Solid-State Electronics 84 (2013) 58–64

Contents lists available at SciVerse ScienceDirect

Solid-State Electronics

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

Two-step annealing effects on ultrathin EOT higher-k (k = 40) ALD-HfO_2 gate stacks

Yukinori Morita *, Shinji Migita, Wataru Mizubayashi, Meishoku Masahara, Hiroyuki Ota

Green Nanoelectronics Center (GNC), Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba West SCR, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

ARTICLE INFO

Article history:
Available online 13 March 2013

Keywords:
High-k
HfO_2
ALD
Cubic
PDA
EOT

ABSTRACT

Ultrathin HfO_2 gate stacks with very high permittivity were fabricated by atomic layer deposition (ALD) and a novel two-step post-deposition annealing (PDA) technique. First, a no-cap pre-crystallization anneal degasses residual contaminations in the ALD layer, and second, a Ti-cap anneal enhances the permittivity of HfO_2 by generating a cubic crystal phase. The Ti-cap layer simultaneously suppresses growth of interfacial SiO_2 during annealing by absorbing residual oxygen released from HfO_2. Using these techniques, the dielectric constant of the ALD-HfO_2 could be enhanced to 40 for 2.4–4.0 nm HfO_2 thickness.

1. Introduction

For equivalent oxide thickness (EOT) scaling in the latest device technology, increasing the dielectric constant (k) of a gate insulator material has been a promising solution ever since "high-k" dielectrics were adopted in a gate stack structure. These high-k dielectrics have greater permittivity than that of SiO_2 and can increase the physical thickness of the gate insulator to suppress direct-tunneling leakage current. In the sub-0.5-nm EOT regime, however, the physical thickness of a high-k HfO_2 (k = 13–20) gate insulator needs to be as small as 2 nm even when using a direct-contact architecture with no interfacial layer (IL) [1–4]. This physical thickness is close to the direct-tunneling limit of the gate leakage current. This implies that for further EOT scaling, further enhancement of the permittivity of high-k dielectrics (higher-k) is needed [5–10].

To implement the higher-k gate stack formation, we have developed an oxygen-controlled cap post-deposition annealing (cap PDA) technique in a previous study [10,11]. A high-permittivity "cubic" phase HfO_2 is used as the dielectric layer. This technique is accomplished by the deposition of HfO_2 followed by abrupt and short-time PDA performed with a Ti-cap layer; the abrupt and short-time PDA generates a metastable cubic phase in the HfO_2. The Ti-cap layer stabilizes the metastable cubic phase and absorbs excess oxygen in the HfO_2 layer during annealing, thereby suppressing SiO_2 IL growth. By using these techniques, IL-less higher-k HfO_2 gate stacks with a dielectric constant of 40 and total gate stack EOT of 0.2 nm could be realized [11].

However, there is a residual problem related to the crystallization of the HfO_2 films deposited by the atomic layer deposition (ALD) technique. The possible thickness for realizing crystallization into the cubic phase of the ALD-HfO_2 layer was thinner than 2.6 nm. In the case of HfO_2 thicker than 2.6 nm, a low permittivity monoclinic phase domain was co-generated with the cubic phase. This severely degraded the dielectric constant of the total gate stacks, suggesting that special attention needs to be paid for crystallization of the ALD films. In the present study, we adopted a novel two-step PDA technique consisting of a no-cap pre-crystallization anneal followed by a Ti-cap crystallization anneal of the ALD-HfO_2 layer, as an improved method to realize higher-k ALD-HfO_2 gate stacks [12].

2. Experimental

Fig. 1 shows the concept of permittivity enhancement by the cap PDA on TiN/HfO_2/Si gate stacks [7,10,11]. The HfO_2 layers were deposited by HfO_2 target sputtering. By abrupt and short-time annealing with a TiN-cap layer, amorphous HfO_2 crystallizes into a cubic phase. X-ray diffraction (XRD) spectra obtained before and after the TiN-cap PDA clearly show that the amorphous phase transforms into the cubic phase, as shown in Fig. 1c and d. However, cross-sectional transmission electron microscopy (X-TEM) observations show that a thick SiO_2 IL grows simultaneously. This is caused by oxygen released from HfO_2 during crystallization. To suppress IL growth, we chose a Ti-cap layer instead of the TiN. Ti can absorb up to 30 at.% oxygen without forming Ti oxide. By controlling the Ti and HfO_2 thicknesses and the PDA temperature, SiO_2 IL growth can be suppressed.

* Corresponding author. Tel.: +81 29 861 2433; fax: +81 29 849 1533.
E-mail address: y.morita@aist.go.jp (Y. Morita).

