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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.

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Introduction

Three-dimensional multi-gate field effect transistors with integrated mobility-enhanced channel materials (i.e. GaAs, $In_xGa_{1-x}As$) and high-κ gate dielectrics (i.e. HfO_2, Al_2O_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-κ 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-κ/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

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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 HfO_2 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 HfO_2 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 HfO_2/GaAs substrates were first spin coated with a 210-nm-thick antireflective coating (ARC), then covered by a 20-nm-thick SiO_2 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 SiO_2 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 LInL. The samples were then introduced in an ICP reactive ion etcher (PlasmaLab80Plus-Oxford Instruments, Oxfordshire, UK) to transfer the pattern to the HfO_2 layer through a series of successive etching steps aimed to selectively remove the exposed areas of SiO_2, ARC, and HfO_2. An initial CF_4 plasma-etching step was used to transfer the pattern from the resist to the SiO_2 layer. This was followed by O_2 plasma etching to transfer the pattern from the SiO_2 to the ARC. During this step, the resist layer is completely eliminated. Finally, the HfO_2 was patterned in a CF_4 plasma using a radio-frequency power of 100 W. The nanostructured HfO_2/GaAs samples were then exposed to a second treatment with O_2 plasma to eliminate all organic residues from the surface. Finally, a dip in a 1:1 HCl/H_2O solution followed by a D.I. H_2O rinse was applied to clean the exposed GaAs bottom trenches.

The surface morphology of the patterned HfO_2/GaAs samples was examined with an AFM microscope (5500 Agilent, Santa Clara, CA, USA) working in the dynamic mode. Si cantilevers (Veeco, Plainview, NY, USA) with a nominal radius of 10 nm were used. An SEM microscope (FEI NovaNanoSEM 230, FEI Co., Hilsboro, OR, USA) was used for HR-SEM sample examination. Cross-sectional specimens suitable for HR-TEM were prepared using a focused ion beam (FIB) FEI Quanta FEG dual-

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 HfO_2/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 HfO_2-etched nanostructures as well as the roughness and compositional integrity of the underlying GaAs surface.

