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Textured Crystallization of Ultrathin Hafnium Oxide Films on Silicon Substrate

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Textured crystallization of ultrathin hafnium oxide films on silicon substrate

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The effects of rapid thermal annealing are reported here on the structure of 2 nm thick hafnium oxide films grown on silicon (100) substrates. The films grown by atomic layer deposition have a 1 nm SiO_2 transition layer between silicon and the HfO_2 layer. The amorphous structure of the as-deposited films is retained after annealing at 600 °C. The HfO_2 films crystallized into an orthorhombic phase with an out-of-plane texture after annealing at 800 °C or higher. In contrast, films grown on thick amorphous SiO_2 substrates crystallize without any texture. The authors attribute the texture of HfO_2 on Si (100) to the role of interfacial SiO_2 transition layer. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2724925]

Thermodynamic stability under high temperature processing is one of the major criteria for the use of high dielectric (high-*k*) oxides in complementary metal-oxide-semiconductor (CMOS) technology. The use of high-*k* oxides leads to lower equivalent oxide thickness and lower leakage current, thus, improving the overall device performance with scaling.[1] Among various oxides considered, hafnium oxide (HfO_2) possesses several desirable properties for CMOS applications.[2] One of the main drawbacks of pure HfO_2 films is their tendency to crystallize upon annealing at fairly low temperatures.[3] Issues related to crystallization, such as the onset temperature, crystal structure, and the role of the underlying interfacial layer, have been controversial or little studied for ultrathin films of a few nanometers thick.[2] In this letter, we examine the structure of 2 nm thick HfO_2 films grown on Si (001) and amorphous SiO_2, subject to different rapid thermal annealing conditions using transmission electron microscopy. We show that under rapid thermal annealing between 800 and 1000 °C, the HfO_2 films crystallized into the metastable orthorhombic phase, textured in case of Si (001) but not on amorphous SiO_2. The crystallization is associated with a small increase in the transition SiO_2 layer thickness on Si (001) and partial ordering of the SiO_2 transition layer.

The HfO_2 films of 2 nm thick studied were deposited on Si (100) and SiO_2 substrates using the atomic layer deposition (ALD) method and subjected to rapid thermal annealing at three different temperatures: 600, 800, and 1000 °C in N_2 environment for 30 s (processed at SEMATECH and provided by Intel). The films grown on Si (100) have a thin interlayer of SiO_2 between the HfO_2 film and the substrate, which is used to improve the interfacial electrical property.[4] The structure of the films was studied by high-resolution electron microscopy (HREM), selected area electron diffraction (SAED), and nanoarea electron diffraction using a JEOL 2010FEG electron microscope. The films were examined in both plan view and cross-sectional geometries. Plan view samples were prepared by wedge polishing the silicon substrate followed by chemical etching in 25% tetramethyl ammonium hydroxide solution at 50 °C for 15 min. Cross-section samples were prepared by wedge polishing followed by precision ion milling to create electron transparent areas.

The effects of rapid thermal annealing on the structure of HfO_2 thin films are first examined in cross section [see Figs. 1(a)–1(c)]. The as-deposited film (not shown) has an amorphous structure, which is maintained until annealing at 600 °C [Fig. 1(a)]. The amorphous structure was confirmed by electron diffraction [inset of Fig. 2(a)]. The 800 and 1000 °C annealed samples [Figs. 1(b) and 1(c)], however, show crystalline fringes in the 2 nm HfO_2 film, indicating a transition from the amorphous to a crystalline phase at temperatures somewhere between 600 and 800 °C. In comparison, 2 nm thick film of HfON crystallizes, while HfSiON

