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Protective capping and surface passivation of III-V nanowires by atomic layer deposition

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Low temperature (~200 °C) grown atomic layer deposition (ALD) films of AlN, TiN, Al2O3, GaN, and TiO2 were tested for protective capping and surface passivation of bottom-up grown III-V (GaAs and InP) nanowires (NWs), and top-down fabricated InP nanopillars. For as-grown GaAs NWs, only the AlN material passivated the GaAs surface as measured by photoluminescence (PL) at low temperatures (15K), and the best passivation was achieved with a few monolayer thick (2Å) film. For InP NWs, the best passivation (~2x enhancement in room-temperature PL) was achieved with a capping of 2nm thick Al2O3. All other ALD capping layers resulted in a de-passivation effect and possible damage to the InP surface. Top-down fabricated InP nanopillars show similar passivation effects as InP NWs. In particular, capping with a 2 nm thick Al2O3 layer increased the carrier decay time from 251 ps (as-etched nanopillars) to about 525 ps. Tests after six months ageing reveal that the capped nanostructures retain their optical properties. Overall, capping of GaAs and InP NWs with high-k dielectrics AlN and Al2O3 provides moderate surface passivation as well as long term protection from oxidation and environmental attack.

I. INTRODUCTION

Semiconductor nanowires (NWs) are being actively pursued as building blocks for next generation nanotechnology enabled systems. Although NWs offer far superior and unique properties than the material in bulk, however, one disadvantage associated with NWs is the presence of high density of surface states1–4 due to a very high surface to volume ratio. The surface states appear because of the un-passivated dangling bonds arising after the formation of the native oxide. The surface states can act as nonradiative recombination centers or surface charge traps, and can make additional electronic states within the band gap causing pinning (bending) of the Fermi level at the surface.1–4 A pinned Fermi level can push the free carriers from surface to the bulk forming an undesirable depletion layer, thereby limiting the movement of free carriers.

The pinning of Fermi level is a common problem observed in III-V NWs.1–4 The severity of the Fermi level pinning depends mainly upon the material native oxide type and the diameter of the NW (smaller the diameter more enhanced the effect of pinning). Among III-Vs, GaAs NWs are known to
have the highest surface recombination velocity of charge carriers \(5.4 \times 10^5 \text{ cm s}^{-1}\), and a strong Fermi level pinning is commonly observed. In fact, according to Demichel et al., for undoped or lightly doped GaAs NWs with diameters less than 100 nm, a depletion layer appears on the surface due to the pinning which extends throughout the NW volume, rendering it completely insulating or highly non-conducting. On the other hand, in sharp contrast, InP NWs have relatively good quality surface with less efficient surface states, and consequently show the lowest surface recombination velocity \((170 \text{ cm s}^{-1})^5,6\) of carrier among all III-V NWs. However, when InP NWs are stored in atmosphere over a long time, a degradation in their optical and electrical properties might occur. For GaAs NWs, to date, the best passivation method is the coating of a high band gap AlGaAs shell.\(^7,7\) For InP NWs, no well-established passivation method exists except for a few chemical passivation methods (sulphur\(^8\) and HF\(^9\)). However, these passivation methods are not stable with time. Thus, to use NW in functional devices, there is a strong need to explore suitable passivating materials that can provide some degree of passivation as well as long-term protection from oxidation and environmental attack.

There exists few previous reports where atomic layer deposition (ALD) grown AlN films were used as gate dielectric layers for the surface passivation of thin film based GaAs materials\(^10–13\) but hardly any systematic report exists studying the effect of different dielectric layers on the surface of III-V NWs and their optical properties. ALD enables depositing thin continuous and uniform films of a variety of materials conformally on topographically complex structures.\(^14,15\) As such, the study of the passivation efficacy of various ALD materials on NWs is an interesting area to pursue. In this study, we have investigated a wide range of ALD grown materials (AlN, TiN, Al\(_2\)O\(_3\), GaN, and TiO\(_2\)) as capping and surface passivating layers for GaAs and InP nanowires and nanopillars. Apart from the bottom up grown III-V NWs, we have also included top-down fabricated InP nanopillars in this study as the etched nanopillars are very interesting from the point of view of surface states.\(^16\) Further, since a high deposition temperature process is detrimental to the III-V NW surface quality, the advantage of using ALD in addition to being a low-cost scalable deposition technique is that most of the ALD capping layers can be deposited at low deposition temperatures \((\sim 200^\circ\text{C})\) which is compatible with most semiconductor device processing technologies. Further, as Al\(_2\)O\(_3\) and AlN are widely used as high-\(k\) gate dielectrics for III-V thin film structures\(^10–13\) they naturally could serve as promising candidates for future gate dielectrics for III-V NWs as well. In the case with GaAs, another additional property both these materials possess is the self-cleaning of the GaAs NW surface (thinning of native oxide after the deposition).\(^12,16,17\) In this study, we have used the photoluminescence (PL) and time-resolved photoluminescence (TRPL) techniques to study the optical properties of III-V NWs after capping them with a wide range of ALD grown materials. The aim was to evaluate if these ALD materials provide some degree of passivation and protection from long term oxidation without having any adverse effect on the NW surface.

