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Passivation of GaAs surface by atomic-layer-deposited titanium nitride

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ABSTRACT

The suitability of titanium nitride (TiN) for GaAs surface passivation and protection is investigated. A 2–6-nm thick TiN passivation layer is deposited by atomic layer deposition (ALD) at 275 °C on top of InGaAs/GaAs near surface quantum well (NSQW) structures to study the surface passivation. X-ray reflectivity measurements are used to determine the physical properties of the passivation layer. TiN passivation does not affect the surface morphology of the samples, but increases significantly the photoluminescence intensity and carrier lifetime of the NSQWs, and also provides long-term protection of the sample surface. This study shows that ALD TiN coating is a promising low-temperature method for ex situ GaAs surface passivation.

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1. Introduction

Technology based on GaAs devices is not fully exploited partly because of the high density of interface and surface states that cause the surface Fermi level pinning near midgap of the forbidden band of bulk GaAs. The surface properties become increasingly important as the dimensions of the devices decrease. Therefore, surface passivation is one of the most important aspects when developing GaAs-based devices. A variety of different surface passivation techniques have been studied. Sulphur passivation methods have been developed but sulphur passivated GaAs surface suffers from a gradual degradation from air and light exposure [1]. Different plasma nitridation methods have faced problems with, e.g. formation of mixture of GaN and Ga_2O_3instead of pure GaN [2]. An ultrathin epitaxial GaN layer has also been used as a passivation layer [3]. However, the process temperature is more than 400 °C which may be too high for many applications. Aluminum nitride (AlN) has been grown by using low temperature metalorganic vapour phase epitaxy (MOVPE) but the growth temperature is still above 370 °C [4].

In this work GaAs surface passivation by ALD grown TiN is investigated. TiN deposition by ALD has been studied extensively in past [5]. This novel passivation technique has the following benefits compared to previously studied methods:

- Uniform growth at large area enables passivation of large amounts of components at the same time.
- Low process temperatures (275 °C), which can be important if passivation must be integrated as a part of component processing.
- Possibility to use as an ex situ passivation method.

Photoluminescence (PL) intensity and carrier lifetime of TiN coated InGaAs/GaAs NSQW structures are used to indicate the passivation efficiency. Passivation film properties like thickness, mass density and interface roughness are studied by X-ray reflectivity measurements. It is shown that TiN not only passivates but also protects the sample surface in the long run.

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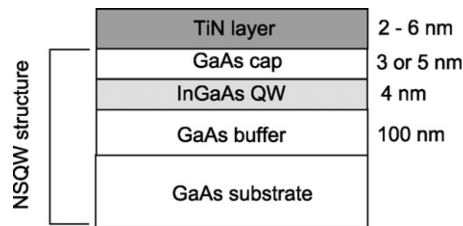

Fig. 1. Schematic diagram of a TiN passivated NSQW structure.

2. Experimental details

2.1. Samples

The schematic graph of a TiN passivated NSQW structure is shown in Fig. 1. A 4-nm-thick $In_{0.2}Ga_{0.8}As$/GaAs NSQW was grown on a semi-insulating GaAs (1 0 0) substrate in a horizontal MOVPE reactor at atmospheric pressure using hydrogen as the carrier gas. Tertiarybutylarsine (TMAs), trimethylgallium (TMGa) and trimethylindium (TMIn) were used as precursors for arsenic, gallium and indium, respectively. The NSQW was sandwiched by a 100 nm buffer and a top GaAs cap layer with thickness of 3 or 5 nm. The growth temperature was 650 °C. The V/III ratio for the $In_{0.2}Ga_{0.8}As$ was 23. The growth rate was 0.42 nm/s and 0.69 nm/s for GaAs and InGaAs, respectively. More details about MOVPE grown NSQWs has been reported elsewhere [6]. After MOVPE growth the NSQW sample was cleaved to several pieces, one was kept as a reference sample while the others were used for different ALD passivation processes. In this way we could avoid possible uniformity problems between different MOVPE growth runs.

Titanium nitride (TiN) was deposited by a flow type ALD apparatus (Beneq TFS 500) with continuous nitrogen carrier gas flow through the reactor. The pressure of the reactor during the growth was about 3.2 mbar. Titanium tetrachloride ($TiCl_4$) and ammonia (NH_3) were used as precursors. Trimethylaluminum ($(CH_3)_3Al$, TMA) was used as a reducing agent between $TiCl_4$and NH_3 pulses. TMA improves the film quality and makes it possible to use lower growth temperature. $TiCl_4$ pulse length was 400 ms and purge time 7 s. TMA pulse length was 200 ms and purge time 2 s. NH_3 pulse time was 300 ms and purge time 7 s. The growth temperature was 275 ° C and the liquid precursors ($TiCl_4$ and TMA) were kept at 20 °C. The vapor pressures for the $TiCl_4$ and TMA at 20 ° C were 11.4 and 9.8 mbar, respectively. Ammonia tank was at room temperature.

