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Enhancement of Piezo-Related Properties of AlN Through

Combinatorial AlN-TiN Nanocolumn Composite Composition

Spread

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ABSTRACT

In this study, a combinatorial AlN–TiN nanocolumn composite composition spread (library) was fabricated using reactive sputtering, and the formation of $Ti_xAl_{1-x}N$ at the interface between AlN and TiN thickness gradients was investigated. Moreover, the intimate coupling between $Ti_xAl_{1-x}N$, AlN, and TiN, which enhanced the piezo-related properties of AlN, was analyzed. Location 1 [(1 - x)AlN - xTiN, 0 < x < 0.03] on the library exhibited superior piezotronic and piezophototronic effects because of the piezopotential modulation at the two ends of the nanocolumn. The location also exhibited excellent reliability and the highest piezophotodegradation coefficient *k* of approximately 7.5×10^{-3} /min for all samples under study. The improved piezophotodegradation reaction was a result of the enhanced optical absorption, reduced recombination of photogenerated electron–hole pairs, and intimate coupling between $Ti_xAl_{1-x}N$, AlN, and TiN. Moreover, the applied bias photon-to-current efficiency of the piezophotoelectrochemical reaction at

Location 1 was approximately 14 times higher than the efficiency of the photoelectrochemical (PEC) reaction under a bias of 0.5 V (versus Pt). The improvement was due to the favorable valence band position for water splitting and the enhanced piezophototronic effect. The study of the PEC reactions indicates the novel environmental sustainability of (1 - x)AIN - xTiN (0 < x < 0.03) on the library.

Keywords: AlN–TiN nanocolumn composite composition spread; Reactive sputtering; $Ti_xAl_{1-x}N$ solid solution; Piezophotocatalysis; Piezophotoelectrochemical reaction.

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1. Introduction

Nitride-based piezoelectric materials are promising because of their outstanding properties [1]. However, these materials are far less frequently studied than oxide-based piezoelectric materials [1,2]. Typical nitride-based piezoelectric materials include wurtzite group III nitrides (e.g., GaN, InN, and AlN) [1]. However, some of the nitrides have certain limitations [1]. For instance, although the energy band gap E_g of GaN and InN exists within the visible light region [3], Ga and In are not abundant on the Earth, and In is biotoxic. These problems considerably limit the application of these nitrides on a wide scale.

By contrast, AlN is ecofriendly and has various exceptional properties, such as high chemical and thermal stabilities, high electrical resistivity, and a low thermal expansion coefficient [4,5]. Thus, many studies have emphasized on the mechanical properties of AlN. For instance, AlN has been widely used for preparing heat dissipation components [5,6], wear-resistant materials [6,7], and corrosion-protective coatings [8]. Moreover, AlN has a high Curie temperature of approximately 1150 °C [9]. Thus, AlN exhibits high sustainability in its piezoelectric response at high temperatures. However, the low piezoelectric coefficient d_{33} (approximately 5.5 pC/N) [10] and large E_g (approximately 6.2 eV) [5] substantially restrict its potential applications in advanced devices, such as piezopotential-modulated field effect transistors [11], high-power or high-frequency transducers [12,13], and light-emitting diodes [14].

Efforts have been devoted to doping TiN into AlN in recent years for modulating its conductivity, piezoelectric property, and E_g , although TiN [15–17] has been extensively investigated as a means of enhancing the mechanical properties of AlN [18]. Iwazaki *et*

