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Chapter 9

Aluminium Doped Zinc Oxide Nanorod Array Ultraviolet Photoconductive Sensors

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Abstract We discussed a novel approach for improving the performance of metal-semiconductor-metal (MSM)–type aluminium (Al)-doped zinc oxide (ZnO) nanorod array-based ultraviolet (UV) photoconductive sensors involving sonicating the precursor solution. The Al-doped ZnO nanorod arrays were deposited onto a glass substrate coated with an Al-doped ZnO thin film as a seed layer using precursor solutions that were sonicated for various amounts of time between 0 to 50 min. We observed that the average diameter of the nanorod decreased with increasing sonication time, decreasing from 59 without sonication to 42 nm after 50 min of sonication. The UV photoconductive sensor using Al-doped ZnO nanorod arrays prepared using the 30 min sonicated precursor solution presents the highest responsivity (4.26 A/W) under 365 nm

UV illumination. This result is attributed to this nanorod array's superior crystallinity properties, improved photogeneration process, lower resistance, and lower compressive stress, as demonstrated by our characterisation results. Notably, the sensitivity or photocurrent-to-dark current ratio of the sensor increased significantly, from 7.8 to 58.0, when the nanorod arrays were prepared using solutions sonicated up to 50 min. Our results demonstrate that high sensitivity of the UV photoconductive sensors can be achieved by growing the nanorod using a precursor solution that has been sonicated for a long time. The sonicated solution produced a smaller nanorod, which enhanced the nanorod surface conditions and induced effective recombination centres for high sensitivity and fast sensing response. In addition, the effects of poly (vinyl alcohol) (PVA) coating on the sensor performance were also discussed.

Keywords Semiconductor, Zinc oxide, Nanorods, Sol-gel preparation, Ultraviolet Photoconductive sensor

1. Introduction

Zinc oxide (ZnO) nanorod arrays have emerged as potential nanomaterials for use in electronic device applications, particularly for ultraviolet (UV) photoconductive sensors [1, 2], solar cells [3, 4], field emitters [5], and gas sensors [6]. Among these applications, the fabrication of ZnO nanorod array-based UV photoconductive sensors has received considerable attention because of their usefulness in various fields, including environmental science, the military, and electronics [7, 8]. Because of the excellent properties of ZnO nanorods, such as high mobility and high surface-to-volume ratio, the performance of the UV photoconductive sensor can be significantly improved compared to conventional devices. Aligned ZnO nanorod arrays can be successfully grown on substrates using a number of methods, including chemical vapour deposition (CVD) [9], metal-organic chemical vapour deposition (MOCVD) [10], sputtering [11], pulsed laser deposition (PLD) [12], and solution-based techniques [13, 14]. Among these methods, solution-based techniques have many advantages because they can produce ZnO nanorod arrays at low temperatures and with a low cost.

The performance of UV photoconductive sensors based on ZnO nanorod arrays can be improved using several strategies. For example, by utilising nanorods with a small diameter in the UV sensor, the surface area of the sensing material could be increased, resulting in a UV sensor with improved performance [15]. In addition, surface treatments have also been shown to increase the UV sensing capability of nanorod arrays because of the enhanced surface conditions, which interact more efficiently with the surrounding environment [8, 16, 17]. It has recently been reported that coating ZnO with certain materials also results in an improved photoresponse of the UV sensing device [18, 19].

Controlling the growth of the ZnO nanorod arrays during the solution-based synthesis for achieving suitable surface conditions is very important for fabricating UV sensors that exhibit high performance. Control of the nanorod growth could be achieved during the solution preparation and/or immersion processes [20]. For example, the diameter of the nanorods can be controlled by lowering the solution molarity and introducing a stabiliser or surfactant agents during the solution preparation process [21-23].

The dispersion of reactants and their reaction in the solution is also through to play an important role for controlling the nanorod growth during the immersion process; thus, producing high-quality ZnO nanorod arrays that are suitable for UV sensor applications. Therefore, to control the morphology and surface conditions of the synthesised product, the reactants in the solution should be thoroughly mixed.

Ultrasonic irradiation can be employed to ensure thorough mixing and is a promising technique for inducing homogeneity in the prepared precursor solution. The sonication process is a well-recognised technique for the fast, simple, and effective production of nanomaterials in powder, which is beneficial for large-scale production [24-28]. The sonication process also promotes the homogenous precipitation of the precursor, highly intensive mixing, morphology control, and reduced agglomeration [28].

Herein, we discuss the fabrication of a UV photoconductive sensor using aligned Al-doped ZnO nanorods grown using the sonicated sol-gel immersion method with different sonication times. Interestingly, we observed that the responsivity of the sensor improved when the Al-doped ZnO nanorods were grown using a sonicated precursor solution. The sensitivity of the device also improved when the Al-doped ZnO nanorod arrays were grown using a solution that was sonicated for a long time.

To the best of our knowledge, the effects of the sonication time of the solution that was used to grow the Al-doped ZnO nanorod array with the immersion process for UV photoconductive sensor applications have not yet been reported.

2. Experimental Details

Al-doped ZnO nanorod arrays were grown on a glass substrate coated with an Al-doped ZnO seed layer using a sonicated sol-gel immersion method. The Al-doped ZnO thin film, which was used as a seed catalyst, was prepared on the glass substrate using sol-gel spin-coating [29]. A 500 ml solution was prepared using 0.1 M zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O; 98% purity; Systerm), 0.001 M aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O; 98% purity; Analar), and 0.1 M hexamethylenetetramine (HMT; C₆H₁₂N₄, 99% purity; Aldrich) in deionised (DI) water.

