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Optical characteristics of GaInP/GaP double-heterostructure core-shell nanowires embedded in polydimethylsiloxane membranes

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The authors report on the optical properties of GaInP/GaP double-heterostructure (DH) core-shell nanowires (NWs) embedded in polydimethylsiloxane (PDMS) membranes. Self-catalyzed NW structures are grown on Si (111) substrates by initiating with the formation of Ga droplets as a catalyst which is followed by the growth of GaP core and GaInP DH shells. Optical characteristics of GaInP/GaP DH core-shell NWs transferred from Si substrates into PDMS membranes show enhanced 77 K light emission at 630 nm. The signal at 775 nm from the surface states of NWs can be mitigated by embedding the NWs in a PDMS membrane that acts as a surface state passivant. © *2010 American Institute of Physics*. [doi:10.1063/1.3455340]

Recent technologies on organic light-emitting diodes (OLEDs) have been attracting growing attention for the realization of low-cost, low-weight, full-color, and flexible flat-panel display as well as other emissive products. Since the first demonstration of organic thin-film electroluminescence in 1987,[1] many researchers have been devoted to the realization and development of high-efficiency OLEDs and flexible displays.[2–4] Furthermore, the integration of organic/inorganic materials into hybrid optoelectronic nanostructures enables active devices that combine the diversity of organic materials with the high-performance and well-established optical/electronic properties of inorganic nanostructures. So far, several groups have demonstrated hybrid light-emitting diodes (LEDs), solar cells, or photovoltaics that combine organic materials with semiconductor nanomaterials such as nanocrystals, colloidal quantum dots, or Si nanowires (NWs).[5–7]

Compound semiconductor NWs, which are crystalline, vertically aligned, and highly oriented crystalline nanostructures utilizing either the vapor-liquid-solid method[8] or the "catalyst-free" method using patterned substrates,[9] have been intensively exploited as a key component for diverse applications in nanophotonics and nanoelectronics such as nanolasers,[10–12] LEDs,[13–16] single-photon emitters,[17] transistors,[18] photodetector,[19] and solar cells.[20] Furthermore, NWs on Si substrates have recently attracted practical interest because of their compatibility with existing Si-based electronic devices using mature and "low-cost" Si technologies. Therefore, hybrid combination of these well-established, intriguing NW technologies with organic materials which includes polymers would enable the realization of flexible organic/inorganic hybrid devices utilizing compound semiconductor NWs such as flexible, low-cost LEDs/displays, detectors, or solar cells which might be able to circumvent the substantial life-time problems of the existing all-organic devices by using semiconductor materials as an active.[5]

In this study, we focus on the development of "self-catalyzed" GaP NWs growth on Si to prevent the contamination from foreign metal catalysts which causes the deep-level trap in III–V NWs and in turn deteriorates device characteristics.[21] GaP has the smallest lattice mismatch to Si substrates (≅0.4%) at room temperature (RT), and GaP-based material systems have been of practical interests for their application to LEDs in visible regimes such as red, yellow, or green. All samples are grown by low-pressure metal-organic chemical vapor deposition on Sb-doped Si (111) substrates at a total pressure of 60 Torr. After sequential cleaning processes with acetone, isopropanol, and deionized water in an ultrasonic bath, the Si wafers are immersed into diluted hydrochloric acid–hydrogen peroxide mixture ($HCl:H_2O_2:H_2O=1:1:1$) to remove the residual microparticles on the surface. Next the wafers are etched in 5% hydrofluoric acid solution to remove a native oxide on the surface and loaded immediately into the reactor. The growth temperature for all the growth including Ga droplets and GaP NWs is 480 °C. First, Ga droplets are deposited by supplying trimethylgallium (TMG) with a mole flow of 2.2×10^{-5} mol/min for 30 s to seed NWs on the Si substrate [Fig. 1(a)]. Next, the GaP core for the growth of GaInP/GaP double-heterostructure (DH) NWs is formed by supplying tertiarybutylphosphine and TMG with a TMG mole flow of 2.9×10^{-5} mol/min at a V/III ratio of 27 for 10 min immediately after the formation of Ga droplets [Fig. 1(b)]. In this growth process, Ga droplets act as a catalyst which allow for vertical NW formation along the ⟨111⟩ direction. After the growth of GaP core, GaInP DH layers are grown at a V/III ratio of 27 which are comprised of thin GaInP layer with a Ga:In flux ratio of 50:50 (GaInP-2) cladded by GaInP layers with a Ga:In flux ratio of 70:30 (GaInP-1). The mole flow of TMG is kept constant at 2.2×10^{-5} mol/min and the growth duration for the growth of GaInP-1 and GaInP-2 are 1 min and 6 s, respectively. The Ga compositions of each layer, GaInP-1 and GaInP-2, can be inferred from the x-ray diffraction analyses of the bulk material growth to be approximately 77% and 61%, respectively. After the growth of NWs, polydimethylsiloxane (PDMS) base, which is a transparent,