al. employed a first-principles calculation to study a codoping strategy by using lowformation-energy dopants, including Ti⁴⁺ and Mg²⁺, to enhance the stability and piezoelectric performance of AlN [10]. Iborra et al. reported the structural and piezoelectric properties of Al_{0.5-x}Ti_xN_{0.5} compounds as a function of the Ti content (x < 6at%) by using reactive alternating current sputtering. Al_{0.5-x}Ti_xN_{0.5} films exhibited features superior to AlN films, including piezoelectric activity, thermal stability of frequency, and temperature resistance [19]. Organometallic chemical vapor deposition was used by Gilles et al. to synthesize nanosized (Ti,Al)N antioxidation coatings at low temperatures. Moreover, thermodynamic calculations were performed to predict the nature of phases [20]. He et al. reported the microstructural evolution, phase development, and chemical composition of fracture toughness-enhanced TiN_{1-x}-AlN composite powders fabricated using high-temperature sintering. These studies pertaining to TiN revealed the positive influence of TiN on the piezoelectric performance of AlN. However, theoretical calculations have mostly been performed, and only a few experimental results have been obtained. Furthermore, no piezotronic, piezophototronic, piezo-related applications, piezophotocatalysis extended including or and piezophotoelectrochemical (PPEC) reactions, were reported. As indicated in the Ti-Al-N ternary phase diagram, the thermodynamically stable phases of Ti₃AlN and Ti₂AlN are centrosymmetric. Thus, they do not exhibit any piezoelectricity. The mutual solubility of TiN and AlN is limited because of their extremely high hardness. In this study, small amounts of TiN were doped into AlN through a novel strategy of combinatorial AlN-TiN nanocolumn composite composition spreads (libraries) by using reactive sputtering. This strategy was used for the following reasons. First, AlN-predominant libraries were fabricated systematically by depositing a substantially thicker natural gradient of AlN than the gradient of TiN. A relatively small amount of nonpiezoelectric TiN was used to distort the lattice of AlN for enhancing the piezoelectricity of the system. The optimal ratio of AlN:TiN was then identified through piezo-related characterizations. Second, the lattice mismatch between the preferred TiN (111) (lattice constant *a* = 0.0300 pm) and AlN (002) (*a* = 0.0311 pm) planes was only approximately 3.6%, which resulted in an excellent interface between them to sustain nanocolumn arrays. Third, the formation of Ti_xAl_{1-x}N was modified at the interface between AlN and TiN thickness gradients. Finally, the intimate coupling between AlN, TiN, and Ti_xAl_{1-x}N improved the piezo-related performance of the system. We observed that Location 1 [(1 – *x*)AlN – *x*TiN, 0 < *x* < 0.03] on the library exhibited the most favorable piezotronic and piezophototronic features and piezophotodegradation and PPEC reactions for all samples under study, thus indicating the promising piezo-related applications of Location 1.

2. Experimental

Combinatorial reactive sputtering was used to synthesize AlN–TiN nanocolumn libraries on fluorine-doped SnO₂ (FTO)–glass substrates (24 mm × 24 mm). FTO–glass substrates were employed because of their excellent conductivity and transparency, which are essential for the characterizations conducted in this study. The substrates were cleaned ultrasonically with acetone, alcohol, isopropyl alcohol, and deionized water, in sequence, for 5 min each. The background pressure of the chamber and working distance between the target and substrate were approximately 1×10^{-6} Torr and 7 cm, respectively. Before deposition, a 10-min presputtering process was conducted using pure Ar plasma

to remove surface contaminants on the Al and Ti targets. Various sputtering parameters, including operation power and pressure, $Ar-N_2$ ratio, and deposition temperature, were modified to obtain crystalline AlN and TiN nanocolumns. A natural AlN thickness gradient [inset of Figure 1(a)] was obtained by optimizing the angle of the Al-target sputtering gun. The AIN thickness gradient was fabricated to couple with the reversed TiN thickness gradient to obtain a combinatorial AlN-TiN nanocolumn composite composition spread, as discussed in TEM analyses. The required crystallinity of AIN nanocolumn arrays was achieved using the following conditions: radio frequency (RF) of 450 W, working pressure of 10 mTorr, and Ar-N₂ flow rate of 10:2 sccm at 450 °C. The reversed natural TiN thickness gradient [inset of Figure 1(a)] was analogously deposited on the AlN layer by using the following conditions: RF of 350 W, working pressure of 10 mTorr, and Ar-N₂ flow rate of 10:1 sccm at 450 °C. To adjust the nanocolumn morphologies and modify the effective coupling between AlN and TiN, both thickness gradients were modulated by tuning the deposition times of each layer (e.g., 5–7 and 2–5 min for AlN (deposition rate: approximately 23 nm/min) and TiN (deposition rate: approximately 18 nm/min), respectively). In total, seven layers were fabricated to achieve the required sample thickness (AlN-rich end: approximately 1100 nm). For the convenience of characterization, the FTO substrate was cut into six equivalent pieces (4 \times 24 mm² each), which were subsequently assembled for library deposition to enable various characterizations on a specific single piece (location) across libraries.