## II. EXPERIMENT

GaAs and InP NWs were fabricated on Si (111) substrates in a horizontal flow atmospheric pressure metal organic vapor phase epitaxy (MOVPE) system with trimethylgallium (TMGa), tertiarybutylarsene (TBAs), trimethylindium (TMIn) and tertiarybutylphosphine (TBP) as precursors for GaAs and InP NWs, respectively.\(^7,18\) Hydrogen was used as a carrier gas and the total reactor gas flow rate was \(~5\ \text{l/min (slm)}\). A 40 nm diameter colloidal gold (Au) nanoparticles were used as catalysts for the vapor-liquid-solid (VLS) growth. The growth time was 5 min for GaAs and 2 min for InP (yielding \(~20\ \text{mm long NWs}\)). The nominal V/III ratio during the growth was \(~25\) for GaAs and \(~200\) for InP NWs, and the growth temperatures were 450°C and 420°C, respectively. High optical quality InP nanopillars were fabricated by nanosphere lithography (NSL) and inductively coupled plasma reactive ion etching (ICP-RIE) etching of InP films.\(^13\) In this process, self-assembled silica particles were used as etch masks. InP nanopillars obtained using this approach were conical in shape (tapered) with length \(~1.5\ \text{um}\).

The ALD AlN, TiN, Al\(_2\)O\(_3\), GaN, and TiO\(_2\) films were deposited using a Beneq TFS-500 system. All films were deposited at 200°C except for TiN, which was deposited at 425°C. AlN and GaN were deposited using plasma-enhanced ALD (PEALD) whereas the rest were deposited using

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standard thermally driven ALD. Here, the growth methods for only AlN and Al$_2$O$_3$ are discussed as the process details are similar for the other nitride and oxides, respectively. For AlN, the deposition temperature was 200 °C with TMA and NH$_3$-plasma enhanced by nitrogen as precursors with nitrogen used as the carrier gas. For Al$_2$O$_3$, the deposition temperature was 200 °C with TMA and H$_2$O as precursors with nitrogen as the carrier gas. TiCl$_4$ was used with H$_2$O and NH$_3$ as precursors for TiO$_2$ and TiN, respectively.

High resolution TEM measurements were carried out with a JEOL 2200FS double aberration corrected FEG microscope operated at 200 kV. Elemental composition in the NWs body was determined using a TEM integrated energy-dispersive X-ray (EDX) spectroscopy tool with a detection limit of 0.2 atomic-%. PL measurements for GaAs and InP NWs were performed using a 532 nm laser with a spot size of ~100 µm (macro-PL). In macro-PL set-up, a liquid nitrogen cooled germanium detector and standard lock-in techniques were used for signal detection and data capture. For InP nanopillars, a micro-PL (µ-PL) set-up at RT was employed. In this case, a Ar$^+$ 514.5 nm laser was used for photoexcitation with a spot size of ~2µm. Time-resolved PL (TRPL) measurements were performed using a synchroscan streak camera with a time-resolution of 2 ps. A tunable mode-locked Ti:Sapphire laser (pulse temporal length ~100fs, repetition rate 76 MHz, wavelength ~800 nm) was used for the excitation.

