ABSTRACT: A design for a heteroepitaxial junction by the way of one-dimensional wurzite on a two-dimensional spinel structure in a low-temperature solution process was introduced, and its capability was confirmed by successful fabrication of a diode consisting of a p-type cobalt oxide (Co$_3$O$_4$) nanoplate/n-type zinc oxide (ZnO) nanorods, showing reasonable electrical performance. During thermal decomposition, the 30° rotated lattice orientation of Co$_3$O$_4$ nanoplates from the orientation of β-Co(OH)$_2$ nanoplates was directly observed using high-resolution transmission electron microscopy. The epitaxial relations and the surface stress-induced ZnO nanowire growth on Co$_3$O$_4$ were well supported using the first-principles calculations. Over the large area, (0001) preferred oriented ZnO nanorods epitaxially grown on the (111) plane of Co$_3$O$_4$ nanoplates were experimentally obtained. Using this epitaxial p−n junction, a diode was fabricated. The ideality factor, turn-on voltage, and rectifying ratio of the diode were measured to be 2.38, 2.5 V and 104, respectively.

KEYWORDS: Epitaxial growth, spinel cobalt (II,III) oxide nanoplate, wurzite ZnO nanorod, heterogeneous p−n junction

As a future electronic materials alternative to silicon, single crystalline metal oxide semiconductor nanomaterials have been noticed as building blocks in many applications, for example, energy harvesting,1–3 photonics,4,5 and electronics,6,7 because of their superior properties, multifunctionality, high crystallinity, quantum size effect, high transparency, stability in air, and so on. Recently, to synthesize these nanomaterials, various solution processes including hydrolysis and condensation of metal cations have been developed and matured for their mass production with control of their size and shape.8–10 However, any route to fabricate a functional device based upon these free-standing nanomaterials has not yet been established due to the difficulties in forming arrays of them as a two-dimensional (2D) monolayer on a substrate and forming electrical junctions between them or a metal electrode.

Discovered by Russell Ohl in 1939, the semiconductor p−n junction has occupied the most important position as an elementary component in current silicon electronics. Therefore, to verify the applicability of single crystalline metal oxide semiconductor nanomaterials in electronics, a reliable fabrication route for a p−n junction device composed of them has to be designed, and also the junction should be epitaxially formed in solution processes to ensure high performance and low process cost. Unfortunately, to date, the fabrication strategy to form this epitaxial junction in a low-temperature solution process has rarely been reported.

Geometrically, 2D single crystalline metal oxide nanomaterials are easy to make as an array with a preferred orientation on a substrate due to its unilamellar micro- and macrostructure. If one can efficiently form arrays of it on a substrate, it can be a good free-standing template for certain one-dimensional (1D) metal oxide nanorods, having an epitaxial relationship with it. Based upon this proposition, as a strategy to solve the above-mentioned issues, we have introduced a design for heteroepitaxial junctions by the way of 1D wurzite on 2D spinel structures in a low-temperature solution process, and its capability was confirmed by successful fabrication of a diode consisting of a p-type cobalt oxide (Co$_3$O$_4$) nanoplate/n-type zinc oxide (ZnO) nanorods showing reasonable electrical performance. Additionally, the mechanism of structural change during preparation of p-type Co$_3$O$_4$ nanorods from single crystalline hexagonal β-Co(OH)$_2$ nanoplates was suggested. Furthermore, first-principles calculations concerning the epitaxial growth of the preferred (0001) oriented n-type ZnO nanorods on a large area 2D array of (111) preferred oriented p-type Co$_3$O$_4$ nanoplates were conducted.

The reason of the choice for Co$_3$O$_4$ and ZnO as test vehicles is that these two materials can be the most significant and
adequate example to verify the capability of our strategy. They show a different semiconducting type as well as have currently been considered as important multifunctional semiconducting materials for various applications, for example, optoelectronic devices,\textsuperscript{11} photoelectrolysis cells,\textsuperscript{12} catalysts,\textsuperscript{13} sensors,\textsuperscript{14} solar cells,\textsuperscript{15} Li ion batteries,\textsuperscript{16} electrochromic devices,\textsuperscript{17} and so on. Furthermore, the flexibility in selection of the connecting metal electrode is a merit of our strategy. The connecting electrode can be sophisticatedly tuned with other p-type ohmic materials instead of gold to match exactly the work function of Co$_3$O$_4$ nanoplates; in the case of a n-type nanoplate, a low work function metallic electrode material should be selected, such as aluminum, indium tin oxide, aluminum-doped ZnO, and so on.

