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Obtaining Niobium Nitride on n-GaN by Surface Mediated Nitridation Technique

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Abstract: In this work the n-GaN(1000) surface is used as a source of nitrogen atoms in order to obtain niobium nitride film by a surface-mediated nitridation technique. To this end, the physical vapor deposition of the niobium film on GaN is followed by sample annealing at 1123 K. A thermally induced decomposition of GaN and interfacial mixing phenomena lead to the formation of a niobium nitride compound, which contains Nb from thin film and N atoms from the substrate. The processes allowed the obtaining of ordered NbN_x films on GaN. Structural and chemical properties of both the GaN substrate and NbN_x films were studied in-situ by surface-sensitive techniques, i.e., X-ray and UV photoelectron spectroscopies (XPS/UPS) and a low-energy electron diffraction (LEED). Then, the NbN_x/GaN surface morphology was investigated ex-situ by scanning tunneling microscopy (STM).

Keywords: gallium nitride; niobium nitride; photoelectron spectroscopy; low energy electron diffraction; scanning tunneling microscopy

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1. Introduction

Many stable phases of niobium nitride (e.g., hexagonal Nb_2N, cubic and hexagonal δ-NbN) reported in the literature exhibit a variety of interesting properties for superconducting and microelectronic devices or hard coatings [1–5]. In such applications, the preparation of a thin film of material is usually required. The thin NbN_x films have been obtained by various well-known methods, such as pulsed laser deposition [6], sputter deposition [7], atomic layer deposition [8], chemical vapor deposition [9,10] or molecular beam epitaxy (MBE) [11–14]. Moreover, the surface-mediated nitridation technique performed on a Si_3N_4/Si(100) substrate has been recently introduced as an additional and easy tool for achieving niobium nitrides [15]. Therein the niobium films were grown on the Si_3N_4/Si(100) substrate kept at 820 °C. After the deposition the sample was subjected to further annealing for 2 h. Elevated temperature activated the following processes: decomposition of Si_3N_4 into Si and N atoms, diffusion of N atoms and their interaction with niobium. The achieved film consists mainly of a hexagonal Nb_2N, which coexists with a minority Nb_4N_5 phase [15].

In this work we propose gallium nitride (GaN) as a source of atomic nitrogen for surface-mediated nitridation of niobium thin films. GaN is a direct band-gap semiconductor. It has a well-established position in optoelectronics and electronics of high power and frequency [16,17]. Annealing of GaN in vacuum leads to surface decomposition [18–20]. Due to different vapor pressure of Ga and N atoms, the surface can be enriched with one of its components. In general, annealing in a 750–1000 °C temperature range can enrich the (0001) surface with gallium atoms, which can form stable coatings of up to a few monolayers thick. The released nitrogen atoms escape into the vacuum. In case of

annealing systems containing metallic thin films (in the range of a few nanometers) on GaN the excess of gallium reacts with a metal of the thin film. This process leads to alloying: Ga atoms dissolve in a thin metallic film deposited on GaN. Longer annealing leads to enriching the alloy with Ga atoms. Such processes are well known and were observed for example in Ni, Pd, Mn films on GaN [21–23]. On the other hand, the released nitrogen atoms can react with a metallic thin film, as was recently shown for an annealed hafnium layer on GaN [24]. Here we show an interfacial mixing in which the nitrogen atoms dissolve into the niobium thin film. This phenomenon allows us to create an ordered NbN_x film on GaN. So far, superstructures with niobium nitride on GaN or AlGaN have been grown by molecular MBE [14,25]. Our observation can be used in a new method of creating these types of structures.

2. Experimental Procedures

All experiments were performed under UHV conditions in two separate systems where base pressures were below 5×10^{-10} Torr. The first system is equipped with a low-energy electron diffraction optic (Er-LEED), a dual anode X-ray source, an UV lamp and a hemispherical electron energy analyzer (Phoibos100 from SPECS Surface Nano Analysis GmbH, Berlin, Germany), whose entrance is normal to the sample surface. A tungsten filament was mounted under a sample holder on a manipulator in order to sample annealing by electron bombardment. The sample temperature was monitored by an optical pyrometer. The XPS measurements were performed with the Mg Kα (1253.6 eV) radiation, whereas the He I line (21.2 eV) was used in the UPS investigations. In the second UHV system the Omicron scanning tunneling microscope (STM) is hosted. All STM images were measured in a constant current mode with a tungsten tip. The XPS, UPS and LEED investigations were performed in-situ, whereas the transfer of the samples for the STM measurements required their exposition to ambient conditions.