Glancing-angle X-ray diffraction (XRD) was used to determine the phase and crystallinity of the libraries. Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were employed to study the microstructures. The morphologies and optical properties of the samples were analyzed by conducting field emission scanning electron microscopy (FE-SEM) and ultraviolet-visible (UV-Vis) spectroscopy. X-ray photoelectron spectroscopy (XPS) was conducted to investigate the bonding states of the constituent elements of the samples. The depth profiling mode was also employed to verify the variation in the Al-Ti ratio and interface between AlN and TiN across the library. The valence band $E_{\rm v}$ positions of libraries were determined using ultraviolet photoelectron spectroscopy (UPS). Photoluminescence (PL) spectroscopy was applied to probe the electronic structure of the samples by studying the recombination of photoinduced electron-hole (e^-h^+) pairs. A custom-made probe station comprising a sensitive stress and voltage tungsten (W) probe, grounded W probe, black box, and light source was used. W is an excellent conductor and ideal for the piezo-related measurement. The grounded and stress-voltage probes were in contact with the bottom electrode (FTO substrate) and library samples, respectively. The current-voltage (I-V) curves were then obtained as a function of the applied stress for the piezotronic properties. When a UVA lamp (power density: approximately 1 mW/cm²) was externally applied, the piezophototronic effect was characterized. The photodegradation activities of the library samples were determined by decomposing methylene blue (MB) solutions (5 ppm and 20 mL) by using a xenon lamp (power density: approximately 130 mW/cm²) as a light source. A cycling test was conducted by performing the degradation procedure thrice to ascertain the stability and reusability of the photocatalysts. The corresponding photoelectrochemical (PEC) activities were measured using a PEC cell that comprised a reference electrode (Pt-coated FTO substrate), a working electrode (library), Na₂SO_{4(aq)} electrolyte (0.5 M and 100 mL), a potentiostat, and two UVA lamps (wavelength:

approximately 324 nm and power density: approximately 1 mW/cm²) [21]. The illuminated sample area was approximately 4×20 mm². A 15-mm-wide binder clip was externally used to supply stress for the PPEC measurement in addition to illumination.

3. Results and discussion

The library, comprising 7- and 3-min natural AIN and TiN thickness gradients in each cycle, respectively, was desirable and subjected to XRD analysis [Figure 1(a)]. Pure AlN (red curve) and TiN (blue curve) nanocolumn arrays were also compared. For Locations 1 to 6 on the library, the AlN characteristic peaks (red dashed lines) gradually shifted to lower diffraction angles. This indicated the successive expansion of interplanar spacing in each corresponding plane based on Bragg's law because of the continuously increasing amount of Ti (ionic sizes of Ti³⁺ and Al³⁺ were 81 and 53 pm, respectively) and the formation of $Ti_xAl_{1-x}N$ solid solutions. This result was further indicated by the TEM (Figure 2) and XPS analyses (Figure 3). However, the intensities of peaks pertaining to the TiN on the library (blue dashed line) were substantially lower compared with the intensities of the peaks pertaining to pure TiN because of poor crystallinity caused by the incorporation of AlN. No other phases were observed. The columnar morphologies, which were enabled under a short working distance and high working pressure [22], were noticed at all locations by conducting SEM analysis [Figure 1(b)]. Due to the nature of thickness gradient, the properties exhibited by each piece varied on the basis of the location. Thus, average properties were measured for each piece on the library [23, 24].

