TOPICAL REVIEW

Measuring, controlling and exploiting heterogeneity in optoelectronic nanowires

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Abstract

Fabricated from ZnO, III-N, chalcogenide-based, III-V, hybrid perovskite or other materials, semiconductor nanowires offer single-element and array functionality as photovoltaic, non-linear, electroluminescent and lasing components. In many applications their advantageous properties emerge from their geometry; a high surface-to-volume ratio for facile access to carriers, wavelength-scale dimensions for waveguiding or a small nanowire-substrate footprint enabling heterogeneous growth. However, inhomogeneity during bottom-up growth is ubiquitous and can impact morphology, geometry, crystal structure, defect density, heterostructure dimensions and ultimately functional performance. In this topical review, we discuss the origin and impact of heterogeneity within and between optoelectronic nanowires, and introduce methods to assess, optimise and ultimately exploit wire-to-wire disorder.

1. Introduction

Single-element functional nanotechnology demands the development of highly-integrated nanoscale materials where each nano-object provides a specified function, such as sensing, detection or light emission. Semiconductor nanowires (NWs) are a highly-studied and important example of this, and the past two decades have seen the development of NW-based lasers [1, 2], photovoltaics [3–7], single-photon sources [8–10], single-photon detectors [11], biomedical sensors [12, 13], terahertz sensors [14, 15] and thermo-electric devices [16]. The benefit of using NWs for functional nanotechnology arises from their size—enabling strong and anisotropic optical interaction [6, 17–19], surface—enabling sensitive environmental interaction [12], shape—enabling directed energy flow [20] and growth mechanism—enabling the production of new material combinations [21]. NWs are typically grown using either colloidal vapour-liquid-solid (VLS) [22–24] or template assisted selective-area epitaxy (SAE) [25], both of which can produce long (micron-scale), thin (10–1000 nm) NWs which can be axially or radially heterostructured. Top-down routes to prepare NW arrays have shown highly promising results using traditional electron beam lithography [26], interferometric lithography and etching [27], masking and sublimation [28] or more through metal-assisted chemical etching (MACE) [29, 30]. While these techniques are of great interest they tend to be less scalable (for electron beam lithography) or less well-controlled (for MACE) than bottom-up techniques for optoelectronics. The question of which approach is best, or ‘to grow or not to grow?’ remains open [31].

NWs produced from many material systems have been studied [32], most notably zinc oxide (ZnO) [33], III-Nitrides [34], silicon [35], chalcogenides [36], III-Vs [37] and more recently hybrid perovskites [38, 39]. The shape and size of the NWs are critical to determining their functional performance—for instance their geometry provides the wavelength scale cavity for laser action [40], their high surface area to volume ratio is required for sensing [41] and a tapered geometry can create structural anti-reflection coating for photo-detectors [11]. Material quality is also highly dependent on NW diameter [42, 43] and local growth conditions [44], leading to potential variations in crystal quality [45], defect density [46, 47], alloy composition [48] and ultimately the functional performance on the dimensionality of the structure. While
Figure 1. Intrawire and interwire inhomogeneity both play a role in determining the ensemble and array properties of semiconductor NWs. This schematic shows the definition of inhomogeneity used herein, with intrawire in blue and interwire in red.

the advantages of the NW architecture are rooted in geometry and material quality, it is clear that variations in NW size, shape or local thermodynamic conditions within a growth will have a significant and non-linear effect on functional performance of NW-based devices.

This strong dependence is not unique to NWs; disorder between individual functional nanomaterials is ubiquitous and characterising ensemble inhomogeneity is challenging [49, 50]. As stated by Stavis, ‘nanoparticle manufacturing is an inherently holistic venture’ [51], where advantages in functionality and scalability are traded for the loss of individual control over the growth of each element. The challenge of measuring, controlling and reducing disorder is widely recognised in the related field of colloidal nanocrystals [52–54], where single-element microscopy and spectroscopy is established as a key measurement methodology [55] and the impact of heterogeneity on emission linewidth [56] and quantum yield has been studied [57] revealing the critical role of low levels of impurity in small objects. While single NW spectroscopy has been developed to a similar level of maturity [58, 59], there has been significantly less focus on the issue of functional heterogeneity in NW-based materials and devices, with limited studies published linking inherent geometrical [60–62], heterostructural [63] or material [64] variations to functional performance.

A key difference between colloidal nanocrystal and NW heterogeneity is the extended dimension for NWs, which allow for both interwire and intrawire variations as depicted in figure 1. The latter is often exploited, for instance in compositional grading [65–67], for stochastic self-assembled photon sources [68] or for producing novel heterostructures [69], however it can more often be unwanted and present an additional challenge to overcome [48, 70]. The first stage in addressing this challenge is developing appropriate characterisation techniques. Study of newly developed NW materials or structures often follows a hierarchy of measurements: morphology (using scanning electron microscopy), crystal structure/heterostructure (using transmission electron microscopy), non-contact optoelectronic measurement (using cathodoluminescence [71], electron-beam induced current [72], photoluminescence [73], scattering [58] or terahertz spectroscopies [74, 75]), contact-based measurement [76] and finally functional study. This presents three challenges; heterogeneity can emerge at any level and must be appropriately quantified, the parameter space for optimisation is wide and highly complex, and the volume of data produced for population studies becomes extremely large.

