

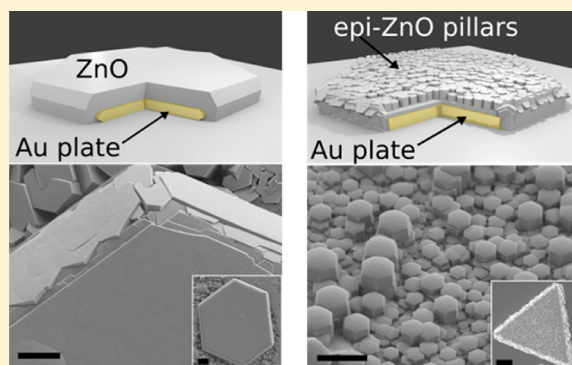
Aqueous Epitaxial Growth of ZnO on Single Crystalline Au Microplates

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S Supporting Information

ABSTRACT: Epitaxial ZnO thin films were grown on single crystalline Au microplates from an aqueous solution at 90 °C. The composite structures were approximately 100 μm wide. The epitaxial ZnO films were smooth, continuous, and several micrometers thick. We examined the epitaxial relationship between the ZnO and Au through scanning electron microscopy, electron backscatter diffraction, high-resolution transmission electron microscopy, and electron diffraction and demonstrated control over the resulting film morphology through the kinetics of growth. An epitaxial relationship of $\text{ZnO}[1100](0002)\parallel\text{Au}[2\bar{1}\bar{1}](111)$ was dominant in the structures.



The quality of metal/oxide interfaces is an important determinant of the efficiency of electrical,¹ plasmonic,^{2,3} and catalytic devices.⁴ Typically, metal/oxide interfaces are formed by vapor-phase deposition, resulting in polycrystalline films with various morphologies, textures, grain sizes, and orientations. Here, we demonstrate a method for growing epitaxial ZnO from an aqueous solution at 90 °C on single crystalline Au microplates. These results could have important implications on the advancement of metal/ZnO-based electronic devices,⁵ plasmonic devices,^{6,7} and heterogeneous catalysts.^{8,9}

While epitaxial growth of ZnO on nearly lattice-matched substrates, including GaN,¹⁰ sapphire,^{11,12} and SiC,¹² has become well-established, heteroepitaxy with metals has not been as well explored. The common challenges of epitaxial growth on highly dissimilar materials¹³ apply to the Au/ZnO system as well. Au and ZnO have different crystal structures, chemical bonding, and lattice constants. Gold has a face-centered cubic (FCC) crystal structure with a lattice constant $a = 0.4079$ nm. ZnO has a hexagonal wurtzite crystal structure with lattice constants $a = b = 0.3250$ nm and $c = 0.5207$ nm. In the close-packed plane of each structure, this yields a lattice mismatch of $(a_{\text{ZnO}} - a_{\text{Au}}\sqrt{2}/2)/(a_{\text{Au}}\sqrt{2}/2) = 12.7\%$.

Despite these challenges, there has been some success in epitaxial growth of ZnO on Au.¹⁴ Because the thermal expansion coefficients of the two materials are so different, low temperature deposition techniques have been crucial in their heteroepitaxy. Aqueous, epitaxial electrodeposition of ZnO nanopillars on large single crystalline gold substrates has been demonstrated.^{15,16} However, smooth ZnO films are often required for most practical optoelectronic applications. Additionally, gold, while ubiquitous in semiconductor technologies and plasmonics, is rarely used as single crystalline substrates.

Recently, a simple thermolysis procedure for producing very large, gold microplates^{17,18} has been developed. These plates are single crystalline, making them atomically smooth and ideal for modular plasmonic¹⁷ and microelectronic devices.

Our technique is a simple solution-based aqueous synthesis and, unlike the previously demonstrated epitaxial electrodeposition of ZnO on Au,^{15,16} does not require an external electrical bias. Another advantage of our work is that we demonstrate the coalescence of epitaxial ZnO columns into a smooth, thin film, which is essential for most device fabrication. The single crystalline gold plates can also be grown on any substrate that can survive the 130 °C deposition and be stable in the growth solution.¹⁸ The simple synthesis method for obtaining epitaxial ZnO therefore opens more opportunities for modular Au/ZnO devices made through bottom-up processes.

Single crystalline Au microplates were first grown on Si substrates by thermolysis of a $(\text{AuCl}_4)^-$ -tetraoctylammonium bromide (TOAB) complex in air.^{17,18} Briefly, 3.2 mL of 25 mM hydrogen tetrachloroaurate(III) hydrate in deionized water were mixed with 8 mL of 50 mM tetraoctylammonium bromide (TOAB) in toluene. After vigorous stirring, the top layer, consisting of a Au-TOAB complex in toluene, was separated and drop-cast onto a Si substrate. The substrate was heated to 130 °C on a hot plate for 24–48 h and gently rinsed with toluene and dried.