The layered structure and microstructures of Locations 1 and 6 on the library were further examined. Figure 2(a) (Location 1) and (c) (Location 6) display typical TEM

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images. Seven layers with distinctive interfaces and columnar structures were ascertained, which was consistent with our experimental design for fabricating sevencycle nanocolumn libraries. The thicknesses of the first five layers were approximately equal but were lower than those of the last two layers. The thickness variation was attributed to the employed fabrication condition that was not completely stabilized in the initial growth phase (first five layers), thus leading to low deposition rates. This condition was not ideal for regular thin-film fabrication. However, the condition was desirable for inducing nanocolumns because of the reduced mobility and mean free path of the generated plasma species [22]. Then, the thickness variation profiles of natural AlN and TiN thickness gradients were determined because the mass variation typically follows a Gaussian distribution [25]. To examine the phase distribution across nanocolumns, SAED was used on three positions, as displayed in Figure 2(b) [enlarged image of the red square presented in Figure 2(a)]. The patterns captured from the left and center positions were verified as the planes (100), (002), and (101) of $Ti_xAl_{1-x}N$ [Figure 2(d)] and AlN [Figure 2(e)], respectively. This indicated that $Ti_x Al_{1-x}N$ formed near the interface between AlN and TiN. The planes indexed at (111), (200), and (220) of TiN were also ascertained from the patterns displayed in Figure 2(f), which was determined from the right position in Figure 2(b). The resolvable spots along the rings in these SAED patterns implied highly textured orientations of the nanocolumns.

XPS was employed to study the chemical and electronic states of constituent elements in the samples (Figure 3). To determine the variation in AlN, TiN, and $Ti_xAl_{1-x}N$ along the nanocolumns, XPS depth profiling was conducted. Four points were characterized for each location: depths of approximately 0, 0.4, 0.7, and 1 µm. Figure 3(a) displays the profiling data of Location 1. The Ti (blue) and Al (red) proportions varied along the nanocolumns; however, the proportion of N (gray) did not vary substantially. The detected O signals (black) were attributed to the O₂ contamination during the sputtering process. Based on the profiling data for each location and the formation of $Ti_xAl_{1-x}N$ at the interface between AlN and TiN (Figures 1 and 2), a schematic of the layered structure of the library, containing AlN (red), TiN (blue), and $Ti_xAl_{1-x}N$ (yellow), was prepared and is presented in Figure 3(b). The black dots in the figure denote the measured points. The atomic proportions of AlN, TiN, and $Ti_xAl_{1-x}N$ were then determined using the following equation: [Thickness \times Location area \times Density]/Molecular weight [26], where the layer thicknesses were determined using SEM, the location area was $4 \times 24 \text{ mm}^2$ for each piece, the molecular weights of AlN, TiN, and $Ti_xAl_{1-x}N$ were 41, 62, and 50 g/mole, respectively, and the densities of AlN, TiN, and $Ti_xAl_{1-x}N$ were 3.26, 5.4, 4.3 g/cm³, respectively [Figure 3(c)]. The AlN-TiN ratio was higher than four across the sample area, in which TiN varied on an average from approximately 0 at.% to approximately 3 at.% at Location 1 [red mark, Figure 3(c)]. Thus, the atomic proportion of TiN (x) at Location 1 on the library [(1 - x)AIN - xTiN] was between approximately 0 and 0.03.

Figure 4(a) displays the UV–Vis diffuse reflectance spectra of the samples. Pure AlN (green) and TiN (purple) were also plotted for comparison. The reflectance edge observed at a short wavelength (one purple star) corresponds to the E_g of pure TiN, and the edge was estimated to be approximately 3.2 eV through a Tauc plot. The other edge at the longer wavelength (two purple stars) was associated with the defect-induced absorption. These observations were ascertained by conducting a subsequent PL analysis. However, the reflectance edge of AlN was not available when the current incident light source was

used because of its extremely large E_g (approximately 6.2 eV). The decay below the wavelength of approximately 350 nm was attributed to the UV absorption by the FTO– glass substrate. The remaining wavelength ranges were effectively reflected. Compared with pure AlN and TiN, Locations 1 to 6 on the library exhibited variations in the reflectance edges. To elucidate the variation, only Locations 1 (red) and 6 (blue) are illustrated. The trend is indicated by two black arrows (two red to two blue stars and one red to one blue star) and shifted toward the TiN edges because of the gradual increase in the Ti content. The two edges of each location were associated with defect-induced recombination, as suggested by subsequent PL analysis.