A schematic diagram shown in Figure 1 illustrates our strategy to build nanorods on individual nanoplates including a 2D array of nanoplates, the electrical addressing, and the formation of an epitaxial p–n junction. As a precursor of p-type Co$_3$O$_4$ nanoplate, the solution of single crystalline hexagonal $\beta$-Co(OH)$_2$ nanoplates dispersed in ethyl-alcohol(EtOH) was suspended on water. During these dropping events, a 2D array of the $\beta$-Co(OH)$_2$ nanoplates was spontaneously formed within a few seconds (see Supporting Information 1). Three sequential steps related to the miscible process of dropping EtOH into the water were employed for the formation of the 2D array: spreading, trapping, and packing. When a droplet of EtOH meets the water, some portion of the EtOH goes into the water, and another portion is spread on the surface because there is a kinetic time delay in the miscible process of EtOH and water. The $\beta$-Co(OH)$_2$ nanoplates in the entering portion are mixed with the water; whereas, those in the spreading portion, as the EtOH is gradually dispersed into the water, are trapped by the net force of the surface tension between the air and water. On the surface area confined by the Petri dish, due to the surface pressure from the EtOH spreading, the trapped $\beta$-Co(OH)$_2$ nanoplates are stacked two dimensionally at the opposite side of the wall from the dropping position. The study of the mechanism of this method, alcohol spreading on water, is beyond the scope of this communication and was demonstrated in our previous report as an easy route to obtain 2D monolayers of various water compatible nanomaterials.

After completing the 2D array of the $\beta$-Co(OH)$_2$ nanoplates on water, the array was transferred on to a gold/silicon substrate. For the ohmic contact of p-type Co$_3$O$_4$, the predeposition of gold having high work function (5.1 eV) was adopted. Given that it is often thought that the electrical contact between $\beta$-Co(OH)$_2$ nanoplates and gold is poor upon the transfer process, we attempt to improve this electrical contact by thermal annealing at 450 °C for 2 h. This improvement comes about by thermally decomposing $\beta$-Co(OH)$_2$ to Co$_3$O$_4$, while heating the interface defects between gold and Co$_3$O$_4$ by promoting atomic diffusion of gold to the metal–oxide interface.

Therefore, to make ohmic contact of p-type metal oxide semiconductor nanoplates, the procedure, putting their hydroxide phase nanoplate precursors on a noble metal and then annealing for the thermal decomposition of the hydroxide, can be thought to be a simple strategy for bottom side metallization of single crystalline p-type metal oxide nanomaterials. Additionally, the reason why the p-type metal oxide nanoplates is placed first, rather than n-type metal oxide nanomaterials in our fabrication process, is that n-type ohmic metal can be easily oxidized during hydrothermal reaction for epitaxial growth, while p-type ohmic metal is inert against alkali or acid water. Finally, our strategy was completed by aqueous solution-based epitaxial growth of n-type ZnO nanorods on the 2D array of Co$_3$O$_4$ nanoplates at 80 °C.

Single crystalline hexagonal $\beta$-Co(OH)$_2$ nanoplates were synthesized by the precipitation of an aqueous solution of cobalt(II) chloride hexahydrate (Aldrich 255599) through hexamethylenetetramine (HMTA) hydrolysis in 200 mL of

Figure 1. Overall process of building ZnO nanorods on a Co$_3$O$_4$ nanoplate, including 2D arrays of the nanoplates, the bottom side electrical addressing, and the formation of an epitaxial p–n junction.
mixing solvent, water/EtOH (9:1, v/v). At a fixed mole fraction of divalent cobalt and HMTA (1:1), the temperature (90 °C), concentration (5 mM), and reaction time (from 0.5 to 3 h) were experimental variables. After synthesis, the β-Co(OH)₂ nanoplates were purified using three-times centrifugation at 4000 rpm and were then dispersed in EtOH. Figure 2a shows an optical microscope (OM) image of a large area 2D monolayer of the synthesized β-Co(OH)₂ nanoplates for 1 h, and the difference in contrast of the image represents the deviation of each β-Co(OH)₂ nanoplate thickness. The scanning electron microscope (SEM) result of well-arrayed monolayer of β-Co(OH)₂ nanoplates is shown in Figure 2b, and from the inset in Figure 2b, the nanoplates were distributed with about a 100–200 nm gap. After thermal annealing at 450 °C for 2 h in air, single crystalline hexagonal β-Co(OH)₂ nanoplates were converted into Co₃O₄ nanoplates, and the 2D array was maintained as shown in Figure 2c. From the inset in Figure 2c, the reduction of the diameter of each hexagonal β-Co(OH)₂ nanoplate was observed.

