Fabrication of HfO$_2$ patterns by laser interference nanolithography and selective dry etching for III-V CMOS application

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Abstract
Nanostructuring of ultrathin HfO$_2$ films deposited on GaAs (001) substrates by high-resolution Lloyd’s mirror laser interference nanolithography is described. Pattern transfer to the HfO$_2$ film was carried out by reactive ion beam etching using CF$_4$ and O$_2$ plasmas. A combination of atomic force microscopy, high-resolution scanning electron microscopy, high-resolution transmission electron microscopy, and energy-dispersive X-ray spectroscopy microanalysis was used to characterise the various etching steps of the process and the resulting HfO$_2$/GaAs pattern morphology, structure, and chemical composition. We show that the patterning process can be applied to fabricate uniform arrays of HfO$_2$ mesa stripes with tapered sidewalls and linewidths of 100 nm. The exposed GaAs trenches were found to be residue-free and atomically smooth with a root-mean-square line roughness of 0.18 nm after plasma etching.

PACS: Dielectric oxides 77.84.Bw, Nanoscale pattern formation 81.16.Rf, Plasma etching 52.77.Bn, Fabrication of III-V semiconductors 81.05.Ea

Introduction
Three-dimensional multi-gate field effect transistors with integrated mobility-enhanced channel materials (i.e. GaAs, In$_x$Ga$_{1-x}$As) and high-$\kappa$ gate dielectrics (i.e. HfO$_2$, Al$_2$O$_3$) are considered as plausible candidates to sustain Si complementary metal-oxide-semiconductor (CMOS) performance gains to and beyond the 22 nm technology generation in the next 5 to 7 years [1,2]. The rapid introduction of these new materials in non-planar transistor architectures will consequently have a high impact on front-end cleaning and etching processes. Cleaning processes thus need to become completely benign, in terms of substrate material removal and surface roughening. Moreover, high-$\kappa$ gate etching offering high across-wafer uniformity, selectivity, and anisotropy will be essential to achieve a tight control over gate-length critical dimensions (CD) while keeping linewidth roughness low in future devices. To attain this goal, an adequate choice of photoresist type, etch bias power, and etch chemistry is necessary [3].

Patterning of HfO$_2$ layers on Si substrates by means of different lithographic techniques and dry etching in F-, Cl-, Br-, CH$_4$-, and CHF$_3$-based plasma chemistries has been extensively investigated [4-7]. Comparatively much less attention has been paid to patterning ultrathin layers of HfO$_2$ deposited on GaAs substrates despite its key role in the fabrication of next generation non-planar high-$\kappa$/III-V transistors. In recent papers, we have studied the nanoscale patterning of HfO$_2$/GaAs by electron beam lithography and inductively coupled plasma reactive ion etching (ICP-RIE) using BCl$_3$/O$_2$ and SF$_6$/Ar chemistries [8,9]. Only the less-reactive F-based chemistry showed good etch selectivity of HfO$_2$ over GaAs (i.e. 1.5) and adequate control of the etching rate. In this letter, we report on the fabrication of nanopatterned HfO$_2$ ultrathin layers on GaAs substrates by laser interference nanolithography (LInL) and selective ICP-RIE in a CF$_4$ plasma chemistry. The main HfO$_2$ etching characteristics studied by a combination of atomic force microscopy (AFM), high-resolution scanning electron
microscopy (HR-SEM), and high-resolution transmission electron microscopy (HR-TEM)/energy-dispersive X-ray spectroscopy microanalysis (EDS) are presented, with specific emphasis on pattern resolution; etch profile; and GaAs surface roughness and composition.