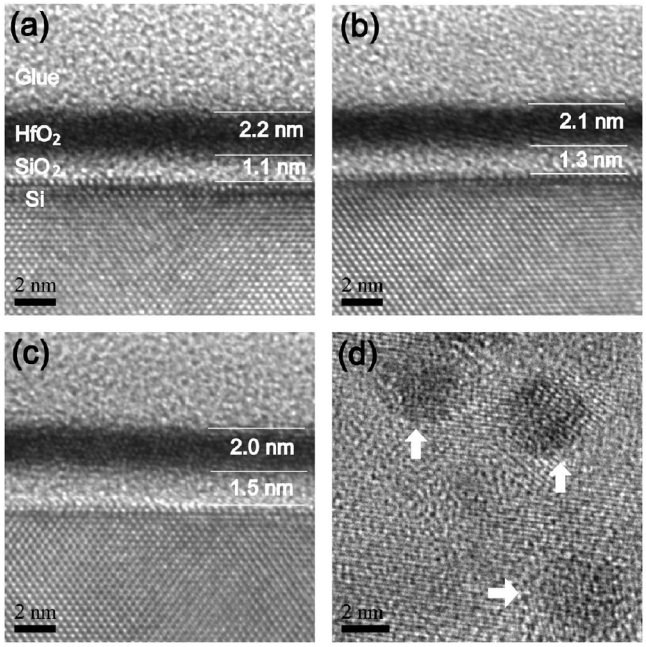

FIG. 1. HREM images. [(a)–(c)] Cross-sectional images of 2 nm HfO_2 on Si (100) substrate annealed at 600 °C (a), 800 °C, (b) and 1000 °C (c). Thickness of the interfacial SiO_2 layer increases, while that of HfO_2 layer decreases with annealing temperature. (d) Image in plan view showing nanocrystals of orthorhombic HfO_2 from the same sample as (c).

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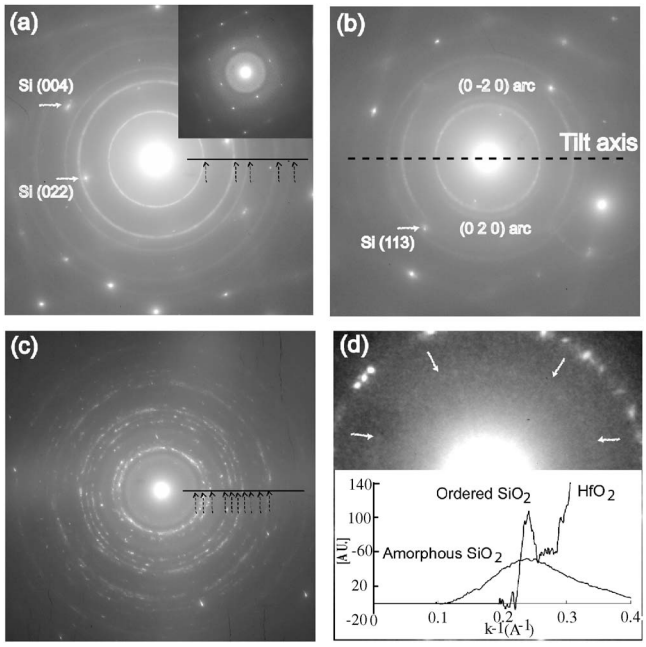

FIG. 2. Recorded electron diffraction patterns from 2 nm thick HfO_2 films. (a) SAED from 800 °C annealed HfO_2 on Si (100) with thin (1 nm) SiO_2 interfacial layer showing polycrystalline diffraction rings from textured orthorhombic crystals. From inwards, the dark arrows mark the (2 1 1), (4 2 0), (2 3 1), (6 3 1), and (4 2 4) reflections, respectively. Amorphous DP from the 600 °C film shown in inset. (b) SAED from the same sample as (a) but tilted by about 25°, showing additional (0 2 0) and (0 −2 0) arcs. (c) SAED from 1000 °C annealed 2 nm HfO_2 on 100 nm thick amorphous SiO_2 substrate, showing no preferred texture of the HfO_2 film. From inwards, the dark arrows indicate (2 1 0), (2 1 1), (0 2 0), (4 2 0), etc., reflections. (d) Extra diffraction ring from the ordered SiO_2 [from 1000 °C annealed HfO_2 film on Si (100) with thin (1 nm) SiO_2 interfacial layer] shown by arrows. Bottom part shows a comparison in the averaged intensity profiles between ordered SiO_2 and amorphous SiO_2 after subtraction of the background.