In this review, we discuss studies of the origin and impact of disorder for functional NWs. We initially focus on the more widely studied area of intrawire disorder, before reviewing research on interwire disorder and introducing opportunities from the emerging fields of big-data [77] and automated experimentation [78]. We focus on NWs with applications sensitive to variations in dimensionality or material quality, including NW-based lasers, photovoltactics, light-emitting diodes (LEDs) and transistors. We conclude with an outline of new high-throughput approaches that can correlate multiple microscopies, exploiting heterogeneity to study fundamental energy processes in functional NWs.

2. Intrawire disorder

Dynamic variation in growth conditions during the production of NWs can lead to disorder within a single NW. Typical examples are changing composition due to the reservoir effects in VLS growth [81], tapering due to competition between radial and axial growth [44], and defect inclusion during growth [47] as schematically shown in figure 2. These effects lead to spatially varying optoelectronic performance, and while
in specific cases can be beneficial (such as graded composition for single-wire spectroscopy [82]) this
disorder is more often unintended and causes degradation in performance.

2.1. Geometry and morphology
NWs are typically produced with radial dimensions of 10–1000 nm. In many cases, true one-dimensional
(1D) quantum confinement of carriers does not occur in such large structures, and variation in geometry is
more significant in its impact on surface faceting, recombination, and scattering. However, 1D quantum
behaviour in free-standing NWs has been studied, where small changes in diameter can lead to large changes
in electronic behaviour.

2.1.1. Quantum confinement
For silicon NWs, quantum confinement requires dimensions of smaller than 10 nm [86] which is
experimentally challenging to produce. Nevertheless, in 2003 Ma et al reported a study on NWs with
diameters below 5 nm using an oxide-assisted growth method [87]. This revealed that above a critical
thickness of 3 nm, the band-gap varied with diameter \( d \) as \( \Delta E \propto d^{-1} \), but below this it increased more
significantly; a change in thickness of 1 lattice constant can lead to a change in energy on the order of 1 eV
for a NW of 1 nm diameter. This has the potential to cause a very large intrawire inhomogeneity for a small
variation in geometry. However, for III-V materials quantum effects can be observed for diameters as high as
\( \sim 40 \) nm, where ballistic conduction has been demonstrated for InAs NWs [88]. In the latter case, small
variations in diameter are less critical for electronic behaviour, although surface roughness, channel length
and scalability of production remained a significant challenge. Recent work by del Giudice [89] demonstrates
the progress made in the templated growth of untapered wires with radial quantum confinement with
diameters in the region of 20 nm, where growth kinetics can be challenging to control. In emerging
applications that depend on precise control of confinement, it is expected that variations in diameter may
play a limiting role for NWs, although an appropriate selection of material with a large carrier or excitonic
wavefunction provides a route to ease this limitation.

2.1.2. Surface effects
With reduced diameter, geometric variations in the surface have a proportionally larger effect on the
electronic properties of NWs. Two key aspects of this are in surface recombination, and surface scattering.

In NWs, the surface provides an often dominant route for the carrier recombination due to high defect
density, therefore the recombination process at the surface and in the core are inherently inhomogeneous
[90, 91]. Measuring the charge carrier recombination is often challenging using photoluminescence due to
the small volume of material and low quantum efficiency of emission; optical pump-terahertz probe (OPTP)
measurements have therefore emerged as a gold-standard for studying carrier lifetime and mobility in NWs.
ensambles [74, 80]. An explicit link between the ensemble carrier lifetime in GaAs, InP and InAs NWs and surface recombination was reported by Joyce et al using this technique [75] (figure 3(a)). However, study of recombination in single NWs requires a local probe. In 2014 Eisele et al successfully captured the time-resolved scattering near-field microscopy images (s-NSOM) of single InAs NWs that shows the ultrafast formation of a 10 nm thick depletion layer at the surface within 50 fs after photo-excitation [84] (figure 3(c)). This depletion layer isolates carriers from the surface, contributing to the long carrier lifetime in InAs wires [84]. More recently Zhang studied transient absorption in InAs NWs as a function of NW diameter to separate surface and interior recombination [91], revealing a nanosecond lifetime at low temperatures. In more emissive NWs, photoluminescence can be used to separate the effect of surface and interior recombination; Ren et al presented a computational approach to study three-dimensional recombination using time-resolved spectroscopy [92].

In electronic applications, carriers are typically driven along the axis of NWs. In the absence of a strong surface depletion field, the carriers can interact strongly with the surface leading to enhanced scattering and a resulting reduction in mobility. Indeed, for the smallest wires surface scattering becomes increasingly important, and Polli et al found that close to the quantum confined regime both surface scattering and gate-dependent effects play a part in limiting transistor performance [93]. Unlike other scattering mechanisms, Ford demonstrated that surface scattering in InAs is independent of temperature, reducing the performance of thin wires at low temperatures [94]. Surface roughness can also be beneficial, and in certain regimes provides an opportunity to limit phonon transport while maintaining high electronic mobility [95]. This ability provides a route to produce new thermoelectric materials with decoupled heat and electronic mobility. When coupled with selective etching, this can provide a method to design axial structures through size variation [96].

The strong electronic interaction with the NW surface can provide unique abilities for sensing [12], controlling thermal transport and the development of proximity-induced superconductivity for quantum applications [97]. However, in many applications surface scattering or recombination require the development of passivation or isolation techniques, and therefore present additional challenges for the development of statistically repeatable NW-based devices.
2.2. Crystal structure
In III-V NWs, two crystal polytypes, zinc-blende (face-centred cubic, ZB, figure 3(d)) and wurtzite (hexagonal, WZ, figure 3(e)) are generally observed [98, 99]. In crystallographic terms, the two structures are distinguished by the stacking periodicity of the atoms [100], and the predominant structure is determined by growth conditions, substrate choice, NW diameter and NW density [101]. Due to the different stacking order, the interface of different polytypes of the same material can show an inhomogeneous band structure [100]; for instance, WZ GaP has a direct band gap, whereas ZB GaP shows an indirect band gap, therefore the optical response from the two polytypes exhibit large differences in the refractive index and resonant absorption behaviour [102]. While this provides a route to bandstructure engineering [103] or may be exploited to form more complex superlattice structures [104, 105], it can also give rise to increased scattering or carrier capture [106] with highly inhomogeneous and random distribution.