To analyze the features observed in the UV–Vis spectra, PL was used to examine the recombination behavior of photoinduced e^-h^+ pairs in the samples [Figure 4(b)]. Pure AlN exhibited extremely high intensities (green, right scale), thus indicating the substantial recombination of e^-h^+ pairs. The two peaks at approximately 410 and 540 nm were associated with the defect-induced recombination. Pure TiN (purple) and Locations 1 to 6 on the library exhibited much weaker intensities (left scale). The minor peak at approximately 410 nm (one purple star) of pure TiN was associated with the intrinsic band-to-band transition. The other peak at approximately 530 nm (two purple stars) was attributed to defect-induced recombination. These observations justified the reflectance behavior of pure TiN, as presented in Figure 4(a). The spectra of Locations 1 to 6 on the library were similar to the spectrum of pure AlN because of predominant AlN in the system [Figure 3(c)]. The two peaks were also associated with the defect-induced recombination. When TiN was continuously doped into AlN from Locations 1 to 6, the two peaks shifted toward the positions of the peaks of pure TiN, as indicated by the black

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arrows in the figure. Both trends indicated the reflectance behavior of the library in Figure 4(a). The substantially reduced PL intensities indicated weak recombination of $e^ h^+$ pairs, which was excellent for enhancing the photodegradation properties (Figure 7).

To derive the energy band diagrams of the samples, the E_v positions were determined by conducting UPS measurements [Figure 4(c)]. The levels negatively decreased from Locations 1 (approximately 1.2 eV) to 6 (approximately 2.1 eV), which is relative to the work function of the facility (approximately –4.9 eV of Au). By combining the PL and UV–Vis results, the energy band diagrams of the library, pure AlN, and TiN were prepared. The conduction band of AlN was determined from a previous study [27]. The tunability of the energy band of the library was clearly based on the amount of TiN. The diagram was also prepared by referring to the energy level of the standard hydrogen electrode, which provided a crucial basis for elucidating the enhanced mechanisms of photodegradation and PEC reactions.

The extended applications to piezotronics and piezophototronics of the materials were inferred using our custom-built I-V system. The insets (a) and (c) of Figure 5 display the side and top views of the measurement configuration, respectively. Two contacts were formed. In the contacts, the stress and bias [inset (b) of Figure 5] and grounded probes were in contact with the sample (S2) and the FTO substrate (S1), respectively. An ohmic contact at S1 was achieved by eroding the coating of the sample surface. Chemical etching was not applied to minimize unexpected chemical reactions during the process. Pure TiN and AlN were also measured as references. Pure TiN exhibited an ohmic behavior in the bias range of -10 to 10 V, thus indicating no piezo-related properties (not shown). However, the asymmetric I-V characteristics of pure AlN as a function of pressure (0.005, 0.05, and 0.25 GPa; solid line) and both pressure and illumination (dashed line) implied weak piezotronic and piezophototronic effects, respectively [inset (d) of Figure 5]. By contrast, Location 1 [(1-x)AlN-xTiN, 0 < x < 0.03] on the library exhibited substantially enhanced piezotronic (solid line) and piezophototronic (dashed line) features (Figure 5) compared with the features of pure AlN, which were almost negligible in the plot (purple line). The Schottky barrier heights at S1 [$\Phi_{S1(F-s)}$, F: FTO, s: sample] and S2 $[\Phi_{S2(W-s)}]$ (pink double-headed arrow) were determined from the measured threshold voltage in the I-V characteristics, for which the current density J_D was activated. When the stress applied at S2 was increased from 0 to 0.25 GPa, the value of J_D under positive bias was substantially enhanced. This increase was attributed to a decrease in $\Phi_{S1(F-s)}$. In this operational mode, electrons flowed from S1 to S2. Thus, $\Phi_{S1(F-s)}$ was crucial for controlling J_D . When a positive piezopotential was generated on the bottom of the sample, $\Phi_{S1(F-s)}$ decreased. Thus, J_D increased. By contrast, the essential $\Phi_{S2(W-s)}$ increased because of the negative piezopotential buildup at the top of the sample when a negative bias and stress were applied at S2 (e⁻ flowed from S2 to S1), although a negative bias increased the electron energy level. Thus, the value of J_D decreased. Other locations were also measured; however, an enhanced ohmic behavior was observed from Locations 1 to 6 [inset (e) of Figure 5] because a higher amount of conducting TiN was involved.