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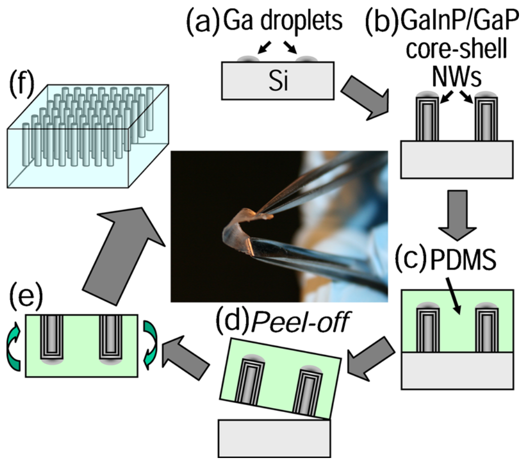

FIG. 1. (Color online) Schematic diagrams of the whole processes which involve (a) the formation of Ga droplets on Si substrates, (b) the growth of GaInP/GaP DH core-shell NWs, (c) PDMS application and curing processes, (d) peeling-off process, and (e) turnover for structural analyses and optical characterization. (f) Schematic and digital camera images of the fabricated NWs embedded in PDMS membranes.

polymeric, and viscous organosilicon compound, is mixed together with a curing agent in a 10:1 ratio and dropped on the samples [Fig. 1(c)]. Next, the sample is left at RT for at least half a day until the polymer penetrates into the grooves among the pillars and incorporates them completely.[22] Then, the sample is cured on a hot plate at 120 °C for 10 min to change the phase of the PDMS from viscous/liquid to solid. Once the sample is cooled down at RT, the PDMS membrane is gently peeled off with tweezers so that it remains intact and does not break [Fig. 1(d)]. The peeled-off sample is then turned over for structural analyses and optical characterization [Fig. 1(e)]. As can be seen in Fig. 1(f), the final structure peeled off from the Si substrate can be easily folded. Structural characterization of the as-grown GaInP/GaP DH NWs and the NWs embedded in PDMS membranes is carried out using transmission electron microscopy (TEM) and high-resolution scanning electron microscopy (SEM), respectively. Optical characterizations of the NW structures are carried out by conventional photoluminescence (PL) setup at 77 K excited by a 6 mW blue semiconductor laser (402 nm) with a beam spot size of approximately 1.5 mm.

The NW density is approximated to be $1.6\times10^{8}/\mathrm{cm}^{2}$ from the top-view SEM image shown in Fig. 2(a). The SEM image in Fig. 2(b) shows the formation of vertical GaP NWs with an average height and diameter of 900 nm and 100 nm, respectively. A TEM image of the GaInP/GaP DH NW shown in Fig. 2(c) clearly proves the existence of core-shell interfaces in the GaInP/GaP DH NW among GaInP-1/GaInP-2 shells and GaP core, along with the formation of Ga droplets on the top of the NW. The thicknesses of GaInP-1 and GaInP-2 are approximated to be 8 nm and 7 nm, respectively, from the high-resolution cross-sectional TEM (not shown). Figure 2(d) shows the SEM image of the NWs embedded in PDMS membranes. The NWs which are contrasted in the white dots can be observed on the surface of the PDMS membrane, while the surface of the PDMS without NWs shows no white contrasts.

Figure 3 shows the PL spectra at 77 K of GaInP/GaP DH core-shell NWs on Si with different incident pump power densities ranging from 390 μW to 6 mW. There are mainly

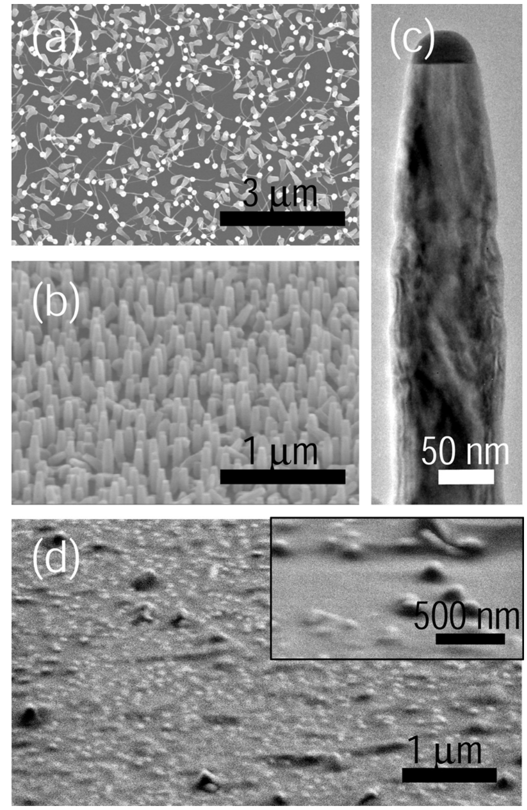

FIG. 2. (a) Top-view and (b) bird-eye-view SEM images of GaInP/GaP DH core-shell NWs on Si (111) substrates. (c) Cross-sectional side-view TEM image of the NWs. (d) Bird-eye-view SEM images of the NWs embedded in PDMS membranes. An inset is the SEM image of the PDMS membranes without NWs.

