Atomic Nature of the Growth Mechanism of Atomic Layer Deposited High-κ Y₂O₃ on GaAs(001)-4 × 6 Based on in Situ Synchrotron Radiation Photoelectron Spectroscopy

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ABSTRACT: Y₂O₃ was in situ deposited on a freshly grown molecular beam epitaxy GaAs(001)-4 × 6 surface by atomic layer deposition (ALD). In situ synchrotron radiation photoemission was used to study the mechanism of the tris-(ethylcyclopentadienyl)yttrium [Y(CpEt)₃] and H₂O process. The exponential attenuation of Ga 3d photoelectrons confirmed the laminar growth of ALD-Y₂O₃. In the embryo stage of the first ALD half-cycle with only Y(CpEt)₃, the precursors reside on the faulted As atoms and undergo a charge transfer to the bonded As atoms. The subsequent ALD half-cycle of H₂O molecules removes the bonded As atoms, and the oxygen atoms bond with the underneath Ga atoms. The product of a line of Ga−O−Y bonds stabilizes the Y₂O₃ films on the GaAs substrate. The resulting coordinatively unsaturated Y−O pairs of Y₂O₃ open the next ALD series. The absence of Ga₂O₃, As₂O₃, and As₂O₅ states may play an important role in the attainment of low interfacial trap densities (Dₜ) of <10¹² cm⁻² eV⁻¹ in our established reports.

1. INTRODUCTION

Atomic layer deposition (ALD) is a technique that uses chemical vapor depositions for the sequential use of self-terminating gas−solid reactions. High-quality ALD high-κ dielectric films, which are effectively deposited on semiconductors with the thickness from sub-monolayer (ML) to a thick film and a conformal coverage, have greatly improved the device performances of complementary metal−oxide−semiconductor field-effect transistors.¹,² The scaling-down oxide layers with nanometer thicknesses are essential to achieve high-performance microelectronic devices. A thin high-quality oxide film demands a high-quality oxide−semiconductor interface. The high-κ/metal gate technology, which is key to the success of Si complementary MOS devices since the 45 nm node, has a thin ALD-HfO₂-based dielectric on silicates (~0.4 nm thick) but not directly on Si. In fact, high-κ materials that are directly grown on an HF-dipped Si surface result in retardation nucleation and rough surfaces.³ A more two-dimensional (2D) growth and better dielectric properties for ALD oxides require a Si surface with more functional groups such as OH⁻ for the high reactivity of the metal precursors.⁴

We may obtain precise knowledge of the interfacial electronic structure and crystallography on an atomic level, with a semiconductor surface with a long-range order and atomic cleanliness. The literature contains many studies on ALD-oxide films, but few studies mention the growth mode of the oxide in the embryo stage at the oxide−semiconductor interface. Thus, the present investigation is motivated to reach the fine region of a single precursor molecule in contact with the single surface atom of a semiconductor substrate.

We specifically selected the system of ALD-Y₂O₃ on freshly molecular beam epitaxy (MBE)-grown pristine GaAs(001)-4 × 6 because the oxide film orients itself along the surface normal (110), which shows a single-domain single-crystalline cubic...
Moreover, the interfacial trap density \((D_{\text{it}})\) is low \((<10^{12} \text{ cm}^{-2} \text{ eV}^{-1})\), and the \(D_{\text{it}}\) distribution within the GaAs band gap is flat without a peak bulge in the midgap.\(^7\) A similar 3+ oxide, such as \(\text{Al}_2\text{O}_3\), fails to return with such excellent electric performances.\(^1\) In situ synchrotron radiation photoelectron spectroscopy (SRPES) was used to study the interfacial electronic structure of the film in sub-ML thickness to bulk. Note that the pristine GaAs(001)-4×6 has no functional OH- group to react with the metal precursors and does not react with pure \(\text{H}_2\text{O}\). We explore how \(\text{Y}_2\text{O}_3\) grows on GaAs on an atomic level under ALD.

