Atomic-scale studies on the growth of palladium and titanium on GaN(0001)

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Abstract

We have used elevated-temperature scanning tunnelling microscopy (STM) to investigate the initial stages of growth of Pd and Ti on GaN(0001). Deposition of Pd onto a Ga-rich GaN(0001) surface followed by annealing at ~600 °C leads to the formation of an ordered Pd/Ga alloy layer, followed by the nucleation and growth of hexagonal Pd nanocrystals. When Pd is deposited on a less Ga-rich surface, the Pd initially wets the surface. With increased Pd coverage the wetted 2D islands coalesce into 3D islands without a wetting layer. The 3D islands have hexagonal shapes with a flat (111) top surface, and STM images of the nanocrystal tops show that they are reconstructed. A separate series of experiments was performed investigating Ti deposition on GaN(0001), where the Ti reacts with GaN to form TiN. Deposition of Ti onto GaN(0001) followed by annealing in UHV results in the formation of 2D irregular TiN islands, which can be transformed into more regular triangular TiN nanocrystals upon annealing in an ammonia atmosphere. This study shows overall that the growth modes of Pd and Ti are strongly influenced by the stoichiometry and cleanliness of the GaN substrate. Therefore, to create reliable electrical contacts between metals and GaN, the atomic level order and stoichiometry of the GaN substrates needs to be controlled.

Keywords: Gallium nitride; Palladium; Titanium; Alloys; Epitaxy; Metal–semiconductor interfaces; Nanostructures; Scanning tunnelling microscopy

1. Introduction

In the past ten years, GaN technology and its device applications have developed rapidly. The performance of these devices (e.g., light emitting diodes, laser diodes and high-power transistors) relies on good metal–GaN contacts. Previous studies have focused on the electrical properties of these contacts, especially on the improvement of ohmic Ti/Al, Ti/Au, Ni/Au and Pt/Pd/Au contacts [1–4]. 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 carried out for silver [5,6] and gold [7]. They reported novel metal-induced reconstructions of the GaN(0001) surface as well as a strong dependence of the Ag growth mode on the metal flux during deposition.

The formation of alloys and interfacial compounds between GaN and the metal contact has an influence on the electrical properties of the contact [3,8,9]. Systematic control of the 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 cleaning treatments on surface reconstruction, morphology and stoichiometry of the GaN(0001) surface [10], whereas, other authors have investigated the effect of specific surface treatments on the electrical properties of ohmic contacts to both n-type and p-type GaN [1,2,11,12].
Here, we have focused on atomic-scale studies of the initial growth stages of palladium and titanium on the GaN(0001) surface depending on deposition conditions and substrate stoichiometry using in situ elevated-temperature STM. Fundamental issues such as adsorption mechanism, wetting behaviour, growth modes and the influence of surface treatments have been investigated.

2. Experimental

Palladium and titanium were deposited from an Oxford Applied Research EGN4 e-beam evaporator onto in situ cleaned GaN(0001)/Al2O3 substrates either at room temperature followed by annealing or at elevated temperature. The GaN/Al2O3(0001) templates consisted of atomically flat 1–5 μm thick n-doped (1018 cm−3) GaN layers grown on Al2O3(0001) by MOCVD. They were cleaned ex situ by sonication in acetone for 1 min followed by rinsing in methanol and dried before being introduced into the UHV chamber. In situ cleaning involved either a 20 min anneal in an ammonia atmosphere (2 × 10−5 Pa) or heating in UHV up to about 700 °C to remove the surface oxide and produce Ga-rich GaN(0001) surfaces with variable amounts of excess gallium. The detailed cleaning procedures and the resulting GaN(0001) surface structures have been described elsewhere [10]. Temperatures were measured using an infra-red pyrometer with an accuracy of ±20 °C. The growth experiments were carried out in the STM chamber of a JEOL 4500XT elevated-temperature STM (base pressure 1 × 10−10 Pa). 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. Due to the low electrical conductivity of the GaN(0001)/Al2O3 samples at room temperature, the STM measurements were carried out at elevated temperatures (200–300 °C).