**Experimental**

All experiments described here were performed on 10-nm-thick HfO2 layers grown by atomic layer deposition (Cambridge NanoTech Inc., Cambridge, MA, USA) on a 2-in.-diameter GaAs (001) wafer (Wafer Technology Ltd., Milton Keynes, UK), where a 400-nm-thick GaAs buffer layer had been previously deposited by metal-organic vapour phase epitaxy. Nanostructuring of the HfO2 thin film was carried out by Lloyd's mirror LInL using a commercial system (Cambridge NanoTools LLC, Somerville, MA, USA) and a He-Cd laser (λ = 325 nm) as the light source. Prior to exposure to the laser source, the HfO2/GaAs substrates were first spin coated with a 210-nm-thick antireflective coating (ARC), then covered by a 20-nm-thick SiO2 layer grown by plasma-enhanced chemical vapour deposition, and finally spin coated with a negative photoresist (OHKA PS4, Tokyo OHKA Kogyo Co., Japan). The ARC has the adequate refractive index to suppress 325-nm reflections from the substrate. The SiO2 layer acts as a mask and improves the pattern transfer from the photoresist to the ARC. Subsequently, a stripe pattern was transferred to the photoresist by a 20-nm-thick SiO2 layer grown by plasma-enhanced chemical vapour deposition, and finally spin coated with a negative photoresist (OHKA PS4, Tokyo OHKA Kogyo Co., Japan). The ARC has the adequate refractive index to suppress 325-nm reflections from the substrate. The SiO2 layer acts as a mask and improves the pattern transfer from the photoresist to the ARC. During this step, the SiO2 layer is completely eliminated. Finally, the HfO2 mesa stripes. The values of the r.m.s. line roughness (R_s) measured along the HfO2 stripes and the etched GaAs trenches were 0.14 ± 0.03 nm and 0.18 ± 0.03 nm, respectively. The value of the GaAs line roughness measured in this work is comparable to that reported previously for HfO2 etching using a SF6/Ar plasma (0.13 nm) [8]. Etching with a CF4 plasma chemistry thus provides an atomically smooth GaAs surface, which is a critical requirement for subsequent selective III-V growth during device fabrication. In fact, preliminary III-V molecular beam epitaxy experiments to be reported elsewhere indicate that both the quality of the starting GaAs surface and the inclined sidewalls of the HfO2 nanopatterns are adequate for selective area growth and the resulting III-V nanostructures do not suffer from microtrench formation near the high-κ gate oxide, reported by other authors [10].

Pattern transfer to the HfO2 ultra thin film was investigated by HR-SEM. The 1.3 × 1.3-μm scanning electron micrographs in Figure 2 illustrate the sample morphology at two different stages of the patterning process. Figure 2a is a plan view of the sample surface after laser lithography showing the patterned resist stripes and the underlying SiO2 layer. The average values of the resist beam system (FEI Co.). In order to protect the surface of interest from milling by the Ga⁺ ion beam during sample preparation, a Pt layer was deposited in the FIB on the HfO2/GaAs nanopatterns. This common procedure is accomplished by introducing an organometallic gas in the vacuum chamber, where it decomposes on the sample surface upon interaction with the ion beam. HR-TEM/EDS compositional maps were acquired using a Philips Tecnai 20 FEG TEM (FEI Co.) operating at 200 keV.

**Results and discussion**

The main characteristics of the nanostructuring process were investigated by a combination of AFM, HR-SEM, HR-TEM, and EDS. In particular, we studied the resolution and anisotropy of the HfO2-etched nanostructures as well as the roughness and compositional integrity of the underlying GaAs surface.

The surface morphology of the as-deposited and nanostructured HfO2/GaAs samples was examined by AFM. The root-mean-square (r.m.s.) surface roughness (σ) extracted from 2 × 2-μm AFM images was found to be 0.7 ± 0.01 nm for the as-deposited HfO2 film and 4.9 ± 0.01 for the nanostructured HfO2/GaAs sample. Figure 1 depicts a three-dimensional image (1.2 × 1.2 μm) of the HfO2/GaAs surface topography after nanostructuring and a typical scan profile across an etched trench. The latter revealed the formation of a tapered sidewall due to directional chemical etching and the presence of re-deposited reaction by-products on the edges of the HfO2 mesa stripes. The values of the r.m.s. line roughness (R_s) measured along the HfO2 stripes and the etched GaAs trenches were 0.14 ± 0.03 nm and 0.18 ± 0.03 nm, respectively. The value of the GaAs line roughness measured in this work is comparable to that reported previously for HfO2 etching using a SF6/Ar plasma (0.13 nm) [8]. Etching with a CF4 plasma chemistry thus provides an atomically smooth GaAs surface, which is a critical requirement for subsequent selective III-V growth during device fabrication. In fact, preliminary III-V molecular beam epitaxy experiments to be reported elsewhere indicate that both the quality of the starting GaAs surface and the inclined sidewalls of the HfO2 nanopatterns are adequate for selective area growth and the resulting III-V nanostructures do not suffer from microtrench formation near the high-κ gate oxide, reported by other authors [10].