As growth time increased from 0.5 to 3 h, the diameter and thickness of the β-Co(OH)₂ nanoplates increased as shown in Figures 2d. The lateral growth of β-Co(OH)₂ nanoplates was rapidly saturated within 1 h, while the vertical growth was linearly proportional to the time. The visible images of the transferred monolayer of the nanoplates on 1 × 1 cm² bare silicon wafers are exhibited in the insets of Figure 2d. The changes of color mean a difference in thickness with growth time, and a single color through the entire substrate is represented by the uniformity of the β-Co(OH)₂ monolayer. Interestingly, after thermal decomposition, the average diameter of β-Co(OH)₂ nanoplates reduced to about 300 nm, as shown in Figures 2e. Before and after thermal annealing, the diameter changes and surface conditions with respect to growth time are shown in the insets of Figure 2e. As the growth time increases, the surface of β-Co(OH)₂ nanoplates was gradually roughened, and after thermal annealing, the surface of Co₃O₄ nanoplates was observed to be rough in all cases.

To investigate the preferred orientation of the monolayer consisting of β-Co(OH)₂ and Co₃O₄ nanoplates on a substrate, X-ray diffractometry (XRD) indexes were measured for each case, and the results are shown in Figure 2f. From the literature [Joint Committee on Powder Diffraction Standards (JCPDS) 30–0443 (β-Co(OH)₂) and JCPDS 74–1657 (Co₃O₄)], the identities of each XRD peak were identified and referenced. As a result, only {0001} planes were determined for the case of β-Co(OH)₂ nanoplates as shown in Figure 2f. This means that all β-Co(OH)₂ nanoplates were placed with (0001) preferred orientation on the substrate. After thermal annealing at 450 °C for 2 h in air, surprisingly, even though β-Co(OH)₂ nanoplates were thermally decomposed into Co₃O₄ nanoplates, the preferred orientation of the monolayer was maintained by {111} planes of Co₃O₄ instead of {0001}, as shown in Figure 2f. This means that all β-Co(OH)₂ nanoplates were placed with {0001} preferred orientation on the substrate. After thermal annealing at 450 °C for 2 h in air, surprisingly, even though β-Co(OH)₂ nanoplates were thermally decomposed into Co₃O₄ nanoplates, the preferred orientation of the monolayer was maintained by {111} planes of Co₃O₄ instead of {0001}, as shown in Figure 2f. From the XRD peak, changes before and after thermal annealing, it is confirmed that {0001} plane oriented β-Co(OH)₂ nanoplates were converted into {111} plane oriented Co₃O₄ nanoplates. Theoretically, volume shrinkage of β-Co(OH)₂ nanoplates occurs because about 33% of oxygen atoms and 100% of hydrogen atoms were eliminated from β-Co(OH)₂ during the thermal decomposition. Therefore, to release the mechanical stress generated by this shrinkage, many
nanocracks are formed in Co₃O₄ nanoplates, as shown in the inset of Figure 2c. Despite the fact that the volume changes of β-Co(OH)₂ nanoplates are dominated by the above-mentioned dehydration, the macroscopic diameter changes of β-Co(OH)₂ nanoplates, as shown in Figure 2e, are thought to be related to the microstructural change from brucite-like (0001) β-Co(OH)₂ nanoplates with minimum oxygen ions (interplanar spacing \(d_{0(0001)} = 2.329\) and \(d_{0(1000)} = 3.182\) Å) to spinel-like (111) Co₃O₄ nanoplates with minimum oxygen ions (interplanar spacing \(d_{s(111)} = 2.333\) and \(d_{s(220)} = 2.858\) Å).