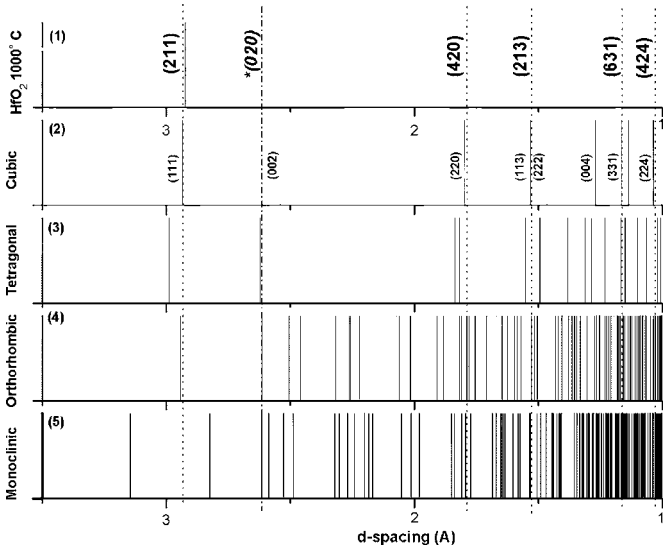

FIG. 3. Comparison between the *d* spacings of different phases of HfO_2 and our 2 nm thick film annealed at 1000 °C. In (1), the reflection marked $^*(020)$ is the extra reflection observed upon tilting of 25°, which is not present in cubic, suggesting the structure to be orthorhombic. The missing orthorhombic reflections suggest a textured growth of HfO_2 nanocrystallites. Cubic reflections are indexed for reference.

does not, under annealing at 1000 °C according to the glancing incidence x-ray diffraction study.[5] The interlayer silicon oxide grown between the HfO_2 film and the silicon substrate is clearly visible in all samples. The thickness of this SiO_2 layer increased from 1.1 to 1.3 to 1.5 nm after annealing at 600, 800, and 1000 °C, respectively. At the same time, the HfO_2 layer decreases from 2.2 to 2.1 to 2.0 nm (see Fig. 1). The film thickness was measured from the half width of the intensity profiles averaged over a 3 nm width. The measurement was repeated at different sample areas and the error was ~1 Å. The growth of the SiO_2 layer and the reduction of the HfO_2 layer can be attributed to the enhanced diffusion of oxygen atoms from the HfO_2 layer towards the interface.[6] It has also been suggested that under coordinated Hf atoms diffuse towards the interface in order to satisfy their dangling bonds.[7–9] A plan view HREM image from the sample annealed at 1000 °C is shown in Fig. 1(d). Crystallites of about 5 nm in diameter are visible with lattice fringes in the HfO_2 thin films. The crystallites were evenly distributed across the entire sample with a narrow size range.

Electron diffraction was used to determine the structure of the crystallites observed in the annealed HfO_2 films. Figure 2(a) shows a SAED diffraction pattern (DP) recorded from the 800 °C annealed sample in plan view close to the Si [110] orientation. The DP of annealed films at 1000 °C (not shown) shows the same polycrystalline diffraction rings. To index the DP, a comparison was made between *d* spacings obtained from our films and bulk x-ray crystallography data from different HfO_2 structures, namely, the monoclinic, orthorhombic, tetragonal, and cubic phases (see Fig. 3). All the observed *d* spacings along the Si [110] orientation can be indexed based on the cubic or orthorhombic phases. In the case of the tetragonal and monoclinic structures, at least one or more *d* spacings do not match. For the orthorhombic indexing, many of the high intensity reflections are clearly missing (see Fig. 3). The reflections indexed belong to either the orthorhombic $[1-2\ 0]_O$ or the cubic $[1-10]_C$ zone axis. In both cases, the crystallites have a preferred growth orientation (texture). To resolve the structure, we tilted the sample by about 25° off Si[110] zone axis and recorded the DP, which is shown in Fig. 2(b). Additional arcs in the DP (marked with * in Fig. 3) are observed in this orientation. The extra reflection corresponds to ±(020) in the orthorhombic phase; no such reflections are present in the cubic HfO_2. Thus, we conclude that the crystallite structure belongs to orthorhombic phase and they have a preferred texture direction along $[1-2\ 0]$ out of plane. There is no in-plane texture as the diffraction rings are continuous.

A list of reflections observed in our DP is given in Table I along with their comparison with the bulk x-ray diffraction data of orthorhombic HfO_2 (orthorhombic structure, space group: Pbca, *a*:10.0177 Å, *b*:5.2276 Å, *c*:5.0599 Å). The difference between the observed *d* spacings and the bulk orthorhombic phase is less than 1%. The experimental error bar is ±0.1% using the Si substrate for calibration. The orthorhombic phase has been observed before in thin HfO_2 films but not in the ultrathin films studied here. The orthorhombic phase is believed to be unstable and their appearance is suggested as stabilized by strain.[10,11] Thicker films usually relax into a monoclinic phase.[12,13] Annealing of HfON and HfSiON films of 2–4 nm thick results in the tetragonal and/or monoclinic HfO_2 phases according to Refs. 5 and 14. Texturing in HfO_2 films has also been reported during ALD deposition and high substrate temperature.[10,15] In our films, orthorhombic phase formed by rapid thermal annealing seems to be the stable phase as the structure is retained upon

TABLE I. List of observed d spacing from 1000 °C annealed orthorhombic HfO_2 phase on Si (100) substrate. Comparison has been made with reported bulk x-ray orthorhombic HfO_2 data, indicating a small (1%) difference in d spacings.