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linewidth and the pitch are $119 \pm 6$ nm and $187 \pm 6$ nm, respectively. The micrograph depicted in Figure 2b is a plan view of the nanostructured surface after exposure to the sequence of CF$_4$ and O$_2$ plasma steps and the final HCl/H$_2$O surface cleaning described above. The image shows well-defined HfO$_2$-etched features on the GaAs substrate. Moreover, no evidence of HfO$_2$ residues on the groove bottom was found when a backscattered electron detector was used to enhance the compositional contrast in the image. The average HfO$_2$ linewidth and pitch of the nanopattern, measured from Figure 2b, were $100 \pm 7$ nm and $192 \pm 6$ nm, respectively.

In order to elucidate the origin of the linewidth narrowing observed in the HfO$_2$ stripes with respect to the original resist pattern, a more detailed study of the intermediate etching steps was undertaken. These were characterised by analysing cross-sectional HR-SEM images of the sample at different stages of the nano-structuring process. Figure 3a depicts the cross-section of the sample after pattern transfer to the SiO$_2$ and ARC layers, showing that the SiO$_2$ linewidth (118 nm) has not varied significantly with respect to that of the resist pattern. In addition, the etched sidewalls are vertical, hence, indicating that the pattern was precisely transferred to the SiO$_2$ layer during the first CF$_4$ etching step. By contrast, O$_2$ plasma etching of the ARC layer proceeds with undercut and inclined sidewall (87°) formation, suggesting that some interaction between radicals from the gas phase and the sidewalls has occurred. The linewidth at the bottom of the ARC is consequently reduced (102 nm) with respect to the original resist pattern, as shown in the image.

Figure 3b illustrates the sample cross-section after HfO$_2$ selective etching with CF$_4$. This process has been estimated to occur at a rate of 0.06 nm/s. Such slow HfO$_2$ etching rate is advantageous with respect to previous reports using SF$_6$/Ar [8] from the process control viewpoint, as it allows to process a typical 2-nm-thick gate oxide in a practicable etching time, i.e.
approximately 30 s. As shown in the image, a tapered etch profile with a 70° inclination angle is achieved by the formation of a sidewall passivation layer comprised of non-volatile reaction by-products of the CF$_4$ etching process. It should be noted here that the patterned resist mask had been completely eliminated during the previous O$_2$ plasma treatment and, consequently, the exposed SiO$_2$ stripes and the ARC layer are gradually etched by the CF$_4$ plasma during pattern transfer to the HfO$_2$ film. This contributes to a further reduction of the pattern linewidth and to the formation of an HfO$_2$ foot on both mesa edges, which is only observable by HR-TEM (see below). The width of the HfO$_2$ mesa top measured from Figure 3b was 98 nm at this stage of the process. The width of the mesa bottom could not be determined from the same image due to the presence of re-deposited material. Notwithstanding, we have estimated that the bottom linewidth is approximately 105 nm, taking into account that the 70° ARC sidewall inclination is transferred to the HfO$_2$ layer without any significant variation. Comparison of this value with the final dimension of the HfO$_2$ stripes (Figure 3c), i.e. 100 nm, suggests that the last HCl/H$_2$O wet etch further contributes to narrow the linewidth. The schematic diagram shown in Figure 4 illustrates the HfO$_2$ nanofabrication process flow.