To critically assess the microstructural changes when β-Co(OH)₂ is thermally transformed to Co₃O₄, we measure and compare the hexagonal lattice orientation of our Co₃O₄ nanoplates (which is topologically derived from β-Co(OH)₂) with that of ideal β-Co(OH)₂ (See Figure 3). Single crystalline β-Co(OH)₂ has a perfect hexagonal plate-shape expanded from hexagonal close-packed system of O²⁻ ions with a Co²⁺ ion in its octahedral interstitial site (CoO₆) and two H⁺ ions in their tetrahedral interstitial site (HO₄), therefore the microscopic in-plane hexagonal lattice orientation can be estimated from the macroscopic hexagonal shape. The bright field image, as shown in the center of Figure 3, represents a perfect hexagonal outline originated from the hexagonal lattice orientation of single crystalline β-Co(OH)₂. To directly investigate the relationship between the side direction and the (111) spinel lattice orientation of Co₃O₄ nanoplates, the hexagonal lattice orientation on the (111) plane of Co₃O₄ nanoplates near each side, from A to F, were determined using high-resolution transmission electron microscopy (HRTEM). From the HRTEM results, it was determined that near the six sides of Co₃O₄ nanoplates, the hexagonal lattice of the (111) spinel plane was presented with an interplanar spacing of 2.86 Å between oxygen ions, as shown in Figure 3. Interestingly, we observed that the orientation of the hexagonal lattice on (111) spinel-like of Co₃O₄ nanoplates is exactly rotated by 30° with respect to the orientation of the hexagonal lattice on (0001) brucite-like of β-Co(OH)₂ nanoplates, as estimated from the direction of the side of a hexagon shape shown in the bright field image of Figure 3. The 30° rotation shown in Figure 3 is thought to be a clue to reveal the mechanism of the kinetic process from brucite (0001) into spinel (111). The formation of Co₃O₄ (i.e., Co²⁺Co³⁺O₄) from Co(OH)₂ is achieved by partially oxidizing the Co²⁺ in Co(OH)₂. In this process, 50% of the octahedral sites are oxidized to the +3 state, while one-eighth of the tetrahedral sites remain in the +2 state. Due to this partial oxidation to its so-called mixed valence oxide, a chemical and structural reordering is observed, manifesting in a
30°-off axis rotation from the original Co(OH)₂ hexagonal template.

For the theoretical prediction of epitaxial relations and surface stress-induced ZnO nanowire growth on Co₃O₄, our first-principles calculations are based on density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP 5.2). We employ the projector augmented-wave method (PAW) and the generalized-gradient approximation (GGA) due to Perdew, Burke, and Ernzerhof (PBE) for the exchange–correlation functional. The wave functions are expanded in a plane-wave basis set with an energy cutoff of 500 eV. For the Brillouin-zone integrations, a Monkhorst–Pack k-point grid of (6 × 6 × 6) is used for bulk Co₃O₄, and a γ-centered k-point grid of (12 × 12 × 8) for bulk ZnO, while a γ-centered k-point grid of (4 × 4 × 1) is used for the interface structures of ZnO(0001)/Co₃O₄(111). A Methfessel–Paxton smearing of 0.1 eV is used to improve the convergence, and the total energy is extrapolated to zero temperature. For all calculations (except for bulk ZnO), a spin-polarization approach is employed. In addition, we include an on-site Coulomb correction within the DFT+U approach for both the Co 3d and Zn 3d states, using an effective U of 3.5 and 5.0 eV, respectively. The calculated bulk lattice parameter of Co₃O₄ is 8.153 Å, while those of ZnO are 3.236 and 5.214 Å (for the a and c lattice constants). These are in good agreement with reported experimental and other theoretical values in the literature.

The interface structures of ZnO(0001)/Co₃O₄(111) are modeled using a symmetric slab with a vacuum region of 12 Å. To construct the atomic geometry of the interface, we consider two models based on previous experimental and theoretical propositions and adapted it for this work. First, based on a thermodynamic stability study of various Co₃O₄ surfaces, it is shown that due to its complex bulk structure, there exist many possible surface terminations for the Co₃O₄(111) surface, with the Co₉ (i.e., Co at the tetrahedral site, referenced to bulk Co₃O₄) termination being most favorable under an oxygen atmosphere. On the other hand, using the plasma-assisted molecular beam approach, epilayers of ZnO (for both O- and Zn-polar films) have been grown epitaxially on MgAl₂O₄, which has a similar bulk spinel structure as Co₃O₄. Based on HRTEM images, the authors propose the epitaxial relationship: ZnO[011]∥MgAl₂O₄[1̅21] and ZnO[21̅1]∥MgAl₂O₄[1̅10]. It also concluded that the surface of the as-prepared substrate should be oxygen terminated. We adopt the similar epitaxial relationship for ZnO/Co₃O₄, given that both Co₃O₄ and MgAl₂O₄ have the same bulk spinel structure. This epitaxial relationship of ZnO(0001) and Co₃O₄(111) is further verified by our own experimental results: The microstructure of a prismatic cross section plane of a ZnO nanorod grown on a Co₃O₄ platelet is determined, as shown in Figure 4.