3. Results and discussion

3.1. Palladium on GaN(0001)

3.1.1. Formation of Pd–Ga surface alloys

During the deposition of sub-monolayer amounts of palladium from an e-beam evaporator onto a Ga-rich GaN(0001) surface [10] (Fig. 1a) at elevated temperature (~300 °C), followed by annealing at ~600 °C, Pd reacts with mobile excess Ga on the surface and is incorporated into the top layer. This results in a rather disordered Pd/Ga alloy surface layer (Fig. 1b). Further deposition and annealing at 600–650 °C in UHV leads to the formation of a strained Pd/Ga alloy overlayer consisting of different domains oriented along the (1120) GaN directions (Fig. 1c and d). Whereas, the lattice directions of the alloy domains correspond to the (1120) GaN directions, the measured periodicity of 1.40 ± 0.05 nm does not match the GaN lattice. It might correspond to a (5 × 5) Ga-adsorbate superstructure on top of a strained Pd(111) layer (5 × 2.75 Å = 1.375 nm) or, possibly, to a Pd/Ga alloy structure. Ga and Pd can form a variety of intermetallic compounds [13], and the exact stoichiometry of the deposited layer is not known. It is thought to be a monolayer (ML) of a Pd-rich alloy. 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 (see Fig. 1d) rather than a complete monolayer.

When palladium is deposited onto a less Ga-rich GaN(0001) surface [10], followed by annealing at 600 °C, the Pd initially wets the surface forming round or irregular two-dimensional (2D) islands with 5–15 nm diameter (Fig. 2a). The height of the islands is 2.1 ± 0.2 Å, which corresponds to the Pd(111) step height (2.25 Å). This indicates that the Pd islands grow epitaxially with their (111) plane parallel to the GaN(0001) surface. Note, the triangular islands in Fig. 2a are GaN or Ga islands with a measured height of 2.5 ± 0.2 Å (cGaN = 5.19 Å). Further Pd deposition and annealing increases the surface coverage with small wetted 2D islands (Fig. 2b), however, the islands do not coalesce into a complete monolayer. Again, this is probably due to the large lattice mismatch between GaN and Pd. Continuing Pd deposition onto Pd/GaN(0001) beyond 1 ML (onto surfaces shown in Fig. 1c and d and Fig. 2b), followed by annealing at 600 °C, results in the nucleation and growth of three-dimensional (3D) hexagonal flat-topped Pd islands (Fig. 2c). During the 3D island formation, the initial partial wetting layer is consumed, inducing a direct transition from the initial stages of Frank–van der Merve growth to Vollmer–Weber growth, rather than Stranks–Krastanov growth. A similar phenomenon has been observed for the deposition of gold on SrTiO3(001) [14].

3.1.2. Growth of 3D palladium nanocrystals

Similarly, after the excess Ga on a Ga-rich GaN(0001) surface is consumed in the formation of an interfacial Pd/Ga alloy layer, further Pd deposition followed by annealing at 600–650 °C leads to the formation of 3D hexagonal flat-topped Pd nanocrystals (Fig. 3a). The logarithmic current STM images in Figs. 3b and c emphasise the shape of the nanocrystals (log I images are formed by switching off the fast feedback circuit in the STM and using the log of the tunnelling current to form an image). The crystallographic orientation of the Pd nanocrystals with respect to the substrate can be described as (111)Pd//[0001]GaN, [110]Pd//[1120]GaN. The (111) face of the Pd nanocrystals shows a periodicity of 5.8 ± 0.2 Å, which may correspond to a (2 × 2) adsorbate superstructure (Fig. 3c). Initially, two sizes of nanocrystals have been observed, smaller ones with a width of 3–4 nm and 4.5 ± 0.2 Å height, and larger ones with a width of 5–6 nm and 9.2 ± 0.2 Å height. The heights of the nanocrystals correspond to twice (4.5 Å) and four times (9.0 Å) the (111) lattice spacing of Pd. Some ripening of the Pd nanocrystals is observed when they are annealed at 600–650 °C in UHV, resulting in three slightly larger...
island sizes: small (width 3–4 nm/height 6.7 ± 0.2 Å), medium (width 5–6 nm/height 9.2 ± 0.2 Å) and large (width 7–8 nm/height 17.8 ± 0.2 Å), as seen in Fig. 3a.

3.2. Titanium on GaN(0001) – formation of TiN

A separate series of experiments was performed investigating titanium deposition on GaN(0001), where Ti reacts with GaN to form TiN [8,9,15,16]. This reaction has already been observed at room temperature [8]. Deposition of Ti onto GaN(0001) at elevated temperatures (~300 °C) leads to the formation of 2D irregular TiN islands (Fig. 4a). Their height (2.4 ± 0.1 Å) corresponds to the TiN(111) step height, suggesting epitaxial growth of TiN(111) on GaN(0001).