The structure of the nanopatterned HfO$_2$/GaAs samples was investigated by HR-TEM. Figure 5a, b, c depicts a series of cross-section HR-TEM images showing the periodic HfO$_2$ nanopattern fabricated on the GaAs epilayer as well as details of an etched trench and a typical HfO$_2$ mesa stripe. The anisotropic nature of the etch profile and the existence of slight variations in sidewall inclination are observable in these images. The HfO$_2$ sidewall angle measured from Figure 5b, i.e. 47°, contrasts with that measured after CF$_4$ etching, i.e. 70°. The HCl/H$_2$O wet etch step thus appears to alter both the HfO$_2$ linewidth and the mesa profile. In addition, Figure 5c clearly shows the formation of an approximately 10-nm-long foot at either side of the HfO$_2$ stripe, due to the progressive erosion of the ARC and SiO$_2$ layers during CF$_4$ etching mentioned above. Note that the total HfO$_2$ width, including the feet at both sides of the mesa, corresponds roughly to the resist linewidth in the original pattern, as indicated in the figure. The HfO$_2$/GaAs interface appears quite abrupt and the underlying GaAs substrate shows no evidence of lattice damage. Nevertheless, an approximately 5-nm-thick amorphous layer is observed in the exposed GaAs regions (Figure 5b), which is likely to have formed as a result of ion damage or oxidation during exposure to the CF$_4$ and O$_2$ plasmas. Further investigation of the chemical composition of the HfO$_2$/GaAs samples was performed by TEM/EDS analysis. The cross-sectional elemental maps corresponding to O (K), Hf (M), Ga (L), and As (K), gathered in Figure 6, indicate that the subsurface layer is mainly constructed of gallium oxide, the less volatile of the oxidation products of GaAs, which is formed during the final exposure to the O$_2$ plasma. This oxide layer can be removed prior to epitaxy by standard
thermal desorption at 600°C. Finally, the composition map corresponding to Hf (M) shows that Hf is concentrated in the mesa stripes, although traces of this element were also detected in the mesa foot.

Conclusions
We have demonstrated the fabrication of HfO$_2$/GaAs patterns with nanoscale resolution using He-Cd laser interference lithography and dry etching using a combination of CF$_4$ and O$_2$ plasmas. The etched GaAs trenches formed by this process were found to be residue-free and atomically smooth after plasma etching. Strong sidewall passivation during HfO$_2$ selective etching and wet cleaning with an HCl/H$_2$O solution results in the formation of tapered HfO$_2$ etch profiles. Optimisation of the CF$_4$ plasma composition and etch bias...
power to lessen the re-deposition of non-volatile by-products, in combination with the use of more benign cleaning solutions than HCl/H2O, are some of the future improvements to be introduced in the current process to reach the approximately 30 nm HfO2 gate lengths and CD control better than 2 nm required for the fabrication of III-V-based CMOS.

Acknowledgements
This work was funded by MICINN (Spain) under projects TEC2007-66955 and FIS2009-12964-C05-04, by Comunidad de Madrid under projects S2009/MAT1158S (Estrumat) and S2009/PPQ-1642, (AVANSENS), and by the EU FP7 MAT ERA-Net “ENGAGE” project, with local support provided by Enterprise Ireland and Fundación Madrid. The use of LinL at FideNa (Pamplona, Spain), the FIB system at CEIT (San Sebastian, Spain), and TEM at Universidad Carlos III (Madrid, Spain) is gratefully acknowledged.

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Authors’ contributions
MB performed the statistical analysis, participated in the interpretation of data, and drafted the manuscript. BG carried out the TEM characterization. PT conceived the study, participated in the interpretation of data, and wrote the manuscript. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

Received: 5 November 2010 Accepted: 31 May 2011 Published: 31 May 2011

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Cite this article as: Benedetto et al.: Fabrication of HfO2 patterns by laser interference nanolithography and selective dry etching for III-V CMOS application. Nanoscale Research Letters 2011 6:400.

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