The surface morphology of the as-deposited and nanostructured HfO_2/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 HfO_2 film and 4.9 ± 0.01 for the nanostructured HfO_2/GaAs sample. Figure 1 depicts a three-dimensional image (1.2 × 1.2 μm) of the HfO_2/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 HfO_2 mesa stripes. The values of the r.m.s. line roughness (R_a) measured along the HfO_2 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 HfO_2 etching using a SF_6/Ar plasma (0.13 nm) [8]. Etching with a CF_4 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 HfO_2 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 HfO_2 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 SiO_2 layer. The average values of the resist
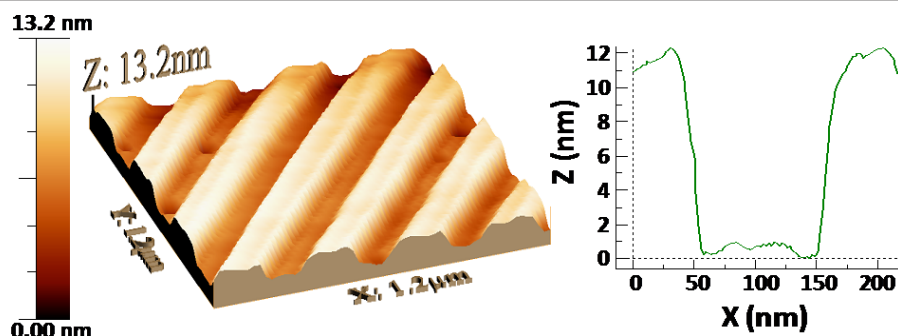
Figure 1 AFM images of the HfO$_2$ nanopattern. (**a**) Three-dimensional view of the nanostructured HfO$_2$/GaAs surface morphology. (**b**) Cross-section scan profile of an etched trench.
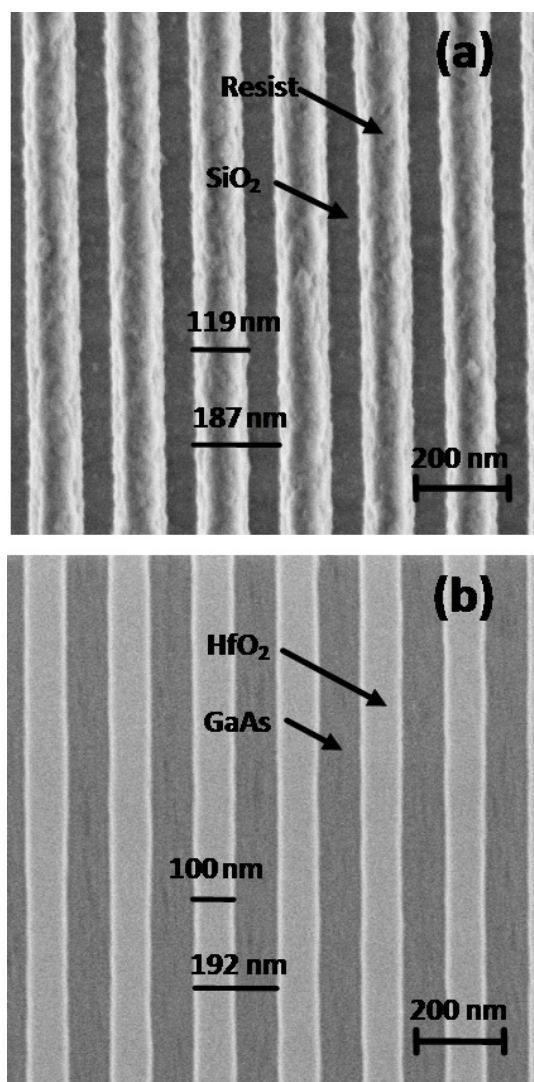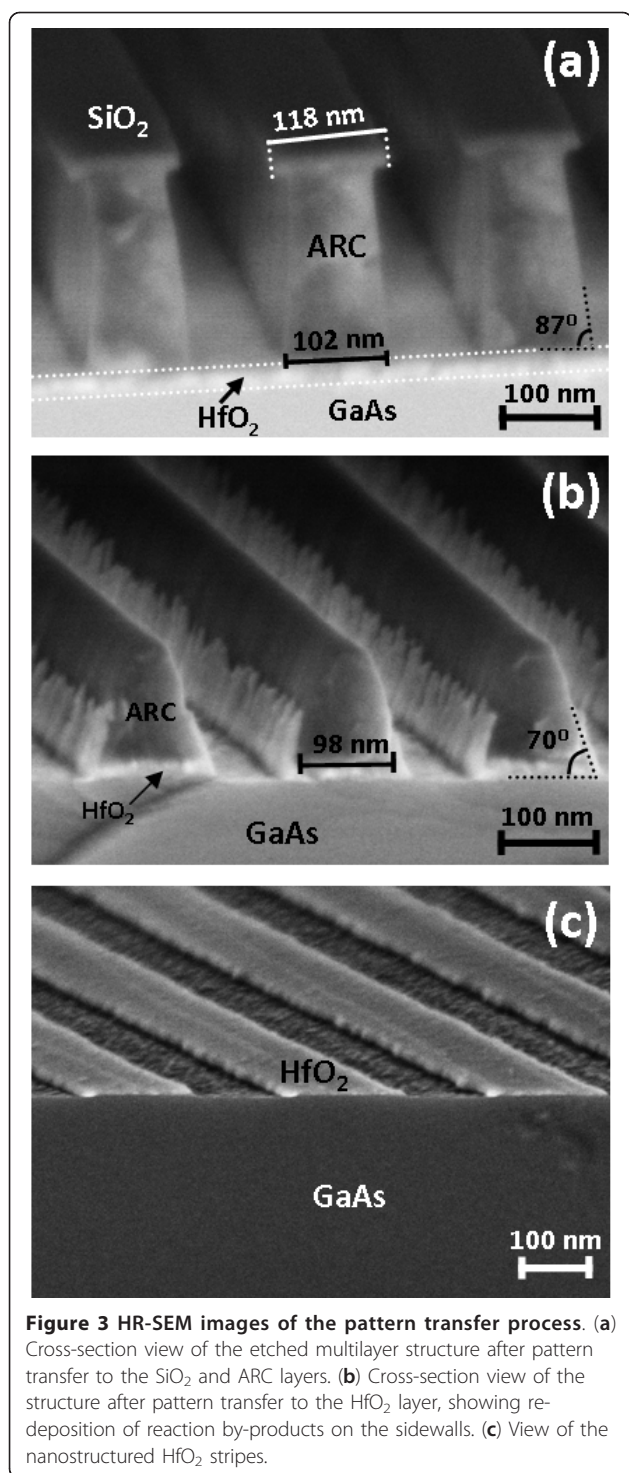

