Scanning probe microscopy studies on the growth of palladium and nickel on GaN(0001)

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Abstract. The performance of GaN-based devices, such as blue LEDs and laser diodes, relies on good metal-GaN contacts. However, little is known about the formation and properties of these contacts on the atomic scale. We have studied the initial stages of growth of Pd and Ni on the GaN(0001) surface using variable temperature UHV-STM. The atomic-scale STM images have been compared with tapping-mode AFM images and point I-V measurements using conductive AFM in order to correlate performance on nano-scale and micro-scale. The growth mode of the metals and formation of alloys and interfacial compounds have important consequences for the electrical contact behaviour. Systematic control of the deposition conditions is therefore crucial for the performance of the contacts.

1. Introduction

Over the past decade, gallium nitride (GaN) technology and its device applications have developed rapidly. The performance of these devices (e.g. LEDs, laser diodes and high-power transistors) relies on high-quality metal-to-GaN contacts. Therefore, ohmic contacts and Schottky barriers to GaN have been studied extensively. Previous studies have focused on the improvement of ohmic contacts, such as Ti/Al and Pd/Al on n-type GaN, or Ni/Au, Ni/Pd/Au, Pd/Au on p-type GaN [1, 2]. Low-resistance, thermally stable ohmic contacts on p-type GaN have been reported using Pd/Ni and Pd/NiO based contacts [3, 4]. However, little is known about the formation and properties of these contacts on the atomic scale. So far, atomic-scale studies of metals on GaN(0001) using scanning tunnelling microscopy (STM) have only been reported for silver [5] and gold [6].

The formation of alloys and interfacial compounds between GaN and a metal contact influences the stability and electrical properties of the contact. For example, the formation of Pd gallides (Ga₂Pd₅ and Ga₅Pd) during annealing of Pd contacts on p-GaN results in enhanced thermal stability and reduced contact resistivity [3]. Control of the metal deposition conditions as well as the effective preparation of clean GaN surfaces is therefore crucial for the performance of the contacts. In a previous study, we have identified the effect of different surface treatments on surface morphology and stoichiometry of the GaN(0001) surface [7], whereas other authors have investigated the effect of specific surface treatments on the electrical properties of ohmic contacts to n- and p-type GaN [1, 8, 9].

Here, we have focused on atomic-scale studies of the initial stages of growth of palladium and nickel on the GaN(0001) surface using in-situ variable-temperature STM. Complementary meso-scale tapping-mode AFM imaging was carried out in order to characterize the density and distribution of structures as a function of processing parameters. Point I-V analysis in the contact mode (SECM) with a conductive Au-coated probe was also undertaken in order to elucidate the resultant point-contact electrical characteristics.
2. Experimental

Pd and Ni were deposited in an ultra-high vacuum (UHV) chamber (base pressure $1 \times 10^{-8}$ Pa) from an e-beam evaporator onto in-situ cleaned GaN(0001)/Al$_2$O$_3$ substrates, either at room temperature followed by annealing or at elevated temperature. The GaN/Al$_2$O$_3$(0001) templates consisted of atomically flat 1-5 µm thick $n$-doped ($10^{18}$ cm$^{-3}$) GaN layers grown on Al$_2$O$_3$(0001) by MOCVD. In-situ cleaning involved either a 20 min anneal in an NH$_3$ atmosphere ($2 \times 10^{-5}$ Pa) or careful heating in UHV up to about 700 °C to remove the surface oxide and produce Ga-rich GaN (0001) surfaces. The detailed cleaning procedures and the resulting GaN(0001) surface structures have been described elsewhere [7]. The growth experiments were carried out in the STM chamber of a JEOL 4500XT UHV STM. The growth was monitored in-situ using RHEED at 12 kV. Immediately after growth, the samples were investigated in-vacuo by STM using electrochemically etched tungsten tips.

AFM imaging was carried out ex-situ under ambient conditions with a Park Autoprobe instrument with a Multitask head and a 100 µm scanner. Tapping-mode ex-situ AFM topographic images were obtained with beam-shaped probes micro-fabricated from highly doped $n$-type Si with force constants in the range 3-10 N/m and resonance frequencies between 140 and 420 kHz. The radius of curvature of the probe at the apex was <10 nm. Point I-V analysis was carried out to elucidate point-contact conductivity. The measurements were carried out with a JEOL 4200D instrument operated in the contact mode with a conductive probe. I-V curves were obtained in contact mode by sweeping the tip-to-surface bias at fixed locations chosen from the topographical image.

3. Results and discussion

3.1. Palladium on GaN(0001)

When sub-monolayer amounts of palladium are deposited onto a Ga-rich GaN(0001) surface, followed by annealing at ca. 600 °C, Pd reacts with mobile excess Ga on the surface and is incorporated into the top layer. The result is the formation of a strained layer consisting of different domains oriented along the <1120> GaN directions (figure 1a). It is thought to be a monolayer (ML) of a Pd-rich alloy, as Ga and Pd can form a variety of intermetallic compounds [10] and the exact stoichiometry of the deposited layer is not known. Due to the large strain at the interface (16% lattice mismatch between Pd(111) and GaN(0001)) the surface consists of a patchwork of small domains rather than a complete monolayer.

Further Pd deposition followed by annealing at 600-650°C leads to the formation of three-dimensional (3-D) hexagonal flat-topped Pd nanocrystals (figure 1b). The crystallographic orientation of the Pd nanocrystals with respect to the substrate can be described as (111)$_{\text{Pd}}$ // (0001)$_{\text{GaN}}$, [110]$_{\text{Pd}}$ // [1120]$_{\text{GaN}}$. The (111) face of the Pd nanocrystals shows a periodicity of 5.8 ± 0.2 Å, which may correspond to a (2x2) adsorbate superstructure (figure 1c).