Epitaxial NWs have a preferred growth direction which is determined by the substrate, and significant effort has been devoted to controlling this [107]. However, the optical and electrical performances of semiconductor NWs can also be significantly affected by the growth orientation of the substrate. Of specific concern is the growth of WZ NWs on conventional ZB substrates, where NWs along the direction of polar ⟨111⟩B have been shown to have limited carrier mobility due to defects arising from twin planes [99]. It had been predicted that the III-V NWs having a non-polar crystal orientation of ⟨100⟩ or ⟨111⟩A might not possess planar defects; Sun et al demonstrated the growth of ZB InP NWs with a non-polar orientation using a vapour-solid-solid approach. This produced nearly defect-free NWs with high electron mobility approaching the theoretical limit [99].

Crystal structure effects are not limited to III-V based materials; in Si NWs, DFT calculations predicted that the growth facet of [100] NWs would exhibit a direct band gap at Γ due to band folding, whereas the [111] has a transition from inherent indirect gap with a large diameter to a direct gap with a narrow diameter, and the gap is larger than that of [100] [86]. Interestingly, strong anisotropic behaviour and an additional absorption peak are manifested in the Si ⟨111⟩ NWs of which the diameter is no more than 2.2 nm [86].

While polytypism remains a concern when targeting high quality and highly homogeneous NWs, a fuller understanding of the stability window for different structures is evolving: recently the effect of shadowing has been identified as playing a role in the crystal structure of self-catalysed NWs [108]. Modern growth approaches tend to make use of the flexibility in crystal structure provided by the bottom-up growth approach for structure such as twinning superlattices [104] with unique properties.

2.3. Materials
Material composition—either through alloying or doping—is key to determining the physical characteristics of NWs, and spatial variation in these has been a common challenge since the start of the semiconductor era [109]. This challenge persists in the NW platform, where careful tuning and control of growth conditions allowed Hertenberger et al to grow highly uniform InGaAs NWs using SAE [48]. Here, a comparison of random-seeded (VLS) and selective-area (SAE) growth showed a doubling in crystal disorder for the SAE method show a more homogeneous crystal quality in comparison to the self-assembled method. More recently, the Aerotaxy growth method [110] has been used to produce GaAsP NWs. In the Aerotaxy process, no substrate is used and alloy composition is determined by growth temperature and gas ratio. Metafaria et al studied GaAsP NWs composition uniformity; similarly to the SAE growth, a high intrawire compositional uniformity was observed under optimized conditions [111].

Recently, research on perovskite NWs have emerged as a highly active field, due to their facile fabrication process, strong band edge absorption, ultra-long carrier diffusion length, and tunability in their band structure by a simple alloying through the choice of precursors [38, 112–116]. One of the great potentials of this material is for lasing applications, where the controllable stoichiometry results in a tunable emission wavelength across the visible spectrum [38, 112, 115, 116]. Perovskite crystals based on lead halide structure (for instance CsPbX$_{3−l}$Y$_l$ or CH$_3$NH$_3$PbX$_{3−l}$Y$_l$, in which X, Y = Cl, Br, I and l = 0, 1, 2) can have a tunable bandgap by substituting the halide ions [114]). Accordingly, several papers have reported wide tunability in the emission wavelength from near infrared to near ultraviolet in mixed halide NWs [112, 113, 116].

However, in spite of the benefit of the tunability of the emission wavelength, mixing more than one halide ion can result in a high density of crystallographic defects forming deep trap states, eventually restricting their performance [83]. In figure 3(b), the current–voltage characteristics show that single halide NWs have higher conductivity mainly attributed to a low density of charge traps. With a high bias, the current increases more steeply in the mixed halide NW, since the high density of defect traps are filled in this regime. In CH$_3$NH$_3$PbX$_3$ NWs, the underlying high rate of ion migration at room temperature and large surface area lead to a comparably poor stability [117].
Material inhomogeneity remains a primary concern in the development of new materials in the NW architecture, whether intrawire doping variation [64] or mixing of mobile halide ions [83]. High resolution characterisation is essential to explore this effect. While in the early stages of development homogeneity is critical, it is notable that exploitation of intrawire compositional grading has been explored for a variety of optoelectronic applications [118] for instance as single-wire spectrometers [82].

2.4. Heterostructures
Much of the early study of III-V NWs suffered due to high surface recombination, and the abundant defects at the surface of bare GaAs NWs limits the carrier lifetimes to a few picoseconds [74, 119]. As such, co-axial heterojunction structures were introduced to reduce this recombination, since the additional layers covering the surface can efficiently passivate surface traps as shown in in figure 3(g) [80, 120–122]. By adding additional shells, other functionality can be introduced, for instance remote doping [123] which can further fill trap states increasing photoconductivity [124]. Unlike planar heterostructures, radial shells must grown on multiple facets, leading to complex nano-structuring. A notable example of this was the generation of self-assembled quantum dots (QDs) in Al-rich barriers by Heiss [68]. While these dots can be have accurate radial position, their axial position is randomly driven by fluctuations in aluminium concentration leading to high intrawire inhomogeneity.