Figure 2 HR-SEM images of the resist and HfO$_2$ patterns. Plan view images of (**a**) the resist pattern after laser interference nanolithography and (**b**) the resulting HfO$_2$ nanopattern after CF$_4$/O$_2$ ICP-RIE and HCl/H$_2$O cleaning.

linewidth and the pitch are 119 ± 6 nm and 187 ± 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 ± 7 nm and 192 ± 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 nanostructuring 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.
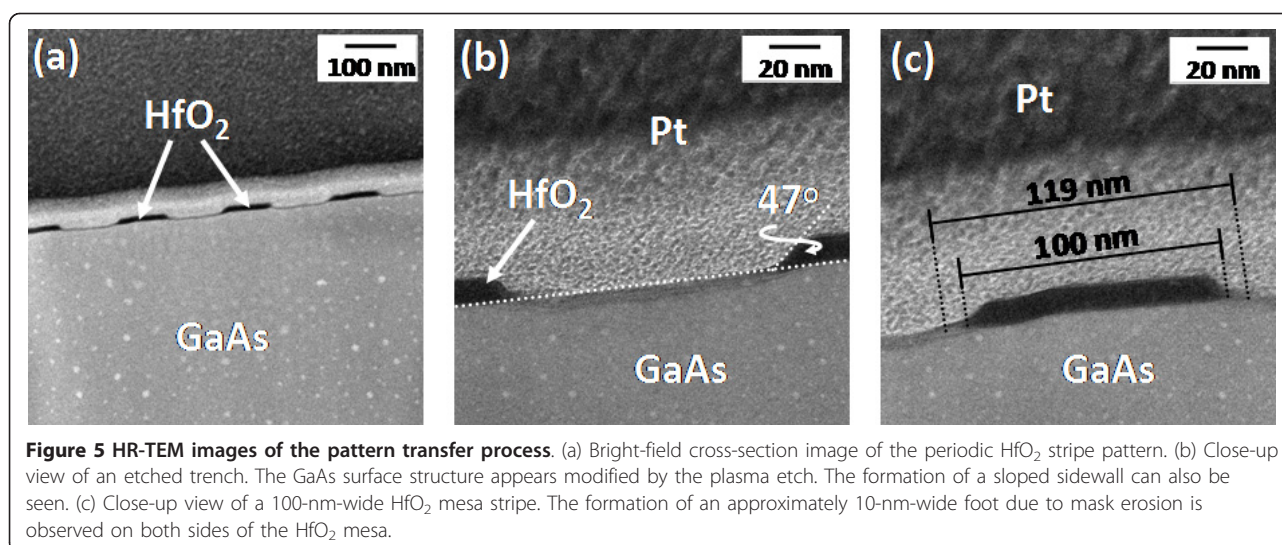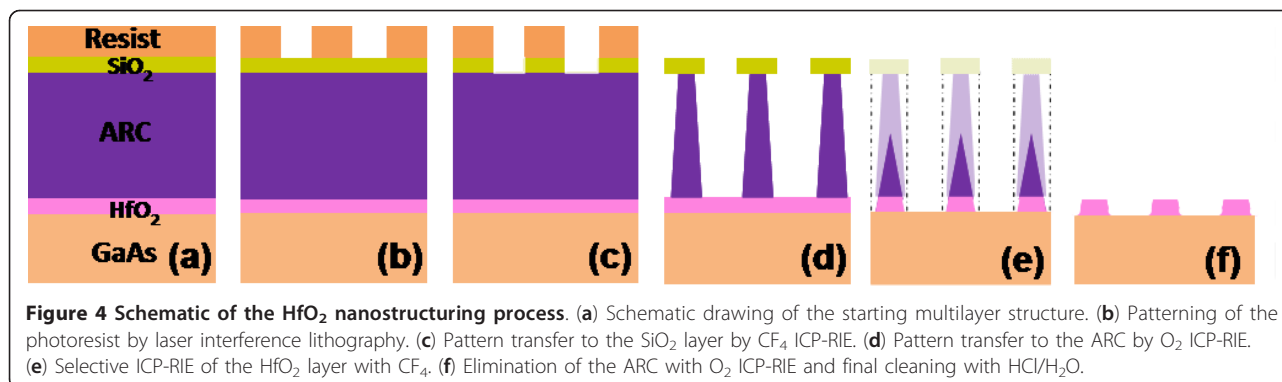
Figure 3b illustrates the sample cross-section after HfO$_2$ selective etching with CF$_4$. This process has been estimated to occur at a rate of 0.06 nm/s. Such slow HfO$_2$ etching rate is advantageous with respect to previous reports using SF$_6$/Ar [8] from the process control viewpoint, as it allows to process a typical 2-nm-thick gate oxide in a practicable etching time, i.e.