We have found that the tris(ethylcyclopentadienyl)yttrium, \(\text{Y(CpEt)}_3\), precursors selectively adsorb onto the faulted terrace of the GaAs(001)-4×6 surface. The \(\text{H}_2\text{O}\) precursors remove the As atoms bonded with \(\text{Y(CpEt)}_3\), and consequently bond with the underneath Ga atoms. A line of Ga−O−Y bonds is generated, which stabilizes the \(\text{Y}_2\text{O}_3\) films on the GaAs substrate. As a result, the coordinatively unsaturated Y−O pairs open the next cycle of the alternated \(\text{Y(CpEt)}_3\) and \(\text{H}_2\text{O}\) process. A complete growth model of a series of sequential self-termination gas-solid reactions for the ALD-\(\text{Y}_2\text{O}_3\)/GaAs(001)-4×6 surface is presented.

2. RESULTS AND DISCUSSION

Figure 1 shows the As 3d, Ga 3d, and Y 4s core level spectra taken with 120 eV photon energy in various \(\text{Y}_2\text{O}_3\) coverages in unit of angstroms on an atomically clean p-type GaAs(001)-4×6 surface. We have normalized the photoelectron intensity to the background height to observe the spectral evolution. The binding energy (BE) is related to the Fermi level \((E_F)\), which is determined by a freshly deposited silver film in bulk and in the ground with the sample holder. As shown in Figure 1, the intensity of the Y 4s peak gradually increases with a simultaneous decrease in the intensity of the As 3d and Ga 3d peaks. Clearly, the \(\text{Y}_2\text{O}_3\) dielectric oxide can be successfully grown on the GaAs(001)-4×6 surface by ALD without being precovered with a functional group as OH-. The core levels show a decrease in the intensity, and the line shape has also dissimilarly revolved from the clean surface. The former behavior indicates the growth mode of the oxide, and the latter indicates the atom-to-atom interaction at the oxide/GaAs interface.

First, let us discuss the growth mode. The summed areas of both As 3d and Ga 3d lines in a given energy window with various \(\text{Y}_2\text{O}_3\) coverages are plotted in Figure 2. The attenuation curve (black solid line) of an ideal layer-by-layer (laminar) growth is included for comparison. Our previous study demonstrated that the ALD-\(\text{Y}_2\text{O}_3\) film was epitaxially grown on GaAs(001)-4×6 along the (110) direction,\(^5\) which is identical to MBE-Gd2O3 on GaAs(001).\(^14\) One ML is defined to be 3.75 Å, which is one-half of the lattice constant of \(\text{Y}_2\text{O}_3\)(110). \(\lambda_{\text{As}}\) and \(\lambda_{\text{Ga}}\) are the inelastic mean free paths (IMFPs) of As and Ga 3d photoelectrons through the \(\text{Y}_2\text{O}_3\) overlayer, respectively. Because the IMFP is a function of the element and kinetic energy, the used photon energy makes the values of \(\lambda_{\text{As}}\) and \(\lambda_{\text{Ga}}\) 15.99 and 17.41 Å, respectively.\(^5\) As displayed in Figure 2a, the Ga 3d signal almost follows the expected characteristics for a laminar \(\text{Y}_2\text{O}_3\) film growth, which is consistent with previous reflection high-energy electron diffraction (RHEED) results.\(^5\) By contrast, the intensity of As 3d decreases below the referenced 2D growth curve (Figure 2b). This behavior is abnormal for the ordered laminar \(\text{Y}_2\text{O}_3\) film and warrants further investigation. Argument on the diffusion of the As atoms to the \(\text{Y}_2\text{O}_3\) overlayer fails to explain the attenuation data under the 2D growth curve because the intensity in the highly surface sensitive scan would be enhanced, and the slower attenuation rate should make the data above the 2D growth curve. One possible explanation is that the surface As atoms have been removed during the ALD process.

For a layer-wise film as the present \(\text{Y}_2\text{O}_3\), the intensity \(I\) of the core level photoelectron emission from the GaAs substrate attenuates with coverage \(\theta\) as follows

\[
I = I_0 \times \exp(-\theta/\lambda)
\]
where $\lambda$ is the IMFP of photoelectrons through the Y$_2$O$_3$ overlayer and $I_0$ is the intensity of the photoelectrons for a clean GaAs surface, which is determined as

$$I_0 = I_i \times (1 - \exp(-d_0/\lambda_o))^{-1}$$

(2)

In eq 2, $I_i$ is the intensity of the photoelectrons emitted from the surface atoms; $d_0$ is the one-ML thickness of GaAs(001), which is defined to be 2.83 Å and one-half of the lattice constant of GaAs(001); and $\lambda_o$ is the IMFP of photoelectrons through the GaAs sample. We assume that the $x$ percentage of the surface atoms is removed, and eq 1 becomes

$$I = (I_o - x \times 100\% \times I_e) \times \exp(-\theta/\lambda)$$

(3)