0038-1101/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.sse.2013.02.020

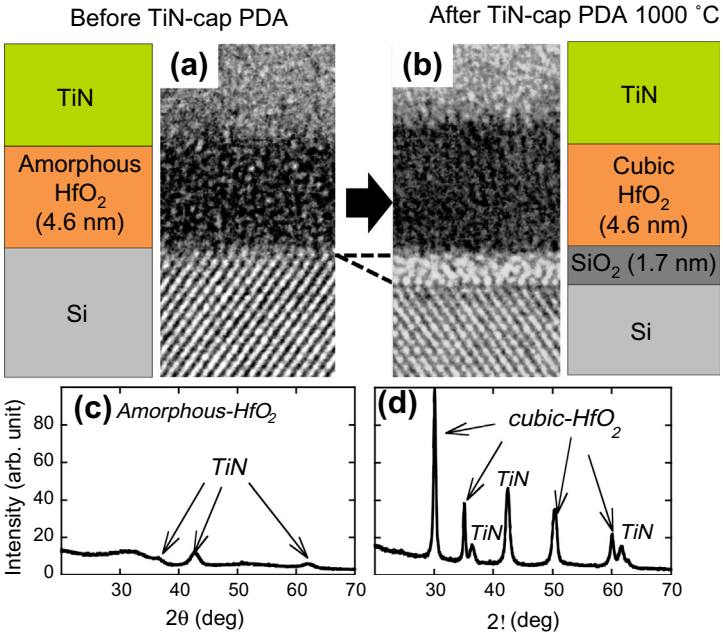

Fig. 1. Concept of *k*-enhancement by the cap PDA method. (a and b) show the X-TEM images of HfO_2 gate stacks obtained before and after the TiN-cap PDA, respectively. The gate stack structures are also shown. (c and d) show in-plane XRD spectra for TiN-cap HfO_2 before and after cap PDA, respectively. By abrupt and short-time annealing with a cap layer, amorphous HfO_2 crystallizes into the cubic phase. The dielectric constant of cubic HfO_2 is increased to 50. However, a SiO_2 IL grew simultaneously because of the oxygen released during crystallization.

Generally, the PDA is an important and critical process not only for crystallization of the film, but also for improvement of the dielectric performance of ALD films: The films deposited by ALD contain considerable amount of fragments from the ALD precursors [13,14]. These ALD-related contaminants severely degrade dielectric performance, and thus, an appropriate annealing process for degassing is needed.

In this study, we use a novel "two-step PDA" technique, a combination of PDAs consisting of no-cap and Ti-cap PDAs. Fig. 2 shows a comparison of three types of PDAs: (a) TiN-cap PDA (see Fig. 1),

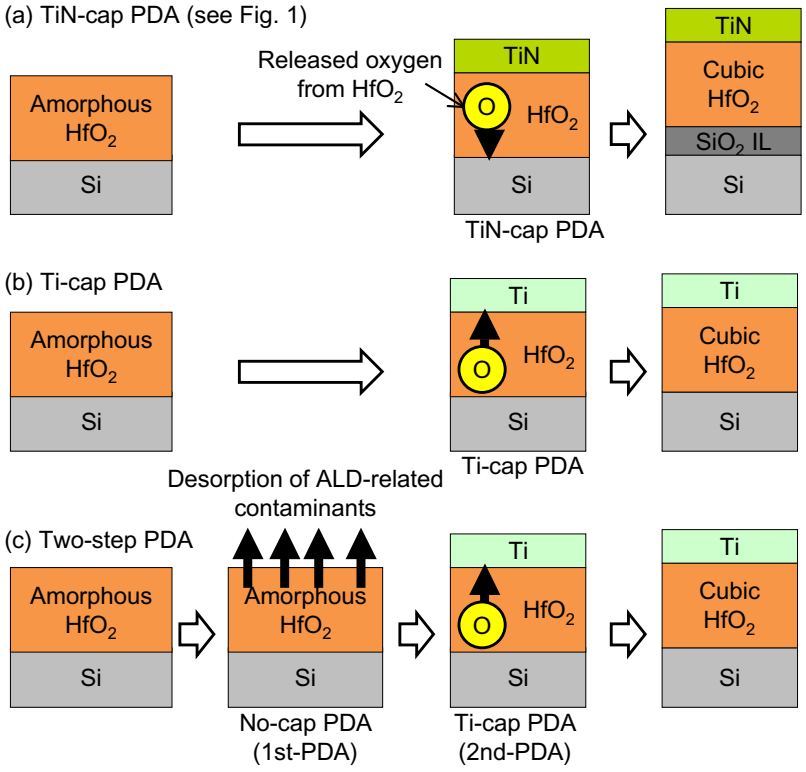

Fig. 2. Schematic illustrations of the concepts for (a) TiN-cap, (b) Ti-cap, and (c) two-step PDAs. (a) TiN barely absorbs oxygen, and then, oxygen released from HfO_2 oxidizes the Si substrate. (b) Ti-cap layer effectively absorbs released oxygen from HfO_2 during PDA, suppressing SiO_2 IL formation. (c) Novel two-step PDA process, wherein the first no-cap PDA removes contaminants in the ALD-HfO_2 layer, and the second Ti-cap PDA crystallizes HfO_2 into the cubic phase without IL formation.