![Figure 4](image_url)
From the information described above, we construct two interface models, preserving the hexagonal symmetry of the substrate oxide Co₃O₄(111), as shown in Figure 5. The first interface structure between ZnO and Co₃O₄ is bridged by a layer of oxygen, sandwiched between a layer of Zn atoms and a layer of Coₓ (i.e., Co at the octahedral site, referenced to bulk Co₃O₄). Thus, we label this structure as O–Co₃O₄(111) and ZnO(0001) during their epitaxial growth. Our calculated interface formation energies are clearly nonstoichiometric to their corresponding bulk counterparts, the formation energies of these structures will have an explicit dependence on the chosen chemical potential value. Here we consider γ for so-called oxygen-rich and oxygen-lean (or Co-rich) conditions. Under oxygen-rich conditions, we equate μO = 1/2E₂O₃ (half the total energy of the O₂ molecule), and under oxygen-lean conditions, we set μO = ECoO, which is the total energy of a bulk Co atom. At thermodynamic equilibrium, we assume μZnO = 3μCo + 4μO and μCoO = μZn + μO, where μCoO, and μZnO are the chemical potentials of bulk CoO₄ and ZnO, respectively. Thus for the O-rich limit, we have μCo = 1/2(ECoOₓ – 2E₂O₃), and μZn = ECoOₓ + 1/2 E₂O₃, where ECoOₓ and E₂O₃ are the total energies of bulk CoO₄ and ZnO. Similarly, at the O-lean limit, we define μO = 1/4(ECoOₓ – 3E₂O₃) and μZn = E₂O₃ + 1/4(ECoOₓ – 2E₂O₃). For the zinc chemical potential, we have also tested taking it from a reservoir of Zn–Co alloy but found it to be more favorable when considered from the ZnO reservoir.

Under O-rich conditions, the interface formation energy of O–Co₃O₄–Zn–O is found to be 0.29 eV/Å², while under O-lean conditions, it is 0.46 eV/Å². The corresponding values for O–Co₃O₄–Zn–O are 0.30 and 0.47 eV/Å², respectively. Our calculated interface formation energies are clearly endothermic, but it is not an insurmountable energy barrier to overcome. It is also clear that both structures have fairly similar formation energies and are more favored under O-rich growth conditions.

It has been reported that when ZnO is grown on MgAl₂O₄, the interface experiences a large lattice mismatch of about 14% which is considerably large. It has been suggested that such a large lattice mismatch induces a large compressive stress at the interface, leading to so-called columnar growth of the deposited material. This has been proposed as a possible mechanism for oxide nanowire growth on its native metal substrate (e.g., CuOₓ/Cu, Fe₂O₇/Fe, etc.), arguing that due to their structural and density differences and associated large volumetric changes upon oxidation induces substantial accumulated stresses at the metal/oxide interface. Once a critical limit is reached, these stresses are often relieved by forming dislocations along appropriate crystal directions (e.g., the maximum shear strength exists along this direction). Atomic migration then occurs, stacking in the corresponding
plane to maintain a nanowire shape. From our calculations, we find that the ZnO layers near the interface are highly compressed to match the basal area of Co$_3$O$_4$(111). The compressed values of the $a$ and $c$ lattice parameters of ZnO are found to be about 2.90 and 5.52 Å, resulting in a large lattice compression ($\sim-10\%$) in the basal plane and a considerable lattice dilation ($\sim6\%$) in the vertical direction. To estimate the strain energy due to lattice distortion in the compressed ZnO layers, we take the total energy difference between an artificially strained crystal of ZnO ($a=2.90$ and $c=5.52$ Å) and that of the fully relaxed one. In this case, the associated strain energy is found to be 0.428 eV per ZnO formula unit. This large compressive stress in the basal plane could then account for the slight tilting ($\sim10^\circ$) seen in our experiments and would also indicate that the tendency of ZnO growing in the (0001) direction on Co$_3$O$_4$(111) substrate template should be favored, as clearly seen in our experiments.

We note that this proposed stress-promoted growth mechanism might not be the full story of our experiments as the presence of solvating ligands could also play an influential role in modifying the relative surface stability, hence directly affecting the growth kinetics to promote preferential growth planes.