III. RESULTS AND DISCUSSION

GaAs NWs with an average length of ~20µm were grown on Si substrates. The NWs display predominantly single phase zinc-blende (ZB) crystal structure and were mostly untampered with ~40 nm diameter but a small variation from this value was also observed. Although the as-grown NWs are of high density, defect-free and long, interestingly no PL emission was detected from them even at low temperatures (15K). Here, we suspect that the as-grown GaAs NWs, owing to their small diameters (~40 nm), are likely to be totally depleted of free carriers with the depletion length extending throughout the NW volume due to the strong Fermi level pinning (high density of surface traps). To address the issue of surface passivation, and further prevention from the long term oxidation of the surface, we studied their optical properties after capping the surface with various ALD grown films of AlN, TiN, Al$_2$O$_3$, GaN, and TiO$_2$, respectively. The native oxide of the NWs reported here was not removed prior to ALD deposition. Nevertheless, removal of the oxide before ALD deposition did not make any difference in their optical properties. For GaAs NWs, only the AlN capping layer resulted in the passivation of GaAs NWs at 15K, and no PL emission was detected with any other ALD capping layer. It is good to note here that the ALD TMA-precursor (even few cycles) is known to clean-up GaAs native oxide by reducing and replacing the native oxide with Al$_2$O$_3$.

As seen in Fig. 1(a), otherwise non-emitters of light, GaAs NWs show PL emission when coated with an ultrathin ~2Å and ~5Å thick layers of AlN. The thickness of the ALD film was
estimated on the number of cycles of growth (typical ALD growth rate for AlN is $\sim 1 \text{Å/cycle}$ at the processed temperature and the real thickness could be higher). As seen in Fig. 1(a), a stronger PL emission was observed for 2Å thick AlN compared to 5Å thick layer. Also, for ALD film thickness exceeding 5Å, no PL emission was detected and the best surface passivation was achieved with a nominal 2Å thick AlN capping layer. We would like to mention here that ALD deposited AlN layer could be polycrystalline or amorphous depending upon the growth temperature.\textsuperscript{20} The AlN used in this work is amorphous as deposition occurred at a temperature of 200°C. This can also be seen in Fig. 1(b), where single phase zinc-blende GaAs NW\textsuperscript{18} is capped with an amorphous looking AlN layer. Discussing further the PL spectra in Fig. 1(a), the PL peak from GaAs NWs capped with 2Å AlN appears at 824 nm, which is red shifted compared to the emission one would expect from single phase ZB GaAs NWs (819 nm). For 5Å AlN, there are two peaks, one appears at 819 nm and the other at 842 nm. The peak at 819 nm is associated with exciton bound-to-acceptors ($D_0^+, X$),\textsuperscript{21} associated with carbon impurity which is normally incorporated during the MOVPE growth. However, the carbon peak might also originate from the carbon content in the AlN layer, which should contain $\sim 1\%$ carbon.\textsuperscript{22} However, since the thickness of AlN is ultrathin, we can attribute the same to the MOVPE growth. It is not clear at the moment why this peak is strongly suppressed when the AlN film thickness decreases to 2Å. The slight red shift (824 nm) in the GaAs PL emission for 2Å thick ALD film could be attributed to the nitridation (GaAsN) and surface coupling effects associated with ultrathin ALD layers, as been observed previously in thin film structures.\textsuperscript{10} Our passivation results are in agreement with previous reports where ALD grown AlN material was previously used as dielectric layer to passivate GaAs thin film structures.\textsuperscript{10–12} It is however interesting that no passivation of GaAs NWs was observed with an Al$_2$O$_3$ capping layer despite clean-up of the native oxide with TMA (Aluminum precursor). The nitridation step that follows TMA exposure for AlN deposition should incorporate nitrogen atoms on the recently formed Al$_2$O$_3$ layer (formed due TMA reducing and replacing the GaAs native oxide with Al$_2$O$_3$), which has the effect of greatly improving the barrier properties of Al$_2$O$_3$.\textsuperscript{23} In addition, employment of plasma has been shown to induce charge compensation at the interface.\textsuperscript{21–25} The details of the atomistic mechanisms leading to Fermi level unpinning and passivation of GaAs by PEALD AlN has been described elsewhere.\textsuperscript{26} Fig. 1(b) shows energy dispersive x-ray (EDX) spectra of single crystal phase GaAs NW capped with an AlN film that appears to be $\sim 1 \text{nm}$ thick and the amorphous nature of the AlN film can be seen clearly. The EDX spectra was taken from a spot located in the middle of the NW diameter. Although, nitrogen and aluminum signals are rather weak in the EDX spectra (because of the ultra-thin layers), nevertheless, the spectra confirms the presence of AlN. In TEM image, the capping layer thickness appears to be $\sim 1 \text{nm}$ instead of the deposited $\sim 5 \text{Å}$ because the surface of PEALD AlN is known to oxidize\textsuperscript{20,22} which could possibly also affect the final thickness, although the TMA precursor is likely to clean-up the native oxide on GaAs NWs completely. Overall, the GaAs surface passivation is mild since no room temperature (RT) PL was detected from GaAs NWs capped with previously mentioned AlN layers.