To quantitatively verify the Schottky barrier height variation at S1 $[\Delta \Phi_{S1(F-s)}]$ and S2 $[\Delta \Phi_{S2(W-s)}]$, the *I*-*V* characteristics were further examined. Based on the thermionic emission-diffusion theory [28], when an applied bias *V* is greater than the built-in

potential V_{bi} and kT/q (k: Boltzmann's constant, T: absolute temperature, and q: electronic charge), a Schottky current J for a Schottky diode can be simplified as follows:

$$\ln I \propto V^{\frac{1}{4}} \tag{1}$$

The details of this equation were explained in our previous study [28]. Figure 6(a) displays the plot of ln $(-J_D)$ as a function of $(-V)^{1/4}$ from approximately -3 to -4 V under varying applied pressures for S1, in which a linear relationship was observed. $\Delta \Phi_{S1(F-s)}$ was also determined [0.005 GPa as a reference pressure, Figure 6(c)]. For example, a decrease in $\Delta \Phi_{S1(F-s)}$ of approximately 60 mV was observed under 0.25 GPa. Analogously, the Schottky behavior at S2 was verified by observing a similar trend in the positive bias range from approximately 5 to 6 V under stress [Figure 6(b)]. $\Delta \Phi_{S2(W-s)}$ was also determined [Figure 6(d)], in which an increase of approximately 30 mV was observed under 0.25 GPa.

Photodegradation [Figure 7(a)] and piezophotodegradation [Figure 7(b)] of MB solutions by using pure TiN, pure AlN, and the library were examined [29]. The first 30 min (indicated by -30 to 0 min) in both plots of Figure 7 denote the dark absorption study. In Figure 7(a), the self-degradation result (black dashed line) indicates a negligible decay of MB under irradiation. Pure AlN (dark green) also exhibited a trivial photodegradation activity because of its extremely large E_g value. Pure TiN (purple) exhibited better performance than AlN. For the library, approximately 50% of MB was photodegraded at Location 6 (blue) within 80 min, and this location outperformed other locations. These results were interpreted using the energy band diagram, as presented in Figure 4(c). Location 6 exhibited a more desirable E_V position to produce the predominant •OH radicals (Figure 8) compared with other locations and TiN.

Piezophotodegradation was studied by externally applying stress (two pieces of FTO substrate) and ultrasonication [Figure 7(b)]. The performance of AlN improved slightly because of its weak piezoelectricity; however, no enhancement was noticed for pure TiN and at Locations 2 to 6 on the library because of their nonpiezoelectricities. By contrast, Location 1 (red line) exhibited substantial improvement. The performance of Location 1 within 80 min was almost comparable with that of Location 6. This considerable enhancement indicated that when the sample was illuminated, light absorption was stronger with Ti_xAl_{1-x}N because of its defect-reduced band gap, thus leading to more photogenerated e^-h^+ pairs. When external stress was applied, the resultant piezopotential buildup and band bending in the piezoelectric components of $Ti_xAl_{1-x}N$ and AlN created smooth migration paths for the photogenerated e^-h^+ pairs and strengthened their separation. The conducting TiN component further facilitated charge carrier transport in the composite system by coupling among the constituent components, which substantially inhibited the recombination of photogenerated e^-h^+ pairs. These features complemented each other and then triggered synergistic piezophotodegradation. To further investigate the piezophotodegradation capability of Locations 1 and 6, the reaction time was extended to 120 min [inset of Figure 7(b)]. Location 1 continued to be active even after 120 min; however, Location 6 became inactive after 90 min. Thus, overall, Location 1 outperformed Location 6. The photodegradation coefficient k of the samples was calculated [Figure 7(c)], and Location 1 on the library was discovered to have the highest k of approximately 7.5×10^{-3} /min.

