Thin Solid Films 518 (2010) 3632–3639

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

High-resolution X-ray photoemission spectroscopy study of AlN nano-columns grown by nitridation of Al nano-squares on Si(111) substrates with ammonia

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ARTICLE INFO

Article history:
Received 23 April 2009
Received in revised form 17 September 2009
Accepted 21 September 2009
Available online 2 October 2009

Keywords:
Nitridation
Nano-structures
Aluminum nitride
X-ray photoemission spectroscopy
Ammonium

ABSTRACT

The growth of AlN nano-columns by ammonium nitridation of Al nano-squares embedded in SiO_2 on Si(111) substrates was studied by high-resolution X-ray photoemission spectroscopy from a synchrotron radiation source and scanning electron microscopy (SEM). Selective nitridation of the Al nano-squares on the SiO_2 mask was obtained in the temperature window of 600 °C–700 °C. The well-shaped AlN nano-column arrays with diameters confined by the lateral size of the Al nano-squares (~100 nm) were observed in SEM.
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1. Introduction

Growth of III-nitride quantum dots (QDs) assemblies has been the subject of intensive research in the past decade or so. This is largely due to their unique properties mainly derived from their strong carrier confinement effect. Quantum dot structures have a high potential for application in future quantum-communication systems [1]. A fabrication technique resulting in QDs with a high packing density and high degree in size, shape and spacing uniformity is crucial to realize future device applications. Selective area growth (SAG), by which the QDs growth is directed and confined inside a highly ordered nano-cavity/hole array that is imprinted into the substrate surface via nanolithography, has been implemented on silicon substrates by molecular-beam epitaxy (MBE) [2–4].

During MBE growth of III-nitrides on silicon substrates, a thin crystalline Al film deposited at temperature higher than 700 °C was found to effectively form a single crystalline AlN layer when nitrated using ammonia [5]. There has therefore been increasing interest in growth of AlN nano-structures by direct nitridation of Al nano-patterns on silicon substrates. S. Ishizawa et al. reported on a SAG technique for fabricating GaN nano-columns by direct nitridation of preformed Al nano-dot-patterns by a radio-frequency (RF) plasma cell and using them as the nucleation sites for GaN nano-column growth to achieve positional control with RF-plasma-assisted MBE [6]. However, the nano-column shape reported in their work was insufficiently controlled owing to the deformation of the Al nano-dots before nitridation. The observed deformation could be due to Al aggregation during temperature ramping across the melting point of metallic Al (660 °C) in the absence of RF-nitrogen plasma.

It is well known that beside RF-nitrogen plasma, ammonia (NH_3) is an efficient nitrogen candidate in III-nitride growth with MBE [7,8]. Thermodynamic calculations using Gibbs free energy changes (ΔG°) data suggest that the favorite pathway to the nitridation reaction of Al using ammonia is through the dissociation of ammonia at the surface of liquid Al particles. High reaction temperature or positive temperature gradient is favorable for a complete Al nitridation. The overall mechanisms can be delineated as follows: Ammonia dissociates into reactive nitrogen (N) and hydrogen (H) radicals at the surface of liquid Al particles. The N radicals react with liquid Al by diffusing into the Al particles to form AlN while H radicals react with other ammonia molecules to promote its decomposition [9]. If ammonia is used for nitridation, the Al nano-columns can be safely heated up with simultaneous supply of ammonia gas, to temperatures above the Al melting point. The hydrogen radical side-products from the ammonia dissociation are beneficial by actively bonding with oxygen from native oxide layer, and by removing carbon impurities on the sample surface during heating.

As a supplement to the work by S. Ishizawa et al. [6], the objective of this study was to investigate the ammonia nitridation efficiency of Al nano-patterns fabricated on SiO_2 platforms by gradually increasing the substrate temperature across the Al melting point in ammonia ambient and studying the nitridation effect using X-ray photoemission spectroscopy (XPS) and scanning electron microscopy (SEM).

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0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.09.088

2. Experimental details

The nano-patterns were prepared on a SiO_2 mask on top of Si(111) substrates using electron-beam lithography (EBL) and reactive ion etching (RIE) in a class 1000 cleanroom facility at the University of Iceland. The Al nano-squares were fabricated in steps shown schematically in Fig. 1. An approximately 50 nm SiO_2 film was prepared on a Si(111) substrate by thermal oxidation at 1000 °C for 1.5 h (Fig. 1a). The SiO_2 surface was spin-coated with around 100 nm of polymethylmethacrylate (950 PMMA dissolved in anisole, MicroChem Corp.), which is a high-resolution positive resist for direct e-beam lithography. The PMMA layer was then cured by baking on a hotplate at 170 °C for 5 min and patterned using EBL (Fig. 1b). PMMA development was performed by immersion in Methyl Isobutyl Ketone:Isopropanol (IPA) (3:1) solution for 45 s followed by immersion in IPA for another 45 s (Fig. 1c). After PMMA development, the exposed SiO_2 wells were etched by RIE in two steps: first in O_2:CHF_3 (30:20 sccm) at 50 W RF power and 6.67 Pa gas pressure for 5 s, then in O_2:CHF_3 (35:25 sccm) at 150 W RF power and 4.00 Pa gas pressure for 10 min, which was sufficient to totally remove the exposed 50 nm thick SiO_2 layer. Thus, arrays of nano-wells (~100 nm × 100 nm × 50 nm) arranged in a 300 nm period hexagonal lattice pattern on the Si(111) substrate surrounded by SiO_2 layer were formed after RIE (Fig. 1d). Next, a ~30 nm thick Al film was deposited by thermal evaporation on the PMMA/SiO_2 mask (Fig. 1e) followed by a lift-off by immersion in acetone and ultrasonic cleaning of the sample in de-ionized water resulting in Al nano-dots of 100 nm × 100 nm in lateral size and ~30 nm thickness (Fig. 1f). The dots were arranged in a 300 nm period hexagonal lattice and grouped into nine 20 μm × 20 μm sub-unit within a square area (300 μm × 300 μm) made of gold frame. Each sub-unit square area consisted of ~5472 Al nano-dots, with the Al covered area density of ~13%.