Aqueous ZnO deposition followed procedures similar to those reported in literature.^{19–21} In order to maintain control over film morphology, a two-step method was used to separate the nucleation and growth of the ZnO films as much as

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possible. The nucleation step was done either by rapid heating using a microwave oven or by slow heating in a conventional oven. Substrates were cleaned with an Anatech 106 oxygen plasma barrel asher for 1 min immediately prior to seed-layer deposition to remove adsorbed organic contaminants. For the microwave-based nucleation, the substrate was suspended with the growth-face facing down in a solution of 0.2 g zinc nitrate hexahydrate, 1.25 mL of 15 M ammonium hydroxide, and 24 mL of deionized water in a Teflon vessel. The vessel was heated on high power for 25 s in a microwave oven (GE model JES738WJ02), heating the solution very rapidly to approximately 95 °C. The substrate was immediately removed from the vessel after heating, gently rinsed in water, and dried. For nucleation in a conventional oven, the substrate was identically suspended face down in a Teflon vessel with the same solution. The vessel was then kept at 90 °C in an oven for at least 1.5 h. Afterward, the sample was removed, gently rinsed in water, and dried.

The second step was to grow the nucleated seed layer into a continuous, coalesced film. The growth solution consisted of 0.2 g of zinc nitrate hexahydrate, 1.25 mL of 15 M ammonium hydroxide, 24 mL of deionized water, and 0.05 g of sodium citrate tribasic dihydrate. Again, the substrate was sealed in a Teflon vessel face down in the solution and heated in a conventional oven to 90 °C for 4–24 h. The growth rate decreases substantially after the first 4 h, but some samples remained in the oven for 24 h to ensure completion of the growth process. Afterward, the substrate was removed, gently rinsed in water, and dried.

To reveal the bottom surface of the ZnO, the sample was flipped and pressed onto a new, resist-coated Si substrate. AZ 5214E (Clariant) photoresist was spun onto the Si substrate at 2000 rpm for 30 s, then soft-baked at 100 °C for 1 min, resulting in a resist thickness of approximately 2 μm . A metal block weighing 1.6 kg was placed on top of the sandwich structure, and the structure was heated to 130 °C, above the glass temperature of the photoresist.²² The sandwiched structure remained at 130 °C for 30 min and was slowly cooled back to room temperature. The metal block was then removed, and the two Si substrates were separated with tweezers. As a result, some of the microplates were transferred into the layer of photoresist on the new Si substrate. This sample, with flipped microplates on it, was dipped into Au etchant Type TFA (Transene Company) until all Au was removed. Since the Au microplates were of various thicknesses, the total etching time also varied from 10 to 60 min. The bottom surface of the ZnO was revealed after all of the Au was removed.

Scanning electron microscopy (SEM) and electron back-scattered diffraction (EBSD) were performed using a Supra55VP field emission SEM (Carl Zeiss AG, Germany) equipped with an EBSD detector. AFM was performed using an Asylum MFP-3D AFM. Photoluminescence (PL) was performed on the grown ZnO using a LabRAM ARAMIS system (HORIBA Scientific, Japan). Samples were excited with a 325 nm (HeCd) laser for PL. Cross-sectional specimens for transmission electron microscopy (TEM) were prepared using the “lift-out” technique in a focused ion beam (FIB) (Zeiss NVision 40) system. TEM (JEOL-2100 at 200 kV) and selected area electron diffraction (SAED) measurements were conducted in order to study the orientational relationship between the Au and the ZnO. The HRTEM micrograph was acquired using a Zeiss Libra 200 monochromic, Cs-corrected

transmission electron microscope (TEM) at 200 kV (Cs-corrected to approximately $-1\text{ }\mu\text{m}$).

ZnO films on the Au microplates were made by a two-step procedure to separate nucleation and growth as much as possible and, therefore, to exercise better control on the structure and morphology of the ZnO. We refer to the ZnO grown on the Au microplates after the nucleation step as the seed layer. Growth of the ZnO proceeded by slowly decreasing

