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Strong surface passivation of GaAs nanowires with ultrathin InP and GaP capping layers
GaAs nanowires grown on Al-doped ZnO buffer layer

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We report a pathway to grow GaAs nanowires on a variety of substrates using a combination of atomic layer deposition and metal-organic vapor phase epitaxy (MOVPE). GaAs nanowires were grown via MOVPE at 430–540 °C on an atomic-layer-deposited Al:ZnO buffer layer. The resulting nanowires were affected only by the properties of the buffer layer, allowing nanowire growth on a number of substrates that withstand ~400 °C. The growth occurred in two phases: initial in-plane growth and subsequent out-plane growth. The nanowires grown exhibited a strong photoluminescence signal both at room temperature and at 12 K. The 12 K photoluminescence peak was at 1.47 eV, which was attributed to Zn autodoping from the buffer layer. The crystal structure was zincblende plagued with either twin planes or diagonal defect planes, which were related to perturbations in the seed particle during the growth. The used method combines substrates with variable properties to nanowire growth on a transparent and conductive Al:ZnO buffer layer. © 2013 AIP Publishing LLC.

I. INTRODUCTION

In recent years, semiconductor nanowires (NWs) have proved to offer novel means to construct a variety of applications including light-emitting diodes, lasers, sensors, and transistors. One of the most studied fields is optoelectronics, where III–V compound semiconductors, such as GaAs, are particularly promising due to their high electron mobilities and direct band gaps. Traditionally, III–V nanowire applications are based on NW fabrication on bulk semiconductors. However, for many of the possible applications, the high cost of bulk semiconductors remains a constraint for mass-scale production. As a result, more research is focused on III–V nanowire growth on low-cost substrates, such as glass. However, glass as such is insulating which limits its use in applications, and is thus often coated with transparent conductive oxides (TCOs) before NW growth. TCOs are attractive candidates as platforms for NW growth, since they can be deposited on numerous substrates with varying properties, and can additionally be used as transparent electrodes. However, the research of TCOs as NW growth platforms remains at relatively immature level and lacks some interesting material combinations.

Among TCOs, aluminium-doped zinc oxide (AZO) has recently gained much interest due to its lower price, abundance of elements and non-toxicity compared to the mainstream TCO used in industry: indium tin oxide (ITO). Furthermore, AZO has been recognized as the most suitable substitute for ITO compared to other available TCOs. AZO can be deposited by a number of methods, including atomic layer deposition (ALD), magnetron sputtering, sol-gel, evaporation, and pulsed laser deposition. Of these methods, ALD offers the most conformal growth and is well established for mass-scale production.

Growing nanowires on ALD-deposited AZO holds great potential, as it enables NW growth on almost any material compatible with ALD and moderately high temperatures. Thus, AZO films offer a path to use a variety of substrates for NW growth, including inexpensive ones, which can additionally be transparent or conductive. Such substrates hold future potential to lower the cost of a number of applications, such as price-sensitive solar cells. AZO is additionally a wide band-gap semiconductor, which allows its use as an active part in devices.

In this paper, we report metallo-organic vapour phase epitaxy (MOVPE) growth of GaAs nanowires on AZO deposited by ALD on various substrates. To the date, only ZnO NWs grown on AZO thin films have been previously reported, and no work has concentrated on the growth of III–V NWs on AZO. We show that the AZO film enables GaAs NW growth on substrates that are intrinsically incompatible with the NW growth. The substrates used include household aluminium foil, which offers an inexpensive platform to produce NWs. Furthermore, the grown NWs show photoluminescence (PL) even at room temperature, despite the high density of surface states in GaAs and frequent stacking faults in the NWs.

II. EXPERIMENTAL METHODS

The sample fabrication required two steps: AZO film deposition and subsequent NW growth. In this study, the AZO films were deposited using an ALD system from Beneq (TFS 500) on following substrates: Si(111), soda lime glass, ITO coated glass, and aluminium foil. Prior to ALD, the samples were rinsed in isopropanol and in deionized (DI) water. Precursors for zinc, aluminium, and oxygen were...
diethylzinc, trimethylaluminium, and H₂O, respectively, and nitrogen was used as carrier gas. Reactor temperature during the deposition was kept at 200°C and the pressure at ~2 mbar. A deposition loop consisted of 30 cycles of ZnO followed by one cycle of Al₂O₃.