Measured d spacing (Å)	$h\ k\ l$	Reported x-ray d spacing (Å)
2.923	2 1 1	2.9423
1.790	4 2 0	1.8083
1.526	2 1 3	1.5286
1.161	6 3 1	1.1727
1.033	4 2 4	1.0365
0.918	8 4 0	0.9042
0.859	6 3 4	0.8727
	8 4 2	0.8514
0.761	4 2 6	0.7643
0.706	6 3 6	0.6910
0.593	12 6 1	0.5985
	4 2 8	0.5970

annealing at both 800 and 1000 °C. The crystallite size is also about the same at these two temperatures.

To study the substrate effect on the crystallization of thin HfO_2 films, we did a comparative study of films grown on SiO_2 substrates. Figure 2(c) shows the SAED pattern from a sample of 2 nm HfO_2 film deposited on amorphous SiO_2 substrate and then rapid thermal annealed at 1000 °C. The amorphous SiO_2 substrate was prepared by chemical vapor deposition of 1000 Å of SiO_2 on Si (100) substrate. The diffraction was taken from a relatively smaller area, which makes the rings look not so continuous, as compared to the pattern in Fig. 2(a). The structure was identified to be orthorhombic again, but without any favored growth direction as indicated by the appearance of additional reflections. It is interesting to note that the 2 nm HfO_2 films transform into an orthorhombic phase irrespective of the substrate SiO_2 thickness. On the other hand, substrate does affect the way in which grains are oriented in the polycrystalline films. In the case of crystalline Si (100) substrate, there is a favorable direction of growth of nanocrystals, which is not observed in the case of an amorphous SiO_2 substrate. It should be mentioned here that grains oriented in similar fashion will have similar dielectric constants and thus would result in a uniform device performance, except for the grain boundaries where the leakage could be an issue.

An extra polycrystalline diffraction ring at d spacing of 4.1 Å was observed in our electron diffraction patterns from 800 and 1000 °C annealed HfO_2 films on Si (100) substrates. Figure 2(d) shows the central part of a DP recorded from 1000 °C annealed HfO_2 film and the extra diffraction ring. This ring cannot be indexed based on the orthorhombic HfO_2. The position of this ring coincides with the first diffuse ring of amorphous SiO_2. The measured full width at half maxima for this peak is 0.0125 $Å^{-1}$ compared to 0.1425 $Å^{-1}$ of the same peak obtained from the 1000 Å thick film of amorphous SiO_2 [see Fig. 2(d) for the comparison]. This diffraction signal comes from the interfacial SiO_2 layer, which is used to separate HfO_2 from silicon substrate. The intensity of this ring is very weak since the interfacial silicon oxide is only 1 nm thick. The narrow peak width is an evidence of ordered SiO_2. This has not been observed at similar $Si-SiO_2$ interfaces, although Wilk and Brar reported ordered SiO_2 grown at 700 °C on Si (001) under UHV conditions.[16] The ordered $Si-SiO_2$ layer explains the strong texture observed in crystallized HfO_2 films on Si (100) but not on SiO_2 films. The transition from Si to amorphous SiO_2 happens through an ordered layer of crystalline oxide, tridymite,[17] was suggested before to explain the low defect density of the $Si-SiO_2$ interface.[18,19]

In conclusion, we have shown that HfO_2 films of 2 nm thickness grown on Si (100) substrate retain its amorphous structure after rapid thermal annealing at 600 °C. Annealings at 800 and 1000 °C lead to the growth of nanometer-sized crystallites with the orthorhombic structure. The crystallites have a preferred out-of-plane orientation of $[1-2\ 0]_O$. Similar films on amorphous SiO_2 substrate upon annealing led to an orthorhombic phase but without any texture. Electron diffraction shows evidence of partially ordered SiO_2 transition layer in annealed films on Si (100).

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