Figure 1. (a) Domains of Pd/Ga alloy strained onto GaN(0001), (b) nucleation of 3-D hexagonal Pd islands on GaN(0001) (sample bias $V_s$ = 1.2 V, tunnelling current $I_t$ = 0.8 nA), (c) higher resolution log I STM image of hexagonal Pd nanocrystals on GaN(0001) with (111)$_{\text{Pd}}$ // (0001)$_{\text{GaN}}$, [110]$_{\text{Pd}}$ // [1120]$_{\text{GaN}}$. 
3.1.1. I-V point analysis by C-AFM

Point I-V analysis was carried out at random locations on samples with 3-D Pd islands. Although particular features could not be targeted due to the small island size and high island density, three types of I-V curves were observed. Representative examples from a large data base are shown in figure 2. Type 1 (blue squares) suggests the presence of shallow electrically active interface states being accessed near zero voltage applied bias. One might speculate that the carrier transport is limited at higher bias by either the density of states and/or by life-time for charge transfer into or out of localized states. Type 2 (black dots) curves show diode behaviour, being forward biased at positive sample bias and reverse biased at negative sample bias. This characteristic is likely to be representative of conduction through the Pd islands, as Pd shows Schottky behaviour on n-type GaN. The effect is also observed in STM, where the best imaging conditions are obtained at large positive sample bias (>1.2 V), tunnelling into empty states, whereas imaging at negative sample bias is very difficult. Type 3 (red triangles) curves show an energy gap behaviour with a bandgap of ca. 4 eV, and then access to filled and unfilled states at ca. -2V and +2V sample bias, respectively. This may be representative of the GaN substrate, as GaN has a bandgap of ca. 3.5 eV, which may be slightly increased due to the presence of native surface oxide, and I-V curves measured on clean GaN look very similar.

Figure 2. Point I-V curves of Pd/GaN(0001) sample measured using conductive AFM
Type 1 (blue squares) suggests the presence of shallow electrically active interface states being accessed near zero applied bias. Type 2 (black dots) curves show diode behaviour, and are likely to be representative of conduction through the Pd islands. Type 3 (red triangles) curves show a bandgap of ca. 4 eV and may be representative of the GaN substrate.

3.2. Nickel nanoislands on GaN(0001)

When nickel is deposited onto GaN(0001) followed by annealing at 600-650°C, it nucleates into mainly hexagonal Ni(111) islands without the formation of a wetting layer (figure 3). Tapping mode AFM (figure 3a, 1µm size) was used to confirm that the nm-scale STM images are representative of the larger surface area. The crystallographic relationship of the Ni islands and the underlying GaN substrate can be described as (111)Ni \(//\) (0001)GaN, [110]Ni \(//\) [1120]GaN. The island sizes are in the range 10-50 nm, with heights up to 2.4 nm, and some ripening has been observed during annealing. Structural detail on the flat island tops can be resolved in the logarithmic current (\(\log I\)) imaging mode (figure 3c). The additional resolution emphasises the shape of the nanocrystals and the atomic corrugation on the flat tops. The measured periodicity along the [110]Ni direction \((// [1120]GaN)\) is 5 Å, which corresponds to twice the Ni [110] periodicity. This does not match the GaN [1120] periodicity (3.2 Å), indicating that the Ni lattice has relaxed in this direction. The distance measured between the ‘stripes’ visible in figure 3(c) is 8.5±0.3 Å. For comparison, the Ni [112] periodicity is 2.16 Å, and the GaN [1100] periodicity is 2.76 Å. It may be possible that four Ni lattice spacings are strained onto three GaN lattice spacings in this direction.
Figure 3. (a) AFM image of Ni islands on GaN (0001), (b) STM image of Ni islands on GaN(0001) (V = 1.8 V, I = 0.3 nA), (c) Log I STM image of Ni islands on GaN (32 nm)

4. Conclusions
We have investigated the deposition of Pd and Ni on GaN (0001) using in-situ elevated-temperature STM in order to elucidate growth modes and the formation of interfacial compounds, as this has been shown to influence the properties and performance of metal-GaN contacts.

The deposition of sub-monolayer amounts of Pd onto a Ga-rich GaN(0001) surface, either at elevated temperature or at room temperature followed by annealing, leads to the formation of a Pd-Ga surface alloy that wets the GaN surface. Further Pd deposition results in the nucleation and epitaxial growth of 3D hexagonal flat-topped Pd(111) nanoislands.

No wetting layer has been observed when nickel was deposited onto GaN(0001) and briefly annealed at 600-650 °C. Instead, nickel nucleates into hexagonal flat-topped Ni(111) islands. The lattice of the islands appears partially relaxed, however high-resolution TEM studies will be necessary to investigate the interface between the islands and the GaN substrate.

The work emphasises that a systematic control of the deposition conditions as well as the cleanliness and stoichiometry of the substrate is important for the control of the composition and morphology of the metal-GaN interface.

Acknowledgements
The authors thank Dr MJ Kappers (Cambridge University) for providing the GaN substrates, Dr RA Oliver and Dr MR Castell for useful discussions, and Prof. CRM Grovenor, Prof. GAD Briggs and Dr JA Crossley for support. An extended version of this paper is due to appear in Microscopy and Analysis (Wiley, 2009).

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