The substrate in this study was Si-doped gallium nitride grown on sapphire (Al_2O_3), which was provided by the Technologies and Devices International, an Oxford Instruments Company. The samples were cleaned under UHV condition by a series of rapid thermal annealing (RTA) up to 1150 K. The surface cleanliness and structure were checked by XPS and LEED, respectively.

Niobium (a powder from Merck with a purity of 99.6%) was deposited by a physical vapor deposition technique from an electron beam evaporator onto the GaN substrate kept at room temperature. During the evaporation the pressure in the chamber was in the range of 10^{-9} mbar.

The XPS and UPS spectra were analyzed in the CasaXPS software version 2.3.25PR1.0. The Nb 3d line was deconvoluted by doublets with the GL(30) peak shape. During the fitting procedure the constant values of spin-orbital splitting (2.7 eV) and the $Nb_{5/2}/Nb_{3/2}$ intensity ratio (1.5) were assumed. The Shirley-typed background was applied. The STM images were analyzed in the WSxM software version 5.0 [26].

3. Results and Discussion

In this work, deposition of 15 nm of niobium film on a n-GaN surface is followed by RTA of sample up to 1123 K. Before and after this procedure, the surface properties of the sample were investigated in-situ by XPS, UPS and LEED. The results from the former technique will be discussed first.

For the bare n-GaN surface, the maxima of Ga $2p_{3/2}$, Ga $2p_{1/2}$ and N 1s peaks are located at binding energies (BEs) of 1118.4, 1145.3 and 398.0 eV, respectively (see Figure 1). On such surface, 15 nm of niobium film was deposited and annealed at 1123 K. The presence of an ad-layer leads to a complete quenching of Ga 2p signal intensity. On the other hand, there is a noticeable amount of nitrogen on the surface. As is visible in Figure 1b, the N 1s line reveals the maximum at BE of 397.5 eV. The line maximum is shifted by 0.5 eV towards a lower BE in comparison to the one obtained for the bare GaN surface. Since the GaN surface is only

a source of nitrogen in the system, its presence on the surface suggests that gallium nitride decomposition and nitrogen vertical diffusion occur during layer preparation.

