Heteroepitaxial Growth of GaN on Unconventional Templates and Layer-Transfer Techniques for Large-Area, Flexible/Stretchable Light-Emitting Diodes

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1. Introduction

Gallium nitride (GaN) can form a continuous alloy system with InN or AlN, in which the direct bandgaps can be varied from 0.65 eV (InN), to 3.43 eV (GaN), to 6.04 eV (AlN) at room temperature. This wide spectral range enables potential applications from the infrared to the deep ultraviolet regions of the electromagnetic spectrum. This makes GaN-based nitrides one of the most important materials for light sources such as light-emitting diodes (LEDs).[1–5] Sapphire has long been used as a substrate for GaN-based LEDs, and silicon (Si) is becoming its strong competitor due to the advantages of its scalability and lower production costs.[6–10] Lattice mismatch values (defined here as \((a_{\text{GaN}} - a_{\text{sub}})/a_{\text{sub}}\)) of GaN on sapphire and Si are as high as 16.1 and −16.9%, respectively. As a consequence, the resulting GaN layers are highly defective, with a typical threading dislocation density (TDD) in the range of about \(1 \times 10^8 –2 \times 10^{10}\) cm\(^{-2}\).[11–13] which is five orders of magnitude larger than that for conventional AlGaAs or AlInGaP LED materials. Nevertheless, GaN-based materials, including In\(_{x}\)Ga\(_{1-x}\)N, exhibit highly efficient photoluminescence (PL) (more than 50% efficiency), which poses interesting questions as to the role of the defects.[14–18] Even polycrystalline In\(_{x}\)Ga\(_{1-x}\)N materials have intriguing PL characteristics.[19,20] Such PL characteristics, which are insensitive to lattice mismatch or the TDD, motivate further studies into the growth of GaN on unconventional substrates such as glass, which are scalable to much larger areas with lower costs than Si.[21,22] However, there remain two major challenges for exploiting glass as a growth template for GaN-based optoelectronic devices: its amorphous nature and its low melting point. The former impedes epitaxial growth, and the latter results in poor crystal quality, yielding randomly oriented, polycrystalline GaN.

Here, we review recent progress in heteroepitaxial growth of GaN, both on amorphous and on large-scale single-crystalline substrates through the use of appropriate interlayers (ILs), as well as progress in low-temperature GaN growth which has enabled successful demonstrations of GaN-based red–green–blue (RGB) LEDs on glass substrates.[23–26] We also review layer-transfer techniques for GaN thin films grown on ILs onto foreign substrates for high-performance flexible/stretchable lighting applications. Large-scale, flexible inorganic LEDs could be applied for flexible LED TV displays, large-scale...
energy-efficient lighting, or window displays in the future. Furthermore, single-crystalline, GaN-based, flexible electronics, which promise higher efficiency, reliability, and a long lifetime, can replace the aim of organic flexible electronics in a range of applications, i.e., biomedical applications exploiting high electron mobility transistor-based sensors or wearable electronics.

2. Template Structures Used for GaN Heteroepitaxy

All device structures discussed in this review consist of a stacked GaN, a nucleation layer (NL), an interlayer (IL), and a substrate (SB). Figure 1 shows an illustration of the atomic arrangements of the four different layer structures that will be discussed. For clarity, only a few atomic layers near the interfaces are shown (see dotted rectangles in the Supporting Information Figure S1; see Figure S2 for all of the superimposed layers). The NL works as a layer that provides uniform nucleation for the growth of GaN, which will be discussed later, and the IL is implemented for heteroepitaxy with GaN.

2.1. Interlayers

ILs have been formed on various substrates, including both amorphous (Figure 1a,c) and single-crystal substrates such as c-sapphire (Figure 1b) and (111) Si (Figure 1d) for the purpose of GaN heteroepitaxy and transfer to foreign substrates. Typical ILs have a hexagonal structure with the basal (001) plane parallel to the surface of the substrate: a simple hexagonal structure (e.g., graphene,[29–33] hexagonal boron nitride (h-BN),[34] aluminium nitride (h-AlN),[35,36] wurtzite), and a hexagonal close-packed structure (alpha titanium (α-Ti)).[37–39] The calculated lattice mismatch (LM) values of GaN on sapphire, Si, ZnO, AlN, and Ti are 16.1, –16.9, –1.9, 2.5, and 8.1%, respectively (see the Supporting Information for further details). The use of hcp zirconium and hafnium provides LMs of –1.3, –0.2%, respectively, thus these are also considered promising candidate materials for ILs. Materials that have a face-centered cubic (fcc) structure with the (111) growth plane are also candidates for ILs. Overall, materials with three-fold or six-fold symmetry and lattice constants close to that of GaN have potential as ILs.