This solution was sonicated at 50°C for 0 (no sonication), 10, 20, 30, 40 and 50 min using an ultrasonic water bath (Hwasin Technology Powersonic 405, 40 kHz, Output power: 350 W). The solution was then aged and stirred for 3 h at room temperature. The sonicated and aged solution was poured into a vessel with the horizontal thin-film-coated glass substrate placed at the bottom. The sealed vessel was then immersed into a 95°C water bath for 50 min. Following the immersion process, the samples were cleaned with DI water before being heated at 150°C for 10 min.

The resulting nanorod arrays were then annealed at 500°C in air. For the Al-doped ZnO nanorod arrays prepared using a solution that was sonicated for

30 min, an extra sample was prepared for poly(vinyl alcohol) (PVA; 98-99% hydrolysed purity; M_w 146,000-186,000; Sigma-Aldrich) coatings. The PVA solution was prepared using DI water as a solvent at a concentration of 4 g/l. The solutions were then heated and stirred for 4 h at 80°C before being stirred at room temperature for 24 h.

The coating procedure was performed by immersing the nanorod arrays into the PVA solution for 1 h at 100°C. The coated nanorod arrays were then dried under ambient conditions. To complete the metal-semiconductor-metal (MSM)-type sensor structure, 60-nm-thick Al-metal contacts were deposited onto the samples using a thermal evaporator at a deposition pressure of 4×10^{-4} Pa.

The sample was characterised using field-emission scanning electron microscopy (FESEM, JEOL JSM-7600F) to observe the surface morphology and the cross-sections of the Al-doped ZnO nanorod arrays. The Raman spectra of the Al-doped ZnO nanorod arrays were measured using a micro-Raman spectrometer with an argon (Ar) laser operating at 514 nm as the excitation source (Horiba Jobin Yvon-79 DU420A-OE-325). The crystallinity of the samples was characterised using X-ray diffraction (XRD, Panalytical X`pert PRO).

The absorbance properties of the sonicated solutions and the optical transmittance of the nanorod arrays were characterised using ultraviolet-visible-near-infrared (UV-vis-NIR) spectrophotometry (Perkin Elmer Lambda 750). The photoluminescence properties of the prepared samples were characterised using a photoluminescence (PL) spectrometer (Horiba Jobin Yvon 79 DU420A-OE-325) equipped with a helium–cadmium (He–Cd) laser excitation source at 325 nm.

The current-voltage (I-V) characteristics of the UV photoconductive sensors were investigated using a two-probe I-V measurement system (Keithley 2400). The UV photoresponse measurements of the fabricated sensor were conducted using a UV photocurrent measurement system (Keithley 2400) operating at 365 nm with a power density of 750 μ W/cm² at a bias voltage of 10 V.

3. Results and Discussion

Figures 1(a-f) present the FESEM images of the Al-doped ZnO nanorod arrays prepared using solutions that were sonicated for different amounts of time between 0 to 50 min. These images indicate that the nanorods were uniformly deposited onto the seed-layer-coated glass substrate after immersion for 50 min. The FESEM images reveal that the diameter of the nanorods decreases incrementally when the nanorods were grown using precursor solutions that were sonicated for longer times.

The average diameter of the nanorods were estimated from the FESEM images as 59, 52, 52, 45, 43, and 42 nm when prepared using solutions that were sonicated for 0 (without sonication), 10, 20, 30, 40, and 50 min, respectively. These results indicate that the diameter of the nanorods could be reduced using precursor solutions that were sonicated for longer times.









Figure 1. The surface morphology of the Al-doped ZnO nanorod arrays that were prepared using precursor solutions sonicated for (a) 0 (no sonication), (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 min

Figures 2 (a-f) present the cross-sectional images of the Al-doped ZnO nanorod arrays prepared using solutions that were sonicated for various times. These images indicated that the Al-doped ZnO nanorods were deposited perpendicular to the substrate with good alignment. The thicknesses of these films were estimated from the FESEM images to be approximately 700 nm.

A previous study has shown that the sonication process can separate individual particles from agglomerated particles [30]. Therefore, for our research, we proposed that the sonication process facilitates the rupture of the agglomerated precursor (i.e., zinc nitrate) particles, dopant (i.e., aluminium nitrate) particles, and the stabiliser (i.e., HMT) particles during an early stage and produces a homogeneous precursor solution.







Figure 2. The cross-sectional image of the Al-doped ZnO nanorod arrays that were prepared using precursor solutions sonicated for (a) 0 (no sonication), (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 min

Furthermore, the sonication process also promotes the dispersion and mixing of the precursor, dopant, and stabiliser, which accelerates the physical- and chemical-reaction activities in the solution. In this case, the long sonication process greatly improved the solution conditions, increasing dispersion and breaking the large precursor, dopant, and stabiliser particles into smaller particles. During sonication process, the collapse of bubbles results in the generation of high speed microjets with very high velocity [31].

