapping due to its densely packed structure. On the other hand, the vertical nanorods exhibit the highest transparency. The top portion of the vertical rods has roughly a pyramid shape (see Fig. 1h) therefore it increases light coupling into the film instead of reflection at the top surface, which happens in the case of the TF. The reflection profiles of TF and nanostructures in Fig. 4 b) also support this idea. If the separation between vertical AZO nanorods were well-defined, then they would be expected to trap the light inside the nanostructure layer and result in high absorption [8]. The vertical nanorods also have high spectral transmission compared to TF because of its high grain size and low strain, indicating less defect and relatively high crystal quality. A more meaningful comparison of both kinds of nanorods (vertical and tilted) is obtained by restricting strain values. The transmittance of tilted nanorods is little bit less than the transmittance of vertical nanorods. It is likely due to a relatively high thickness value of tilted nanorods. We propose that the tilted AZO nanorods trap the light effectively in the nanostructure layer and transmit less light and thus absorb more light compared to vertical nanorods. The nanostructure arrays in spiral and zigzag shapes suggest a change in nature of strain as pointed out before. Taking into account high strain values, porosity is more effective on the transmittance than crystal quality for nanostructure arrays with spiral and zigzag shapes. Therefore, spiral shapes with relatively low porosity exhibit greater transmittance value than zigzag shapes.

Generally, porosity in conventional films is dominated by small pores or atomic voids in the bulk and provides an effective medium of lower density and refractive index for increased light penetration transmission. On the other hand, the porosity in GLAD nanostructures is mainly dominated by larger gaps among them, individual structures can act as light scattering centers, hinder the transmission, and hence result in high absorption of light. Therefore, a typical film is expected to transmit more compared to the nanostructured layer of the same material produced by GLAD. However, in our study, vertical nanorods are exception, because of their closely packed nature, which does not seem to provide sufficient light scattering.

The nanostructured arrays of zigzag shapes deserve attention with a huge optical absorption in the visible region as can be seen in Fig. 4 c). Also, the spectral behavior of the transmission in this sample is unusual; there is a monotonic increase of its transmittance. A similar behavior was reported by Zhao *et al.* for ZnO nanostructures [30]. This behavior may be related to highly scattering of light inside the sample due to its porous structure as discussed above [10]. The disappearance of interferences in the transmission spectrum suggests a highly light trapping among the zigzags. We believe that their complicated structure enhance the light scattering inside the nanostructure layer more than the other nanostructures and result in high optical absorption through both UV and visible spectrum. However, a further and detail study is needed for exploring the other reasons behind the monotonic behavior, if there is any.

4. Conclusion

AZO nanostructures in different shapes were deposited by GLAD by utilizing different substrate rotation speeds. Effect of the shape of the nanostructure arrays on morphological, micro-structural, and optical properties of AZO nanostructures was

investigated by XRD, SEM, and UV-Vis-NIR measurements. The crystal quality and layer porosity of the AZO nanostructures are the dominant factors that influence the optical properties. Our results indicate that vertical AZO nanorods show relatively high crystal quality, less lattice strain, and low layer porosity, which leads to an enhanced optical transmittance compared to other shapes of nanostructure arrays under normal incidence of light. For further investigation of optical characterization of AZO nanostructures, different polarization or incoming angle of light can be utilized in optical measurements.

Acknowledgements

One of the authors (A. Y.) acknowledges support from the Turkish Academy of Sciences (2219). This work was supported by NASA (grant no: NNX09AW22A) and NSF (grant numbers: EPS-1003970 and 1159830). The authors thank UALR Center for Integrative Nanotechnology Sciences for helping with SEM images and UV-Vis-NIR measurements.