Most hetero-interfaces (including those shown in Figure 1a,c,d) are formed by connecting the dangling bonds of the two surfaces (left side panel, Figure 1e). There is a different type of hetero-epitaxial interface (center and right panels, Figure 1) termed van der Waals epitaxy (vdWE), in which the role of dangling bonds is minor. In a broad sense, epitaxial growth of 2D layered materials on 2D (center and right panels, Figure 1b) or passivated 3D substrates (right side panel, Figure 1e), as well as 3D materials on 2D substrates, can be classified as vdWE, in which the material on at least one side of the interface does not have dangling bonds. Both 3D on 2D (e.g., ZnO or AlN on graphene, or AlGaN on BN) and 2D on 3D (h-BN on sapphire) interfaces, vdWE have been reported. The requirement for the lattice matching conditions for vdWE is drastically released, allowing a large variety of different heterostructures,[40–47] even for highly lattice mismatched systems (e.g., LM = 58% for MoSe2 on mica).[48] Moreover, such 2D materials can act as excellent IL layers not only for single-crystals but also for amorphous substrates.[32,33] For example, multilayered graphene can be easily synthesized on Ni foil and
transferred to an amorphous substrate for GaN growth (this will be discussed in detail later). As shown in Figure 1, the LMs for GaN on graphene, ZnO on graphene, GaN on h-BN, and h-AlN on h-BN are 29.8, 32.3, 26.5, and 23.4%, respectively. These LM values may be too high to achieve conventional epitaxy, however, high-quality deposited layers can be achieved via vdWE.

2.2. Internal Quantum Efficiencies of In$_x$Ga$_{1-x}$N on Various Templates vs. the Dislocation Density

Figure 2 shows the internal quantum efficiency (IQE) of various In$_x$Ga$_{1-x}$N-based materials as a function of the different indium composition $x$ that changes the PL peak
wavelength,

InGaN can have various forms, including 2D and 3D multiple quantum wells (MQWs) or double heterojunctions (DHs), formed on different substrates including sapphire, Si, and glass. In the plot, the IQE is approximated as the ratio of the integrated PL intensity at room temperature (300 K) to that at low temperature (e.g., 8, 10, or 15 K); in some cases (marked by the asterisks in Figure 2a), x is estimated from (b). By increasing x, 2D InGaN MQWs formed on c-plane sapphire can achieve a high IQE of more than 75%, especially in the blue-emitting region (0.14 < x < 0.18), despite the high dislocation density of 1×10^9 cm\(^{-2}\).[49] With further increases in x, the IQE gradually decreases because of the large lattice mismatch between GaN and InGaN. 2D MQWs on (111) Si exhibit similar IQEs of 75% and 64%, with respective dislocation densities of 1×10^9 cm\(^{-2}\) and 3×10^9 cm\(^{-2}\).[50] 3D MQWs of a nanorod formed on c-plane sapphire also exhibit similar IQEs of ≈20–50%.[51,52] Interestingly, 2D or 3D MQWs and DHs grown even on amorphous substrates exhibit high IQEs, with the estimated dislocation densities in the range 0.5–9×10^9 cm\(^{-2}\); 3D MQWs on micro-pyramid/Ti/glass exhibit IQEs in the range 32–52%.[37] More surprisingly, 2D DHs formed at low temperatures on sapphire exhibited an IQE of 24% in the red part of the electromagnetic spectrum,[26] and 2D MQWs on graphene/glass formed even at low temperatures exhibited 7.4%.[27] With green region emission. As shown in Figure 2a, the dislocation densities of the 3D MQWs on micro-pyramid/Ti/glass substrates, 2D DHs on sapphire, and 2D MQWs on graphene/glass were estimated from the top[39] and bottom[44,46–51] panels of Figure 2b. These unusually high IQEs can be explained by considering the following. First, optical emission from InGaN on glass substrates occurs via a defect-insensitive mechanism,[14]

Second, InGaN formed on graphene IL/glass may actually have a significantly lower defect density than expected due to vdW growth, which allows large LMs, as well as the use of glass instead of a single-crystal substrate, which alleviates epitaxial strains backwards to the substrate. Such a high IQE shows the potential for the realization of true RGB electroluminescent (EL) devices on glass, which will be discussed in detail later.

2.3. Available Nucleation Layers in the Templates

With conventional metal organic vapor deposition (MOCVD), uniform nucleation of high-temperature (≈1040 °C) GaN (HT-GaN) is essential to form uniform, highly crystalline, 2D GaN, which often requires the use of a NL. Low-temperature (<600 °C) GaN (LT-GaN) or AlN is typically used as the NL on sapphire or Si (111) prior to HT-GaN growth. Here, we discuss whether the above mentioned ILs, including 2D layered materials, form effective NLs for HT-GaN growth. First, it has been shown that titanium (Ti) IL is a poor NL. For example, in radio-frequency (RF)-plasma assisted molecular beam epitaxy, a Ti layer is used, even as an HT-GaN growth mask, as HT-GaN rarely nucleates on Ti.[59,60] With MOCVD, LT-GaN (560 °C) is formed on a Ti IL as a uniform NL for HT-GaN.[1] Only at a sufficiently low temperature, surface diffusion of Ga sources and desorption of Ga can be minimized so as to react with a nitrogen source such as NH\(_3\), which serves as a GaN nucleation site (Figure 3a).