Next, we tested the effect of previously mentioned ALD grown capping layers on the optical properties of InP NWs. In contrast to GaAs NWs, the InP NW surface is reasonably good quality (comparatively less surface states), and the as-grown NWs display a strong PL emission at RT. In contrast to GaAs NWs, as-grown InP NWs display high density of defects (twin faults) throughout the NW length. Further, the native oxide was not removed prior to the ALD deposition using hydrofluoric acid (HF) as the same is used to passivate the InP NWs and we did not want to influence the results with other sample pretreatments. In this case, as shown in Fig. 2(a), among all the ALD materials tested as capping layers, Al$_2$O$_3$ was found to be the best passivating material for InP surface. Compared to the as-grown sample, the best passivation was achieved for the InP NWs when capped with a 2nm thick Al$_2$O$_3$ film. Also, a two times enhancement in the PL peak intensity can also be seen. Further, with increasing thickness of Al$_2$O$_3$ capping layers, the PL emission first increases then decreases with no change in the PL peak position (922 nm). For example, with a 3 nm thick Al$_2$O$_3$, the PL emission was strongly quenched by almost a factor of five. The existence of optimum thickness is perhaps related to the incorporation of strain and/or surface coupling effects beyond a critical thickness. Notably, Al$_2$O$_3$ has been used previously as dielectric layers to passivate
the InP thin film structures. Among the ALD capping layers, 1nm thick AlN displayed the same PL as the as-grown sample but did not result in the enhancement of the PL (not shown here). Thus, it can be concluded that after Al₂O₃, AlN is probably the second best material which do not damage the InP surface when an optimum thickness is used (1nm). On the contrary, all other ALD material resulted in rapid PL quenching with a strong de-passivation effect and possible damage to the InP surface. For simplicity, we have excluded the PL data for ALD materials which did not result in enhancement of PL. Fig. 2(b), shows HRTEM image of InP NWs capped with a 2nm thick ALD grown Al₂O₃ layer. The perpendicular lines observed along the NW are twin faults in as-grown InP NWs. The ALD films shown in this work were grown via standard thermal assisted ALD.

We further tested the effect of capping layers on the optical properties of the top down fabricated (etched) InP nanopillars. Since nanopillars are formed by etching the bulk thin films, the surface formed is very rough compared to the bottom-up grown NWs, and as a result more surface defects are incorporated. Fig. 3(a), shows the PL spectra from InP nanopillars capped with AlN and Al₂O₃ grown ALD films. The inset is the SEM image of as-etched InP nanopillars. A mild enhancement in the peak PL intensity can be seen with 5Å AlN and 2 nm thick Al₂O₃. In this case also, an optimum ALD layer exists beyond which a decrease in PL emission was observed. These

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FIG. 2. InP NWs capped with thermal-assisted ALD grown layers of Al₂O₃ (a) RTPL spectra and (b) HRTEM image of a ~50 nm diameter InP NW coated with a ~2nm thick Al₂O₃ layer. The perpendicular lines seen in the NW are the defects (twin faults). Scale bar corresponds to 10 nm.

FIG. 3. (a) RT PL spectra from top-down fabricated InP nanopillars capped with different thicknesses of PEALD grown AlN and thermal-assisted ALD Al₂O₃ layers. A bump in PL spectra at around 900nm is an artifact due to the InGaAs detector response. Inset shows SEM image of as-etched InP nanopillars. (b) TRPL carrier decay profiles in logarithmic scale from as-etched, Al₂O₃ & TiN capped InP pillars. A two times enhancement in carrier lifetime can be seen in NWs coated with 2nm Al₂O₃ layer.
TABLE I. Summary of passivation results for wide range of ALD grown capping layers deposited on bottom-up grown (GaAs and InP) NWs and top-down faricated InP nanopillars. PL measurements temperatures are indicated in parenthesis for each material system. The average length and diameters of untampered GaAs and InP NWs were 20 µm and 40 nm, respectively. InP nanopillars were tapered with and an average length of 1.5 µm. The best passivating material layer thickness for GaAs NWs was 2Å, and 2nm for InP NWs.