three peaks in the PL spectrum of the NWs on Si at 565, 625, and around 775 nm. From our detailed investigation which is discussed in Ref. 21, the PL peak at 625 nm originates from GaInP DH core-shell structure in the NWs, and the light emission at around 775 nm originates from surface states of GaP (or GaInP).[23] At lower pump power densities, only the peak from GaInP-2 shell is observed at 625 nm. The PL peak at 565 nm as well as the PL peak from the surface state at 775 nm emerges at higher pump power densities. This might be due to an excess of photopumped carriers that diffused from the GaInP-2 shell to the surface of NWs where the

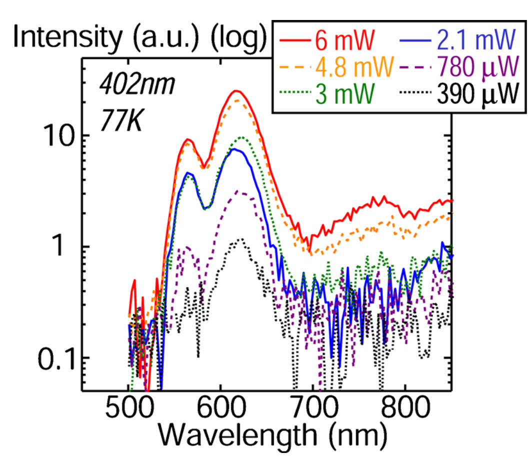

FIG. 3. (Color online) PL spectra at 77 K of GaInP/GaP DH core-shell NWs on Si substrates with different incident pump power densities ranging from 390 μW to 6 mW.

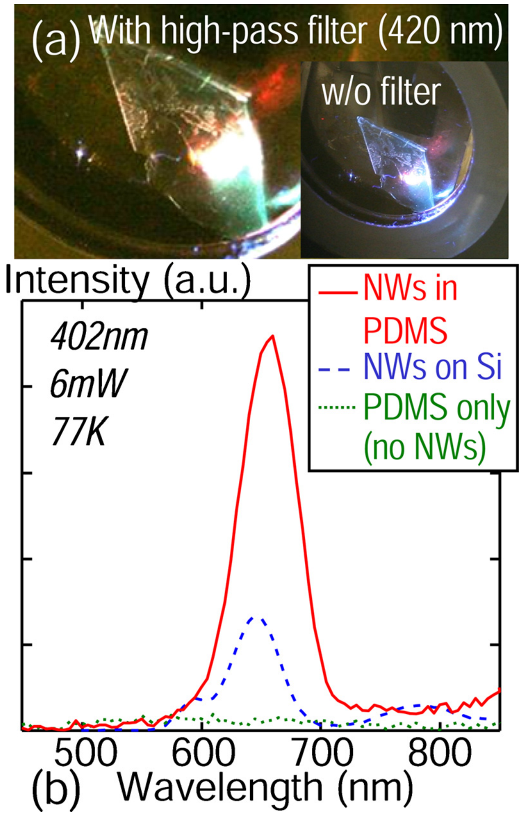

FIG. 4. (Color online) (a) Digital camera images of the NWs in PDMS membranes measured at 77 K with an excitation by a 6 mW blue 403 nm semiconductor lasers through a high-pass filter which cuts the signal below 420 nm. An inset is the image without the high-pass filter. (b) PL spectra at 77 K of GaInP/GaP DH core-shell NWs on Si substrates, the NWs in PDMS membranes, and PDMS membranes without NWs.

carriers can be trapped, resulting in an increase in the PL signal from both of the GaInP-1 barrier and the surface state of NWs. Therefore, the PL peak at 565 nm is likely originated from the light emission from GaInP-1 barrier.

Figure 4 shows the PL spectra at 77 K of the NW samples along with the digital camera images with an excitation by a blue laser through a high-pass filter which cuts off the signal below 420 nm. The digital camera image with the high-pass filter in Fig. 4(a) clearly shows the visible light emission in red from the NWs embedded in the PDMS membrane. The NWs embedded in the PDMS membrane have only one enhanced peak at 635 nm whose PL intensity is 3.5 times stronger than that of the NWs on Si substrates while there is no PL peak from the PDMS membrane without NWs, as can be seen in Fig. 4(b). It is noted that the peak from the surface state disappears after embedding NWs in PDMS membranes. It is likely because PDMS polymers acts as a passivant for the surface state of the NWs during both the drop-casting and curing processes.[24] Further investigation will be required to elucidate the mechanism of the surface state on NWs.

In summary, we report on the optical properties of GaInP/GaP DH core-shell NWs embedded in PDMS membranes. Self-catalyzed NWs are grown on Si (111) substrates by initiating with the formation of Ga droplets as a catalyst which is followed by the growth of GaP core and GaInP DH shells, and are then transferred into PDMS membranes. The optical characteristics of the NWs in PDMS membranes show enhanced light emission at 635 nm whose PL intensity is 3.5 times stronger than that of the NWs on Si substrates. The signal at 775 nm from the surface states of NWs is mitigated by embedding NWs in PDMS membranes that acts as a surface state passivant. These results would enable the realization of organic/inorganic hybrid nanophotonic devices such as flexible LEDs/displays, detectors, and solar cells.

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