Under this circumstance, the chance of collision between the reactants and also the reactants with beaker walls increases [32]. Therefore, dissolution and dispersion of the reactants in the solution increase. This process enables the Zn^{2+} ions to effectively react with HMT to produce a Zn-HMT complex, as shown by the following reaction [33]:

$$Zn(NO_3)_2 + C_6H_{12}N_4 \rightarrow [Zn(C_6H_{12}N_4)]^{2+} + 2NO_3^{-}.$$
 (1)

The formation of Zn-HMT complexes (i.e., $[Zn(C_6H_{12}N_4)]^{2+}$) is essential for slowing the formation of ZnO and thus reducing particle agglomeration in solution. During the immersion process, the reactions can be described as follows [33, 34]:

$$C_6H_{12}N_4 + 4H_2O \rightleftharpoons C_6H_{12}N_4H_4^+ + 4OH^-,$$
 (2)

$$\left[Zn(C_{6}H_{12}N_{4})\right]^{2+} + 4OH^{-} \rightarrow Zn(OH)_{4}^{2-} + C_{6}H_{12}N_{4},$$
(3)

$$\operatorname{Zn}(\operatorname{OH})_{4}^{2^{-}} \to \operatorname{Zn}^{2^{+}} + 4\operatorname{OH}^{-}, \tag{4}$$

 $Zn^{2+} + 2OH^{-} \rightleftharpoons ZnO + H_2O \text{ or } Zn^{2+} + 2OH^{-} \rightleftharpoons Zn(OH)_2 \rightleftharpoons ZnO + H_2O.$ (5)

When the saturation levels of the Zn^{2+} and OH^- ions exceed supersaturation conditions, ZnO nuclei are formed on the seed-layer surface. As a result, the growth of the aligned ZnO nanorods is initiated. During this stage, HMT, which functions as a chelating agent, can immediately attach to the surfaces (the six prismatic side planes) of the ZnO nanorods following the ZnO nanorod-nucleation process on the seed layer [35].

Because the long sonication process creates a well dispersed solution, the immediate attachment of HMT to the surfaces of the ZnO nanorods was possible; this attachment inhibited the subsequent deposition of ZnO on these surfaces but permitted the deposition of ZnO on the polar surface or in the

(0001) direction. Therefore, the average nanorod diameter was reduced. Based on this result, longer sonication produced better solution conditions with greater homogeneity, which yields smaller nanorods during the immersion process.

Figure 3 presents the Raman spectra of the Al-doped ZnO nanorod arrays prepared by a 50 min immersion using solutions that were sonicated for different times. The Raman spectra exhibit two prominent peaks, which are attributed to the E_2 (High) and A_1 (LO) mode peaks. For intrinsic ZnO, the E_2 (High) mode peak is generally centred at 437 cm⁻¹ and represents the characteristic peak of the Raman-active mode of the wurtzite hexagonal ZnO or the oxygen atom in the ZnO hexagonal structure [36, 37]. However, the A_1 (LO) mode peak, which is normally centred between 570 to 590 cm⁻¹, is caused by defects such as oxygen vacancies, zinc interstitials, their complexes or free carriers [38, 39].



Figure 3. Raman spectra of the Al-doped ZnO nanorod arrays that were prepared using solutions sonicated for various times under a 514 nm Ar laser excitation

A broad, weak peak also appeared between 750 to 850 cm⁻¹ and may be attributed to Al-doping [2, 40]. The Raman spectra reveal that the intensity of the E_2 (High) mode peak of the nanorod arrays initially increased slightly when the nanorod was grown using solutions that were sonicated from 0 (no sonication) to 30 min but decreased when the sonication times approached 50 min.

The increase in the intensity of the $E_2(High)$ mode peak indicates that the crystallinity of the sample was improved by sonicating the precursor solution up to certain time, which in this case is 30 min. However, the crystallinity of the nanorod decreased when the nanorod was prepared using solutions that were sonicated for longer times of up to 50 min.

The position of the $E_2(High)$ mode peak in the Raman spectra also exhibits a shift for the nanorod arrays compared to the bulk ZnO Raman spectrum. The Al-doped ZnO nanorod arrays prepared using the solution that was not sonicated presents the $E_2(High)$ mode peak centred at 438.5 cm⁻¹, which is an upward shifted compared to bulk ZnO. When the solution that was sonicated for 10 min was used, the peak for the $E_2(High)$ mode of Al-doped ZnO in the Raman spectra shifted towards 438.0 cm⁻¹.

This trend was also observed for the samples prepared using solutions that were sonicated for 20 and 30 min, with the Raman shifts to 437.8 and 437.2 cm⁻¹, respectively. However, the Raman position of the nanorod arrays returns to higher Raman positions for the solutions that were sonicated for over 30 min. The Al-doped ZnO nanorod arrays prepared using solutions that were sonicated for 40 and 50 min present the E_2 (High) mode centred at 437.3 and 437.5 cm⁻¹, respectively.

Generally, the shift towards higher wave numbers is attributed to compressive stress in the lattice, whereas the shift to positions lower than the E_2 (High) mode of bulk ZnO results from tensile stress [39, 41, 42]. The results indicate that the Al-doped ZnO nanorod arrays, which were prepared using solution sonicated for 30 min, possess good-quality nanorod arrays that have less compressive stress than do the other samples.

The XRD patterns of the Al-doped ZnO nanorod arrays prepared using solutions sonicated for different times are shown in Figure 4. The diffraction

peaks of the nanorod arrays can be indexed to the hexagonal phase of ZnO with a wurtzite structure (JCPDS 36-1451). The results indicate that all samples present a very intense (002) reflection, which indicates that the preferential growth of ZnO is along the c-axis, perpendicular to the substrate.



Figure 4. XRD patterns of the Al-doped ZnO nanorod arrays prepared using solutions sonicated for 0 (no sonication), 10, 30, and 50 min

The diffraction patterns reveal noticeable changes in the crystallinity of the Al-doped ZnO prepared using solutions that were sonicated for different times, which could be observed in the changes in the (002) reflection intensity. The samples prepared using the solution that was sonicated for 10 min show an increased (002) reflection intensity compared to the sample prepared using the solution that was also observed for the sample prepared using the solution sonicated for 30 min.