A three-run cycling test of the piezophotodegradation activity was conducted to verify the photostability and reusability of Location 1 on the library [Figure 8(a)]. No discernible deterioration was observed, thus indicating the sample's reliable piezophotocatalysis. This result suggests that the material has the potential to be used for environmental sustainability related applications. Tert-butanol [hydroxyl radical (•OH) scavenger] and sodium disulfate [superoxide radical (•O₂⁻) scavenger] were added to the MB solution in the scavenger study to evaluate the crucial radicals in the photodegradation and piezophotodegradation mechanisms of Locations 1 and 6. In the photodegradation study, no evident differences were discovered between •OH and •O₂⁻ scavengers for Location 1 because of its poor photodegradation activity [Figure 8(b)] and unfavorable energy band position for generating •OH radicals [Figure 4(c)]. However, •OH scavengers exhibited inferior photodegradation activity to •O₂⁻ scavengers for Location 6 [Figure 8(c)], thus indicating the predominant role of •OH in the process. This observation is supported by the favorable energy band position of Location 6 [Figure 4(c)]. For the piezophotodegradation activity, •OH radicals again predominated for both locations [Figures 8(d) and (e)]. Thus, •OH radicals were determined to be crucial for decomposition reactions.

Another potential application of the material is its application as a photoelectrode for PEC water spitting. The photocurrent density J_{ph} of various samples was measured as a function of the applied voltage (versus Pt) with and without stress and illumination [inset of Figure 9(a)]. In general, pure AIN and pure TiN exhibited a negligible J_{ph} value under illumination or under both stress and illumination (data not shown). Although Location 1 also exhibited a trivial J_{ph} value under illumination (PEC, solid red line), J_{ph} was substantially enhanced when stress was applied (PPEC, red dashed line). A similar trend was observed for Location 6; however, the enhancement was not as substantial as that for

Location 1. These observations were also interpreted from the locations' energy band positions [Figure 4(c)] and I-V characteristics (Figure 5). Both locations exhibited favorable $\underline{E}_{\underline{v}}$ positions for water splitting. However, under stress, the strong piezophototronic effect exhibited by Location 1 caused substantial enhancement of J_{ph} . This enhancement was larger than that for Location 6 under stress. The PEC and PPEC capabilities of both locations were elucidated in the corresponding applied bias photonto-current efficiency (ABPE) [Figure 9(a)]. In general, the PPEC performance (dashed lines) was considerably superior to the PEC performance (solid lines), thus indicating the positive influence of external stress. Although the ABPE of both PEC and PPEC reactions of Location 1 was lower than that of Location 6, the PPEC performance of Location 1 was approximately 14 times higher than the PEC performance under 0.5 V (versus Pt). Such improvement substantially exceeded the improvement obtained for Location 6, in which an approximate fivefold enhancement was obtained under the same bias. To determine the photostability of the two locations, five cycles with light-on (60 s) and light-off (60 s) modes for each cycle were conducted under a bias of 0.5 V [Figure 9(b)]. Both locations exhibited stable and reliable J_{ph} in both PEC and PPEC reactions, thus indicating their use in novel PEC-related applications. The dramatic increase in J_{ph} at the beginning of each cycle was attributed to the rapid generation of e^-h^+ pairs. J_{ph} gradually stabilized once equilibrium was attained.

4. Conclusions

Combinatorial AlN–TiN nanocolumn libraries were fabricated using magnetron sputtering, and their various properties were investigated. Highly textured orientations of

the nanocolumns comprising AlN, TiN, and $Ti_xAl_{1-x}N$ were observed by conducting XRD and TEM analyses. By combining the XPS depth profiling results, the layered structure and atomic proportions of the constituent components of the library were ascertained, and AlN was found to be predominant. Location 1 [(1 - x)AlN - xTiN, 0 < x < 0.03] on the library exhibited substantially enhanced piezotronic and piezophototronic features compared with other samples because of piezopotential modulation, and $\Delta \Phi_{S1(F-s)}$ and $\Delta \Phi_{S2(W-s)}$ were quantitatively verified in this study. Location 1 also exhibited reliable piezophotocatalysis and exhibited the highest k value of approximately 7.5×10^{-3} /min. This study determined that •OH radicals are crucial to photodecomposition reactions. The enhancement of the piezophotocatalytic reaction was attributed to the coupling between $Ti_xAl_{1-x}N$, AlN, and TiN. A stable and reliable J_{ph} was obtained for both PEC and PPEC reactions. For Location 1, the ABPE of the PPEC reaction was approximately 14 times higher than that of the PEC reaction under 0.5 V. This result was attributed to the favorable E_{ν} position for water splitting and the enhanced piezophototronic effect. The study of the PEC reactions [21] indicates the novel environmental sustainability of (1x)AlN – x TiN (0 < x < 0.03) on the library.