2.2. Measurements

TiN film properties like thickness, mass density and surface roughness were studied by using X-ray reflectivity (XRR) measurements. Philips X'pert Pro instrument was used at 40 kV voltage and 40 mA current settings. The measurement assembly consisted of Ni and Cu attenuators (Cu attenuator factor 180), a X-ray mirror, a Soller slit (0.04 rad) and a programmable divergence slit at 1/32° fixed aperture and a 10 mm X-ray mask at incident beam setup. The reflected beam was collected by using a thin film collimator, a 0.04 radian Soller slit, a flat graphite crystal monochromator and a scintillation detector assembly.

The low temperature (10 K) continuous-wave photoluminescence (PL) measurements were made by using a diode-pumped frequency doubled $Nd:YVO_4$ laser emitting at 532 nm wavelength for excitation. A monochromator, a liquid-nitrogen-cooled germanium detector and a lock-in amplifier were used to record the PL spectra. The low temperature time-resolved photoluminescence (TRPL) measurements were performed by exciting the samples

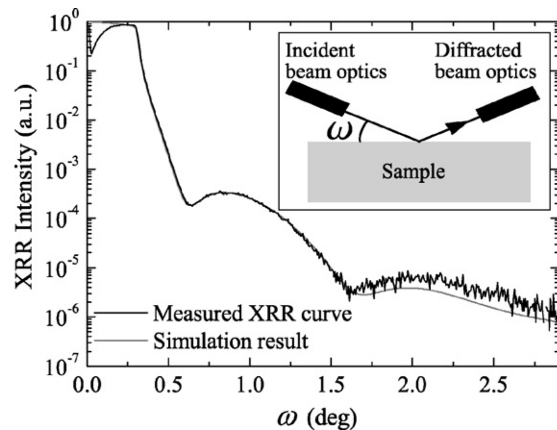

Fig. 2. Measured and simulated XRR curves of a 60 cycles TiN layer on GaAs (1 0 0) substrate. The schematic picture of the measurement setup is shown in the inset.

with 150 fs pulses at 780 nm from a mode locked Ti:Sapphire laser and by detecting the signal using a Peltier-cooled microchannel plate multiplier and time-correlated single photon counting electronics.

Contact mode atomic force microscopy was used to study the surface morphology of the samples.

3. Results and discussion

3.1. Physical propetries of ALD grown TiN

The linearity of the TiN growth (at 275 °C) on GaAs (1 0 0) substrate was studied by changing the number of ALD growth cycles. Fig. 2 shows the measured and simulated XRR curves of a 60 cycles TiN layer. The simulated curve is based on Parrat's formalism [7] and the Nevot–Croce roughness model [8]. The physical model differs from the real measurement because the sample area is not infinite and X-ray thickness is not zero. That effect is largest when the angle ω is less than 0.2°. However, the most interesting point in this study is the layer thickness which is related to the XRR curve fringe spacing. The dependence of the TiN layer thickness on the number of ALD growth cycles is shown in Fig. 3. TiN layer thickness is linearly increasing when the number of the growth cycles is more than 20. The intercept of the fitted line with the thickness-axis is 1.1 nm which is typically a consequence of substrate native oxide formation before growth or so called

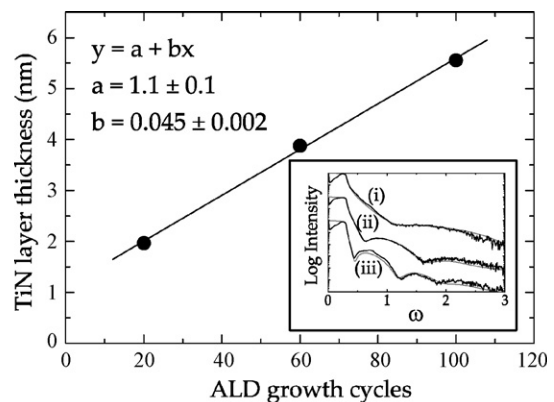

Fig. 3. TiN layer thickness on GaAs substrate as a function of growth cycles based on the XRR measurements. A linear fitting formula is represented so that y is layer thickness, x is number of cycles and a and b are linear fitting parameters in nanometer scale. The inset shows measured (black) and simulated (gray) curves for (i) 20 cycles, (ii) 60 cycles and (iii) 100 cycles of TiN on GaAs.

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