In the case of the ILs of 2D layered materials, such as graphene and h-BN, uniform nucleation of HT-GaN is much more difficult. This is due to the absence of dangling bonds in these 2D materials, which leads to an extremely low surface energy γ in vacuum or air (γ); Table 1 lists γ for several materials considered in this review.[61–69] Adsorption or nucleation of
foreign atoms on such 2D materials is thermodynamically unfavorable, i.e., it increases the total free energy of the system, which is expressed as follows:

\[
\Delta G = G_f - G_i = \gamma(NL) + \gamma_{IL-NL} - \gamma(2DIL) >> 0
\]  

where \( G_f \) and \( G_i \) are the total Gibbs free energies before and after the formation of a uniform NL, respectively, \( \gamma(NL) \), \( \gamma(2DIL) \), and \( \gamma_{IL-NL} \) are surface energies of the NL and IL in vacuum and the interfacial energy between NL and IL, respectively. Therefore, the nucleation of GaN on such a 2D material is extremely challenging. Indeed, it has been found that direct LT-GaN growth (530 °C) on highly oriented pyrolytic graphite leads to nucleation only at grain boundaries. One way to circumvent this problem is to generate defects in the 2D materials. Chung

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**Figure 3.** Process for uniform GaN nucleation and film growth. a) Schematic diagram of GaN nucleation process on a specific underlayer. b) Schematics of GaN growth on graphene IL using \( O_2 \) plasma and ZnO nanowall NL. Reproduced with permission.\cite{29} Copyright 2010, AAAS. c) Optical microscope image of GaN growth on BN IL: (left) with and (right) without \( Al_xGa_{1-x}N \) NL. \( T, D_{UL}, \gamma_{GaN} \) represent GaN growth temperature, defect density of the underlayer, surface energy of GaN, respectively. Adapted with permission.\cite{34} Copyright 2012, Nature Publishing Group.

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**Table 1.** Surface energies of different materials considered in the article.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Surface free energy [mJ m(^{-2})]</th>
</tr>
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<tbody>
<tr>
<td>Si (111)\cite{81}</td>
<td>1467</td>
</tr>
<tr>
<td>Sapphire (001)\cite{82}</td>
<td>4800 (before relaxation), 1850 (after relaxation)</td>
</tr>
<tr>
<td>w-ZnO (001)\cite{83}</td>
<td>( \approx 2025-2040 )</td>
</tr>
<tr>
<td>w-GaN (001)\cite{84}</td>
<td>1970</td>
</tr>
<tr>
<td>w-AlN (001)\cite{85}</td>
<td>5840</td>
</tr>
<tr>
<td>h-BN (001)\cite{86}</td>
<td>( \approx 37-57 ) (cubic BN)</td>
</tr>
<tr>
<td>graphene (001)\cite{87}</td>
<td>52 (multilayer)</td>
</tr>
<tr>
<td>( \alpha )-Ti (001)\cite{88}</td>
<td>2048</td>
</tr>
<tr>
<td>glass\cite{89}</td>
<td>2000-4000</td>
</tr>
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et al. reported that ZnO nanowalls (NWs) can form uniformly on O$_2$-plasma-treated graphene,[29] and that the resulting ZnO NWs act as an excellent NL for GaN (Figure 3b). The O$_2$ plasma treatment is believed to increase the defect density (D$_{UL}$) in graphene, which should enhance Ga adsorption and GaN nucleation. Following the defect generation process, $\gamma$ of the graphene IL will increase significantly, such that $\Delta G$ will be close to zero; hence nucleation will be energetically favorable. Kobayashi et al. reported that an Al$_x$Ga$_{1-x}$N ($x > 0.1$) layer can be uniformly formed on h-BN, resulting in an excellent NL for GaN and a significantly improved growth morphology, as shown in Figure 3c.[34] Shon et al. reported a uniform AlN NL on graphene.[27] Although not depicted explicitly, we may expect that similar defect generation processes in graphene such as an O$_2$ plasma or ozone treatment were employed prior to the NL growth. Note that the NLS discussed here, including ZnO, AlN, and Al$_x$Ga$_{1-x}$N, have sufficient dangling bonds, and hence have comparable $\gamma$ to that of GaN, enabling uniform nucleation of GaN.

3. High-Quality GaN Growth on Amorphous Substrates for Large-Area LEDs

Here, we now review high-quality GaN grown on amorphous substrates. It is particularly challenging to achieve single-crystal epitaxial growth of GaN on glass as the NL/IL is polycrystalline. We first discuss highly ordered polycrystalline GaN using a textured NL/IL, and then nearly or fully single-crystal GaN using the concept of evolutionary selection or predominant growth (ESPG).

