Applied Surface Science 258 (2012) 4497–4506

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

A micro-spectroscopy study on the influence of chemical residues from nanofabrication on the nitridation chemistry of Al nanopatterns

B. Qi[a,*], S. Ólafsson[a], A.A. Zakharov[b], B. Agnarsson[a,d], H.P. Gislason[a], M. Göthelid[c]

[a] Physics Department, Science Institute, University of Iceland, Dunhaga 3,107 Reykjavík, Iceland
[b] MAX-lab, Lund University, S-22100 Lund, Sweden
[c] Materialfysik, MAP, ICT, KTH, ELECTRUM 229, 16440 Kista, Sweden
[d] Department of Applied Physics, Chalmers University of Technology, S-41296 Gothenburg, Sweden

ARTICLE INFO

Article history:
Received 17 August 2011
Received in revised form 8 December 2011
Accepted 3 January 2012
Available online 20 January 2012

Keywords:
X-ray photoemission electron microscopy
e-Beam lithography
Micro-spectroscopy
Nanopatterns
Nitridation

ABSTRACT

We applied spatially resolved photoelectron spectroscopy implemented with an X-ray photoemission electron microscopy (XPEEM) using soft X-ray synchrotron radiation to identify the compositional and morphological inhomogeneities of a SiO_2/Si substrate surface nanopatterned with Al before and after nitridation. The nanofabrication was conducted by a polymethylmethacrylate (PMMA)-based e-beam lithography and a fluorine-based reactive ion etching (RIE), followed by Al metalization and acetone lift-off. Three types of chemical residues were identified before nitridation: (1) fluorocarbons produced and accumulated mainly during RIE process on the sidewalls of the nanopatterns; (2) a thick Al-bearing PMMA layer and/or (3) a thin PMMA residue layer owing to unsuccessful or partial lift-off of the e-beam unexposed PMMA between the nanopatterns. The fluorocarbons actively influenced the surface chemical composition of the nanopatterns by forming Al—F compounds. After nitridation, in the PMMA residue-free area, the Al—F compounds on the sidewalls were decomposed and transformed to AlN. The PMMA residues between the nanopatterns had no obvious influence on the surface chemical composition and nitridation properties of the Al nanopatterns. They were only partially decomposed by the nitridation. The regional surface morphology of the nanopatterns revealed by the secondary electron XPEEM was consistent with the scanning electron microscopy results.

1. Introduction

Selective area growth is of great importance in nanostructure fabrication. Various techniques, such as photolithography, e-beam lithography (EBL), micro-contact printing and shadow masking have been utilized in nanofabrication [1–4]. Among those, EBL is frequently adopted to generate nanoscale templates for selective area growth. Polymethylmethacrylate (PMMA) is widely used as a high-resolution positive resist in EBL. The pattern written in the resist is developed by removing the irradiated areas in an organic solvent. Subsequent processing steps may include plasma-based etching, metalization, or epitaxial regrowth, and finally stripping off the resist by aggressive solvents (often acetone) to form nanoscale structures on substrates. It is notorious, the surface cleanliness of the patterned substrate at the end of nanofabrication influences the quality and post-processing of the nanostructures.

Macintyre et al. [5] observed two sorts of residual resist layers in PMMA: exposed and unexposed. They presented evidence of a residual layer in regions of unexposed resist which have been subject to a standard solvent-based resist stripping and cleaning procedure. Exposed residues have been observed by many groups in e-beam exposed and developed regions of PMMA. For example, Maximov et al. [6] found that the correctly exposed and developed PMMA leaves residues with an average thickness of about 1 nm. Even under overexposure conditions, about 0.5 nm of PMMA residue remained on the SiO_2 surface. Our previous study [7] on nitridation of Al nanopatterns fabricated by EBL indicated that the fluorine impurities which most probably originated from the fluorine-based reactive ion etching (RIE) process were introduced into the nanopatterns.

