

Short communication

Atomic scale microstructures of high-k HfSiO thin films fabricated by magnetron sputtering

Etienne Talbot^{a,*}, Manuel Roussel^a, Larysa Khomenkova^b, Fabrice Gourbilleau^b, Philippe Pareige^a^a Groupe de Physique des Matériaux (GPM), Université et INSA de Rouen, UMR CNRS 6634, Av. de l'Université, BP 12, 76801 Saint Etienne du Rouvray, France^b Centre de Recherche sur les Ions, les Matériaux et la Photonique (CIMAP), CEA/CNRS/ENSICAEN/UCBN, 6 Bd. Maréchal Juin, 14050 Caen Cedex 4, France

ARTICLE INFO

Article history:

Received 7 July 2011

Received in revised form 11 October 2011

Accepted 31 October 2011

Available online 12 November 2011

Keywords:

Hafnium silicates

Silicon nanoclusters

High-k dielectric

Magnetron sputtering

Atom probe tomography

Transmission electron microscopy

ABSTRACT

High-k hafnium-silicate films were deposited by RF magnetron sputtering approach on silicon wafer. The microstructure has been investigated using the combination of transmission electron microscopy and atom probe tomography. It was evidenced that the elaborated HfSiO thin films subsequently annealed at 950 °C during 15 min leads to a complex phase separated nanostructure where silica, hafnia and silicon nanoclusters coexist. The formation of silicon nanoclusters in hafnia-based host was never reported before. The results demonstrate the capability of RF magnetron sputtering to pave the way for realization of nanomemory devices based on silicon clusters embedded in high-k matrix.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The development and improvement of nanoclusters based devices compatible with the silicon-based CMOS technology is a large and active research area [1]. One of the specific topics deals with group IV semiconductor nanoclusters diluted in dielectric matrix for photonic and microelectronic devices, for example, for third generation of photovoltaic cells or nanomemory devices. However, in the last case, silicon dioxide (SiO₂) met its physical limit as a gate dielectric (calculated to be 0.7 nm [2]) due to an unacceptable leakage current for reliable and high performance devices. To overcome this problem, new materials with a higher dielectric constant (high-k materials) have been proposed. Among them, hafnia (HfO₂) and its silicates appear as the most promising high-k dielectrics to replace silica. They offer good chemical and thermal stability, as well as the good interfacial quality with Si channel [2–5]. Nevertheless, from the point of view of the electrical properties of the devices, a deeper analysis of the high-k dielectrics is required. In this regard, to reveal the nature of the high-k layer/silicon channel interface is one of the main tasks to achieve the high reliability of the devices.

An application of high-k materials was also extended to floating gate non-volatile memory devices containing semiconductor

nanoclusters embedded in SiO₂ host [6]. However, till present time the formation of such clusters in high-k host is questionable. In spite of reported elaboration and fine characterization of Si-rich-HfO₂ systems over a large composition range, any formation of Si nanoclusters was not revealed [7–9]. In the present article, the atomic scale characterization of HfSiO thin films prepared by magnetron sputtering has been performed by transmission electron microscopy and atom probe tomography. We demonstrate that the growth of nanometric silicon clusters can occur in hafnium silicate elaborated by magnetron sputtering.

2. Experimental technique

2.1. Magnetron sputtering elaboration

A 230 nm high-k HfSiO thin films were deposited on a (100) p-type CZ Si wafers by radio-frequency (RF) magnetron co-sputtering of HfO₂ (99.99%) target topped with Si chips placed on the electron 'race track'. The films were fabricated under a RF power density of 0.74 W/cm² and a substrate temperature of 100 °C in mixed Ar–H₂ plasma. The use of hydrogen is due to its ability to remove the oxygen from plasma and consequently, to reach higher Si excess in the layers. More details on the reactive fabrication process can be found elsewhere [10,11]. The total plasma pressure was kept at 0.04 mbar. Finally, the sample was annealed under a nitrogen flow in a conventional furnace at 950 °C during 15 min.

* Corresponding author. Tel.: +33 2 32 95 51 32; fax: +33 2 32 95 50 32.

E-mail address: etienne.talbot@univ-rouen.fr (E. Talbot).

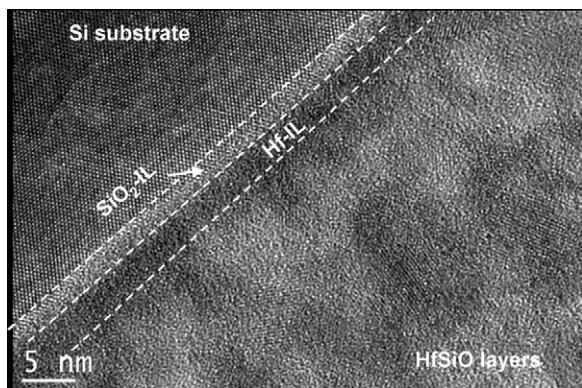


Fig. 1. Cross-section HR-TEM micrograph of the HfSiO layer. SiO₂-IL and Hf-IL denote SiO₂ rich and Hf rich interface layers respectively.

2.2. Atom probe tomography

Atom probe tomography (APT) is a three dimensional high-resolution analytic microscopy offered spatial mapping of atoms in materials [12]. Nowadays, this technique is increasingly used for the study of semiconductor and dielectric materials [13,14]. The APT technique is based on the field evaporation of surface atoms from tip-shaped specimen with a curvature radius lower than 50 nm. Tips preparation was realized in a dual-beam FIB-SEM, using a lift out method following by annular milling procedure [15]. The experiments were performed with in a Laser Assisted Wide Angle Atom Probe (LAWATAP – CAMECA) at a temperature of 80 K, using a laser-wavelength of $\lambda = 343$ nm with femtosecond pulses duration (350 fs, 50 nJ) at 100 kHz pulse rate.