3.1. Microstructure of NL Layers and GaN Growth Morphology

In order to achieve GaN growth with a controlled morphology on amorphous glass, it is essential to control the degree of crystallographic orientation of the NL/IL. When the orientation of the NL/IL is completely random (top panel, Figure 4a), there are three degrees of freedom (DOF) with respect to the orientation of GaN; thus, the resulting GaN morphology is simply an assembly of randomly oriented grains with their density variable depending on the NL. For example, direct HT-GaN growth on glass, on untextured ZnO/glass, and on LT-GaN/glass should lead to such a morphology, as shown in the left, center, and right panels, respectively, of Figure 4b.

When the NL/IL orientation is $c$-axis textured (i.e., the $c$ axes are aligned in the out-of-plane direction and $a$ axes are randomly oriented in the in-plane directions), the number of DOF for GaN growth is reduced to two, and the resulting GaN morphology is a $c$-axis textured pyramid or an uneven film (top and middle panels, Figure 4c). It is well known that GaN typically grows on a NL as truncated 3D islands in the Stranski–Krastanov (SK) growth mode; however, when the nucleation sites are dense and uniform (such as with sputtered AlN/SiO$_2$),[35,36] the 3D islands soon merge into a nearly 2D film (middle panel, Figure 4c). On the other hand, when the nucleation density is low (such as with LT-GaN/Ti/glass,[37–39] the 3D islands evolve into pyramids and do not merge. As the grain size of the $c$-axis textured NL/IL increases (such as with ZnO nanowall/transferred graphene or AlN/graphene, as shown in the bottom panel of Figure 4c),[27,29] it becomes more feasible to obtain a 2D like GaN morphology. The resulting GaN layers grown on ZnO NW/graphene can be extremely flat like epitaxial GaN. Nevertheless, because the sputtered AlN IL is deposited on glass, and the transferred graphene IL is typically grown on a polycrystalline Ni foil, although flat, the resulting GaN is inherently polycrystalline. Inspection of an inverse pole Figure of GaN grown on a textured AlN IL (middle panels, Figure 4a,c) reveals that GaN is $c$-axis textured, but completely random in the in-plane directions (Figure 4d). Surprisingly, despite the extremely flat GaN on ZnO NW/graphene being polycrystalline, electron backscatter diffraction (EBSD) analyses reveals that GaN has fairly large grains (of the order of 10 µm) with high-angle grain boundaries, although some low-angle grain boundaries also exist inside (left and middle panels, Figure 4e).[31] X-ray diffraction (XRD) phi scanning also shows that the GaN is not only $c$-axis textured, but also $a$-axis textured to some extent. Inspection of the right side panel of Figure 4e reveals two main sets of peaks, with six-fold symmetry of the (1–12) planes, and with additional minor peaks; this indicates that GaN has only two in-plane orientations. Although a set of six-fold symmetric (1–12) planes similar to that of a single crystal has recently been reported for GaN on AlN NL/transferred graphene IL,[27] it appears that this is an exceptional case. Therefore, defects in GaN on AlN/graphene or ZnO nanowall/graphene can be categorized into low-angle grain boundaries, high-angle grain boundaries, and threading dislocations (with densities on the order of $1 \times 10^{10}$ cm$^{-2}$). We may infer that the transferred graphene from copper or nickel foils has a similar morphology, with $\approx 10 \mu$m high-angle grain boundaries divided by several low-angle grain boundaries. Despite such defects, the IQE is significant (see Figure 2a). Therefore, defect-insensitive emission from In$_x$Ga$_{1-x}$N is assumed to occur, even for 2D defects such as grain boundaries.[19,20] This intriguing In$_x$Ga$_{1-x}$N will be discussed in more detail later.