The (002) reflection of the Al-doped ZnO nanorod arrays, which were prepared using the solution sonicated for 30 min, has the highest intensity. However, the intensity of the XRD peaks is reduced for the nanorod arrays that were prepared using the solution that was sonicated for 50 min. This result indicates that an appropriate sonication duration helps produce Al-doped ZnO nanorod arrays with good crystallinity.

It was also observed that the (002) reflection of the Al-doped ZnO nanorod arrays prepared using solutions sonicated for different durations have different diffraction angles. The centres of the (002) reflection for the Al-doped ZnO nanorod arrays prepared using solutions that were sonicated for 0 (no sonication), 10, 30, and 50 min were 35.05, 35.03, 34.92, and 35.07°, respectively. The centres of these (002) reflections for all samples are shifted to higher diffraction angles compared to the standard data in JCPDS, which cites a (002) reflection centred at 34.42° .

This shift results from the Al-doping, which reduces the lattice constant and induces compressive stress in the lattice [43]. Because the ionic radius differs between Al^{3+} (0.054 nm) and Zn^{2+} (0.074 nm) [44, 45], the presence of Al in the ZnO lattice may influence attractive forces between the atoms, thereby reducing the lattice constant of the ZnO nanorods and inducing compressive stress in the lattice. Based on these results, the nanorod arrays prepared using the solution that was sonicated for 30 min present the lowest diffraction angle shift compared to the other samples.

This result is consistent with the Raman measurement results, which indicate that the solution sonicated for 30 min provides the best conditions for producing Al-doped ZnO nanorod arrays with good crystallinity and less lattice stress.

The deterioration in the crystallinity of the Al-doped ZnO nanorod arrays following the increases in the solution sonication time beyond 30 min may be explained as follows. When the solution has not been sonicated, Al may occupy both the Zn sites and the interstitial position, which results in nanorod arrays with poor crystallinity. However, sonicating the solution improves the doping process, producing highly crystalline Al-doped ZnO nanorod arrays.

This sonication process produced a well-dispersed solution that allows Al to substitute into the Zn sites with lower free energy and little stresses during the nanorod growth. This condition increases the crystallinity of the ZnO, as evidenced in the XRD patterns and the Raman spectra. However, when the sonication time is increased beyond 30 min, the Al may again occupy both the Zn sites and the interstitial position or other impurities may absorb into the nanorod arrays, which decreases the crystallinity of the nanorod array.

We proposed that this phenomenon may attributed to the excessive energy resulting from the long ultrasonic irradiation time, which may have formed some of the dopants (i.e., Al^{3+} ions) into another species, such as Al_2O_x , in the solution because the sonication technique is reported to be capable of producing Al_2O_3 [46]. Furthermore, the enthalpies of formation for aluminium oxide (Al_2O_3) are much smaller than those of ZnO [47].

These molecules may then absorb into the nanorod arrays and diffuse at the interstitial position as a dopant or form amorphous Al_2O_3 during the annealing process, which degrades the ZnO crystallinity. However, the long sonication process may also produce ZnO nanoparticles that could be absorbed into the nanorod array during the immersion process, thereby producing stress in the Al-doped ZnO nanorod array. This theory was based on a previous report that showed that the ZnO nanoparticles in a powder form could also be synthesised using the sonication process after a certain period of sonication time in addition to the stabiliser [48, 49].

To investigate this theory, the UV-vis absorption spectra of the solution prepared using different sonication times were studied. Figure 5 presents the UV-vis absorption spectra of the solution after sonication for different periods of time. The spectra indicate that after 40 and 50 min of sonication, a faint absorption edge appeared at approximately 360 nm. This absorption edge,

which corresponded to the ZnO nanoparticles, is formed by ultrasonic irradiation [48]. However, this absorption edge did not appear for the solution that was sonicated for 30 min or less.



Figure 5. UV-vis absorption spectra of the precursor solutions that were sonicated for different lengths of time

This result indicates that the use of an appropriate sonication time will yield a solution that is highly homogeneous and contains fewer impurities, which initiates the growth of highly crystalline Al-doped ZnO nanorod arrays during the immersion process. However, an excessively long sonication time produces impurities in the solution, which might disturb the growth of the Al-doped ZnO nanorod arrays during the immersion process, thereby deteriorating the crystallinity of the samples.

Ultrasonic energy is derived from a powerful ultrasonic radiation wave, ranging from 20 kHz to 10 MHz [50]. The sonication process produces energy through acoustic cavitation, which is a process involving the creation, growth, and collapse of bubbles formed in the sonicated liquid. When a liquid is ultrasonically irradiated, bubbles (i.e., cavities) are created due to the alternating expansive and compressive acoustic waves, which force the bubbles

to oscillate [51]. The oscillating bubbles accumulate ultrasonic energy, effectively growing to a certain size (typically tens of microns). However, the bubbles tend to collapse after they have grown to excess, releasing the concentrated energy stored within the bubble in a very short period of time.

When a bubble collapses, the locally produced temperature is claimed to be extremely high, in the range of 5,000 to 25,000 K [50]; because of this high temperature, it is possible that the chemical bonds of the sonicated material can be broken. Additionally, because the bubbles collapse in times of less than a nanosecond, very fast cooling rates (in excess of 10^{11} K/s) are also produced [52]. Under these extreme conditions, even the water bath can undergo hemolytic bond cleavage to form radicals, such as H⁻ and OH⁻ [53, 54].

The reactions for the formation of the impurities can be described as follows. During the early stage of the sonication process (up to 30 min), the HMT effectively reacts with the Zn^{2+} ions to produce the Zn-HMT complex, as shown in Equation 1. During the sonication process, the collapse of bubbles promotes the reaction between HMT and Zn^{2+} ions because the released energy can be used to complete the reaction process in the solution.