2.3. Transmission electron microscopy

High-resolution Transmission Electron Microscopy (HR-TEM) was performed in a JEOL ARM-200F operated at 200 kV. TEM lamellas were prepared by conventional in situ lift-out technique.

3. Results and discussion

3.1. TEM experiments

Fig. 1 shows a cross-sectional HR-TEM image of the HfSiO films. The revealed bright and dark contrast can be associated with Si-rich (bright regions) and Hf-rich (dark ones). This gives a direct evidence of Hf segregation process already reported in the literature [5,7]. The Hf-rich regions appear to be crystallized. In addition, the interfacial region between HfSiO film and Si substrate demonstrates the presence of two layers, i.e. 2-nm thick SiO_x layer followed by 3-nm-thick Hf-rich layer parallel to the Si substrate. Similar structure has been already observed in the case of ultrathin HfSiO layers [5].

3.2. APT experiments

Atom probe tomography is one of the most accurate techniques to measure chemical compositions in nanostructured materials. The mass spectrum obtained on the HfSiO sample is shown in Fig. 2. All the mass peaks are identified and well associated to the chemical species. In regard with the dielectric nature of the sample, we should note that the mass resolution is relatively good ($m/\Delta m = 400$ at full width half maximum on the O₂²⁺ peak). Moreover, hafnium atoms were detected as molecular ions (HfO₂³⁺ and HfO₂²⁺). Finally, no Ga atoms have been detected, indicating that the FIB-SEM use for tip preparation has not created any damage in the microstructure. The chemical composition has

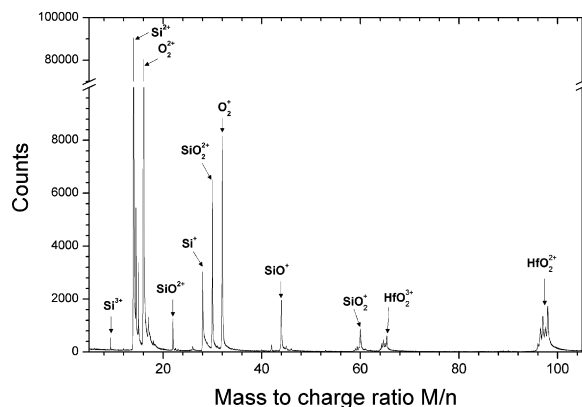


Fig. 2. Mass spectrum collected during APT experiment on the HfSiO layers.

been determined from the mass spectrum and the Si, O and Hf contents are respectively estimated to $X_{\text{Si}} = 30.6 \pm 0.3$ at.%, $X_{\text{O}} = 61.5 \pm 0.3$ at.% and $X_{\text{Hf}} = 7.9 \pm 0.3$ at.%.

Fig. 3 shows the 3D reconstructed spatial distribution of Si, O and Hf atoms in the HfSiO thin layers. Silicon and Hafnium atoms are non-homogeneously distributed in the analysed volume indicating clearly phase separation upon sample annealing. The presence of Hf-rich and Si-rich zones is revealed and is consistent with the microstructure deduced from TEM experiments (Fig. 1).

In order to identify the microstructure of the HfSiO layer and to measure the composition of the different chemical zones and their spatial distributions, we have calculated iso-concentration surface on Hf and Si atoms. Fig. 4a shows the surface for $X_{\text{Hf}} > 25$ at.% (in the blue) and $X_{\text{Si}} > 33$ at.% (in the red). These data provide the evidence of phase separation between SiO₂-rich and HfO₂-rich phases induced by the annealing treatment. Moreover, increasing the concentration threshold of iso-concentration (Fig. 4b where the threshold are $X_{\text{Hf}} > 40$ at.% and $X_{\text{Si}} > 75$ at.%) does not evidence Hf zones containing more than 40 at.% but only very rich-Si clusters. Fig. 4c displays a top view in a selected region of the analysed volume which contains the different chemical zones mentioned previously. Compositions of the three chemical regions were measured and reported in Table 1. We should note that APT experiment can lead to a bias in the concentration measurement in the case of multi-phase sample analysis. This effect is due to the difference in evaporation field between the different phases [16]. All the concentration

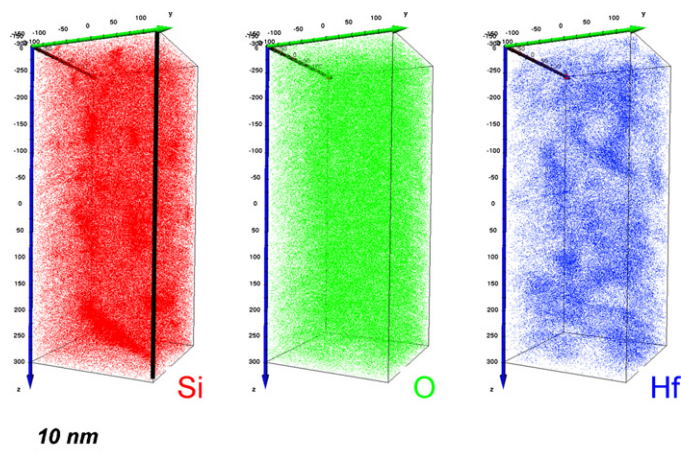


Fig. 3. 3D chemical maps (Si in red, O in green and Hf in blue) of the HfSiO layer obtained by APT analyses. For clarity of the figures, only 50% of Si and O are represented. The volume is 25 nm × 25 nm × 60 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Download English Version:

<https://daneshyari.com/en/article/1529292>

Download Persian Version:

<https://daneshyari.com/article/1529292>

[Daneshyari.com](https://daneshyari.com)