Through the addition of multiple shells, radial quantum wells (QWs) can be produced. These structures are known to be beneficial for producing optoelectronic devices such as NW lasers [125]. However, the optical transition energy in radial QWs is highly dependant on the well thickness and barrier composition; as such, disorder in a NW tends to be amplified in a radial QW [63]. Figure 3(h) shows that intrawire disorder in radial QWs can be visualised using low-temperature cathodoluminescence, as reported by Gustafsson [70]. Within single NWs, a thickness variation of up to 30% was measured, and for the thinnest QWs (1.5 nm thickness) the well becomes discontinuous due to incomplete coverage or confinement.

3. Interwire disorder
Unlike intrawire disorder, which may be studied using conventional methodology developed for planar heterostructure growth, interwire disorder presents a new challenge. Inhomogeneity in structure, defects, and doping across the NW ensemble emerge from the bottom-up growth technique; therefore, in either seeded or templated growth it is essential to measure and understand interwire disorder and link it to the functional properties of the NWs. Neither single-wire nor ensemble measurements can provide insight into interwire disorder, as the relative contribution of each wire to an ensemble is not necessarily equal. It is essential that many single-wire measurements are conducted, and through large-scale statistical methods, the overall behaviour of the sample can be understood and correlations between different parameters can be revealed.

3.1. Geometry and growth
During the growth or fabrication process, interwire inhomogeneity can be introduced due to the spacing or size of the seed, or from small local variations during growth (e.g. material flux, temperature). It is known that interwire distance and NW density significantly affect the morphology and optical properties of the NWs. This is associated with the dependence of the rate of atom adsorption with NW density which consequently affects the axial and radial growth rates [24]. Rudolph et al [126] varied the GaAs NW spacing by controlling the density of the NW grown on SiO$_2$ mask-patterned Si (111), using SAE-MBE By increasing the GaAs NW spacing, the length and diameter of the NWs were found to increase and the size of the Ga droplet and degree of inverse tapering increased. The study also demonstrated that the radial and axial growth rate increase with the interwire distances, of critical importance during heterostructure growth. This was also observed in a study by Gibson and LaPierre [44] that linked the effect of the interwire distance on the radial growth rate to both the shadowing effect and competition for the material flux desorbing from the surface between the NWs. As a result, the total flux impinging on the surface and sidewalls of NWs decreases for small interwire distance, affecting the growth rate, tapering, and the geometry of the NWs [44].

Rudolph et al studied the impact of the interwire distance on the optical properties of individual NWs by $\mu$-PL spectroscopy [126]. The findings demonstrated that with interwire distances of 0.5 $\mu$m and 1 $\mu$m, the PL spectra are symmetric with peak emission at $\sim$1.515 eV which is a characteristic of high-quality ZB GaAs with low twin defect densities, as shown in figure 4(a). With the interwire distance increased to 2 $\mu$m and 3 $\mu$m, the PL spectra appeared more asymmetric and additional peaks arise at $\sim$1.46 eV. This suggests the existence of WZ phase and high density of twin-plane defects in the ZB-GaAs NWs. This confirms the substantial change of the microstructure from nearly phase-pure ZB-phase NWs at a small interwire distance to defected NWs for large interwire distance [126]. The observed dependence of the PL spectra on the Ga flux
Interwire disorder can be used to modify the optical absorption or emission of NW arrays. (a) The typical PL emission of GaAs NW arrays with different interwire distances $p$ [126], indicating the role of NW spacing on material quality (reprinted with permission from Applied Physics Letters 105, 033111. Copyright 2014, AIP Publishing). (b) The absorption spectra of Si NW arrays showing induced disorder in (top) radius, (middle) location, and (bottom) orientation of the NWs. A random change in the radius of each NW was introduced with maximum percentage change equal to $\Delta$ with absorption calculated by averaging 10 configurations. The dotted, solid, and dashed lines represent $\Delta = 0$, 20%, and 40% for both radius and location disorder. The orientation disorder $\Delta = 0$, $\pi/10$, and $\pi/15$ for dash, solid and dotted lines, respectively [133] (reprinted with permission from Photonics and Nanostructures, 9, 163. Copyright 2010 Elsevier B.V). (c) Random arrays of GaAs NWs can be used for resonant absorption: (left) simulated 3D absorption profiles of a NW-based photon sieve at wavelengths of 455, 555, 650, and 800 nm. (right) Diameter distributions of NWs under incident light of different wavelengths (dot) and fit curve (solid line) [19] (reprinted with permission from Advanced Optical Materials 8, 2000198. Copyright 2020, Wiley).