After AZO deposition by ALD, the samples were prepared for nanowire growth by MOVPE. Prior to the growth, the samples were immersed in acetone and in isopropanol and ultrasonicated for 2 min each, followed by a 5 min rinse in DI water. The clean samples were treated with poly-L-lysine (PLL) solution, which was used to deposit Au nanoparticles from a colloidal solution (from BBI International). After 1–7 min of Au particle deposition, the samples were transferred to the MOVPE reactor, where the Au nanoparticles acted as seeds for vapour-liquid-solid growth process.²⁴ The precursor for Ga was trimethylgallium (TMG) and for As tertiarybutylarsine (TBA). During a growth run, the reactor temperature was first raised to 410–540 °C, and subsequently TMG (6.1 μmol/min) and TBA (150 μmol/min) flows were switched on simultaneously to initiate NW growth. For a Zn doped reference sample, additional diethylzinc flow of 0.1 μmol/min was used. Growth time varied from 30 s to 5 min, after which the TMG flow was switched off and the TBA flow was kept on until the reactor cooled down to 300 °C. Temperature values reported in this work are thermocouple readings from graphite susceptor and therefore tens of °C higher than actual sample surface temperatures. Additionally, the actual growth temperature was higher for Si samples than glass samples, since Si conducts heat significantly better and the Si samples were thinner (300 μm for Si and 1.1 mm for glass and ITO coated glass).

Morphological characteristics of the AZO films and the NWs were studied using scanning electron microscopy (SEM) (Zeiss Supra 40). SEM was used to image the samples from top-view and side-view. Crystallographic information, high-resolution imaging and energy-dispersive X-ray spectrometry (EDX) data was obtained from transmission electron microscopy (TEM) (JEOL JEM-2200FS operated at 200 kV). TEM samples were prepared by gently rubbing a copper-supported holey carbon grid against a substrate with nanowires. Crystal structure was additionally investigated from TEM images with Fourier transformations (FT) performed in Imagej software. Furthermore, powder X-ray diffraction (XRD) (Cu Kα radiation) was used to probe crystal structure of large nanowire volumes.

Optical properties of the nanowires were studied with PL measurements. Nanowires were excited using a continuous wave laser with a wavelength of 532 nm, a spot size of ~100 μm, and a typical laser excitation power of ~250 W/cm². The PL signal was detected using a lock-in amplifier, a monochromator, and a liquid nitrogen cooled germanium p-i-n detector. A closed cycle helium cryostat was used for cooling the samples down to 12 K.

III. RESULTS AND DISCUSSION

The first step of the fabrication process is AZO film deposition on a desired substrate. Figure 1 shows a top-view SEM image of a typical AZO film, in this case deposited on Al foil. A rough polycrystalline structure can be seen with grainy features, corresponding to previously reported ALD grown AZO films.¹⁴,¹⁵ The grainy structure is visible also in the inset, which presents a cross-sectional image of a film grown on Si. Based on SEM, the film thickness measures ~350–380 nm. The films were deposited conformally on all surfaces of the samples including cracks and hillocks, and the morphology appeared identical throughout the samples. AZO film resistivity was measured using van der Pauw geometry and indium contacts. The measured value was 2.4 × 10⁻⁵ Ωm, which is in the same order of magnitude as previously reported values.¹⁶,¹⁹,²⁰,²⁵

In order to confirm that the AZO film enables the growth of nanowires on intrinsically incompatible substrates, NWs were grown on ITO with and without AZO deposited on top. With the used methods, scarcely any nanowires grew on bare ITO (Figure 2(a)). On the other hand, the AZO film deposited on ITO enabled NW growth with significantly higher yield, consistency, and length (Figure 2(b)). This indicates that the NW growth is not dependent on the properties of the underlying substrate, but only on the properties of the AZO film. Thus, a variety of substrates can be used for III-V NW growth simply by depositing AZO. To demonstrate further, NWs were grown on an AZO film deposited on common household Al foil, which is illustrated in Figure 2(c).