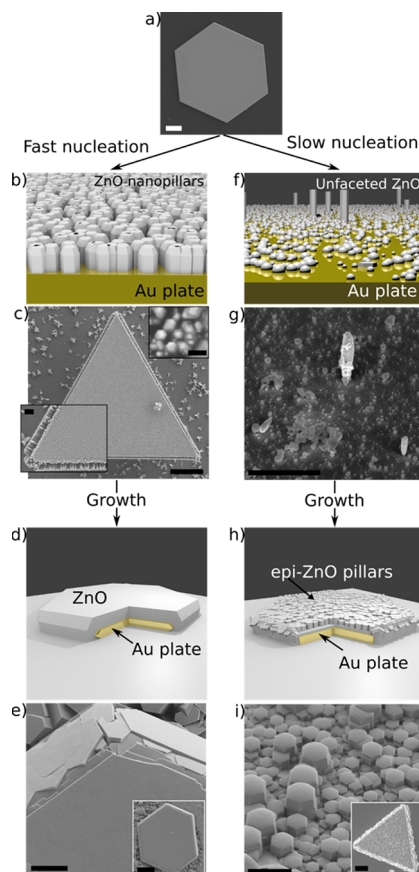


Figure 1. Overall film morphology of epitaxial ZnO on Au controlled through growth kinetics. (a) SEM micrograph of the initial Au microplate. Scale bar = 10 μm . Left column: Nucleation and growth steps of microwave-nucleated ZnO on Au. (b) Schematic of dense nanopillars formed on the Au microplate during the fast nucleation step. (c) SEM micrograph showing ZnO on Au microplate after the fast nucleation step. Scale bar = 5 μm . Insets show high magnification views of the corner of the plate, showing the uniform height of the nanopillars (lower left, scale bar = 1 μm), and middle of the plate, showing the crystal habits (top right, scale bar = 200 nm) of the ZnO. (d) Schematic of flat ZnO on Au, showing the Au substrate underneath a smooth ZnO film. (e) SEM micrograph showing the smooth and flat morphology of microwave-nucleated ZnO after the growth step. Scale bar = 5 μm . Inset shows a low magnification view of the entire film on the Au microplate. Scale bar = 40 μm . Right column: Nucleation and growth steps of oven-nucleated ZnO on Au. (f) Schematic of sparse, unfaceted ZnO of varying sizes on a Au microplate formed during the slow nucleation step. (g) SEM micrograph showing the Au microplate after the slow nucleation step, viewed at a tilt of 45°. Scale bar = 1 μm . (h) Schematic of ZnO on Au showing the Au substrate underneath a highly faceted ZnO film. (i) SEM micrograph showing rough and faceted morphology of oven-nucleated ZnO after the growth step viewed at a tilt of 45°. Scale bar = 5 μm . Inset shows a low magnification view of the entire film on the Au microplate. Scale bar = 20 μm .