Figure 4. Interwire disorder can be used to modify the optical absorption or emission of NW arrays. (a) The typical PL emission of GaAs NW arrays with different interwire distances $p$ [126], indicating the role of NW spacing on material quality (reprinted with permission from Applied Physics Letters 105, 033111. Copyright 2014, AIP Publishing). (b) The absorption spectra of Si NW arrays showing induced disorder in (top) radius, (middle) location, and (bottom) orientation of the NWs. A random change in the radius of each NW was introduced with maximum percentage change equal to $\Delta$ with absorption calculated by averaging 10 configurations. The dotted, solid, and dashed lines represent $\Delta = 0$, 20%, and 40% for both radius and location disorder. The orientation disorder $\Delta = 0$, $\pi/10$, and $\pi/15$ for dash, solid and dotted lines, respectively [133] (reprinted with permission from Photonics and Nanostructures, 9, 163. Copyright 2010 Elsevier B.V). (c) Random arrays of GaAs NWs can be used for resonant absorption: (left) simulated 3D absorption profiles of a NW-based photon sieve at wavelengths of 455, 555, 650, and 800 nm. (right) Diameter distributions of NWs under incident light of different wavelengths (dot) and fit curve (solid line) [19] (reprinted with permission from Advanced Optical Materials 8, 2000198. Copyright 2020, Wiley).
random structure. The three arrangements show wavelength selectivity and light absorption sensitivity in the visible-NIR range. The results show that the PS with too high density loses the selective absorption feature and the optimum density of the PS is $\sim 10\%$. Computation models of the fabricated PS confirm the wavelength selectivity at wavelengths of 455, 555, 650, and 800 nm as depicted in figure 4(c). These disordered GaAs NW arrays show that small diameter NW absorbs short wavelength and larger diameter NWs absorbs longer wavelength, confirming wavelength absorption selectivity. Diameter distributions of NWs under incident light of different wavelengths is illustrated at the right panel of figure 4(c) [19].

While disordered GaAs NW arrays can be used to optimize absorption due to their direct bandgap, highly disordered silicon NW arrays have been developed to achieve enhanced light trapping. Fractal arrays such as those reported by Fazio [29] have been demonstrated to provide both extremely low reflectance as well as demonstrations of novel optical effects such as coherent back-scattering of Raman radiation [30].

These studies emphasise that the performance of the overall ensemble array is largely affected by the structure and the geometry of the NWs which are manipulated at the early stages of the growth process. For single-wire devices however, structural disorder is a more significant challenge. For applications where high geometrical control is required, it is likely that SAE growth or top-down approaches [27] may provide a better route to homogeneity.

3.2. Material and surface quality
Charge carrier mobility and minority carrier lifetime are strongly affected by the material quality of the NWs [80]. The variance in the minority charge carrier lifetimes can be attributed to interwire or intrawire surface quality variations [119, 123, 124], and this is often used as a proxy to understand growth quality.

3.2.1. Surface effects
Surface recombination dynamics on 301 Si NWs were investigated by Cating and colleagues [62]. Eight batches of wires were explored in this study, each batch included a mixture of different catalyst sizes resulting in a distribution of NW diameters ranging from 25 to 120 nm. Pump-probe microscopy was used to measure carrier lifetime of an ensemble. The study revealed that surface recombination velocity ($S$) varies by a factor of 50–100 from wire-to-wire from the same batch and varies by a factor of 2-3 in a single NW within the diameter range as illustrated in figure 5(a), where each colour represents one of eight growth batches. There is considerable variation in surface defect density even when NWs are synthesised at the same time.
Histograms of surface recombination velocity values for NWs with diameters smaller than 48 nm (top) and larger than 48 nm (bottom) demonstrate that larger diameter NWs have a more consistent surface quality than smaller diameter NWs as might be expected upon reducing the surface-to-volume ratio. The variation of recombination velocities at different locations within the NWs was also reported for different NWs sets as shown in figure 5(b). Surface recombination velocity is measured in 23 NWs at locations within 10 µm of the catalyst (red) where little variation is observed in S compared with the wider NW population (gray). In figure 5(b), S is measured at 2–6 locations along 5–20 µm segments in each of 40 NWs, 12 of which are indicated by different colours. This shows that there is little difference in the spread of S values compared with the population as a whole, confirming that the surface recombination velocity variation observed in population is mainly between wires, rather than intrawire.

In two different studies, a broad distribution of carrier lifetimes has been observed that is predominantly linked to interwire variation in diameter. Pump-probe measurements of individual Si NWs [137] show longer lifetimes than ensemble measurements by transient absorption spectroscopy of the same NWs [61]. This might be attributed due to side products, residual reactants or catalysts which may remain in the structures, as these can skew the decay to shorter times compared to that of the individual NWs.

A similar study was conducted on single GaN NWs by Upadhya where ultrafast pump-probe was used to study carrier relaxation through yellow luminescence (YL) [59]. Figure 5(c) compares ultraviolet-pump, visible-probe measurements on single and ensemble GaN NWs. Counter-intuitively, it was observed that single NWs show slower recombination when compared with the ensemble. A fast dynamic was attributed to the relaxation of electrons out of the conduction band into near-conduction band defect states, while a slower dynamic is linked to the radiative and non-radiative recombination processes. Variation in relaxation times is related to the inhomogeneous distribution of the NW diameter, length, and orientation in the ensemble; this observation disagrees with a previous study on the same sample where the single NW dynamic was observed to be is faster than ensemble [138]. The comparison between single and ensemble NWs can give different results depending on measurement locations of the ensemble and the properties of individual NWs. The study also compared the effect of the state of the polarization of the pump on the NWs sample [59]. Compared with a similar study performed by the group on ensemble [139], it was found that ultrafast dynamics in GaN ensemble is independent of the polarization of the pump and probe. This was not the case for single NWs, which revealed that the relaxation is faster when both beams are polarized parallel to the NW. This is because the photoexcited carrier density will be much higher for parallel polarization than perpendicular polarization resulting in fast relaxation.

Variation in surface recombination is attributable to either geometrical or facet-related differences between wires. As such, improved control over geometry and local growth conditions provides a route to better interwire homogeneity.