The NWs were observed to grow in two different modes: in-plane growth (NWs growing along the surface) and out-plane growth (NWs growing outwards from the surface). The NW growth on AZO begins as in-plane growth and transits to out-plane growth after few tens of seconds. Figure 3 shows SEM images of GaAs NWs grown for 30–120 s at 470 °C on an AZO film on Si. The two stages are visible as grey wormlike trails (in-plane growth) and straight brighter features (out-plane growth). Based on SEM observations, the growth mode for majority of the NWs was in-plane after 30 s and out-plane after 60 s, and after 120 s practically all NWs had transited to out-plane growth.

The growth process we propose for GaAs NWs on AZO is further clarified in Figure 4. When the reactor temperature
is raised to several hundred °C, Zn dissolves into the Au seed particle, since Zn is abundant in the AZO film and readily alloys with Au (Figure 4(a)). The presence of Zn in the NWs was supported by PL and EDX measurements, as will be discussed later in this paper. Next, Ga and As species are introduced to the system at the desired growth temperature. At this point also Ga alloys with the seed particle. The intake of Ga species to the seed substantially exceeds that of Zn, since Zn is chemically bonded in the AZO film, whereas Ga is diffusing freely on the surface. Eventually, the seed particle precipitates the alloyed species, i.e., mainly Ga and small amounts of Zn, initiating the NW growth. Arsenic species have poor solubility to Au and they arrive to the growth interface directly from the gas phase. Figure 4(b) depicts this in-plane NW growth process. In an earlier study, NW bending during in-plane growth was attributed to the seed particle precipitating NW crystal faster than the seed particle itself is moving on the surface. As a result, the NW crystal protrudes into the seed particle until it is quickly pushed to a new location. At this point, the seed particle location can change in respect with the NW crystal, and the NW growth proceeds to a new direction. Eventually, the growth direction changes to one that points outwards from the surface and the NW growth proceeds as out-plane growth, as shown in Figure 4(c). This growth model is supported by SEM observations; the out-plane growth tends to follow the in-plane growth, i.e., when viewed from above, the out-plane growth tends to proceed to approximately the same direction as the final part of the in-plane growth.

Finally, the out-plane growth was observed to proceed as straight or kinked NWs depending on the growth temperature (Figures 4(d) and 4(e)). The kinked or straight NW morphology was found to stem from different types of defect planes: diagonal or perpendicular to the growth direction. Kinked NWs and diagonal defects were observed with relatively low growth temperatures, as shown in Figure 5 for NWs grown at 470 °C on an AZO film grown on glass for 5 min (compared...
to NWs on an AZO film on Si, the actual growth temperature was lower due to poor heat conductance of glass). The kinked growth is apparent in Figure 5(a), which shows a side-view SEM image of the NWs. Additionally, the AZO film is visible as a bright layer underneath the NWs.

In order to reveal more details about the crystalline structure, kinks, and stacking faults, the NWs were investigated with TEM. Figures 5(b)–5(d) show TEM images from a top section of a NW with defect planes and kinks. The diagonal defects were tilted approximately 20° from the axis of the growth direction, and the defects in the same NW were always parallel to each other. The defects were few to tens of monolayers thick and some nanowires were severely defected with some areas having only few nm of the original crystal between the defects, whereas other nanowires had defect-free sections micrometers long. Interestingly, the kinks in the NWs were found to occur at the defects (Figures 5(b) and 5(c)).

Figures 5(e) and 5(f) present FT of a defect crystal and the NW crystal, respectively. For clarity, the crystal planes in the defect are marked with italic. The FT pattern in both corresponds to the zincblende (ZB) crystal structure and the nanowire growth direction was [111]. Comparing the FT images of the original crystal and the defect, it is clear that the defect crystal nucleated to the [11−1] direction of the original crystal (parallel to [111] in the defect), which deviates 70.53° from the [111] axis. Additionally, a twin plane separates the two crystals, since the defect FT is rotated by 180°. The nanowire growth direction typically being ⟨111⟩B, the facet opening to this [11−1] direction becomes ⟨111⟩A,27 which is a less favourable nucleation site. After the defect has nucleated, there are three {111} facets underneath the seed particle: (111) and (11−1) of the original crystal (Figure 5(f)), and (−1−11) of the defect crystal (Figure 5(e)). Evidently, the growth to the [11−1] direction of the original crystal (or [111] of the defect crystal) ceases shortly, i.e., the defect crystal ceases to widen as seen in Figures 5(c) and 5(d). When growth towards [11−1] ceases, the remaining [111] facets seen by the seed particle are (111) and (−1−11). The growth continues on these two facets until another crystal finally nucleates on the edge of the defect to the original [111] direction, and the growth continues as before the defect. Earlier studies report (11−1) oriented twin planes, but only as twin planes (no crystal growth towards [11−1]) and without relation to NW kinking.28,29 These twin planes were attributed to abrupt compositional changes28 or gold clustering.29 Metal clustering is a more likely cause for such defects in the NWs grown on AZO, since they exhibit no abrupt changes in composition.