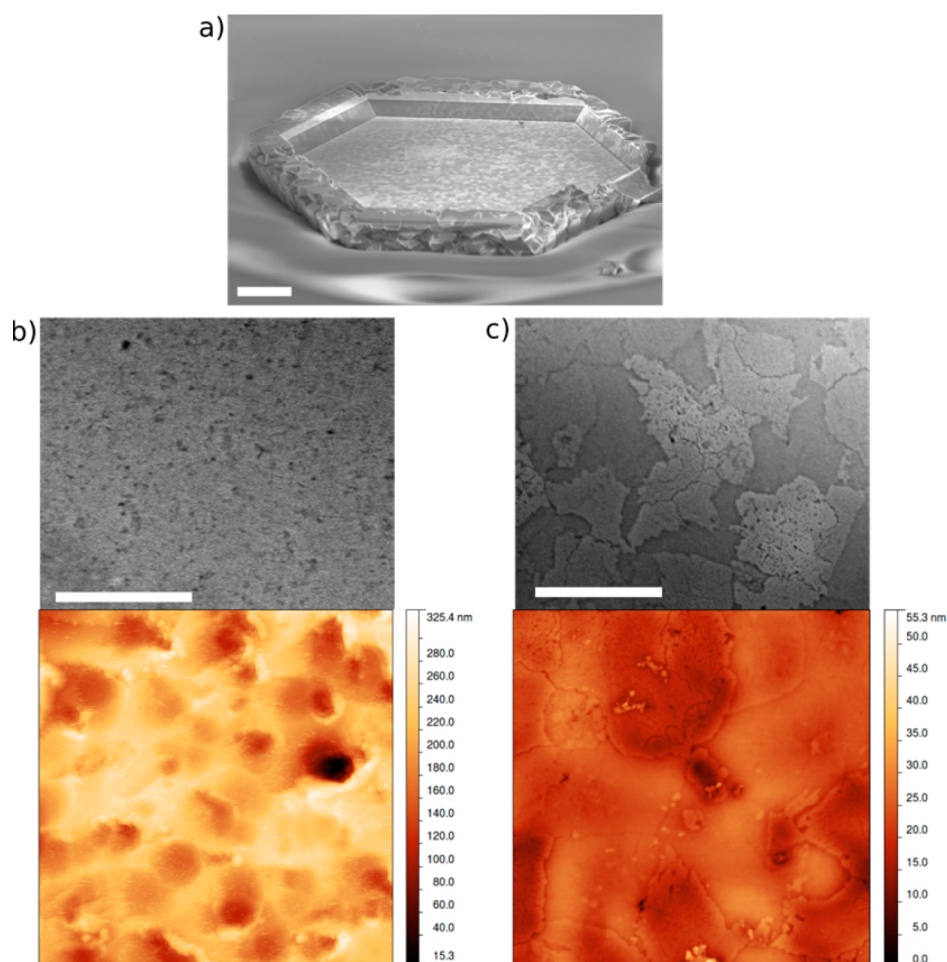


Figure 2. Bottom surface of ZnO. SEM and AFM micrographs of the flipped ZnO/Au microplates after the Au has been removed. (a) Low magnification, 45° tilt view (SEM) of the entire flipped ZnO membrane embedded in photoresist after Au has been etched away. Scale bar = 10 μm. (b) Bottom surface of ZnO nucleated rapidly by microwave heating. (Top: SEM, scale bar = 1 μm; bottom: AFM, 5 μm × 5 μm image.) (c) Bottom surface of ZnO nucleated slowly by heating in a conventional oven. (Top: SEM, scale bar = 1 μm; bottom: AFM, 5 μm × 5 μm image).

the solubility of zinc species in solution through the gradual elevation of temperature.^{19,23} The main difference between the nucleation step and the growth step was the speed at which the temperature was raised. Figure 1 (panels b, d, f, and h) shows schematics of the overall structure of ZnO grown on Au microplates at the different stages of synthesis. Also shown are micrographs from scanning electron microscopy (SEM) of the ZnO film at various stages of growth. Overall film morphology could be changed from flat and smooth (Figure 1, panels b–e) to rough and faceted (Figure 1, panels f–i) by altering the kinetics of the nucleation step.

When the nucleation step was fast, the resulting ZnO film after the growth step was smooth (AFM RMS roughness was ~7 nm) and uniform in height. Individual grains were nearly impossible to discern by SEM (Figure 1e). Microwave heating was used to raise the temperature to 90 °C in 25 s in order to make the nucleation step fast and increase the rate of ZnO formation. Figure 1c shows that the initial seed layer was composed of small densely packed ZnO crystallites on the Au surface. The crystallites were faceted with the expected hexagonal crystal habits and had a columnar structure. The height of each crystallite was uniform across the surface of each Au microplate. Each crystallite grew and coalesced during the growth stage at the same rate, resulting in a smooth ZnO film.

Conversely, a conventional oven raised the sample temperature to 90 °C over 1.5 h, resulting in a much slower nucleation rate. It has been previously shown by Wen et al. that ZnO nanowire arrays may grow without the aid of a seed layer on metal films.²⁴ The nucleation step in the oven described in this work is akin to a very short growth by the method described by these authors. The final ZnO film morphology was composed of many large, hexagonal grains of ZnO with each hexagonal grain oriented in the same direction (Figure 1i). The alignment of each grain indicates that there was an epitaxial relationship between the film and the substrate. Each grain appears smooth and sharply faceted, but since the film is composed of many of these grains, each with a different height, the overall film is extremely rough. ZnO grown on the Si substrate, but not on the Au microplates, shows no signature of alignment. Figure 1g shows that the initial seed layer was composed of islands of ZnO that formed over the course of the nucleation step. ZnO crystallites sparsely populated the surface of the Au. The crystallites that formed were columnar and tall. Because the nucleation did not occur all at the same time, the height of each ZnO column depended on when it was formed during the 1.5 h period. The largest crystallites were ~1 μm tall. A large portion of the surface after the slow nucleation step was populated by granular ZnO particles that lacked any obvious crystal facets.

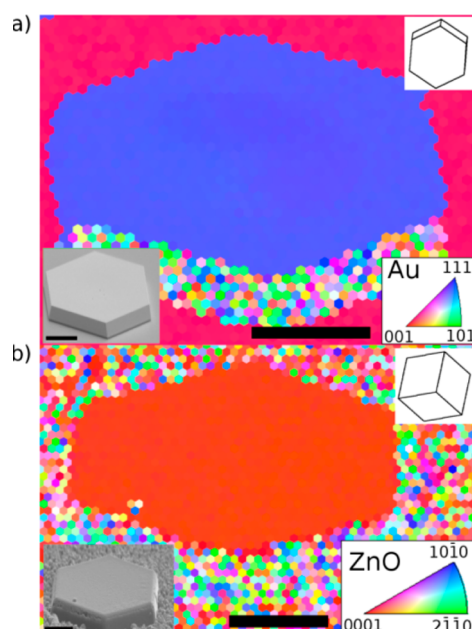


Figure 3. EBSD of a Au microplate before and after ZnO growth. (a) EBSD IPF map of a single crystalline Au microplate. (b) EBSD IPF map of ZnO grown on the same Au microplate. Insets for (a) and (b): top right indicates the orientation of the unit cell of the Au microplate; bottom left is the corresponding SEM micrograph for the EBSD IPF map. Scale bars = 25 μm .