The intensity $I_{As}$ over $I_{Ga}$ in a given thickness is calculated as

$$I_{As}/I_{Ga} = [(I_{As} - x \times 100\% \times I_{Ga}) \times \exp(-\theta/\lambda_{As})] / [I_{As} \times \exp(-\theta/\lambda_{Ga})]$$

(4)

The As–Ga signal ratio was measured in a scan that simultaneously covered the As 3d and Ga 3d core levels to avoid the fluctuated photon flux in different measurements of $I$ and $I_o$. The As–Ga intensity ratios for the clean and 23 Å covered surfaces are 0.53 and 0.45, respectively. A thick film is selected to bypass the interfacial reaction. The values of $\lambda_{As}$ and $\lambda_{Ga}$ are 10.41, 15.99, and 17.41 Å, respectively. The insertion of these values to eqs 2 and 4 returns the value of $x$, which is approximately 18%.

Ohtake et al. proposed a model for the GaAs(001)-4 × 6 surface (Figure 3a). There are 24 As atoms per unit cell above the almost undisturbed Ga layer, which amounts to 1 atomic layer of As atoms. Twelve of these As atoms have four Ga neighbors and properties similar to those of the bulk As. The remaining 12 As atoms have 3 Ga neighbors and exist in 4 different environments (3 environments if a minor difference is ignored), which correspond to populations of 2, 4, and 6 and are marked as As(3), As(1), and As(2), respectively. In the established reports, we have demonstrated that the As(1), As(2), and As(3) atoms are parts of the As 3d core level spectrum with the bulk component.

The detailed energy positions of the surface As atoms are shown in Figure 3b. The As(1) component predominates the emission on the high BE side and is shifted by 0.14 eV, whereas both As(2) and As(3) components are on the low BE side and are shifted by 0.19 and 0.59 eV, respectively. The $x$ value of 18% is the occupancy of the faulted terrace As(1) atoms in the surface unit cell. In other words, the As(1) atoms are subjected to be totally removed upon deposition of one ML of ALD-Y$_2$O$_3$.

Now, we discuss the change in the line shape. An analysis of the line shape of the As 3d and Ga 3d core level spectra in the embryo stage will justify the aforementioned proposal. Figure 4a displays the half-cycle Y(CpEt)$_3$–only spectra plotted on top of the clean surface counterparts (black curves) for close comparisons. The BE calibration maintains the same precision as in Figure 1. As displayed in Figure 4a, the Y(CpEt)$_3$ precursors have different effects on the Ga and As surface atoms. They simply bypass the Ga atoms and leave the energy position and line shape of the Ga 3d core level spectrum virtually unaltered. However, the precursors introduce a tail to the As 3d core level spectrum mainly in the high-energy region but not in the low-energy region. Clearly, the Y(CpEt)$_3$ precursors tend to affiliate to the As(1) atoms instead of As(2) and As(3) atoms. Furthermore, the inset of Figure 4a shows the spectral cutoff region, where the Y(CpEt)$_3$/GaAs(001) system distinctly marks the cutoff shift from the GaAs(001) surface. Because the band-bending effect is absent in the Ga 3d states induced by the Y(CpEt)$_3$ precursors, the 0.35 eV downward movement indicates that the local vacuum level drops because of the presence of the surface dipoles with the direction pointing outward. The surface dipoles are generated between the Y(CpEt)$_3$ and As(1) atoms. Because Y(CpEt)$_3$ is not a polar molecule, the surface dipole likely results from the charge-transfer effect. Recently, we have illustrated a unique surface characteristic of GaAs(001), which exhibits high surface electronegativity. With this characteristic and the direction of the surface dipole, a bonding state will appear at a lower energy position than the As(1) component. Indeed, a fit to the Y(CpEt)$_3$–covered As 3d core level spectrum would resolve an induced As*–Y component at a few tenth million electronvolts from the As(1) component (Figure 4b). The strength of the As*–Y component grows with the expense of the As(1) component. Note that neither As(2) nor As(3) components in Figure 4b show any intensity decrease in a fit. The As* component must be included in the model function for a proper fit (see below). The interfacial reaction schematic is drawn in Figure 4c.