3.2.2. Doping

The optoelectronic performance of the NWs can be enhanced by doping [124]. Alanis et al [64] studied the effect of doping on the quantum efficiency (QE) of Zn-doped GaAs NWs [140]. Based on large-scale statistical measurements, NW emission was found to be brighter for higher doping concentration, evidencing an enhancement in QE. It was further shown that doping level is negatively correlated with the lasing threshold; in other words, a reduced lasing threshold is achievable by use of a high doping concentration. Wires with a mean doping level \( p > p_{\text{cut}} = 3 \times 10^{18} \text{ cm}^{-3} \) had the highest chance of lasing with a yield of \(~65\%\). Furthermore, the likelihood of lasing increases to 70% for NWs with a length \((L > L_{\text{cut}} = 4 \text{ µm})\). Figure 5(d) shows a sub-population selected from the ensemble \((p > p_{\text{cut}})\) and \((L > L_{\text{cut}})\) where the yield is expected to be over 70%.

3.2.3. Photoelectrochemistry

Wire-to-wire variation can also influence the electrochemistry of an ensemble array as found by Su [141] during their study of developing single NWs for photoelectrochemistry (PEC). In this study, Si NWs with two doping profiles \( p - Si \) and \( n^+ p - Si \) were exploited which were further decorated with platinum nanoparticles. Using PEC measurements on the NW arrays, it was found for both devices that \( V_{\text{oc}} \) (open circuit voltage) of the array devices is comparable to that of the worst single NW device. This is illustrated in figure 5(e) for \( n^+ p - Si \) device. This would indicate that the performance of the ensemble array photoelectrode is largely affected by the worst-performance of the individual NW. This is further supported by the equivalent circuit model which shows the correlation between the \( V_{\text{oc}} \) of the ensemble with the distribution of the \( V_{\text{oc}} \) of single NWs as demonstrated in figure 5(f). As these single NWs have similar dimensions and underwent the same doping process, the wire-to-wire variance should be attributed to the heterogeneity of the material quality introduced during the growth or fabrication processes or both. These findings suggest the importance of enhancing NW homogeneity within an array.
3.3. Heterostructures

Many heterostructural designs have been created using the NW architecture: QW, multiple quantum well (MQW), core–shell and QDs are common examples. Disorder and inhomogeneity are increasingly relevant when quantum confinement determines optoelectronic functionality, due to the highly non-linear relationship between energy levels and confinement.

Fluctuation of the thickness of a QW in a NW structure has an impact on the optical and electrical properties. Radial heterostructure QWs can exhibit significant thickness fluctuations which lead to the formation of unintentional QDs (for a QW thickness $\leq 4$ nm) [142]. Wavelength tunability of the QW emission can be achieved by varying thickness [143], and small variation of the perfect hexagonal shape of the NW-QW can lead electrons and holes to be localised on the facets where QW is the thickest instead of at the corners. As investigated on hexagonal QW system in the commonly grown GaAs/Al$_{1-x}$Ga$_x$As core/shell NW heterostructure, the 6-fold corner symmetry of a perfect hexagon is rapidly lifted due to thickness variation and charge localisation at the side facets [142].

Davies [63] examined the disorder in the GaAs core and GaAs quantum well tubes (QWT) in core-multishell GaAs/Al$_{0.3}$Ga$_{0.7}$As NWs. Fluctuations in the QWT thickness were linked to variations in Al alloy fraction, and the photoluminescence disorder parameter in the core and the QWT were examined and correlated. The disorder parameter describes the broadening of PL emission beyond thermal effects due to defects and inhomogeneity existing in the structure. The disorder of the QWT is larger than the disorder of the core which is attributed primarily to inhomogeneity in the QWT thickness. The strong correlation of the core and QWT disorder parameters indicates that variations in core structure can effectively propagate to the shell layers. Given that well growth rate (and hence thickness) is dependant upon core diameter, special attention must be taken to produce high-quality and uniform core growth before shell deposition.

A study by Alanis on GaAs/AlGaAs MQW NW lasers [144] revealed that a strong positive correlation was found between MQW disorder parameter and lasing threshold as illustrated in figure 6(a). It was proposed that a reduction in the threshold could be achieved by reducing MQW disorder, through a variation in growth conditions [63]. The study also showed a weak correlation between lasing threshold and the length of the NW, suggesting that distributed losses may dominate, interwire disorder in reflectivity is large or both. These parameters are strongly dependant on initial growth conditions, and interwire disorder in length directly impacts on threshold in this case.

Recently we reported that large-scale statistical measurements in MQW structures can be implemented to study loss mechanisms in nanolasers [73]. In this study, two MQW samples with different core material—GaAs-core and AlGaAs/GaAs QWs and GaAsP-core and GaAs/GaAsP QWs—were investigated. By correlating the inverse of the NW length to the NW lasing threshold, the study shows that the correlation is weak for GaAs-cored wires and a positive correlation for GaAsP-cored NWs; this supports distributed losses and end-facet dominated losses in these cases, respectively. The study claims that the primary loss mechanism for GaAs-cored NW lasers is core-reabsorption, which can be eliminated to achieve low lasing threshold.

Different nano-structures of the same material can have significantly different behaviour. InGaN/GaN nanopillars have been fabricated from InGaN/GaN MQW [145]. Here, temperature-dependent PL measurements showed different PL spectra compared with the original MQW, with the ensemble nanopillars showing several peaks which are attributed to the size-dependent effects. It was proposed that InGaN layers with different strains and quantum confinements will exhibit different emission wavelengths, and nanostructuring introduced significant material inhomogeneity. A blueshift was also observed in the nanopillar PL emission which is most likely due to the strain relaxation and the quantum confinement effects.