Each of these crystallites, which started growing at different times within the 1.5 h nucleation period, eventually coalesced into a film during the growth step, resulting in a film composed of large hexagonal grains of different heights.

The final thickness of the film grown by fast nucleation was approximately 3 μm (Figure 1a of the Supporting Information), whereas the final thickness of films grown by slow nucleation was approximately 10 μm (Figure 1b of the Supporting Information). The discrepancy in the thickness is due to the selectivity of ZnO growth. The amount of ZnO precursor was the same in both growth solutions, and so we expected to see the total volume of ZnO grown to be equal. When fast nucleation was used, nonselective nucleation occurred on the Si substrate in addition to the nucleation on the Au microplates. Therefore, during the growth step, ZnO was deposited over a large area. In contrast, during slow nucleation, ZnO only nucleated on the metal, which is similar to a previous report.²⁴ Hence, all of the ZnO growth occurred only on the Au microplates. As a result, the ZnO grown on the slow nucleated samples are much thicker because the ZnO grew over a smaller area.

To examine the bottom surfaces of films produced by both techniques, the films were inverted and the Au was removed using a gold wet etch. The bottom surfaces of the films indicate the quality of the interface on a larger scale than cross-sectional TEM and reveal some of the kinetics at the beginning of ZnO growth. The bottom surface of the film produced by fast nucleation was porous (Figure 2b) and had a root-mean-squared roughness of approximately 50 nm, as measured by atomic force microscopy (AFM) (Figure 2b). Rapid nucleation and growth of the ZnO using microwave heating caused gaps to form between each ZnO nanopillar in the initial ZnO layer. Growth of the ZnO nanopillars and their eventual coalescence occurs as zinc species in solution undergo a condensation

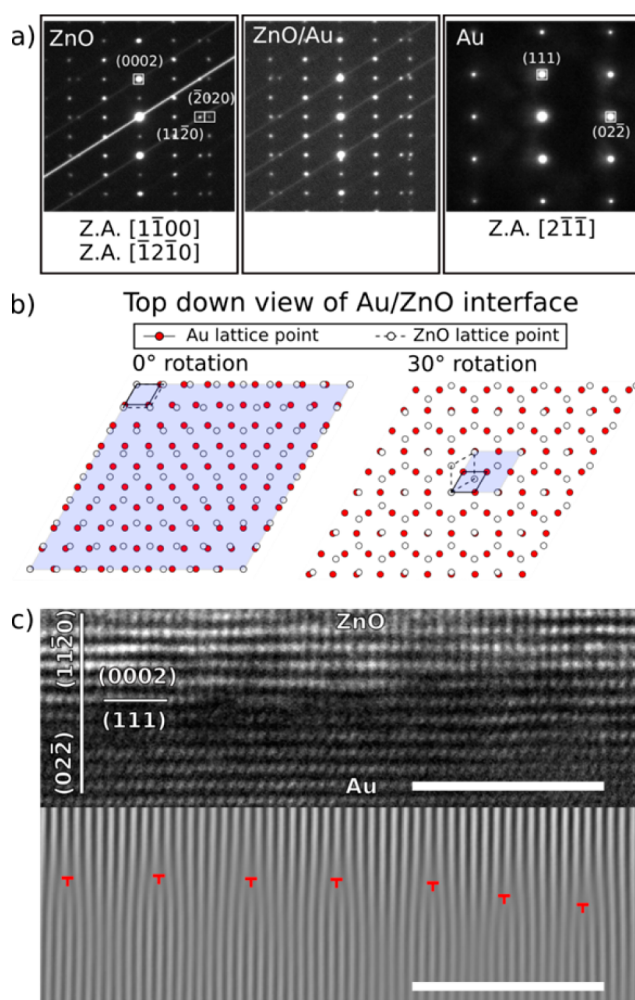


Figure 4. Cross-sectional TEM and SAED confirm epitaxial relationship between Au and ZnO. (a) SAED of ZnO only (left), ZnO and Au (middle), and Au only near the interface (right). (b) Schematic of the 2D projection of the close-packed planes of ZnO(0001) and Au(111) at the interface. The solid line represents the unit cell for Au. The dashed line represents the unit cell for ZnO. The shaded region represents the coincidence lattice. The two possible orientations are those with the ZnO lattice rotated 0° and 30° about the [0001] axis with respect to the (111)[111] Au lattice. These orientations correspond to the two epitaxial relationships found in the SAED. (c) The top panel shows a high resolution TEM micrograph of the ZnO/Au interface. The bottom panel is a Fourier-filtered image of the top panel, which highlights the misfit dislocations present at the interface. Scale bars = 5 nm.