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Figure Captions

Figure 1. (a) XRD results of the library (Locations 1 to 6 indicated by #1 to #6, respectively). Pure AlN and TiN were compared. Red, blue, and green dashed lines indicate the characteristic peaks of AlN, TiN, and the FTO substrate, respectively. A schematic of the layered structure is displayed in the top inset (not to scale). (b) Sideview SEM images of Locations 1 to 6.

Figure 2. TEM results of the library. (a) Typical image of Location 1. (b) Three positions for conducting SAED analyses [enlarged image of the red square in (a)]. (c) Typical image of Location 6. (d)–(f) SAED patterns captured from positions indicated in (b).

Figure 3. (a) XPS depth profiling of Location 1 on the library. (b) Detailed schematic of the layered structure of the library. (c) Calculated atomic proportions of AlN, TiN, and $Ti_xAl_{1-x}N$ in the library.

Figure 4. Optical and electronic properties of pure AlN, pure TiN, and the library. (a) UV–Vis diffuse reflectance spectra, (b) PL spectra, and (c) energy band diagram.

Figure 5. *I*–*V* characteristics of Location 1 as a function of stress (0, 0.005, 0.05, and 0.25 GPa; solid lines) and both stress and illumination (dashed lines) on the library. The characteristics of pure AlN (purple line) are presented for comparison. Inset (a) and (c): side and top views of the measurement configuration, respectively. Inset (b): photo of the stress probe. Inset (d): *I*–*V* characteristics of pure AlN. Inset (e): *I*–*V* characteristics under a pressure value of 0.05 GPa from Locations 1 to 6.

Figure 6. Analysis of Schottky behavior under various stresses. (a) $\ln (-J_D)$ versus $(-V)^{1/4}$ at S1. (b) $\ln (J_D)$ versus $(V)^{1/4}$ at S2. (c), (d) Schottky barrier height variation at S1 $[\Delta \Phi_{S1(F-s)}]$ and S2 $[\Delta \Phi_{S2(W-s)}]$.

Figure 7. Photodegradation study of pure AlN, pure TiN, and the library (a) under illumination and (b) under stress and illumination. The inset presents a comparison between Locations 1 and 6 over 120 min. (c) Calculated photodegradation coefficient k. Stress and illumination are denoted by s and i, respectively.

Figure 8. (a) Cycling test of Location 1 on the library. (b), (c) Photodegradation scavenger test for Locations 1 and 6, respectively. (d), (e) Piezophotodegradation scavenger test for Locations 1 and 6, respectively.

Figure 9. PEC and PPEC performance of Locations 1 and 6 on the library. (a) Calculated ABPE. J_{ph} values are presented in the inset. (b) Cycling test. Stress and illumination are denoted by *s* and *i*, respectively.

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Figure 1. Hsin-Yi Lee et al.



(b)

Location 1	FTO	- <u>1μm</u>	Location 2	FTO	544μm 1 μm	Location 3	FTO	1µm
Location 4	FTO	īμm	Location 5	FTO		Location 6	FTO	1 µm

Figure 2. Hsin-Yi Lee *et al*.



Figure 3. Hsin-Yi Lee *et al*.



Figure 4. Hsin-Yi Lee *et al*.



Figure 5. Hsin-Yi Lee *et al*.





Figure 6. Hsin-Yi Lee et al.

Figure 7. Hsin-Yi Lee *et al*.



Figure 8. Hsin-Yi Lee et al.



Figure 9. Hsin-Yi Lee *et al*.