3.2. ESPG Growth

The concept of ESPG has been suggested as an alternative approach for the growth of single-crystal GaN.[35–37] With ESPG, the growth of certain crystallites (3D islands) is favored, leading to arrays of single-crystal GaN and blocking the growth of other crystallites (also known as geometrical selection). The key requirements for ESPG are the use of a growth mask and a $c$-axis textured NL (Figure 5a). The former is required to reduce the number of DOF of GaN growth, and the latter for geometrical selection. Under the masked region, the $c$-axis textured GaN crystallites grow predominantly, while blocking the growth of other crystallites, as shown in Figure 5a. However, when the aspect ratio (AR) is $h_2/D$, two crystallites emerge out of the mask and break the single-crystallinity. When the AR increases to $h_2/D$, only one crystallite remains, and the layer becomes a single crystal ($h_2$ and $h_3$ are shown in Figure 5a). The effect of the growth mask is evident when we compare a GaN array grown without masks (AR = 0, left panel, Figure 5b),[31] with that using a microhole-patterned growth mask (AR < 1, right
panel, Figure 5b), and with a microtunnel-patterned growth mask (AR > 1, Figure 5c). For AR = 0, the degree of ESPG is relatively weak, which means that growth competition occurs only among GaN crystallites. Therefore, the growth morphology is similar to a continuous film on the same NL/IL. Inspection of the left panel of Figure 5d reveals that the GaN array on the ZnO NL/graphene IL pattern exhibits a flat-top morphology; however, the orientation of the hexagonal facets exhibits a partially polycrystalline nature. ESPG growth is evident with microhole patterned epitaxy. With AR = 0.13 and LT-GaN NL/Ti IL, pyramidal GaN arrays form, with slight side fragments (right top panel, Figure 5d). With AR = 0.5, even the side fragments completely disappear (right bottom panel, Figure 5d). With microhole patterned growth (AR > 5), ESPG becomes nearly perfect, as confirmed by the EBDS data shown in Figure 5e. Note that each element in the GaN array formed using ESPG has a common c axis, but does not have a common a axis (see the arrows in the left upper panel of Figure 4d). This is because EBSD is based on the local heteroepitaxy between GaN and an NL/IL (see Figure 5a for a and c axes of HT-GaN and the NL/IL).
Microhole-patterned growth is a simple process but has a low achievable AR, whereas microtunnel growth can be achieved with a high AR, but it is a more complex process with a slower growth rate. The former is suitable for pyramidal or rod-shaped arrays on an NL/IL with large grains (e.g., ZnO NL/graphene IL), and the latter is suitable for plate-shaped arrays on an NL/IL with small grains (e.g., AlN NL/IL).

4. Low-Temperature Growth of GaN on Glass

The recent research discussed has been focused on overcoming the limitations associated with the amorphous nature of glass. However, glass typically has a maximum processing temperature of around 675 °C,[70,71] which necessitates the low-temperature growth of GaN. Here, we discuss recent developments of low-temperature growth of GaN/In<sub>x</sub>Ga<sub>1−x</sub>N/AlN/GaN:Mg, which is applicable to glass substrates. In the early 1990s, Khan et al. used pulsed MOCVD to synthesize single-crystal GaN on sapphire at 450 °C, the crystallinity of which was comparable to that of GaN grown by conventional MOCVD at 1040 °C.[72] With pulsed growth, triethylgallium (TEG) and NH<sub>3</sub> are supplied alternately with time intervals (upper panel, Figure 6a), which enables diffusion of the precursor gases and the formation of GaN. The key points with pulsed growth are improvements in the diffusion or surface migration of reactants, and reduction in the pre-reactions between the reactants. At low temperatures, NH<sub>3</sub> does not readily decompose to the active nitrogen species required for the growth reaction. In the mid 2000s, Blu-glass Inc. reported a remote nitrogen plasma technique for supplying active nitrogen,[73,74] and reported high-quality GaN grown at 600 °C.
4.1. Pulsed Sputtering

In the early 2000s, a team at the University of Tokyo developed a low-temperature group III nitride growth process called pulsed sputtering (PS), and reported room-temperature growth of GaN,[23] AlN,[24] and InN[25] films with high structural quality, as well as LED-compatible p-type GaN grown at $480^\circ \text{C}$ and annealed in $N_2$ at $450^\circ \text{C}$. They realized full LED structures using the PS system at temperatures in the range of $550–760^\circ \text{C}$. With the PS system, metallic elements such as Ga are ablated via a pulsed KrF laser similarly to pulsed laser deposition (PLD); a nitrogen source is supplied using RF plasma excitation of high-purity $N_2$ (Figure 6b). The PS enables the growth of high-quality GaN at low temperatures, as the reactants of both Ga and N are sufficiently energetic (ablated Ga will have a high kinetic energy, and the plasma-assisted N radicals are highly reactive). In the PS system, not only Ga but also other metallic radicals including In, Al, and Mg may form independently or simultaneously with N to create various group III nitrides, such as AlN, In$_x$Ga$_{1-x}$N, and Mg-doped GaN, using laser ablation. The team combined their PS group III nitrides with transferred multilayer graphene ILs on glass substrates to realize LED structures grown solely via PS (Figure 6c). Each layer was polycrystalline, with a grain size of the order of 10 µm (Figure 6e).