It is clear that as long as the EBL and RIE are involved in the nanofabrication, the potential impurities from e-beam resist residues and RIE processing gases cannot be ignored. It is therefore important to identify these contaminants in nanostructures and to monitor their behavior during post-processing of the nanostructures. In many cases of nanostructure analysis, the important properties change from place to place, and key phenomena can be confined to small areas. The normal standard photoemission spectroscopy probing wide regions (scale of 1000 μm in diameter) often misses crucial elements and can even be misleading.

* Corresponding author.
E-mail address: bing@raunvis.hi.is (B. Qi).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2012.01.015

Upon increasing demand for the spectroscopy with a high spatial resolution capability, the research and development of spectromicroscopy which refers to a broad class of experimental techniques that combine the analytical power of spectroscopy with high spatial resolution has greatly advanced over the past decades [8]. The combination of X-ray photoemission electron microscopy (XPEEM) and low-energy electron microscopy (LEEM), with the option of μ-sized photoelectron spectroscopy (μ-PES), called SPELEEM (spectroscopic photoemission low-energy electron microscopy) [9–11] is one of the most recent developed prototypes of synchrotron-based spectromicroscopy. Another XPEEM technique complementary to SPELEEM is the energy-filtered NanoESCA XPEEM method, which in particular uses both laboratory and synchrotron X-ray sources [12]. They both allow elemental and chemical information on the nanopatterned surfaces to be acquired with a high spatial resolution [12–14].

In this article, the Al nanopatterns fabricated by PMMA-based EBL and fluorine-based RIE process on SiO_2 covered Si substrates were adopted as a prototypical system to exploit the versatility of XPEEM combined with μ-PES to identify the potential contaminants from nanofabrication and their influences on the chemistry and nitridation of the nanopatterns.

2. Experimental work

The overall nanopattern fabrication is schematically shown in Fig. 1. In step (a), Si (1 1 1) substrates (p-type, 0.0001–3.0 *Omega*-cm) were cleaned in H_2O:27% NH_4OH:30% H_2O_2 (5:1:1 by volume) solution, at 70 °C for 15 min, then rinsed with deionized water and dried with N_2. This resulted in a native SiO_2 layer about 6–7 nm thick (measured by ellipsometry), on which, in step (b), about 200 nm PMMA (950 molecular weight, 3% concentration dissolved in anisole, MicroChem Corp.) was spin-coated and cured at 170 °C for 5 min. The PMMA layer was then patterned by EBL using a Raith 150 e-beam writing system (Raith GmbH) integrated with a LEO SUPRA-25 scanning electron microscopy (SEM) system (Carl Zeiss AG). In step (c), the patterned PMMA layer was developed in methyl isobutyl ketone:isopropanol (IPA) (3:1) solution and rinsed in IPA, for 45 s, respectively. This resulted in the featured nanowells embedded in PMMA layer. Afterwards, in step (d), two types of RIE were carried out: first in an O_2:CHF_3 (30:20 standard cubic centimeter (sccm)) mixture at 6.67 Pa applied by 50 W RF plasma for 5–10 s to clear the PMMA residues from the bottoms of the nanowells; and secondly in an Ar:CHF_3 (25:25 sccm) mixture at 4.00 Pa applied with a 150 W RF plasma for 10–15 min to selectively etch away the SiO_2 layer from the bottoms of the nanowells [15]. In step (e), 20–30 nm thick Al was thermally deposited on the patterned surface held at room temperature. In step (f), acetone soaking and a gentle ultrasound agitation were performed in order to lift-off the Al layer outside the nanowells (Fig. 1(f)). The overall process resulted in arrays of Al nanopatterns of 100 nm × 150 nm in lateral size and 20–30 nm in height, and arranged in a hexagonal pattern with a lattice period of 200–300 nm.