At a higher growth temperature, defect planes occurred only perpendicularly to the growth direction and the kinking tendency diminished. Figure 6(a) shows a side-view SEM
image of NWs grown at 510 °C on an AZO film on Si for 5 min. The NWs have straight morphology with little tendency to kink. However, the defect planes plagued the NWs also at this higher growth temperature, as seen in Figures 6(b) and 6(c). Again, some of the NWs had more frequent defect planes than others, which is seen in nanowires NW1, NW2, and NW3 in Figure 6(b). The three NWs have clearly different density of defect planes, which are visible as darker lines perpendicular to the growth direction. Additionally, the defects appear more frequently closer to the base of the NW. The defect planes at 510 °C were identified as twin planes from diffraction patterns. A diffraction pattern taken over a defect plane is presented in Figure 6(e). Clearly, the crystal structure is ZB on both sides and the defect rotates the pattern by 180° over the [111] axis, which indicates a twin plane, a common defect in ZB nanowires.30

As mentioned above, the defect density varied between NWs and within NWs. Intriguingly, the defects appeared more frequently closer to the base of the nanowire. This suggests that the growth process is altered in the later stages of the growth. This alteration could be caused by changes in the seed particle. Indeed, some of the seed particles were found to have diagonal perturbations, as shown in Figure 6(d). Such perturbations were not observed in Au particles on top of the nanowires grown directly on Si, and the nanowires on Si presented only infrequent twin planes. The fundamental difference is thus expected to stem from the growth substrate and its constituents. In earlier studies, indium background has been observed to affect Ga supersaturation in the seed particle, which in turn affects crystal structure of the NW.31

Similarly, Zn background might affect the Ga supersaturation level. Furthermore, Ga supersaturation has been reported to affect the phase of the Au-Ga alloy and hence the crystal structure of the resulting NWs.32 When Zn is present in the seed particle, the alloy becomes Au-Ga-Zn, which might further alter the phase of the seed particle. The presence of Zn is thus expected to affect the delicate growth process of the NWs. Since the defects are more frequent closer to the base of the NW and the Zn is depleted during the growth, Zn appears to cause defects in the NW crystal. This also explains the varying defect density between separate nanowires; the faster the growth transits from in-plane to out-plane growth, the smaller amount of Zn is incorporated to the seed during the in-plane growth and the fewer defects are introduced to the NW.

Besides the resulting crystal structure, the growth temperature affected the in-plane growth and the transition from in-plane growth to out-plane growth. Figure 7 presents top-view SEM images of GaAs NWs grown for 60 s on an AZO film on Si between 430 °C and 540 °C and a reference sample of NWs grown directly on Si at 470 °C. The growth temperature had three notable effects; higher temperatures caused faster transition from in-plane to out-plane growth, out-plane NWs grew more vertically and tapering increased. Based on the morphology and yield of the NWs, the growth window is deemed 450 °C–510 °C. Similar temperature series were studied also on AZO films on ITO and glass. The substrate underneath the AZO film was observed to play little role on the NW growth, only the onset temperature of different visible effects was higher on glass and ITO coated glass due to poorer heat conductance. The actual surface temperature was estimated to be few tens of °C higher for Si samples compared to glass or ITO coated glass.

In order to obtain information of the crystalline structure of large NW volumes, the NWs were characterized using powder XRD. First, the presence of polycrystalline AZO was verified by measuring a glass sample with an AZO film (Figure 8(a)). Second, an identical sample with nanowires grown at 470 °C on the AZO film showed additional peaks corresponding to the GaAs ZB phase (Figure 8(b)). Finally, nanowires grown on an AZO film on Si at 470 °C, 490 °C, and 510 °C (Figures 8(c), 8(d) and 8(e), respectively) revealed only one additional peak corresponding to Si(111) plane. Thus, all of the scans on nanowires showed peaks corresponding to the GaAs ZB phase, whereas no wurtzite (WZ) phase was observed. This indicates that no polytypism is present and the crystal structure of nanowires as ensembles resemble those imaged with TEM.