As heterostructured NWs provide a method to produce varied optoelectronic properties, interwire variation continues to present a significant challenge to scale-up. While highly homogeneous axial structure can be produced using top-down approaches [146], radial structures are less amenable to this technique. Routes to more uniform radial profiles have been explored through high-speed growth [122] and this remains an active area of research.

3.4. Strain

Inhomogeneity in the NW structure due to variation in the alloy stoichiometry or variation in the dimensional properties can induces strain [147–151]. Mapping the variation in strain between NWs remains an outstanding challenge in the field, however a number of studies have explored the impact of strain on the electronic behaviour of individual [152] or ensemble NWs. Balaghi demonstrated that changing the composition of In$_x$Ga$_{1-x}$As shell can be used to tune the PL emission in a GaAs core by up to 40% [153]. Both GaAs/In$_x$Ga$_{1-x}$As and GaAs/In$_x$Al$_{1-x}$As core/shell NWs were studied, grown by molecular beam epitaxy (MBE). The strain induced on the core arises from lattice mismatch between the core and shell in which the shell composition plays a crucial role. The results demonstrate that strain in the core is increases linearly with $x$ content for both GaAs/In$_x$Ga$_{1-x}$As and GaAs/In$_x$Al$_{1-x}$As NW structures suggesting that no
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= for NWs with a fixed diameter, as illustrated − of thickness of 70 nm and 0.15 were shown to have carrier lifetimes ranges from 1 to [\[40–80 \text{ nm; closed symbols} \] and the corresponding core/shell misfit \[153\]. (c) The correlation of peak lasing wavelength between two measurements for printed and unprinted NWs. Dashed line represents the ideal correlation \[166\] (reprinted with permission from Nano Letters, 20, 1862. Copyright 2020 American Chemical Society).

apparent plastic relaxation occurs; such relaxation often limits the use of higher strain for bandgap engineering \[154\]. PL emission is red-shifted with increasing \(x\) for NWs with a fixed diameter, as illustrated in figure 6(b) for GaAs/In\(_x\)Al\(_{1-x}\)As NWs ensemble.

The effect of alloy inhomogeneity on the NW properties can be regulated by the means of thermal annealing which reduced alloy disorder \[155\] and hence controls the strain induced in the NW. Tuning the nitrogen composition in core/multishell GaAs/GaAsP/GaP reduces the local strain which can cause three-dimensional confinement of excitons. This can be used to create partial relaxation of the global strain caused by the lattice mismatch \[156\]. Annealing should be considered carefully since it is one important factor involved in the fabrication process which can reduce interwire inhomogeneity.

Strain is indicated as one of the factors which affects the carrier dynamics. By using strain, carriers can be efficiently confined in the core, enhancing the electrical and optical properties \[147, 157, 158\] of the NW. Couto et al demonstrated this approach in strained GaAs/GaAsP core/shell NWs \[159\]. GaAs core capped with GaAs/P\(_{1-x}\) of thickness of 70 nm and \(x = 0.15\) were shown to have carrier lifetimes ranges from 1 to 1.5 ns at low temperature. This is comparable to type-1 QDs indicating that strained NWs exhibit carrier localisation in QD-like nanoscale potential. Efficient carrier confinement in the strained GaAs core was confirmed by the absence of PL emission corresponding to the GaAsP shell. Strong carrier confinement was also observed on highly strained GaAsP/GaAs coaxial NW QWs which exhibits low lasing threshold which is observed by the dominance of QW emission \[160\].

3.5. Fabrication

Many applications for NWs require transferring the NWs from the growth substrate to a different low-index or flexible substrate. The transferring process and subsequent fabrication can strongly influence the properties and performance of the transferred NWs. Different techniques can be utilised to transfer NWs where some are superior compared with other techniques.

Four different NW transfer approaches have been studied by Alanis \[161\]. The four approaches are ultrasonication for 5 s and 100 s, mechanical rubbing, and PMDS stamping onto z-cut quartz substrates. The impact of the transfer process was examined on p-doped GaAs core-only NW lasers ensemble. This involved studying the effect of the transfer on the NW length, lasing yield, and lasing threshold and correlate it with end-facet quality. Employing large-scale statistical measurements, it was been found that ultrasound transferred samples had the longest average length. This indicates that wires transferred by solution-based methods seem to fracture closer to the base resulting in longer wires. On lasing characterisation, short ultrasound showed the lowest median lasing threshold followed by PDMS transfer. This reduction in the threshold is attributed to the improved end-facet quality at the base of the NWs as confirmed further by SEM, which is a significant source of interwire inhomogeneity for NW lasers.

There is great attention to applications of flexible electronics \[162\]. A study of transferring GaAs NWs onto a flexible substrate while maintaining vertical orientation was conducted by Valente \[163\]. The fabrication process involved the growth of GaAs on a Si substrate, embedding the GaAs NW array within a dielectric solution, releasing NW layer by reactive ion etching, transferring NWs to an intermediate glass substrate, and finally to a flexible substrate. The structural properties of the transferred GaAs NWs are not significantly altered as confirmed by Raman spectroscopy. Nevertheless, the PL emission of the transferred NWs is enhanced indicated by the high PL emission, which is likely due to the reduced non-radiative
recombination as a result of the modification of surface states. This enhancement is also observed in power-dependent PL spectra, where low power is required to observe the sharp NW emission.

Interwire disorder can be caused by changes in individual NW fabrication. Guilhabert demonstrated that single InP NWs lasing emission was retained after controlled transfer-printing onto a target substrate [164], and the differently oriented NWs can support different modes and hence tuning the lasing emission of the NWs [165]. However, a study of the effect of transfer-printing process on the lasing properties of GaAs/AlGaAs core/shell NW lasers showed a heterogeneous process [166]. The population of NWs was transferred from the growth substrate onto a second substrate with random orientation, then optically characterised and spatially mapped to allow device binning by lasing threshold or lasing wavelength. From the a statistical measurement, around 81% of the NWs show lasing emission on the first substrate.