The characterizations were carried out using the SPELEEM III microscope (Elmitec, GmbH) at beamline I311 at the Swedish National Synchrotron Radiation facility Max-lab. The beamline is an undulator-based soft X-ray source, providing horizontally polarized light in an energy range from 30 to 1500 eV. A simplified scheme of the microscope layout can be found in Ref. [16]. A unique feature of the SPELEEM which allows X-ray photoemission spectromicroscopy is its capability of energy filtering, which is enabled by the hemispherical electron energy analyzer with a pass energy of about 908 eV. The band-pass filter is implemented by the energy slit placed at the dispersive plane of the analyzer. The two slits available in the microscope correspond to resolutions of 0.3 and 0.6 eV. In real-space imaging mode, the microscope reaches a lateral resolution of about 10 nm in LEEM and 30 nm in XPEEM [14]. The SPELEEM can also be operated in the micro-diffraction mode and selected-area spectroscopy or micro-spectroscopy (μ-PES) mode. The latter is implemented by imaging the dispersive plane of the energy analyzer directly onto the detector, providing the snapshot of a 15 eV-wide spectral window. The μ-PES measurements in our case were restricted to a spot of 0.8 or 8 μm in diameter selected

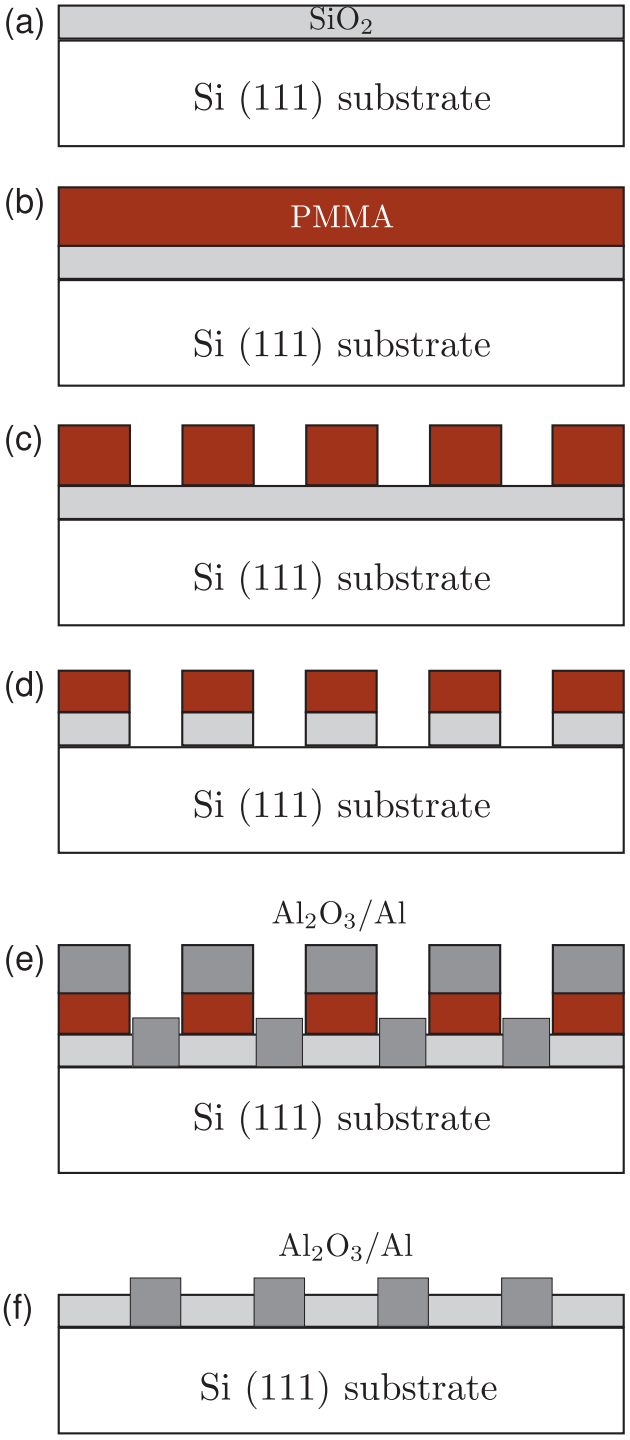

Fig. 1. Schematic diagram of nanopattern fabrication, including: chemical cleaning with H_2O:27% NH_4OH:30% H_2O_2 (5:1:1 by volume) solution (a), spin-coating with PMMA about 200 nm thick (b), e-beam lithography (c), RIE in O_2:CHF_3 (30:20 sccm) and Ar:CHF_3 (25:25 sccm) (d), Al deposition by thermal evaporation (e) and PMMA lift-off with acetone (f).