reaction at the surface of the nanopillars. However, for films produced by fast nucleation, we believe that the high density of nanopillars makes it difficult for the zinc species to diffuse to the bottom of the pillars, preventing coalescence of the ZnO near the Au surface before access to the solution is cut off by the growing film. SEM and AFM (Figure 2c) of the film produced by slow nucleation revealed a much smoother surface (RMS roughness of approximately 4 nm) compared to the film prepared by fast nucleation. Here, the nucleation process is much slower and the seed layer is much less dense. Therefore, zinc species more readily access the space between the ZnO seeds, creating intimate contact with the Au surface. Large grains are visible in the SEM and AFM micrographs, but the boundaries do not correspond to a specific crystallographic

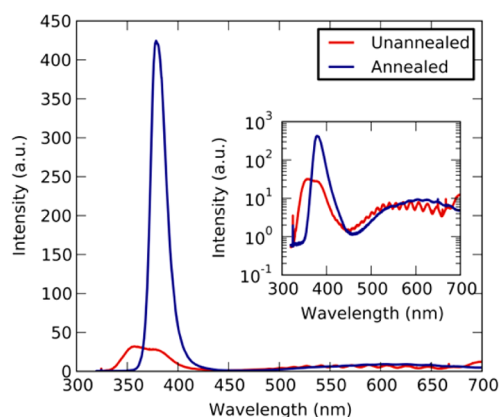


Figure 5. Effects of annealing on photoluminescence of ZnO grown on Au microplates. Photoluminescence spectra of ZnO grown on Au microplates as-grown and after a stepped anneal. The fast nucleation method was chosen to produce the ZnO film for this sample. Inset: A logarithmic-linear scale shows the effects of thin film interference in the defect band of the ZnO.

direction. We are currently investigating the origin of the boundaries which may result from disturbances in the solution growth during the long nucleation period, such as loose precipitates adhering to the substrate or deformation in the Au microplate.

Electron backscatter diffraction (EBSD) was used to reveal the single crystalline nature of the ZnO film on the Au(111) surface and infer the epitaxial relationship over large areas. EBSD inverse pole figure (IPF) determined the surface of the ZnO to be a single grain of ZnO(0001) (Figure 3b) on monocrystalline Au(111) (Figure 3a). Relative misorientation in ZnO and Au at each measured point on the plate was negligible (Figure 2 of the Supporting Information), confirming the absence of large-angle grain boundaries. After accounting for the slight difference of rotation between the two SEM micrographs, the unit cell orientations corresponding to the Au microplate and the ZnO are shown in the insets of Figure 3 (panels a and b), which demonstrate the epitaxial relationship. From the EBSD data, we can infer the full epitaxial relationship between the ZnO film and the Au substrate, $\text{ZnO}[1\bar{1}00](0002)\parallel\text{Au}[2\bar{1}\bar{1}](111)$, which persists over the entire area of the Au microplate. The fast nucleation method was used to produce the film shown in Figure 3. However, ZnO films produced by the slow nucleation method also showed the same epitaxial relationship as probed by EBSD. Ultimately, due to the low angular resolution in EBSD, we relied on TEM and electron diffraction to confirm the epitaxial relationship.

Cross-sectional TEM was acquired to confirm the epitaxy between the ZnO film and the Au microplate. The ZnO film used in cross-sectional TEM was produced by the fast nucleation process. The high-resolution cross-sectional TEM (HRTEM) micrograph (Figure 4c) shows alignment between the Au and the ZnO planes and a fully crystalline interface between Au and ZnO. By Fourier filtering the HRTEM image using only the $\text{ZnO}(11\bar{2}0)$ and $\text{Au}(02\bar{2})$ planes (Figure 3 of the Supporting Information), we obtained an image that highlights the dislocations. On average, dislocations were present for every 8.7 planes of Au and for every 7.7 planes of ZnO ($s_{\text{Au planes}} = 1.4$, $s_{\text{ZnO planes}} = 1.3$, and $n = 38$ dislocations). The observed frequency of dislocations corresponds closely with the expected frequency of dislocations when the two lattices are not rotated with respect to each other, 9 Au planes for every 8 ZnO planes