This condition inhibits the growth of ZnO in the solution because the Zn^{2+} ions are captured by HMT, and thus, no absorption edge is observed in the UV–vis absorption spectra, which reflects the absence of ZnO nanoparticles. With increased sonication time (i.e., more than 30 min), the Zn-HMT complex bonds may be broken to produce Zn^{2+} ions. Simultaneously, the water may decompose into extremely reactive radicals, such as H⁺, OH⁺, O₂⁻⁺, and HO₂⁻⁻ radicals, under ultrasonic irradiation [24, 55].

This process is due to cavity implosion, which produces heat; this thermal energy is consumed to vaporise the water and transform the water molecules into radicals. According to the literature, ZnO nanoparticles may be produced by the reaction between Zn^{2+} ions and radicals such as OH and O_2^{--} [24, 55, 56]. According to Jia et al., the ZnO particles can be formed under ultrasonic irradiation by the following reaction [55]:

$$2Zn^{2+} + 4O_2^{\bullet} \rightarrow 2ZnO + 3O_2 \tag{6}$$

However, Mazloumi et al. proposed that ZnO particles could be produced by the following reaction [24]:

$$Zn^{2+} + 2OH^{\bullet} \to ZnO + H_2O \tag{7}$$

Similarly, these radicals may react with the small concentration of Al^{3+} ions in the solution to produce Al_2O_3 particles, as shown by the following equations:

$$4Al^{3+} + 12O_2^{\bullet} \rightarrow 2Al_2O_3 + 9O_2$$

or/and
$$2Al^{3+} + 6OH^{\bullet} \rightarrow Al_2O_3 + 3H_2O$$
 (8)

Figure 6 displays the PL spectra of the Al-doped ZnO nanorod arrays prepared using solutions that were sonicated for different lengths of time. The spectra reveal that the Al-doped ZnO nanorod arrays show two emission peaks: the prominent UV emission and the broad, weak visible emission peaks. The UV emission peak centred at 387 nm corresponds to the direct recombination of the free excitons, whereas the visible emission peak is attributed to the defects in the Al-doped ZnO nanorod arrays.

The weak and almost negligible visible emission peak centred at 600 nm compared to the UV emission indicates that the Al doping suppressed the defects in ZnO, particularly the zinc interstitials and oxygen vacancies [57, 58].

The spectra indicate that the prepared nanorod has UV emission that incrementally improved when the nanorod was grown using solutions that were sonicated between 0 to 30 min. However, the UV emission intensity decreased for the Al-doped ZnO nanorod that were prepared using solutions sonicated for 40 and 50 min.

We believe that increasing the sonication time to 30 min for the precursor solution improves the solution conditions (i.e., dispersion and reaction activities), thereby enabling the growth of Al-doped ZnO with improved crystallinity. Therefore, the nanorod prepared using a solution that was sonicated for 30 min presents the highest UV emission intensity because of the highly crystalline properties and less compressive stress experienced by this sample, which is in agreement with other reports [59].



Figure 6. Room-temperature PL spectra of the Al-doped ZnO nanorod arrays that were prepared using solutions sonicated for different lengths of time and excited with a 325 nm He-Cd laser

The reduction of the UV emission peak from the nanorod arrays, which were prepared using a solution that was sonicated for longer than 30 min, might be due to the existence of impurities that formed in the solution, which absorbed into the Al-doped ZnO nanorod arrays and acted as recombination centres for decreasing the UV emission intensity. The Al-doping of ZnO has been reported to produce yellow emission centred at approximately 600 nm [60].

Generally, the yellow emission that is centred at 600 nm has contributions from interstitial oxygen or excess oxygen at the nanorod surface [61, 62]. The Al doping process produces charge defects because of an excess of free electrons. Therefore, the oxygen will be introduced as interstitial oxygen to produce charge equilibrium [60].

The PL spectra were used to calculate the ratio of the UV emission intensity, I_{UV} , to the visible emission intensity, I_{vis} . These ratios were determined to be 9.8, 13.3, 22.3, 23.3, 18.4, and 13.9 for the Al-doped ZnO nanorod arrays prepared using 0, 10, 20, 30, 40, and 50 min of sonication for the precursor solution,

respectively.

The result indicates that the nanorod arrays produced using a sonicated solution have improved optical properties with a higher I_{UV}/I_{vis} ratio compared to the nanorod arrays prepared using a solution that was not sonicated. The result also indicates that the Al-doped ZnO nanorod prepared using a solution sonicated for 30 min has better optical properties and is more stoichiometric than the other samples, which is indicated by the high I_{UV}/I_{vis} ratio.

Figure 7(a) shows the transmittance spectra of the Al-doped ZnO nanorod arrays prepared using solutions that were sonicated for different lengths of time. The spectra indicate that the transmittance of the nanorod arrays is excellent in the visible region, with the average transmittance greater than 80 %. In the UV region (below 400 nm), the transmittance significantly decreased with a sharp absorption edge at a wavelength of approximately 380 nm.

This absorption edge is attributed to the bandgap absorption of ZnO. From these spectra, the bandgap of the Al-doped ZnO nanorod arrays were calculated using a Tauc's plot, as shown in Fig. 7(b). The Tauc's plot was constructed using the following equation:

$$\alpha hv = A \left(hv - E_g \right)^{\frac{1}{2}},\tag{9}$$

where α is the absorption coefficient, hv is the photon energy, A is a constant, and E_g is the optical bandgap energy. The absorption coefficient, α , was calculated based on Lambert's law using transmittance data, as shown in the following equation [29, 63]:

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{T} \right), \tag{10}$$

where *t* is the film thickness and *T* is the film transmittance. According to the Tauc's plot, the calculated bandgap energy of the Al-doped ZnO nanorod arrays prepared using solutions that were sonicated for different lengths of time is nearly constant with a value of 3.28 eV.