A large EL spectral width is often reported for PS LEDs, with a full width at half maximum greater than 50 nm at emission wavelengths of 640 nm[26] and 515 nm. This is related to the structural and compositional variation: the film morphology obtained using PS exhibits a 3D-like nanostructure (such as a nanorod) rather than a flat geometry (bottom panel, Figure 4c), and the In fraction and/or the layer thickness across the 3D typically varies.[27,38,75] Despite the large spectral width in PS LEDs, the 3D structure exhibits a high IQE even in the red-emitting region (with a large $x$ in In$_x$Ga$_{1-x}$N) as shown in Figure 2a and Figure 6d. The elastic strain arising from the...
lattice mismatch between GaN and InGa\textsubscript{x}N is expected to increase with increasing x, and, for this reason, only blue and green emission is available for In\textsubscript{x}Ga\textsubscript{1-x}N grown on sapphire (see Figure 2a). With a 3D structure, the elastic strain will be greatly reduced compared to that in a 2D structure, even with a large x. There remain a number of technological issues, including a further reduction in the processing temperature, passivation of grain boundaries to replace 600 nm-thick p-GaN for minimizing leakage currents, and the growth of In\textsubscript{x}Ga\textsubscript{1-x}N with uniform x and uniform thickness for minimizing the spectral width. The development of single-crystal graphene synthesis and reliable layer-transfer processes may be a key step to address these issues.\textsuperscript{[77,78]} Despite all the disadvantages, RGB EL characteristics were demonstrated for devices grown on glass using group III nitride layers (Figure 6d). This successful demonstration paves the way for the realization of true RGB LEDs on ordinary glass substrates for large-area lighting applications.

4.2. Selective Synthesis

Selective synthesis is a low-temperature growth technique for GaN in which GaN forms from precursor gases only near the selectively or locally heated regions by electric currents (Figure 7a), while maintaining a low substrate temperature. The growth of single-walled carbon nanotubes (SWCNTs), tungsten oxide, and silicon nanowires on microheater bridges...
has been demonstrated.[79–86] We have also demonstrated that an array of metallic microbridges such as molybdenum on ordinary glass substrates can be selectively heated up to 1200 °C while maintaining the substrate temperature below 100 °C (Figure 7b), and have used the bridges for the synthesis of various materials, including polycrystalline silicon (p-Si)[87] and SWCNTs,[88] as well as for the annealing of lanthanum hexaboride (LaB₆)[89] and EL patterning.[90] We also successfully synthesized ZnO nanorods and ZnO/GaN core–shell nanorod heterostructures (Figure 7c).[91,92] The ZnO/GaN heterointerface was structurally evident (Figure 7d) although photoluminescence was observed only at low temperatures (Figure 7e).

Selective synthesis is more suitable for low heat-capacity materials, such as sparsely dispersed arrays of nanorods.[79,80] When the synthesized material is larger than the microbridges, precise control of the synthesis temperature becomes challenging due to the significant heat capacity. With local synthesis of p-Si using silane (SiH₄), it was found that variations in the synthesis temperature did not significantly degrade the quality of the p-Si layer, and that growth occurred in a concentric mode[87] around the microheater (Figure 7f), which should be due to the uniform decomposition of SiH₄ around the microheater. With GaN, only amorphous GaN has a smooth surface (left panel, Figure 7g). Moreover, inspection of this Figure reveals that GaN did not grow in a concentric fashion like p-Si, but mainly grew on the upper side of the bridge. This suggests that the reaction between trimethyl gallium (TMG) and NH₃ mainly occurred above the microheater. A randomly oriented polycrystalline GaN morphology is observed without a moderate IL (center panel, Figure 7g). Moreover, as growth proceeds with constant-voltage heating, the well-faceted GaN morphology abruptly changes to small grains (right panel, Figure 7g), implying that accurate temperature control is challenging for the selective synthesis of large regions. We conclude that selective synthesis of GaN is useful for the realization of nanorod LEDs when adopting an appropriate IL and core–shell nanorod array form.

5. GaN-based Flexible/Stretchable LEDs

5.1. Layer Transfer

Here, we focus on layer-transfer methods for hetero-epitaxial GaN. Exploiting layered materials with weak van der Waals interactions is a promising strategy, which can be applied to the structures shown in Figures 1a,b (see the left side panel, Figure 8a). Layer structures such as GaN/BN/substrate have been analyzed using density functional theory, and it was shown that the BN/BN homo-interface had a much lower energy barrier for interlayer sliding than the BN/GaN hetero-interface.[93] This suggests that the shear mechanical forces lead to structural release or separation not at the GaN/BN or BN/sapphire hetero-interface, but at the BN/BN homo-interface (right side panel, Figure 8a). This was experimentally verified, as shown in Figure 8b.[94] X-ray photoelectron spectroscopy analyses were carried out following the release process, which clearly reveals that both the host sapphire substrate and the foreign substrate exhibit clear B-1s and N-1s peaks (note that only the B-1s peak is shown in Figure 8b), indicating that separation occurred within the 30 nm-thick BN. This transfer mechanism is also expected to be valid for the GaN/graphene system. It has recently been reported that even monolayer graphene formed on hydrogen terminated germanium can be easily transferred by mechanical force.[77] Therefore, GaN-based LEDs on such 2D-layered materials and mechanical layer transfer are highly promising, once high quality growth of 2D materials and GaN is secured.