Coincided with the theoretical prediction, (0001) preferred oriented ZnO nanorods were epitaxially grown on (111) plane of Co$_3$O$_4$ nanoplates, as shown in Figures 6a–g. The ZnO nanorods were grown in a 20 mL mixed aqueous solution of zinc nitrate hexahydrate (Alrich 96482) (70 mM) and HMTA (70 mM) at 80 °C. The temporal growth features of ZnO nanorods on the Co$_3$O$_4$ nanoplates were shown in Figures 6a–e. In the initial state for 10 min, tiny ZnO nanorods were observed at several points on the Co$_3$O$_4$ nanoplates. As growth time increases, the shape of ZnO nanorods became thicker and longer than their initial state. Figure 6f shows vertically grown ZnO on the large area for 300 min. As observing results from the hexagonal cross sections of all ZnO nanorods on the Co$_3$O$_4$ nanoplates shown in Figure 6f, the 30° rotating relationship between hexagons for ZnO and Co$_3$O$_4$ nanoplates were determined, as shown as red and yellow hexagons in Figure 6g and Supporting Information, 2-1. Because ZnO nanorods are epitaxially grown based on the (111) plane of Co$_3$O$_4$ nanoplates, the orientation of the lattice in (0001) plane of ZnO nanorods has to be coincident with that in the (111) plane of Co$_3$O$_4$. Therefore, the 30° rotating relationship between the ZnO nanorod’s hexagon and the Co$_3$O$_4$ nanoplate’s hexagonal outline inherited from $\beta$-Co(OH)$_2$ is a natural consequence.

Finally, to verify the capability of our strategy for the large scale epitaxial p–n junction based up on single crystalline metal oxide semiconductor nanomaterials, a heteroepitaxial junction diode consisted of p-type Co$_3$O$_4$ nanoplate/n-type ZnO nanorods was fabricated, as shown in the inset in Figure 7.
evaporator. The electrical characteristics of this device are exhibited in Figure 7, and turn-on voltage and rectifying ratio were measured as 2.5 V and 10^4, respectively. Using the plot of the ln(current) vs voltage, the ideality factor was calculated as 2.38 within the voltage range 0.01 < V < 0.5 V. To investigate the electrical property of each junction of this device, we determined I–V characteristics of Au/Co3O4 platelet/Au, Al/ITO/ZnO nanorod/AI, and Al/ZnO nanorod/Au. From the linearity of the I–V characteristics for Au/Co3O4 platelet/Au and Al/ITO/ZnO nanorod/AI shown in Supporting Information 2-2a,b, it is confirmed that the junctions of Al/ZnO nanorod and Au/Co3O4 platelet are ohmic contacts. Additionally, the I–V characteristics of Al/ZnO nanorod/Au shown in Supporting Information 2-2c represent a typical electrical junction property of metal/semiconductor Schottky diode, in which the turn-on voltage is lower than 1 V. Therefore, it is convinced that the rectifying characteristics of p–n diode, ZnO nanorod/Co3O4 platelet shown in Figure 7 is different from that of Schottky diode of ZnO nanorod/Au.

In summary, a design for a heteroepitaxial junction by the way of 1D wurzite on a 2D spinel structure in a low-temperature solution process was introduced, and it’s capability was confirmed by successful fabrication of a diode consisting of p-type cobalt oxide (Co(OH)2) nanoplate/n-type zinc oxide (ZnO) nanorods, showing reasonable electrical performance. From the thermal decomposition of the 2D arrayed β-Co(OH)2 nanorods, (111) spinel Co3O4 nanorods were obtained, and the 30° rotated lattice orientation of Co3O4 nanorods from the orientation of β-Co(OH)2 nanorods was directly observed using HRTEM. This nanoscale structural change was revealed by the macroscopic geometrical relation between the hexagonal ZnO nanorods and that of hexagonal Co3O4 nanorods. The epitaxial relations and surface stress-induced ZnO nanowire growth on Co3O4 were well supported using the first-principles calculations. Coincided with the theoretical prediction, (0001) preferred oriented ZnO nanorods epitaxially grown on the (111) plane of Co3O4 nanorods were experimentally obtained. Using this epitaxial p–n junction, a diode was fabricated. The ideality factor, turn-on voltage, and rectifying ratio of the diode were measured to be 2.38, 2.5 V, and 10^4, respectively. We expected that the epitaxial p–n junction of p-type Co3O4 nanoplate/n-type ZnO nanorods may have future application in electronic devices. Furthermore, we believe that our design rule, 1D wurzite on 2D spinel using solution processes, can be adopted as a fabrication strategy for various single crystalline metal oxide nanomaterials based heteroepitaxial junction devices.

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