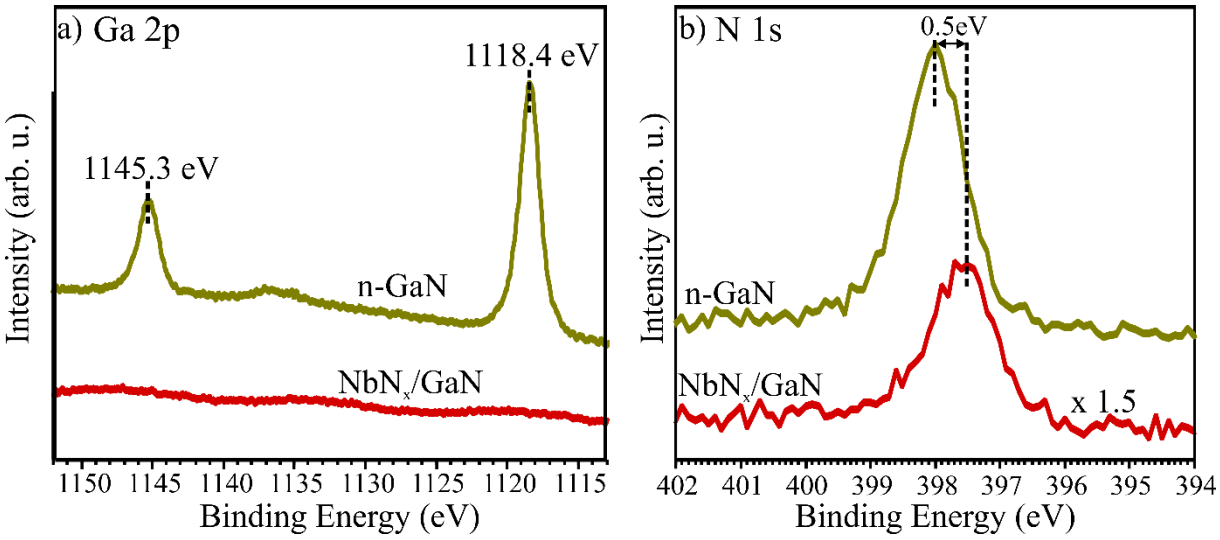

Figure 1. XPS results for bare GaN surface and after NbN_x layer preparation: (**a**) Ga 2p; (**b**) N 1s.

To rule out whether nitrogen present on the surface reacts with niobium, the Nb 3d core level and valence band (VB) spectra after layer preparation were analyzed. The Nb 3d spectrum shape, presented in Figure 2a, is complex and reveals two maxima located at 204.0 and 206.8 eV. A fitting procedure enables distinguishing three doublets associated with various Nb chemical environments. The majority doublet exhibits the lowest BE position, at 204.0 eV for Nb $3d_{5/2}$. The peak full width at half maximum (FWHM) is 1.4 eV. This BE value is higher by about 1.7 eV in comparison to the one reported for niobium metal (Nb), which is ~202.3 eV (for Nb $3d_{5/2}$) [27]. On the other hand, the Nb $3d_{5/2}$ BE value is in agreement with those reported for NbN_x films, which lie in the range from 203.3 to 204.2 eV [2,28,29]. Thus, we assigned the main doublet to the NbN_x compound. The N/Nb intensity ratio is 0.57, which indicates a niobium-rich phase of NbN_x, i.e., $x < 1$.

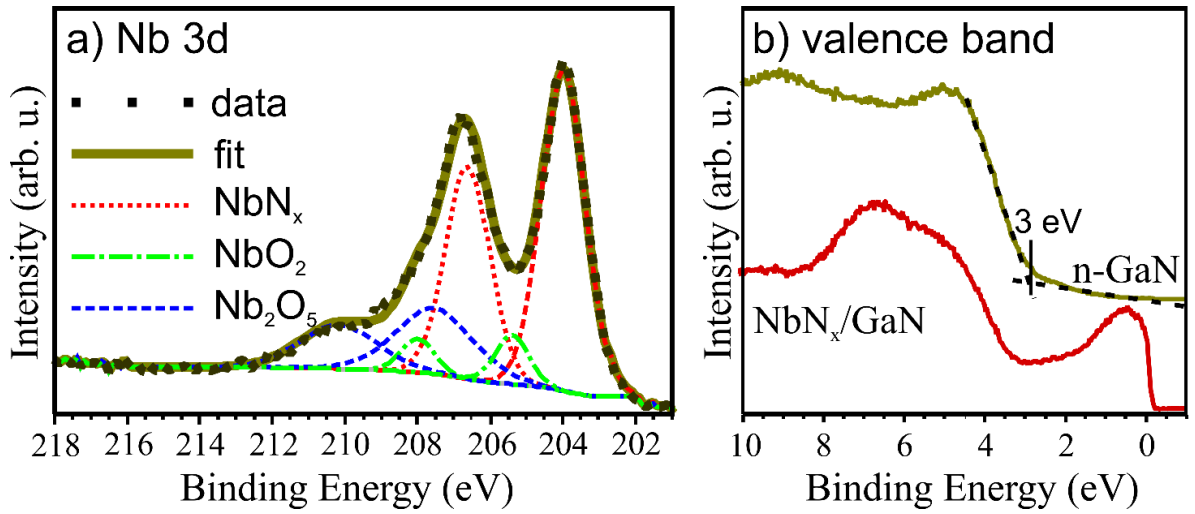

Figure 2. (**a**) XPS Nb 3d line with its deconvolution; (**b**) UPS VB spectra obtained before and after NbN_x layer preparation on GaN.