Next, we discuss selective wet etching of GaN on Si (Figure 1c), where the underlying layer was selectively wet etched relative to the overlying LED structure that was weakly fixed to the anchoring layer (Figure 8c).[94,95] Rectangular patterning of the LED structure was performed, followed by patterning of a photoresist anchoring layer (top-left and top-right panels, Figure 8c). Isotropic, selective wet etching was used to etch beneath the GaN layer (bottom-right panel, Figure 8c), leaving the overlying GaN-based LED structure. Potassium hydroxide (KOH) is a good selective wet etchant of Si and does not attack the overlying GaN-based LED structure.[94] With GaAs-based LEDs, hydrofluoric acid-based etchant is commonly used to selectively wet etch a sacrificial layer of AlₓGa₁₋ₓAs.[95] Finally, the weakly anchored LED structure is released and transfer-printed to foreign substrates, allowing accurate layer transfer of discrete arrays onto a desired location of foreign substrates (Figure 8d). However, additional patterning of the LED array and the anchoring layer increases the process complexity, and relatively long etching times are required to completely undercut typical array units; ≈4 h for a 50 µm × 50 µm area and ≈5.5 h for a 100 µm × 100 µm area.[95]

Finally, we discuss the nanovoid-mediated transfer method for GaN-based LED arrays on Ti, as shown in Figure 1d (also see the top panel of Figure 8e).[39] Modulating the processing conditions, including the Ti thickness and the annealing temperature, can create variable-sized nanovoids at the Ti/GaN interface via the following reaction: Ti + GaN à Ga + TiN (bottom-left panel, Figure 1e). The nanovoids are created during diffusion out of the generated Ga atoms along the nanocolumn boundaries of LT-GaN. This weakens the Ti/GaN interface, where the LED structure can be easily released (bottom-right panel, Figure 1e). Following release, it was experimentally verified that the TiN layer remained on the source substrate, with a slight trace of the GaN array (top panel, Figure 1f), and the GaN arrays were transferred onto the foreign substrates (bottom panels, Figure 1f). This transfer process can be used to transfer any LED form, including patterned or unpatterned 2D and 3D LEDs. One disadvantage, however, is the small process window for precise control of the interfacial strength between Ti and GaN layers. Table 2 lists a comparison of the layer-transfer processes.

5.2. Requirements of Flexibility and Stretchability

Among the foreign substrates for the LED structure to be transferred onto, flexible and stretchable materials have become increasingly popular. The design rules for flexible devices (less
Figure 8. GaN release process by using inherently weak interfaces or generating weak interfaces. a) Separation at a certain homo-interface within 30 nm-thick BN with weak van der Waals bonds between neighbouring layers. Adapted with permission.\textsuperscript{[34]} Copyright 2012, Nature Publishing Group. b) B 1s XPS spectra for the surfaces of 1 and 2 in (a) marked by red arrows. Reproduced with permission.\textsuperscript{[34]} Copyright 2012, Nature Publishing Group. c) Selective KOH wet etching of silicon relative to GaN at the AlN/Si interface, where GaN LED arrays are tentatively anchored by the supporting pattern. Adapted with permission.\textsuperscript{[34]} Copyright 2011, NAS. d) Microscope images of (top) source and (bottom) target substrates after the transfer in (c). Reproduced with permission.\textsuperscript{[34]} Copyright 2011, NAS. e) Nanovoid formation at the GaN/Ti interface. f) Microscope images of (top) source and (bottom) target substrates after the transfer in (e). Reproduced with permission.\textsuperscript{[39]} Copyright 2014, Wiley-VCH Verlag.

Table 2. Summary of discussed transfer methods for flexible GaN LEDs.

<table>
<thead>
<tr>
<th>Principle</th>
<th>wet etching selectivity</th>
<th>weak van der Waals bond in multi-layered graphene or BN</th>
<th>nanovoid formation in the LT-GaN/Ti interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Key release process</td>
<td>anchoring wet etching nd stamping</td>
<td>mechanical cleaving</td>
<td>thermal annealing ND post mechanical treatment</td>
</tr>
</tbody>
</table>
than a few percent strain) are such that important and brittle elements, (e.g., indium tin oxide (ITO) transparent electrode) are located in the neutral-mechanical plane (Figure 9a) where there is zero strain. The optimum structure for any given set of materials can be designed by modeling the strain distribution in the device (Figure 9b). With stretchable devices (with a strain of less than ≈30%), a number of different approaches have been investigated. The first was to use pre-straining of the stretchable substrate to generate a buckled or wrinkled structure (Figure 9c). Tensile strain is applied to the foreign stretchable substrate during the transfer process, after which the strain is released to form a buckled structure that is wavy in the out-of-plane direction. The buckled structure may either be periodic [96–98] (see the top panel of Figure 9c) or random [99,100] (see the bottom panel of Figure 9c), and can withstand significant strain. The second was a serpentine structure [101–103] (Figure 9d), which can be accurately designed using lithographic patterning. Therefore, not only electrodes [104] (right side panel, Figure 9d) but also full devices [105] (left side panel, Figure 9d) can be formed with a serpentine structure. Due to such controllability, these serpentine structures are commonly used in many applications including Li-ion batteries, [101] GaAs-LEDs, [95] and GaN-LEDs. [94] Because of the wavy structure in the in-plane direction, there is some spatial loss of the active element; thus, this technique is suitable for less dense devices (right side panel, Figure 9d).