Figure 5a shows the acquired core level spectra of a complete ALD cycle, which includes the H$_2$O precursors with representations of one and three cycles of depositions. The growth rate of Y$_2$O$_3$ is 0.4 Å per cycle in the sub-ML region. The plot is normalized to a constant peak height in reference to a zero background. Here, we discuss the a priori evolution of the Ga 3d core level spectra. Figure 5a shows that the H$_2$O purge affects the Ga 3d line shape to show an induced state (Ga*) at a high BE tail, which gradually increases in strength with increasing cycles of deposition. The line shape with a fit is
analyzed in Figure 5b. Three surface-related Ga(1), Ga(2), and Ga(3) components are found at −0.19, +0.22, and +0.44 eV, respectively, relative to the bulk component Ga(B). Upon the growth of the ALD-Y$_2$O$_3$ oxide, the Ga$^*$ component grows at the expense of the Ga(1) component. According to the resolved energy position at 20.10 eV, the Ga$^*$ component is likely associated with Ga$_2$O (Ga$^+$). In other words, the Ga(1) atoms begin to bond with oxygen, that is, the oxygen atom in H$_2$O has replaced the bonding role of Y(CpEt)$_3$ to bond with the Ga atoms. Because the Ga(1) atoms are beneath the As(1) atoms in the faulted terrace, the As(1) atoms become stripped off in the exchange reaction. The removed As atoms appear as the As$^*$ component on the high-energy tail of the 3d spectrum (left panel of Figure 5b). The increased cycles of deposition gradually decrease the intensity of the As(1) component and enhance the strength of the As$^*$ region. Note that the As−Y component in the half-cycle spectrum is no longer present. The bonding role of Ga is not unreasonable because the bonded As(1) atom with extra charge from Y(CpEt)$_3$ in it has weakened the original As−Ga bonds because of charge redistribution. Consequently, the following N$_2$ purge and high pressure of the H$_2$O vapor in the ALD processes easily remove the bonded As(1) atoms. The 41.5 eV BE of As$^*$ suggests that it is neither from As$_2$O$_3$ (44.3 eV) nor from As$_2$O$_5$ (45.3 eV), but instead from pure As. In a separate experiment on an annealed ALD-Y$_2$O$_3$ (8 cycles)/GaAs(001)-4 $\times$ 6, as shown in Figure 6, heat immediately wipes off the As$^*$ component, suggesting that it could not be associated with the interfacial bonding state, but rather with the freed As in the oxide overlayer. It is noted that the Ga$_2$O (Ga$^+$)-like state, Ga$^*$, does not result in the gap state. The absence of the interface defect state from the Ga$_2$O$_3$ (Ga$^{3+}$)-like gap state (20.70 eV) explains well the low $D_{it}$ (<10$^{12}$ cm$^{-2}$ eV$^{-1}$) in our previous study (ref 7). Figure 7 shows the development of the Y 3d core level spectra at a photon energy of 190 eV from sub-ML to a thick Y$_2$O$_3$ film. The BE of the Y 3d$_{3/2}$ state below 4.6 Å of thickness appears at approximately 158.20 eV, which suggests that the stoichiometric Y$_2$O$_3$ oxide has already formed at this sub-ML

Figure 4. (a) As 3d and Ga 3d core level spectra for the Y(CpEt)$_3$-only deposition (half cycle) compared to the clean surface spectra; (b) fit to the As 3d core level spectrum for half cycle; (c) schematic drawing for the reaction between Y(CpEt)$_3$ and the GaAs(001)-4 $\times$ 6 surface.

Figure 5. (a) As 3d and Ga 3d core level spectra for the complete Y(CpEt)$_3$ and H$_2$O reaction (one and three cycles) compared to the clean surface spectra; (b) corresponding fitting results.
Nevertheless, the energy position is 0.68 eV higher than that of a thick Y₂O₃ film. The behavior is not unusual but reflects a change of the Y chemical environment. A similar phenomenon occurs at the Y₂O₃/Si interface, where Y shows a transition from yttrium silicate at the interface to pure Y₂O₃ when the film grows. Presently, the Y atom has the Ga atom as the second nearest neighbor for the Y−O−Ga bonding configuration at the interface, which is in contrast to Y in Y₂O₃ in the Y−O−Y configuration. The differences in the electronegativity of Ga, O, and Y further cause the observed energy shift. Note that the shift occurs after one ML of coverage.