Figure 7. (a) Transmittance spectra of the Al-doped ZnO nanorod arrays prepared using sonicated solutions. (b) Tauc's plot of the Al-doped ZnO nanorod array used to estimate the optical bandgap

Figure 8 shows the current-voltage (I-V) characteristics of the Al-doped ZnO nanorod arrays prepared using solutions that were sonicated for different lengths of time. The I-V curves indicate that the nanorod arrays form good ohmic contact with the Al metal as the measurement produced linear curves. The result also indicates that the current, with respect to the supplied voltage, increases for the nanorod arrays that were prepared using a solution that was sonicated for up to 30 min. However, the current decreases when the sonication time of the solution used to grow the nanorod arrays was further increased to 50 min.

The resistances of the Al-doped ZnO nanorod arrays prepared using solutions that were sonicated for 0, 10, 20, 30, 40, and 50 min were 0.84, 0.43, 0.31, 0.12, 0.40, and 0.87 M Ω , respectively.



Figure 8. Current-voltage (I-V) plots of the Al-doped ZnO nanorod arrays that were prepared using solutions sonicated for different lengths of time

Figure 9 presents the structure of the UV photoconductive sensor using the Al-doped ZnO nanorod arrays that were prepared in this study. The structure consists of a glass substrate at the bottom, onto which an Al-doped ZnO nanoparticle thin film or seed layer is deposited using sol-gel spin-coating. The Al-doped ZnO nanorod arrays were grown on the seed-layer-coated glass

substrate by immersion.

The Al metal contacts were then deposited on top of the Al-doped ZnO nanorod arrays using a thermal evaporator. The flow of the electrons that were photogenerated during UV illumination, as proposed by Zhou et al., could be explained as follows [64]. During UV illumination, electrons are photogenerated from the nanorod and then flow to the seed layer. The electrons from the seed layer then move towards the nanorod underneath the Al metal contacts before reaching the metal contacts as a photocurrent.



Figure 9. Schematic configuration of the Al-doped ZnO nanorod array-based UV sensor and the flow of photogenerated electrons during UV illumination

The spectra from the photocurrent measurement for the Al-doped ZnO nanorod arrays that were deposited using solutions sonicated for different times are shown in Figure 10. The results indicate that the photocurrent of the sensors increased when using the nanorod arrays that were prepared using solutions sonicated for times up to 30 min. However, the photocurrent of the sensor decreased when the nanorod arrays that were prepared using solutions that were sonicated for 40 and 50 min were used.



Figure 10. Photoresponse spectra of the UV photoconductive sensor using Al-doped ZnO nanorod arrays that were prepared with solutions sonicated for different lengths of time under UV illumination (365 nm, 750 μ W/cm²) and a 10 V bias

The photocurrents (dark current) of the sensors are 6.77×10^{-5} (8.64×10^{-6}), 8.09×10^{-5} (9.12×10^{-6}), 9.34×10^{-5} (9.82×10^{-6}), 2.09×10^{-4} (1.25×10^{-5}), 8.94×10^{-5} (1.81×10^{-6}), and 6.46×10^{-5} (1.11×10^{-6}) A for the nanorod arrays prepared using solutions that were sonicated for 0 (no sonication), 10, 20, 30, 40, and 50 min, respectively. From these results, the responsivity of the devices was calculated using following equation [65]:

$$R = \frac{I_{ph} - I_{dark}}{P_{op}},$$
(11)

where I_{ph} is the photocurrent, I_{dark} is the dark current, and P_{op} is the optical power of the UV source. This result indicates that the nanorod arrays prepared using the solution sonicated for 30 min has the highest responsivity, with a value of 4.36 A/W.

The responsivity of the other sensors are 1.32, 1.60, 1.86, 1.95, and 1.41 A/W for the nanorod arrays prepared using solutions that were sonicated for 0 (no sonication), 10, 20, 40, and 50 min, respectively.

Interestingly, the sensitivity of the sensors, which is defined as the photocurrent-to-dark-current ratio, increased when using Al-doped ZnO nanorod arrays prepared from solutions that were sonicated for a long period of time. The sensitivity of the sensors was 7.8, 8.9, 9.5, 16.6, 49.4, and 58.0 after being immersed with solution sonicated for 0 (no sonication), 10, 20, 30, 40, and 50 min, respectively.

This result indicates that the sensitivity of the Al-doped ZnO nanorod array-based UV photoconductive sensor can be enhanced using a precursor solution that is sonicated for long time. Based on several reports, the sensitivity of the sensor is generally influenced by the surface area availability and the surface conditions of the nanorod that is capable of promptly adsorbing and desorbing oxygen [1, 15, 66].