(Figure 4b). Bright field TEM imaging (Figure 4 of the Supporting Information) shows a columnar microstructure, signaling that ZnO on Au initially grew in islands before coalescing. Selected area electron diffraction (SAED) was used to index the planes present in the cross-sectional TEM micrograph at the interface (Figure 4a). (Streaks in the SAED are camera artifacts.) Unexpectedly, two zone axes of ZnO were present in the SAED, indicating that two orientations of ZnO were epitaxial to the Au substrate at the interface: $\text{ZnO}[1\bar{1}00](0002)\parallel\text{Au}[2\bar{1}\bar{1}](111)$, which has no rotation between the two close-packed lattices, and $\text{ZnO}[\bar{1}2\bar{1}0](0002)\parallel\text{Au}[2\bar{1}\bar{1}](111)$, which has a 30° rotation between the two close-packed lattices (Figure 4b). The $[1\bar{1}00]$ reflections from the ZnO were much stronger than the $[\bar{1}2\bar{1}0]$ reflections, indicating a preferred and dominant crystal orientation. While the 30° rotation is favored in some epitaxial wurtzite films on cubic (111) surfaces, such as ZnO on MgAl_2O_4 ,²⁰ it is slightly more unusual for an analogous epitaxial system, Ag/ZnO.²⁵ Both Ag and Au have similar lattice constants, 4.08 and 4.09 Å, respectively, and the same crystal structure. For the Ag/ZnO system, both epitaxial relationships had similar interfacial energies and the resulting structure was dependent on surface conditions. In experiments of Ag nanocrystal deposition on ZnO,²⁶ both variants were initially observed, but the 30° epitaxial growth was strongly inhibited by the compressive strain in the Ag. In other cases of ZnO grown on textured Ag films by solution growth, the 30° rotated growth was not observed at all.²⁷ Similarly, since we did not observe evidence of the 30° rotation in EBSD after complete growth of the ZnO films, we believe that the nonrotated variant also dominated our growth process.

Finally, to confirm the quality of the ZnO, photoluminescence spectra were measured (Figure 5). Data presented in Figure 5 are from ZnO films produced after a fast nucleation step. Similar PL spectra were also obtained from films produced after a slow nucleation step. As-grown ZnO films showed photoluminescence at unexpectedly low wavelengths. Two peaks were resolved at 354 and 377 nm corresponding to energies of 3.50 and 3.28 eV, respectively, with the peak at 377 nm being more intense. After a stepped annealing of the sample on a hot plate at 250°C for 30 min and then at 300°C for 30 min, an asymmetric peak was observed around 380 nm (3.26 eV). The shift in photoluminescence was attributed to the effects of residual water, remaining in the film after growth in an aqueous solution.²⁸ After annealing, residual $\text{Zn}(\text{OH})_2$ was dehydrated and the remaining water was expelled from the film. With quenching defects from the excess water eliminated by the short anneal, the annealed ZnO exhibited strong UV band edge photoluminescence, characteristic of high quality ZnO, with a small defect band centered around 600 nm.

In summary, heteroepitaxial deposition of continuous ZnO films on single crystalline Au microplates through solution-based techniques has been demonstrated. Our method improves on previous work of epitaxial deposition of ZnO on Au by using a deposition technique without a need for electrical contacts and by obtaining a fully continuous and smooth film. Nucleation of the ZnO seed layer was also investigated and shown to dramatically affect the morphology of the resulting film after growth. Our method of producing modular single-crystalline ZnO/Au plates, which may be formed on a large range of substrates, can facilitate detailed study of metal-semiconductor junctions and new devices, such as micro-

systems-enabled photovoltaics,²⁹ micrometer-scale metal/oxide catalysts, or fully epitaxial ZnO nanopiezoelectric generators.³⁰ These promising results will enable further studies of the electrical and optical properties of the epitaxial ZnO/Au junction.