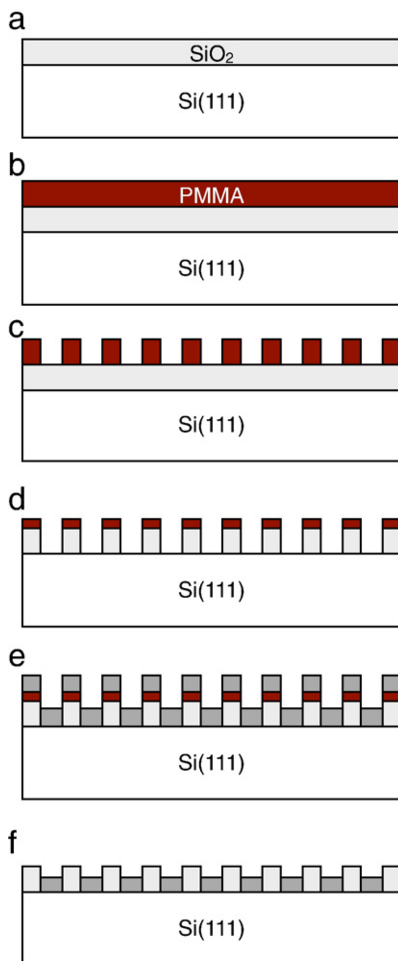

Fig. 1. Schematic showing the relevant steps in the fabrication process of the Al nano-squares. (a) Thermal oxidation at 1000 °C in O_2 for 1.5 h, resulting in approximately 50 nm SiO_2. (b) 100 nm PMMA spin-coating. (c) E-beam lithography. (d) Reactive ion etching of SiO_2. (e) ~30 nm Al deposition. (f) Acetone PMMA lift-off.

The high-resolution XPS measurements were carried out at the Swedish National Synchrotron radiation facility Maxlab in Lund, at beamline D1011, which is located on a bending magnet on the MAX-II storage ring. It delivers photons in the energy range 50–1500 eV from a modified SX-700 monochromator. Electron spectra were recorded using a hemispherical Scienta 200 analyzer in normal emission mode. The energy scale in all spectra was related to the Fermi level of the tantalum sample holder that was in electrical contact with the sample. The energy resolution was 100 meV.

The system consisted of separate analyzer and preparation chambers. After the sample had been loaded into the preparation chamber, ammonia gas was gradually introduced into the chamber through a leak valve until chamber-pressure had stabilized at ~5–6 × 10^{-3} Pa. At that point, the sample was gradually heated up to the desired nitridation temperature by the electron bombardment on the backside of the substrate holder from a hot tungsten filament. The temperature was measured with a thermocouple in contact with the tantalum substrate holder. The ammonia pressure was maintained at 5–6 × 10^{-3} Pa throughout the whole nitridation process. The sample underwent three nitridation treatments. In the first treatment, the sample temperature was ramped up to ~600 °C over one and half hour and kept at that temperature for 1 h. In the second treatment, the sample was ramped up to ~700 °C over one and half hour and kept at that temperature for about 2 h. In the third treatment, the sample was ramped up to 600 °C over 1 h, then increased to 730 °C over 1 h and kept at 730 °C for 1 h. The overall temperature profile for the sample treatment is delineated in Fig. 2. After each nitridation treatment, the sample was allowed to cool down before being transferred to the analyzer chamber for XPS measurement carried out in ultra high vacuum (~7.0 × 10^{-8} Pa).

The morphological characterization of Al nano-squares induced by ammonia nitridation was done with SEM using a LEO SUPRA-25 scanning electrical microscope system (Oxford Instruments) at the Innovation Center Iceland.

3. Results and discussions

The XPS studies provide information concerning the composition and chemical states of the elements in the specimen being probed. However, it is difficult to find a consistent energy reference for the core electron peaks in question because their location varies depending on film thickness, method of nitridation, substrate etc.

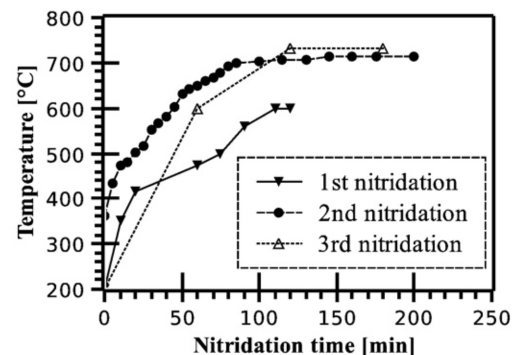

Fig. 2. Temperature profile for the three nitridation processes. For the first nitridation the substrate temperature was ramped to ~600 °C and kept at this temperature for 1 h. For the second nitridation treatment the same substrate was ramped to ~700 °C and kept at this temperature for 2 h. For the third and final nitridation treatment the substrate was ramped to ~730 °C and kept at this temperature for 1 h.

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