References

- [1] H. Kim, C. M. Gilmore, J. S. Horwitz, A. Pique, H. Murata, G. P. Kushto, R. Schlaf, Z. H. Kafafi, D. B. Chrisey, Transparent conducting aluminum-doped zinc oxide thin films for organic light-emitting devices, *Appl. Phys. Lett.* 76 (2000) 259.
- [2] J. Zhao, S. Xie, S. Han, Z. Yang, L. Ye, T. Yang, Organic light-emitting diodes with AZO films as electrodes, *Synthetic Metals* 114 (2000) 251.
- [3] A. Crossay, S. Buecheler, L. Kranz, J. Perrenoud, C. M. Fella, Y. E. Romanyuk, A. N. Tiwari, Spray-deposited Al-doped ZnO transparent contacts for CdTe solar cells, *Solar Energy Mater. and Solar Cells* 101 (2012) 283.
- [4] S. H. Kim, A. Umar, S. H. Al-Heniti, A. Al-Hajry, A. A. Al-Ghamdi, Growth, structural and optical properties of well-crystalline Al-doped ZnO nanowire and their based field effect transistor (FET), *Science of Advanced Mater.* 3 (2011) 719.
- [5] J. M. LaForge, M. T. Taschuk, M. J. Brett, Glancing angle deposition of crystalline zinc oxide nanorods, *Thin Solid Films* 519 (2011) 3530.
- [6] J.J. Hassan, M.A. Mahdi, C.W. Chin, H. Abu-Hassan, Z. Hassan, A high-sensitivity room-temperature hydrogen gas sensor based on oblique and vertical ZnO nanorod arrays, *Sensors and Actuators B* 176 (2013) 360.
- [7] Y-J. Lee, Z-P. Yang, F-Y. Lo, J-J. Siao, Z-H. Xie, Y-L. Chuang, T-Y. Lin, J-K. Sheu, Slanted n-ZnO/p-GaN nanorod arrays light-emitting diodes grown by oblique-angle deposition, *APL Mater.* 2 (2014) 056101.

- [8] H. Cansizoglu, M. F. Cansizoglu, M. Finckenor, T. Karabacak, Optical Absorption Properties of Semiconducting Nanostructures with Different Shapes, *Advanced Optical Mater.* 1 (2013) 158.
- [9] T. Karabacak, G. C. Wang, T. M. Lu, Physical self-assembly and the nucleation of 3D nanostructures by oblique angle deposition, *J. Vac. Sci. Technol. A* 22 (2004) 1778.
- [10] Y. F. Hsu, Y. Y. Xi, A. B. Djuricic, W. K. Chan, ZnO nanorods for solar cells: Hydrothermal growth versus vapor deposition, *Appl. Phys. Lett.* 92 (2008) 133507.
- [11] K-K. Kim, S-dong Lee, H. Kim, J-C. Park, S-N. Lee, Y. Park, S-J. Park, S-W. Kim, Enhanced light extraction efficiency of GaN-based light-emitting diodes with ZnO nanorod arrays grown using aqueous solution, *Appl. Phys. Lett.* 94 (2009) 071118.
- [12] T. Smya, D. Vick, M. J. Brett, S. K. Dew, A. T. Wu, J. C. Sit, K. D. Harris, Three-dimensional simulation of film microstructure produced by glancing angle deposition, *J. Vac. Sci. Technol. A*, 18 (2000) 2507.
- [13] T. Karabacak, P.-I. Wang, G.-C. Wang, T.-M. Lu, Phase transformation of single crystal tungsten nanorods at elevated temperatures, *Thin Solid Films*, 493 (2005) 293.
- [14] T. Karabacak, P.-I. Wang, G.-C. Wang, T.-M. Lu, Growth of single crystal tungsten nanorods by oblique angle sputter deposition, *Mat. Res. Soc. Symp. Proc.* 788 (2004) 75.

- [15] F. Tang, T. Karabacak, P. Morrow, C. Gaire, G.-C. Wang, T.-M. Lu, Texture evolution during shadowing growth of isolated Ru columns, *Phys. Rev. B*, 72 (2005) 165402.
- [16] P. Morrow, F. Tang, T. Karabacak, P.-I. Wang, D.-X. Ye, G.-C. Wang, T.-M. Lu, Texture of Ru columns grown by oblique angle sputter deposition”, *J. Vac. Sci. Technol. A*, 24 (2006) 205.
- [17] F. Tang, T. Karabacak, P. Morrow, C. Gaire, G.-C. Wang, T.-M. Lu, Texture evolution during shadowing growth of isolated Ru columns, *Physical Review B* 72 (2005) 165402.
- [18] P. Morrow, F. Tang, T. Karabacak, P.-I. Wang, D.-X. Ye, G.-C. Wang, T.-M. Lu, Texture of Ru columns grown by oblique angle sputter deposition, *J. Vac. Sci. Technol. A* 24 (2006) 235.
- [19] F. Tang, C. Gaire, D.-X. Ye, T. Karabacak, T.-M. Lu, G.-C. Wang, AFM, SEM and in situ RHEED study of Cu texture evolution on amorphous carbon by oblique angle vapor deposition, *Physical Review B* 72 (2005) 035430.
- [20] B.D. Cullity, *Elements of X-ray Diffraction*, 2nd ed. Addison-Wesley, Reading, MA, 1978.
- [21] V. Biju V, N. Sugathan, V. Vrinda, S. L. Salini, Estimation of lattice strain in nanocrystalline silver from X-ray diffraction line broadening, *J. Mater. Sci.* 43 (2008) 1175.
- [22] G.J. Fang, D.J. Li, B.L. Yao, Effect of Vacuum Annealing on the Properties of Transparent Conductive AZO Thin Films Prepared by DC Magnetron Sputtering , *Phys. Stat. Sol. A* 193 (2002) 139.