The oxygen adsorption and desorption processes could be explained as follows. In the dark, oxygen molecules tend to adsorb onto nanorod surfaces by capturing free electrons and producing adsorbed oxygen ions, as shown by the following equation:

$$\mathbf{O}_2 + \mathbf{e}^{-} \to \mathbf{O}_2^{-},\tag{9}$$

where O_2 is the oxygen molecule, e^- is the free electron, and O_2^- is the adsorbed oxygen ion on the nanorod surface. The adsorbed oxygen ions create a barrier near the surface that generates a low current before UV illumination. When UV light is irradiated onto the nanorods, photogenerated electron-holes pairs are produced at the surface according to the following equation:

$$hv \to h^+ + e^-, \tag{10}$$

where hv is the photon energy of UV light, h^+ is the photogenerated hole in the valence band, and e^- is the photogenerated electron in the conduction band. The photogenerated holes recombine with the adsorbed oxygen ions on the surface, producing oxygen molecules; this reaction also eliminates the barrier near the nanorod surface. This process is described by the following equation:

$$O_2^- + h^+ \to O_2. \tag{11}$$

Simultaneously, the desorption of adsorbed oxygen ions on the nanorod surface produces photogenerated electrons in the conduction band, which increases the film conductivity and contributes to the photocurrent. When the UV light is switched off, the oxygen once again starts to adsorb onto the nanorod surface, which decreases the conductivity of the sensor.

The rise (decay) time constants of the sensor were calculated from the photocurrent spectra using the following equations:

$$I = I_0 \left[1 - \exp\left(-\frac{t}{\tau_r}\right) \right]: \text{ rise process with UV illumination on} \quad (12)$$

$$I = I_0 \exp\left(-\frac{t}{\tau_d}\right)$$
: decay process with UV illumination off. (13)

Here, *I* is the magnitude of the current, I_0 is the saturated photocurrent, *t* is the time, τ_r is the rise time constant and τ_d is the decay time constant. The rise (decay) time constants of the sensors were estimated to be 20 (70), 16 (41), 15 (36), 19 (30), 8 (15), and 2 (10) s after being immersed into the solution that was sonicated for 0 (no sonication), 10, 20, 30, 40, and 50 min, respectively.

According to our analysis, the highest photocurrent properties of the sensor using Al-doped ZnO nanorod arrays fabricated using the solution that was sonicated for 30 min may be attributed to the reduced compressive stress in the ZnO lattice compared to that in the other samples. We suspect that this condition produces an effective photogeneration process in the nanorod when it was irradiated with UV light.

This result is also consistent with the PL spectra, whereby the UV emission intensity was observed to be the highest for the nanorod arrays that were prepared using the solution sonicated for 30 min. This condition indicates that the nanorod arrays prepared using the solution that was sonicated for 30 min produce more photogenerated charge carriers than the other samples. In addition, the Al-doped ZnO nanorod arrays prepared using the solution that was sonicated for 30 min has better crystallinity than the other samples, which contributes to these nanorod arrays' low resistance, thereby producing the

highest sensor responsivity.

However, the photocurrent of the sensor using nanorod arrays that were prepared using the solutions that were sonicated for 40 and 50 min decreased significantly; their photocurrents are close to those of the sensors prepared using the solution that was sonicated for 20 and 0 min, respectively. Nevertheless, the rise (decay) time constant of these sensors that used the solution that was sonicated for a long time is much lower than that of any of the other samples.

In addition, the sensitivity of these samples to UV light is greater than that of the others. This observation indicates that the surface conditions of the nanorod arrays that were prepared using the solution that was sonicated for less than 30 min (i.e., 0 (no sonication), 10, and 20 min) and greater than 30 min (i.e., 40 and 50 min) are different. This observation might be a result of the smaller diameter of the Al-doped ZnO nanorod that results from the long ultrasonic irradiation time and provides a larger surface area for the sensors.

This large surface area enhanced the surface conditions of the nanorod arrays that were prepared using the solution that was sonicated for a long time, which increases the affinity for oxygen and the number of oxygen molecules trapped; therefore, UV sensors comprised of these arrays exhibit high sensitivity and a fast response. Han et al. explained that the electron from the ZnO may be consumed in two competitive ways: the electrons are consumed by intrinsic acceptors or used to adsorb oxygen from the surroundings [67]. If fewer electrons are consumed by the intrinsic acceptors, more adsorbed oxygen is ionised, and vice versa. The reduced rise and decay time constants might also be favoured by a reduction in the nanorod diameter with the increase of sonication times, which produces large surface areas for the oxygen adsorption and desorption processes.

We also proposed that the impurities formed during the long sonication times of 40 and 50 min and absorbed into the nanorod arrays may have contributed to the fast time constants of the sensors. These impurities serve as effective recombination centres for electrons during the switching off of the UV light and improved the response of the UV sensor.

In addition, these impurities might also be responsible for the low dark

current of the sensor, improving the sensitivity of the sensor. Kim et al. previously reported that by introducing impurities (i.e., TiO_2 nanoparticles) into the Al-doped ZnO nanowire network, the response time and sensitivity could be enhanced significantly [68]. Similarly, Seo et al. explained that by having deep traps or recombination centres in the ZnO, a fast photoresponse could be achieved [69].

Interestingly, the photocurrent of the sensors could be further increased by coating the nanorod array with PVA. PVA is generally used to create a barrier that reduces the oxygen adsorption onto the nanorod surface [70-72]. PVA is also used to passivate the remaining defects after the annealing process by decreasing the number of holes in the deep level.

Figure 11 (a-b) presents the FESEM images of the Al-doped ZnO nanorod arrays after coating with PVA at magnifications of 30,000x and 100,000x. These images show that the PVA was uniformly coated onto the nanorod arrays using the immersion process.





Figure 11. (a) 30,000x and (b) 100,000x magnified FESEM images of Al-doped ZnO nanorod arrays prepared using the 30 min sonicated solution and coated with PVA

The I-V measurement spectra of the uncoated and PVA-coated Al-doped ZnO nanorod arrays are shown in Figure 12. The spectra reveal that the Al metal contacts also form ohmic contacts with the PVA-coated Al-doped ZnO nanorod arrays. The current, with respect to the supplied voltage, also improved with PVA coatings, which indicates that the PVA modified the surface conditions of the nanorods. The resistance of the PVA-coated Al-doped-ZnO nanorod arrays was calculated to be 0.09 M Ω , which is smaller than the uncoated Al-doped ZnO nanorod array.