Two minority layer components are associated with doublets, of which the BE (FWHM) of Nb $3d_{5/2}$ lines are 207.5 eV (2.5 eV) and 205.4 eV (1.2 eV). The highest BE peaks correspond to the Nb_2O_5 compound, whereas the latter are ascribed to NbO_2 [30,31]. The appearance of oxides on the surface is associated with high reactivity of niobium with oxygen. Oxygen appears from the residual gases in the vacuum chamber as the sample is annealed.

The presence of metallic gallium or an Nb-Ga alloy is not detected in our XPS investigations. However, we cannot exclude the presence of such components closer to the NbN_x/GaN interface. The film nonhomogeneity was observed for TiN obtained by surface-mediated nitridation technique on Si_3N_4 [32]. Therein the atomic Si and $TiSi_2$ were found across the interface. The amount of those components varies with layer preparation conditions and layer depth. However, TiN was always the major component [32].

The UPS valence band spectra for the bare GaN and as-deposited layer are shown in Figure 2b. The valence band maximum for the cleaned n-GaN surface amounts to 3.0 eV, which is consistent with previous investigations [20]. After the layer preparation the UPS spectrum exhibits the metallic nature of the surface. Knowing the photon energy ($h\nu = 21.2$ eV) and the width of the spectrum (W = 16.6 eV), the work function (WF) can be determined from the formula $WF = h\nu - W = 4.6$ eV. Our WF value is close to those reported in the literature for NbN_x films, which range from 4.7 to 4.9 eV [33,34]. Two emission structures are distinguishable in the spectrum. The first feature is centered at about 0.5 eV and can be attributed to the Nb 4d state [31]. The second is a double shoulder feature, centered at about 5.5 and 7.0 eV, which can be attributed to the Nb 4p state hybridized with the N 2 p one and the O 2p state, respectively [29,31,35].

The structural properties of the surfaces were investigated in-situ by the LEED technique; the representative images for the bare GaN and as-prepared layer are presented in Figure 3. The reciprocal unit vectors are marked by the arrows. As it is visible in Figure 3a, at the beginning of the experiment, the patterns exhibit a hexagonal structure of the pristine GaN. After the layer preparation the images still reveal the hexagonal structure, whose unit vectors are rotated by 30° in comparison to those obtained for GaN. The ratio between lengths of reciprocal lattice vectors for the as-prepared layer/GaN is 0.63. Given the length of the GaN unit vector, which is 3.186 Å [36], the above ratio allows us to determine the in-plane unit vector length for the structure obtained after the NbN_x creation, i.e., ~5.1 Å. The obtained value is compared with those reported in the literature for NbN_x [35,37–40]. Our lattice parameter is closest to one found for the Nb_5N_6 phase, which is 5.19 Å [37]. Due to the fact that LEED is a surface-sensitive method, the possibility of an NbN_x surface reconstruction should be also addressed. The (2×2) surface reconstruction was reported, in Refs. [11,41], based on high-energy electron diffraction images, for hexagonal niobium-rich Nb_2N thin films grown on SiC by MBE. Depending on the growth conditions, the (2×2) and $\left(\sqrt{3} \times \sqrt{3}\right)$R30° reconstructions were found for the NbN(111) films obtained on the $SrTiO_3$(111) substrate by plasma-assisted MBE [12]. Further ex-situ structural bulk sensitive investigations, which are beyond the scope of this work, are needed to rule out whether the surface of our thin film is reconstructed.

The NbN_x/GaN surface morphology and structure were also characterized ex-situ by STM. Two representative STM images are presented in Figure 4. Based on the large-scaled images, an example is shown in Figure 4a; the surface root mean square roughness obtained was of the order of 0.9 nm. The images with higher resolution (see Figure 4b) reveal that the film consists of elongated crystallites. The angles between the crystallites' edges are i.a. 120° and 60° in accord with the six-fold symmetry of the LEED patterns.