- [23] R. Ghosh, D. Basak, S. Fujihara, Effect of substrate-induced strain on the structural, electrical, and optical properties of polycrystalline ZnO thin films, *J. Appl. Phys.* 96 (2004) 2689.
- [24] G. C. A. M. Janssen, J.-D. Kamminga, Stress in hard metal films, *Appl. Phys. Lett.* 85 (2004) 3086.
- [25] T. Karabacak, J. J. Senkevich, G.-C. Wang, T.-M. Lu, Stress reduction in sputter deposited films using nanostructured compliant layers by high working-gas pressures, *J. Vac. Sci. Technol. A* 23 (2005) 986.
- [26] A. S. Alagoz, J.D. Kamminga, S. Grachev, T.-M. Lu, T. Karabacak, Residual stress reduction in sputter deposited thin films by density modulation, *Materials Research Society* 1224 (2010) 27.
- [27] T. Karabacak, C. R. Picu, J.J. Senkevich, G.-C. Wang, T.-M. Lu, Stress reduction in tungsten films using nanostructured compliant layers by oblique angle sputter deposition, *J. Appl. Phys.* 96 (2004) 5740.
- [28] S. P. Cao, F. Ye, B. Hou, A. Y. Xu, Aluminum-doped zinc oxide film with gradient property deposited at oblique angle, *Thin Solid Films* 545 (2013) 205.
- [29] S. Flickyngerova, M. Netrvalova, P. Sutta, I. Novotny, V. Tvarozek, P. Gaspierik, J. Bruncko, Effects of sputtering power and pressure on properties of ZnO:Ga thin films prepared by oblique-angle deposition, *Thin Solid Films* 520 (2011) 1233.
- [30] Q. Zhao, T. Xie, L. Peng, Y. Lin, P. Wang, L. Peng, D. Wang, Size- and Orientation-Dependent Photovoltaic Properties of ZnO Nanorods, *J. Phys. Chem. C* 111 (2007) 17136.

Table Captions:

Table 1. Characteristics of the samples estimated from SEM and XRD data.

Table 1.

AZO Samples	Thickness /Length (nm)	Diameter (nm)	Layer Density (%)	Mas Loading (mg/cm ²)	(002) 2 θ (°)	Deconvoluted FWHM (°)	Grain size (nm)
Thin film (TF)	460 $\pm$ 7.0	NA	95.7 $\pm$ 5.0	0.23 $\pm$ 0.012	33.92	0.26	30.5
Tilted	760 $\pm$ 40	190	48.8 $\pm$ 3.5	0.20 $\pm$ 0.010	34.40	0.13	61.1
Vertical	550 $\pm$ 15	90	76.0 $\pm$ 4.6	0.22 $\pm$ 0.012	34.39	0.11	72.2
Spiral	600 $\pm$ 20	145	78.1 $\pm$ 4.8	0.25 $\pm$ 0.013	34.70	0.14	56.7
Zigzag	1000 $\pm$ 13	190	58.3 $\pm$ 3.0	0.31 $\pm$ 0.015	34.50	0.18	44.1

Figures Captions:

Fig. 1. Top-view (top row) and cross-sectional (bottom row) SEM images of the AZO samples of (a) and (f) thin film (TF), (b) and (g) tilted nanorods, (c) and (h) vertical nanorods, (d) and (i) spirals, and (e) and (j) zigzags. Nanostructures of different shapes were fabricated by glancing angle deposition (GLAD) at different substrate rotation speeds.

Fig. 2. XRD profiles of the TF and nanostructured AZO samples. The inset shows an enlarged region of XRD patterns.

Fig. 3. Strain and grain sizes calculated for TF AZO and GLAD AZO nanostructures of different shapes.

Fig. 4. Optical transmission, reflection and absorption profiles of TF AZO and GLAD AZO nanostructures of different shapes, which were normalized to the mass loading values.

Figures:

Fig. 1

Fig. 2

Fig. 3

Fig. 4