An alternative approach to forming stretchable devices with wavy structures is to use a percolated electrode material that consists of a percolated network of 1D metallic nanostructures embedded in a polymer matrix, with silver nanowires (NWs)
and carbon nanotubes (Figure 9e,f). Such electrodes can maintain stretchability under significant elongation, with only a slight increase in the electric resistivity, provided that the percolation network is maintained (Figure 9e). In general, the metallic NWs are slightly aligned in the elongation direction following repetitive application of tensile strain (Figure 9f). Mixed AgNW–polyurethane acrylate electrodes coupled to blended continuous yellow light-emitting polymer electrochemical cells have been recently reported, which exhibited bright yellow emission under a tensile strain of 120%. Following layer transfer of GaN arrays (Figures 8c,e) onto percolated electrodes with good ohmic contacts, the percolated structure can be coupled onto stretchable arrays of GaN-based LEDs (Figure 9b). The p-GaN (outer shell) and n-GaN (core) in pyramid arrays can be electrically connected to the upper and lower percolated electrodes, respectively.

5.3. Device Performance

Figure 10 shows the EL from GaN LEDs grown on unconventional templates, as well as that from devices transferred onto foreign substrates. Immediately following growth on the unconventional templates, as well as following layer transfer, all of the LEDs exhibited clear green or blue EL. We recently achieved a luminance of 11 700 cd m⁻² with a peak wavelength of 494 nm via optimization of GaN arrays formed on a Ti/glass template (top-left panel, Figure 10c). Figure 10c also shows the performance of these devices; assuming a Lambertian (cosine) distribution, we obtained an efficiency of 4.8 lm W⁻¹ (inset, Figure 10c), which is equivalent to 11% with respect to state-of-the-art LEDs with a similar peak wavelength (see Supporting Information Table S1 for the calculations and data). Such high efficiency demonstrates the potentials of GaN-based LEDs.
on unconventional substrates for commercialized large-area lighting applications, when combined with low-temperature growth.

Note that the layer-transfer process (Figures 8a,c) does not affect EL performance. The current–voltage (I–V) characteristics were similar, only with a slight increase in the voltage for a given current (left side panel, Figure 10b), and in some cases, the luminescence was even enhanced following layer transfer at the same injection current (left and center panels, Figure 10a, and the left panel of Figure 10b). This is probably due to the reflection or improved light-extraction efficiency in the geometry of the transferred device. Following transfer, clear blue EL could be seen in both the flat and flexible foreign substrates (right-side panels, Figure 10a,b). However, we often found a significant increase in the leakage current and a decrease in the maximum luminance following layer transfer. This is attributed to imperfect layer transfer, whereby some small portion of the GaN pyramids remain on the host substrate, leaving holes in the transferred structure that result in electrical leakage current pathways between the upper and lower electrodes during the lower electrode deposition, which is performed after the layer transfer process. Nevertheless, we could find the case that the EL performance was almost identical before and after the layer-transfer process (top-right and bottom panels, Figure 10c).

Another technical issue in GaN-based devices is thermal management. The low thermal conductivity of the conventional sapphire or glass substrates makes it difficult to dissipate heat generated in packages or high-power electronic devices. This can be resolved by layer transfer of GaN onto Cu or graphene, with high thermal conductivity as well as excellent flexibility. Exploiting graphene as an IL would also be a good alternative.

6. Conclusions

We have discussed the heteroepitaxy of GaN on unconventional templates, and layer transfer onto foreign substrates for large-area, flexible/stretchable GaN-based LEDs. Successful heteroepitaxial growth of GaN-based materials has been achieved, as well as the successful demonstration of RGB LEDs on glass substrates using 2D graphene ILs and a low-temperature PS system. Layer-transfer techniques were examined and demonstrated for flexible/stretchable lighting applications. Luminance of GaN arrays on a Ti/glass template of 11 700 cd m\(^{-2}\) with a peak wavelength of 494 nm was achieved. A calculated efficiency of 4.8 lm W\(^{-1}\) of such GaN arrays is equivalent to 11% efficiency for state-of-the-art conventional LEDs.

Currently, we can conclude that large-scale, single-crystal graphene as an IL together with a ZnO nanostructure as an NL promises the best GaN morphology. The dislocation density of GaN can also be further reduced because strain between the substrate and the film is much less important in vdWES. Furthermore, exploiting graphene as an IL facilitates layer transfer to foreign substrates, e.g., Cu molds, thus applicable to vertical stacked high-power LED devices. Additionally, the PS technique that enables the growth of high-quality GaN at low temperature would lead to highly efficient GaN-based LEDs on large-scale glass. We anticipate that the technologies discussed here will be commercially available in the near future.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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