Fig. 4b shows an even distribution of small titanium or TiN clusters on a GaN(0001) surface after deposition at room temperature. The outline of the GaN surface with its typical triangular features is still visible underneath. During subsequent annealing at 600 °C in UHV, titanium strongly reacts with the underlying GaN to form TiN clusters and small irregular islands (Fig. 4c). More regular triangular TiN nanocrystals are formed during annealing of the Ti/GaN surface in an ammonia atmosphere (2 × 10^-5 Pa) at ~700 °C (Fig. 4d). The epitaxial relationship of the TiN nanocrystals with the GaN(0001) substrate is (111)_{TiN}/(0001)_{GaN}, (110)_{TiN}/(1120)_{GaN}. 

Fig. 1. (a) STM image of Ga-rich NH3-etched GaN(0001) surface (image size 100 nm, sample bias $V_s = 1.4$ V, $I_t = 0.6$ nA). (b) Disordered alloyed GaN(0001) + Pd surface after sub-ML palladium deposition at ~300 °C (image size 72 nm, $V_s = 1.2$ V, $I_t = 0.8$ nA). (c) Domains of Pd/Ga alloy strained onto GaN(0001) after Pd deposition at room temperature (RT) + 650 °C anneal (image size 100 nm, $V_s = 1.5$ V, $I_t = 0.8$ nA). (d) Log I image (70 nm) of strained Pd/Ga alloy domains parallel to (1120) GaN directions.
Fig. 2. (a) Round and irregular shaped 2D Pd or Pd-rich alloy islands (width 5–15 nm, height 2.1 ± 0.2 Å) on GaN(0001) formed by RT deposition + 600 °C anneal. Note, triangular islands are GaN. (image size 140 nm, $V_s = 1.2$ V, $I_t = 0.5$ nA). (b) GaN(0001) surface covered in 2D irregular ML-high Pd or Pd-rich alloy islands (width 5–10 nm, height 2.0 ± 0.2 Å) after further Pd deposition at RT followed by annealing at 600 °C (image size 200 nm, $V_s = 1.1$ V, $I_t = 0.8$ nA). (c) Further RT Pd deposition onto Pd/GaN surfaces shown in Fig. 1b–d and Fig. 2b, followed by annealing at 600 °C, leads to the formation of 3D hexagonal Pd islands (image size 200 nm, $V_s = 1.2$ V, $I_t = 0.8$ nA).

Fig. 3. (a) Hexagonal flat-topped Pd nanocrystals on GaN(0001) formed on top of an initial Pd/Ga alloy interface layer (image size 190 nm, $V_s = 1.2$ V, $I_t = 0.8$ nA). (b) Logarithmic current image of Fig. 3a emphasising the shape of the nanocrystals (image size 190 nm). (c) Higher resolution log $I$ image of hexagonal Pd nanocrystals on GaN(0001) with $(111)_{Pd}//(0001)_{GaN}$, $(110)_{Pd}//[1120]_{GaN}$. The periodicity on the islands might correspond to a $(2 \times 2)$ adsorbate superstructure (image size 32 nm).
4. Conclusions

We have investigated the deposition of palladium and titanium 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. Depending on the amount of excess Ga on the GaN surface, this alloy can either form a complete monolayer, consisting of differently oriented domains, or consist of small irregular monolayer-high islands. Once the excess Ga is consumed, further Pd deposition results in the nucleation and epitaxial growth of 3D hexagonal Pd nanocrystals.

The deposition of Ti onto GaN(0001), on the other hand, leads to the formation of TiN, already at low temperatures, and epitaxial TiN nanocrystals can be grown by subsequent annealing in NH$_3$.

We have shown that the systematic control over 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. Since the formation of alloys and interfacial compounds between GaN and a metal contact has an influence on the electrical properties of the contact, the systematic control of the deposition conditions is crucial for the performance of these contacts.

Fig. 4. (a) TiN on GaN(0001) formed at ~300 °C (image size 100 nm, $V_s = 1.5$ V, $I_t = 0.2$ nA). (b) Ti deposited onto GaN(0001) at room temperature (image size 200 nm, $V_s = 1.6$ V, $I_t = 0.2$ nA). (c) Annealing of (b) at 600 °C in UHV leads to the formation of TiN clusters (image size 100 nm, $V_s = 1.2$ V, $I_t = 0.5$ nA). (d) More regular TiN nanocrystals form during anneal in NH$_3$ at ~700 °C (image size 70 nm, $V_s = 1.6$ V, $I_t = 0.8$ nA).
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