The development of the O 1s core level spectra acquired by in situ X-ray photoelectron spectroscopy (XPS) is shown in Figure 8. Two peaks appear in every Y₂O₃ coverage. Components O−Y and O* appear at approximately 529.8 and 531.8 eV, respectively. O in the O−Y component is emitted from the stoichiometric Y₂O₃ film, whereas O in the O* component is emitted from the Ga−O−Y bonding configuration at the interfacial layer and O−H on the surface originates from water absorption. The Ga−O−Y bond dominates the O* component in the sub-ML coverage, which is replaced by O−H in a thick Y₂O₃ film.

The schematic drawing of the interfacial reaction in the embryo stage is plotted in Figure 9. First, the Y(CpEt)₃ precursors bond with the surface As(1) atoms, and the listed reaction is written as

$$\|\text{GaAs} + \text{Y(C₇H₉)₃}(g) \rightarrow \|\text{GaAs} - (\text{C₇H₉})₃$$  (S)

where the symbol \(\|\) denotes the surface group and (g) denotes the molecule in the gas phase. The next water vapor deposition activates the ligand-exchange reaction to remove the As(1) atom. Y₂O₃ is produced and bonds with Ga via oxygen as follows

$$2\|\text{GaAs} - \text{Y(C₇H₉)₃}(g) + 3\text{H₂O}(g) \rightarrow (\|\text{Ga})₂ - \text{Y₂O₃} + 6\text{C₇H₁₀}(g) + 2\text{As}$$  (6)

Gaseous \(\text{C₇H₁₀}\) and most freed As atoms are readily purged oFF by nitrogen in the ALD processes. Note that Ga−O bonds provide a strong bonding strength to stabilize the Y₂O₃ layer bonded with GaAs. However, the size of the Y₂O₃ unit is 5.3 Å, which is close to the lattice constant of 5.65 Å of GaAs(001). The steric hindrance effects caused by the ligands promote the growth of Y₂O₃ films, which tilt into the (110) direction to relax in a spacious region.

After the GaAs surface is completely covered with Y₂O₃, the growth of the Y₂O₃ film can be referred to that of the Al₂O₃ film using trimethylaluminum and water as the precursors. In other words, the Y(CpEt)₃ precursor in the next cycle dissociatively reacts with coordinatively unsaturated Y−O pairs and becomes

$$\|\text{Y−O}||\text{Y(C₇H₉)₃}(g) \rightarrow \||\text{Y−C₇H₉}) + ||\text{O−Y(C₇H₉)(g)}$$  (7)

The H₂O deposition to complete the ALD cycle becomes

$$||\text{Y−C₇H₉}) + \text{H₂O}(g) \rightarrow ||\text{Y−OH} + \text{C₇H₁₀}(g)$$  (8)

and

$$||\text{O−Y(C₇H₉)₂} + 2\text{H₂O}(g) \rightarrow ||\text{O−Y−(OH)₂}) + 2\text{C₇H₁₀}(g)$$  (9)

Again, the gaseous products are removed from the ALD chamber by the nitrogen purges. Equations 8 and 9 show that the Y₂O₃ film surface is always terminated with an \(\text{OH}^-\).
OH deposition and N2 purge. The oxygen atom in H2O takes over followed in the study. We have found that the Y(CpEt)3 change of Ga 3d, As 3d, Y 3d, and O 1s states are coherently the cycling agents. The intensity evolution and line shape terrace. The attainment of low interface forms with the Ga 2O (Ga+)-like bonds along the faulted As atoms are removed, and the Y2O3/GaAs(001) the bonding role with the Ga atom. In the present system, the As2O3, and As2O5 states. In contrast to the high- the ALD-Y2O3 oxide was successfully grown on the GaAs(001)-×4. EXPERIMENTAL SECTION