Twenty-five NW laser devices were individually picked and printed onto a second substrate in a regular array and recharacterised. The printed and unprinted samples were characterised after 6 months of storage at room temperature, showing that 24 out of 25 of the printed device group retained their lasing properties, while 74 out of 155 of unprinted devices showed lasing behaviour. This decrease in the lasing population is likely to be due to thermal effects on the polymer layer at the surface during repeated measurements.

Figure 6(c) shows a correlation of laser threshold values between two measurements for printed and unprinted NW lasers. The results show an increase in the threshold level for printed NWs and a decrease for unprinted NWs, whereas the correlation of the peak lasing wavelength shows no significant variation in the PL for first and second measurements for both printed and unprinted groups which indicates that the printing process does not dominate variations in peak lasing wavelength. This is promising for fabrication of highly sensitive and uniform devices using the micro-printing approach.

4. Exploiting heterogeneity

Heterogeneity is a major challenge in industrial take-up of functional nanomaterials [50, 51]. However, from a fundamental materials and physics perspective it also provides an opportunity [73]. Given appropriate measurements, deviations in performance of individual NWs from the ensemble average can be linked to microscopic causes such as variations in geometry [63, 167], heterostructuring [144], doping [64], facetting [161] or surface quality. A typical alloy-based (VLS) growth may produce $>10^4$ NWs, while SAE growth may produce $10^2$–$10^4$ NWs; in either case, this provides an opportunity for big-data approaches [77] if sufficient data can be collected. Exploiting large datasets by using automated approaches to experimentation is an increasingly studied area of science [168], and while this was initially focused on traditionally big-data areas such as bioinformatics, climate science and astrophysics, the development of robot scientists [169], Bayesian experimental design [78, 170] and machine learning in materials science [171] has enabled advanced computational and analytical methods to be applied in materials physics and nanotechnology [77].

4.1. High-throughput experimentation

Producing large datasets for analysis requires specific experimental methodology. Of primary importance is the identification and repeated characterisation of materials. Two approaches to high-throughput are typically taken: online study in flowing fluid on a microfluidic or ‘lab-on-a-chip’ platform, or dispersal of particles onto a planar substrate and microscopic identification. The former has emerged from early optofluidic [172] and micro-synthetic techniques [173] and the fusion of these with photonics platforms for analysis [174], and has been successfully applied to nanocrystal synthesis [175, 176]. In this approach, the sequential passing of nanodroplet containing one or more nanoparticles through a microfluidic channel allows for in-line absorption and fluorescence studies, which can be used for kinetics or monitoring, however to date it does not allow for deterministic single particle measurements and has not been applied to NWs.

Removal and re-dispersal of as-grown NWs from their growth substrate onto an inert support substrate is typically used for the isolation and characterisation of single NWs. This may be performed via micro-mechanical cleavage, ultrasonication, or using a soft polymer stamp, and typically results in the random distribution of NWs (although precision methods exist [164]). Identification of single NWs can be achieved using a machine vision approach in SEM [76, 177] or optical microscopy [73], with the latter based on object identification techniques originally developed for astrophysical imaging analysis [178]. More recently, neural network based techniques are being applied to 2D material flakes [179, 180] which are likely to be adopted more widely. Once identified, common high-throughput techniques including imaging and fluorescence spectroscopy [63, 73] which can be correlated if a registered co-ordinate system can be produced. Re-location of single wires can be achieved using marked substrates or more general computational approaches based on the relative position of wires [167].

Of critical importance to this field is the linkage of simple characterisation with evaluation of functional performance. For NW-based lasers this performance is lasing threshold and yield; by correlating imaging and
spectroscopy with a lasing study we have reported the dependence of NW laser threshold on reabsorption losses [144], doping [64] and end-facet reflectivity [181]. These studies provide for a deeper physical understanding, identification of best-in-class materials for in-depth study, and a true measure of yield for using these NWs in industrial or commercial applications. For electronic devices multiplexing can be achieved for randomly placed materials using automated four-point probe [182] or electron-beam lithography [76], both of which can measure electrical properties across tens of wires. More recently, the integration of pick-and-place techniques provides a route to the accurate and repeatable production of single NW optical [183, 184] and electronic [15] devices.

5. Outlook

Semiconductor NWs have well-established promise for optoelectronic and photonic technologies. Bottom-up, thermodynamically driven growth enables their production at scale, however, functional disorder arising from intrawire or interwire variations is an under-explored area which is critical to address for industrial application. High-throughput and data-assisted scientific experimentation is a rapidly growing field, and its application to disorder in semiconductor NWs presents clear opportunities both for characterisation, and for providing a deeper physics understanding. Challenges do remain: while exciting progress on experimental and analytic tools has begun, a unified framework for treating and exploiting multimodal and disordered data is lacking. Much can be learnt from projects in other materials systems, such as the dark reactions project [185], autonomous experimentation in 2D materials [179] and semi-supervised approaches from semiconductor manufacturing [186]. Uniting these approaches under a single methodology will provide an opportunities to use big-data to address heterogeneity challenges for a range of material applications spanning thin film [187] to colloidal QDs. Disorder in NWs presents a real challenge, but modern experimental and analytical techniques are enabling significant advances and provide a new route to functionally homogeneous and industrially relevant single-NW devices.

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