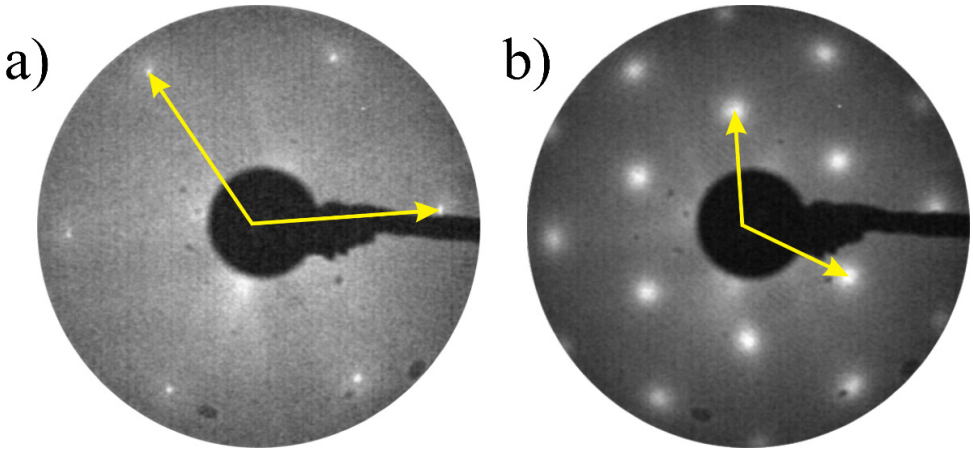

Figure 3. LEED patterns of: (**a**) pristine n-GaN surface; (**b**) as-prepared NbN_x layer. Images taken at 60 eV.

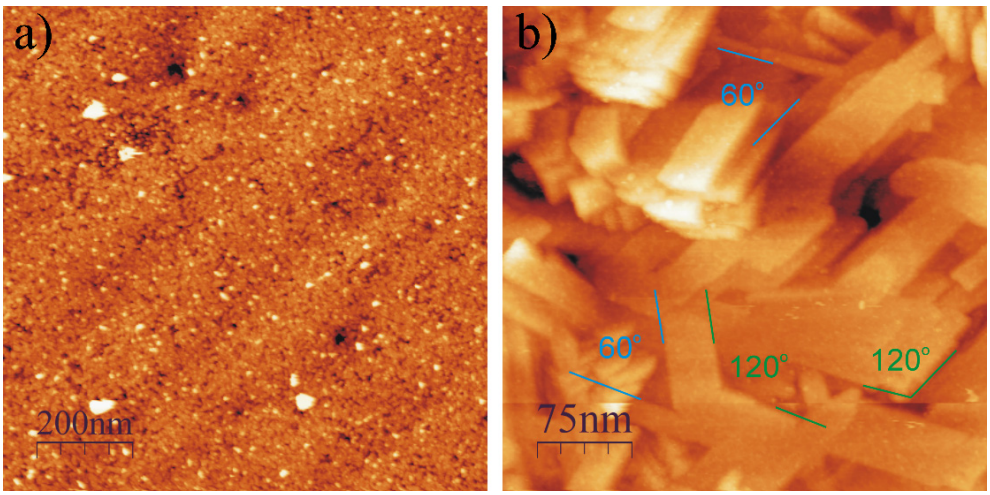

Figure 4. STM images of NbN_x/GaN surface. Images taken for: (**a**) U = 1.26 V; I = 0.042 nA; (**b**) U = 1.26 V; I = 0.103 nA.

4. Conclusions

The possibility of NbN_x thin film preparation on the GaN substrate by surface-mediated nitridation technique was presented. For this purpose, the as-deposited niobium film was annealed at 1123 K. Then, the surface properties of the obtained layer were in-situ explored by XPS, UPS and LEED methods. The chemical composition analysis based on XPS reveals that the obtained NbN_x layer is nitrogen-poor, i.e., $x < 1$. The film exhibits hexagonal LEED patterns with the in-plane lattice parameter of 5.1 Å. The UPS data shows the metallic nature of the layer, the work function of which is 4.6 eV. Additional studies are planned to investigate the homogeneity and crystallographic structure of NbN_x on GaN obtained with our method using more sensitive bulk techniques.

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