4.1. ALD-Y2O3 Growth. The MBE chamber, ALD reactor, and analysis chamber of XPS were in a multichamber ultrahigh vacuum (UHV) growth/analysis system. All chambers were connected via transfer modules, which were maintained at 10⁻¹⁰ Torr to ensure that the sample surfaces are free of contamination in the entire process. GaAs epi-layers (Be-doped, 1 × 10¹⁷ cm⁻³) were grown on 2in. diameter p-type GaAs(001) substrates using a solid-source GaAs-based MBE. A 4 × 6 reconstructed GaAs surface was obtained by annealing the samples to 550 °C, as examined by RHEED. The freshly MBE-grown GaAs(001)-4 × 6 sample was in situ transferred to the ALD reactor under UHV. The ALD-Y2O3 process was performed with the precursors, Y(CpEt)3 and H2O. Y(CpEt)3 was injected into the reactor with a pulse time of 2.1 s; then, high-purity N2 (99.9999%) purge was performed for 10 s. To increase the dosage of Y(CpEt)3 precursors in an ALD cycle, the aforementioned sequence was repeated three times before introducing H2O vapor to complete the ALD cycle. The dosage of H2O vapor per ALD cycle was maintained once with a pulse time of 2.1 s; however, the subsequent N2 purge time was reduced to 8 s. The ambient temperature of growth was set at 270 °C.

4.2. Transfer. The SRPES experiments were performed at the National Synchrotron Radiation Research Center in Taiwan, which is approximately 7 km from the film growth laboratory. Thus, the Y2O3/GaAs(001)-4 × 6 sample was transferred to the SRPES end station via a portable UHV chamber, in which a pressure below 5 × 10⁻¹⁰ Torr was maintained to retain the contamination-free surface.

4.3. Characterization. The SRPES photoelectrons were collected and analyzed using a 150 mm hemispherical analyzer (SPECS) in a UHV chamber, in which the base pressure was less than 5.0 × 10⁻¹⁰ Torr. Monochromatic radiation was provided via a low-energy spherical grating monochromator with photon energies of 20–200 eV. The energy resolution was estimated by the full width at half-maximum of a Gaussian function, which was fitted with the Fermi edge slope of the valence band spectrum of the Ag reference film mounted on the metal sample holder. Here, the resolution of approximately 70 meV for a photon energy of 120 eV was obtained. The O 1s core level spectra were analyzed using in situ high-resolution XPS with an Al Kα (1486.7 eV) monochromatic X-ray source. An energy resolution of approximately 0.25 eV was obtained by fitting the Fermi edge of the Au reference film. The atomic ratio of Y–O in the Y2O3 film was deduced from a comparison of the relative signal area of the Y 3d and O 1s states in the survey XPS data. The sensitivity factors for a photon energy of 1486.7 eV were obtained from the tabulated cross-sections and had values of 0.082 for Y 3d and 0.04 for O 1s. As a result, the atomic ratio of Y–O is 0.65 ± 0.02 for the Y2O3 thickness of above 9 Å, which is identical to that of stoichiometric Y2O3.

3. CONCLUSIONS
We have investigated the embryo stage of ALD precursor adsorption on GaAs(001)-4 × 6 using Y(CpEt)3 and H2O as the cycling agents. The intensity evolution and line shape change of Ga 3d, As 3d, Y 3d, and O 1s states are coherently followed in the study. We have found that the Y(CpEt)3 precursors mainly reside on the faulted terrace in the embryo stage. The footed As atoms are readily removed upon H2O adsorption on GaAs(001)-4 × 4 and analysis chamber of XPS were in a multichamber ultrahigh vacuum chamber, in which a pressure below 5 × 10⁻¹⁰ Torr was maintained to retain the contamination-free surface. The O 1s core level spectra were analyzed using in situ high-resolution XPS with an Al Kα (1486.7 eV) monochromatic X-ray source. An energy resolution of approximately 0.25 eV was obtained by fitting the Fermi edge of the Au reference film. The atomic ratio of Y–O in the Y2O3 film was deduced from a comparison of the relative signal area of the Y 3d and O 1s states in the survey XPS data. The sensitivity factors for a photon energy of 1486.7 eV were obtained from the tabulated cross-sections and had values of 0.082 for Y 3d and 0.04 for O 1s.

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Figure 9. Schematic drawing of Y(CpEt)3 precursors (a) deposited on GaAs(001)-4 × 6, (b) with subsequent H2O deposition.
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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by the Ministry of Science and Technology, Taiwan with Grants MOST 105-2112-M-415-005, 106-2112-M-002-010, 105-2112-M-007-014-MY3, 106-2622-8-002-001, and 105-2112-M-213-007-MY3. We also acknowledge the technical support from Ten-Hsun Lin, Keng-Yung Lin, and Lawrence B. Young.

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