This result indicates that the amount of defects and the amount of oxygen adsorbed onto the nanorod surface has been reduced by the PVA coating, which increases the conductivity of the sensors.

Figure 13 shows the photocurrent measurement spectra of the Al-doped ZnO nanorod array-based UV photoconductive sensors before and after being

coated with PVA under 365 nm UV illumination. The spectra reveal that the photocurrent was much better for the PVA-coated UV sensor, nearly double that of the uncoated UV sensor. The photocurrent (dark current) of the PVA-coated Al-doped ZnO nanorod-array-based UV photoconductive sensor was 3.82×10^{-4} (3.88×10^{-5}) A, and the responsivity of the device were calculated to be 7.64 A/W.



Figure 2. Current-voltage (I-V) characteristic of uncoated and PVA-coated Al-doped ZnO nanorod arrays

These effects have been described in the literature: the photocurrent of the sensor has been shown to improve significantly when less oxygen is adsorbed onto the ZnO surface [73]. This photocurrent increase could be explained as follows. The PVA molecules attach onto the nanorod surface through a weak electrostatic interaction and passivate the remaining surface defects of Al-doped ZnO, such as zinc vacancies [72, 74].

This process also reduces the oxygen adsorption on the nanorod surface because of the barrier created by the PVA coatings, which consequently decreases the resistance of the nanorod. Therefore, more photogenerated electrons could be collected at the metal contacts, increasing the photocurrent of the sensor. In addition, the dark current also increased after the PVA coatings due to less carrier trapping on the nanorod surface.

However, this surface passivation produces an UV photoconductive sensor that has a slow response because of the decrease in the oxygen adsorption and desorption processes on the nanorod surface. The rise (decay) time constant of the PVA-coated Al-doped ZnO nanorod array-based UV photoconductive sensor was calculated from the photocurrent spectra to be 31 (64) s.



Figure 13. Photoresponse spectra of the UV photoconductive sensor using uncoated and PVA-coated Al-doped ZnO nanorod arrays under UV illumination (365 nm, 750 μ W/cm²) and a 10 V bias

Similarly, the sensitivity or photocurrent-to-dark current ratio also decreases after PVA coatings, with the value of 9.8. This result may indicate that the oxygen adsorption and desorption process on the nanorod surface plays an important role in the performance of the UV photoconductive sensor.

4. Conclusions

The fabrication of MSM-type UV photoconductive sensors was performed using aligned Al-doped ZnO nanorods prepared through sonicated sol-gel and immersion methods. These nanorod arrays were grown on a glass substrate that was coated with an Al-doped ZnO thin film as a seed layer using a precursor solution that was sonicated for different periods of time.

The FESEM images reveal that the average diameter of the prepared nanorods decreases with increasing sonication time; the size was estimated to be between 59 to 42 nm using solution sonicated between 0 to 50 min. This result is due to the effective dispersion and mixing of the reactants promoted by sonication.

The Raman spectra reveal that the Al-doped ZnO nanorod arrays produced using solutions that were sonicated up to 30 min show a reduction in compressive stress, which is indicated by the gradual shift of the E_2 (high) mode towards the ZnO bulk value of 437 cm⁻¹. However, the compressive stress then increases for the nanorods prepared using the solution 40 min and 50 min, which may be due to the interstitial Al-doping and the absorbed impurities that formed in the solution during the long sonication process. This result is consistent with the XRD measurements.

The XRD measurements also indicate that the Al-doped ZnO nanorod arrays prepared using the sonicated solution show improved crystallinity when the nanorod arrays were prepared using the solution that was sonicated for 30 min, which is indicated by more intense, prominent (002) reflections compared to the other samples.

The resistance of the Al-doped ZnO nanorod arrays decreased from 0.84 to 0.12 M Ω when the nanorods were prepared using solutions that were sonicated between 0 min to 30 min; however, this value increased to 0.12 M Ω for the nanorod prepared using the solution that was sonicated for 50 min.

This trend was also observed for the responsivity of the Al-doped ZnO nanorod array-based UV photoconductive sensors, whereby the sensor containing Al-doped ZnO nanorod arrays prepared using the solution that was sonicated for 30 min as the sensing element presents the highest responsivity

value of 4.36 A/W.

This result is attributed to the higher crystallinity properties, improved photogeneration process, lower resistance, and less compressive stress experienced by these nanorod arrays. Notably, the sensitivity of the sensor significantly increased from 7.8 to 58.0 when the nanorod arrays were prepared using solutions sonicated between 0 to 50 min. The rise and decay time constants were also improved with the increasing duration of the sonication process.

These improvements in the sensitivity and time constants were contributed to by suitable surface conditions and large surface area that were induced by the small size of the nanorod arrays prepared using the solution that was sonicated for a long time. This condition also contributed to the existence of impurities, which formed during the long solution sonication, that were absorbed into the nanorod arrays and decreased the dark current value of the sensor and improved sensitivity.

By coating the nanorod arrays prepared using the 30 min sonicated solution with PVA, the photocurrent and responsivity of the sensor could be significantly increased to 3.82×10^{-4} A and 7.64 A/W, respectively, as the result of the surface defect passivation and barrier formation from oxygen adsorption process. However, this coating reduces the sensitivity of the sensor, which may be due to less oxygen adsorption and desorption activities on the nanorod surface during switching the UV illumination on and off.

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