<table>
<thead>
<tr>
<th>Passivation</th>
<th>AlN</th>
<th>Al₂O₃</th>
<th>TiN</th>
<th>GaN</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs NWs (15K)</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>InP NWs (RT)</td>
<td>Yes</td>
<td>Yes (best)</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>InP nanopillars (RT)</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

results are quite similar to the InP NWs and it can be concluded that indeed, AlN and Al₂O₃ are good material for mild surface passivation. On the other hand, for all other capping layers, a strong quenching of the PL emission was observed (data not shown here for the sake of brevity).

Time-resolved photoluminescence (TRPL) measurements were performed to study the carrier lifetime dynamics in as-etched and capped nanopillars. Surface states have dramatic effect on the optical properties of nanostructures, for instance, the bulk InP before etching display a carrier decay time of ~2.5 ns, while the as-etched InP nanopillars show a lifetime of only ~251 ps (Fig. 3(b)) due to a high density of surface states/defects after the dry etching. Further, as seen in (Fig. 3(b)), capping the as-etched InP nanopillars with a 5Å thick Al₂O₃ layer resulted in carrier decay time of ~226 ps, which is quite similar to the as-etched nanopillars. On the other hand, capping with a 2nm thick Al₂O₃ resulted in two times enhancement of the carrier lifetime (~523 ps), signifying that significant number of surface traps were successfully removed. Notably, similar to as-etched nanopillars, the carriers decay profile after the photoexcitation is mostly mono-exponential after capping with Al₂O₃. However, in contrast, after capping with a 2 nm thick TiN layer, the carriers decay profile is bi-exponential with an initial very fast decay of carriers followed by a slower decay. Here, the carrier lifetime is reduced to only 23 ps and the extremely rapid decay of carriers initially is attributed to the presence of additional trapping centers/defects at the InP-TiN interface induced by capping. Similar to TiN, capping of nanopillars with other ALD layers (except AlN) drastically reduced the decay time with respect to the as-etched nanopillars and is not shown here for simplicity. In case of AlN, a 1nm thick capping layer at best retain the carriers decay time comparable to the as-etched pillars and the carrier lifetime decrease beyond this optimum thickness (not shown here). Summarizing, a 2nm thick Al₂O₃ capping was found to be the best passivating layer, followed by 5Å thick AlN as the second best passivating material. A detailed summary of all the passivation results is provided in Table I.

Finally, we again measured the PL emission from III-V NWs and nanopillars after 6 months of exposure to the environment. We find that the samples capped with an optimum AlN and Al₂O₃ ALD layers retain their original optical properties. This indicates that AlN and Al₂O₃ are promising capping materials for GaAs and InP NWs providing moderate passivation and serving as protective cappings for long term protection from the oxidation and environmental attack.

IV. CONCLUSION

In conclusion, we have explored the suitability of a wide range of ALD materials that include AlN, TiN, Al₂O₃, GaN and TiO₂ for use as protective capping layers as well as the surface passivation for bottom-up grown III-V NWs and top down fabricated InP nanopillars. For GaAs NWs, only AlN passivated the GaAs surface at low-temperatures and the best passivation was achieved with a 2Å thick layer. For InP NWs and nanopillars, which displayed similar surface passivation results, Al₂O₃ was found to be the most promising surface passivating material followed by AlN. All other capping layers were found to be non-suitable for InP surface, and resulted in strong de-passivation effect and possible damage to the surface. An important aspect of ALD surface passivation and protective capping was the presence of an optimum capping layer thickness. Aging tests after six months show that the capped nanostructures retain their original optical properties.
Overall, ALD grown AlN and Al₂O₃ as capping layers provides mild passivation as well as long term protection from oxidation and environmental attack, which is desirable for long-term stability of NW based devices. Additionally, low (∼200 °C) growth deposition temperature of ALD capping layers makes them compatible with most semiconductor device processing technologies.

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