Finally, PL measurements were used to study optical properties of the NWs. Figure 9(a) presents room-temperature PL spectra from GaAs NWs grown for 300 s at different
temperatures on different AZO coated substrates: at 470 °C on glass (sample 1), at 470 °C on Si (sample 2), at 510 °C on ITO coated glass (sample 3), and at 510 °C on Si (sample 4). In principle, the only effective difference between the samples was the actual growth temperature, which resulted from the susceptor temperature (the temperature reading) and the heat conductance of the substrate. The actual growth temperature is expected to be higher with increasing sample number.

The room temperature spectra exhibit broad peaks with a maximum at approximately 890 nm–900 nm (1.39 eV–1.38 eV). The breadth of the peaks and the variation of peak position are attributed to random occurrences of strain, impurities, and surface states in the NWs. The PL intensity increases by a factor of ~6 from sample 1 to sample 4 (i.e., when the growth temperature is increased). At higher growth temperatures, tapering becomes more imminent leading to thicker nanowires and larger average separation of charge carriers from the surface. GaAs surface is known to introduce trap states inhibiting radiative recombination. Thus, the increased thickness enhances the PL intensity. Another factor affecting the intensity is twin planes, which are considered detrimental to carrier lifetimes and mobility. Thus, the increased thickness enhances the PL intensity. Another factor affecting the intensity is twin planes, which are considered detrimental to carrier lifetimes and mobility.

In the case of twin planes, the incorporated Zn was apparent in PL studies, confirming that the observed signal originated from NWs. The presence of Zn was further studied by measuring EDX signal from NWs grown on AZO. Since EDX has a moderately high detection limit and the measured spot in TEM is small, only a faint signal is expected from the Zn species. Indeed a faint signal corresponding to Zn energies was seen in the NW crystal at some of the measured locations, supporting that Zn was incorporated in the NWs.

Figure 9(b) shows PL spectra taken at 12 K from the same samples. The peak positions emerge at approximately 845 nm (1.47 eV). Studies of the optical properties of GaAs/AlGaAs core-shell nanowires report low-temperature free exciton peak at ~1.518 eV (Refs. 34 and 38–40) and donor-acceptor pair (DAP) peak at 1.48–1.49 eV.24,38,40 The DAP peak is commonly associated with carbon,38,40 which is an inherent impurity in MOVPE. As discussed above, Zn is expected to be incorporated in the NWs. Zn is a shallow acceptor in GaAs, and a PL peak has been previously observed at ~1.49 eV in both Zn doped GaAs nanowires41 and bulk material.42 Comparing to previously reported values, the measured PL peak position of 1.47 eV is close to the DAP peak and the zinc-related peak, but is more likely to be Zn-related, since Zn is expected to be present in the NWs, and PL was observed only from doped NWs on bare Si.

IV. CONCLUSIONS

We demonstrated successful MOVPE growth of GaAs nanowires on atomic-layer-deposited transparent and conductive (resistivity 2.4 × 10⁻⁵ 2Ωm) AZO films. The AZO films were deposited on Si, glass, ITO, and household aluminum foil, demonstrating the variability of possible substrates. The NWs grew in a 2-phase growth mode, which included initial in-plane growth and following out-plane growth. The in-plane growth resulted in Zn incorporation from the AZO film to the seed particle and subsequently to the NW. Depending on the growth temperature, the out-plane growth exhibited either kinked wires with diagonal defect planes or straight wires with perpendicular twin planes. The incorporated Zn was apparent in PL studies, which showed a low-temperature peak at ~1.47 eV, corresponding to Zn-related peak in GaAs. The PL properties of the NWs on AZO were deemed good, since they luminated at room temperature, whereas no signal was acquired from undoped NWs grown on bare Si even at low temperature. The diagonal defects and the kinks caused by them add to the observed phenomena of NW growth process. The possibility of using an AZO film as a NW growth platform allows the use of inexpensive substrates and low-cost fabrication of devices where vertical NWs are not a necessity, such as solar cells.
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