Figure 3 HR-SEM images of the pattern transfer process. (**a**) Cross-section view of the etched multilayer structure after pattern transfer to the SiO$_2$ and ARC layers. (**b**) Cross-section view of the structure after pattern transfer to the HfO$_2$ layer, showing re-deposition of reaction by-products on the sidewalls. (**c**) View of the nanostructured HfO$_2$ stripes.

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 a 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 sub-surface 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

Figure 4 Schematic of the HfO2 nanostructuring process. (**a**) Schematic drawing of the starting multilayer structure. (**b**) Patterning of the photoresist by laser interference lithography. (**c**) Pattern transfer to the SiO_2 layer by CF_4 ICP-RIE. (**d**) Pattern transfer to the ARC by O_2 ICP-RIE. (**e**) Selective ICP-RIE of the HfO_2 layer with CF_4. (**f**) Elimination of the ARC with O_2 ICP-RIE and final cleaning with HCl/H_2O.

Figure 5 HR-TEM images of the pattern transfer process. (a) Bright-field cross-section image of the periodic HfO_2 stripe pattern. (b) Close-up view of an etched trench. The GaAs surface structure appears modified by the plasma etch. The formation of a sloped sidewall can also be seen. (c) Close-up view of a 100-nm-wide HfO_2 mesa stripe. The formation of an approximately 10-nm-wide foot due to mask erosion is observed on both sides of the HfO_2 mesa.
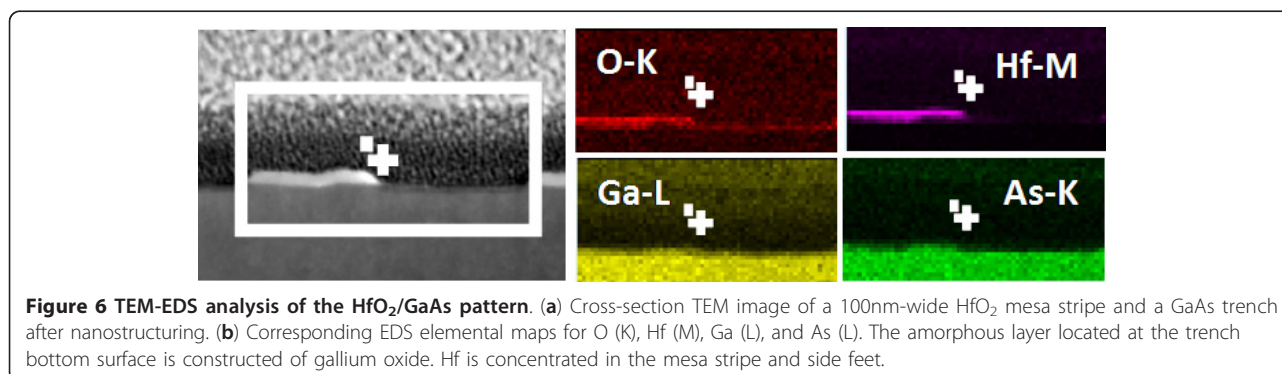
thermal desorption at 600°C. Finally, the composition map corresponding to Hf (M) shows that Hf is concentrated in the mesa stripes, although traces of this element were also detected in the mesa foot.

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_2O solution results in the formation of tapered HfO_2 etch profiles. Optimisation of the CF_4 plasma composition and etch bias

Figure 6 TEM-EDS analysis of the HfO2/GaAs pattern. (**a**) Cross-section TEM image of a 100nm-wide HfO_2 mesa stripe and a GaAs trench after nanostructuring. (**b**) Corresponding EDS elemental maps for O (K), Hf (M), Ga (L), and As (L). The amorphous layer located at the trench bottom surface is constructed of gallium oxide. Hf is concentrated in the mesa stripe and side feet.

power to lessen the re-deposition of non-volatile by-products, in combination with the use of more benign cleaning solutions than HCl/H_2O, are some of the future improvements to be introduced in the current process to reach the approximately 30 nm HfO_2 gate lengths and CD control better than 2 nm required for the fabrication of III-V-based CMOS.

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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 and participated in the interpretation of the data. JMMA carried out the TEM sample preparation and analysis. SM, PKH, and KC participated in the deposition of the GaAs and HfO_2 layers. LV was responsible for AFM 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.

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