■ ASSOCIATED CONTENT

● Supporting Information

FIB cross-section of the Au/ZnO structures; pole figures of electron backscattered diffraction of ZnO and Au; method for Fourier filtering of the HRTEM image; and bright-field TEM image of the Au/ZnO interface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Tung, R. T. Proceedings of the 20th Annual Conference on the Physics and Chemistry of Semiconductors Interfaces, Williamsburg, VA, Jan 25–29, 1993. *J. Vac. Sci. Technol.* **1993**, *11*, 1546–1552.
- (2) Russell, K. J.; Liu, T.-L.; Cui, S.; Hu, E. L. *Nat. Photonics* **2012**, *6*, 459–462.
- (3) Lu, Y.-J.; Kim, J.; Chen, H.-Y.; Wu, C.; Dabidian, N.; Sanders, C. E.; Wang, C.-Y.; Lu, M.-Y.; Li, B.-H.; Qiu, X.; Chang, W.-H.; Chen, L.-J.; Shvets, G.; Shih, C.-K.; Gwo, S. *Science* **2012**, *337*, 450–453.
- (4) Badyal, J. P. S.; Nix, R. M.; Rayment, T.; Lambert, R. M. *Faraday Discuss. Chem. Soc.* **1989**, *87*, 121.
- (5) Ip, K.; Thaler, G. T.; Yang, H.; Youn Han, S.; Li, Y.; Norton, D. P.; Pearton, S. J.; Jang, S.; Ren, F. *J. Cryst. Growth* **2006**, *287*, 149–156.
- (6) Gwon, M.; Lee, E.; Kim, D.-W.; Yee, K.-J.; Lee, M. J.; Kim, Y. S. *Opt. Express* **2011**, *19*, 5895–5901.
- (7) Lawrie, B. J.; Mu, R.; Haglund, R. F. *Opt. Lett.* **2012**, *37*, 1538.
- (8) Li, P.; Wei, Z.; Wu, T.; Peng, Q.; Li, Y. *J. Am. Chem. Soc.* **2011**, *133*, 5660–5663.
- (9) Kundu, P.; Singhania, N.; Madras, G.; Ravishankar, N. *Dalton Trans.* **2012**, *41*, 8762–8766.
- (10) Vispute, R. D.; Talyansky, V.; Choopun, S.; Sharma, R. P.; Venkatesan, T.; He, M.; Tang, X.; Halpern, J. B.; Spencer, M. G.; Li, Y. X.; Salamanca-Riba, L. G.; Iliadis, A. A.; Jones, K. A. *Appl. Phys. Lett.* **1998**, *73*, 348–350.
- (11) Gorla, C. R.; Emanetoglu, N. W.; Liang, S.; Mayo, W. E.; Lu, Y.; Wraback, M.; Shen, H. *J. Appl. Phys.* **1999**, *85*, 2595–2602.
- (12) Johnson, M.; Fujita, S.; Rowland, W.; Hughes, W.; Cook, J.; Schetzina, J. *J. Electron. Mater.* **1996**, *25*, 855–862.
- (13) Palmstrom, C. J. *Annu. Rev. Mater. Sci.* **1995**, *25*, 389–415.
- (14) Yoshino, Y.; Inoue, K.; Takeuchi, M.; Ohwada, K. *Vacuum* **1998**, *51*, 601–607.
- (15) Liu, R.; Vertegel, A. A.; Bohannon, E. W.; Sorenson, T. A.; Switzer, J. A. *Chem. Mater.* **2001**, *13*, 508–512.
- (16) Limmer, S. J.; Kulp, E. A.; Switzer, J. A. *Langmuir* **2006**, *22*, 10535–10539.
- (17) Radha, B.; Arif, M.; Datta, R.; Kundu, T.; Kulkarni, G. *Nano Res.* **2010**, *3*, 738–747.
- (18) Radha, B.; Kulkarni, G. U. *Cryst. Growth Des.* **2011**, *11*, 320–327.
- (19) Richardson, J. J.; Lange, F. F. *J. Mater. Chem.* **2011**, *21*, 1859–1865.
- (20) Andeen, D.; Loeffler, L.; Padture, N.; Lange, F. F. *J. Cryst. Growth* **2003**, *259*, 103–109.
- (21) Thompson, D. B.; Richardson, J. J.; DenBaars, S. P.; Lange, F. F. *Appl. Phys. Express* **2009**, *2*, 042101.
- (22) Dammel, R. R. Diazonaphthoquinone-Based Resists. *SPIE Tutorial Texts in Optical Engineering*; SPIE Publications: Bellingham, WA, 1993; Vol. TT11.
- (23) Richardson, J. J.; Lange, F. F. *Cryst. Growth Des.* **2009**, *9*, 2570–2575.
- (24) Wen, X.; Wu, W.; Ding, Y.; Wang, Z. L. *J. Mater. Chem.* **2012**, *22*, 9469–9476.
- (25) Lin, Z.; Bristowe, P. D. *Phys. Rev. B: Condes. Matter Mater. Phys.* **2007**, *75*, 205423.
- (26) Jedrecy, N.; Renaud, G.; Lazzari, R.; Jupille, J. *Phys. Rev. B: Condes. Matter Mater. Phys.* **2005**, *72*, 195404.
- (27) Floro, J. a.; Michael, J. r.; Brewer, L. n.; Hsu, J. w. p. *J. Mater. Res.* **2010**, *25*, 1352–1361.
- (28) Saito, N.; Haneda, H.; Sekiguchi, T.; Ishigaki, T.; Koumoto, K. *J. Electrochem. Soc.* **2004**, *151*, H169–H173.
- (29) Cruz-Campa, J. L.; Okandan, M.; Resnick, P. J.; Clews, P.; Pluym, T.; Grubbs, R. K.; Gupta, V. P.; Zubia, D.; Nielson, G. N. *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 551–558.
- (30) Volk, J.; Nagata, T.; Erdélyi, R.; Bárony, I.; Tóth, A.; Lukács, I.; Czigány, Z.; Tomimoto, H.; Shingaya, Y.; Chikyow, T. *Nanoscale Res. Lett.* **2009**, *4*, 699–704.