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Epitaxial growth of yttrium-stabilized HfO_2 high-*k* gate dielectric thin films on Si

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Epitaxial yttrium-stabilized HfO_2 thin films were deposited on *p*-type (100) Si substrates by pulsed laser deposition at a relatively lower substrate temperature of 550 °C. Transmission electron microscopy observation revealed a fixed orientation relationship between the epitaxial film and Si; that is, $(100)\mathrm{Si}//(100)\mathrm{HfO_2}$ and $[001]\mathrm{Si}//[001]\mathrm{HfO_2}$. The film/Si interface is not atomically flat, suggesting possible interfacial reaction and diffusion. X-ray photoelectron spectrum analysis also revealed the interfacial reaction and diffusion evidenced by Hf silicate and Hf–Si bond formation at the interface. The epitaxial growth of the yttrium stabilized HfO_2 thin film on bare Si is via a direct growth mechanism without involving the reaction between Hf atoms and SiO_2 layer. High-frequency capacitance–voltage measurement on an as-grown 40-Å yttrium-stabilized HfO_2 epitaxial film yielded an effective dielectric constant of about 14 and equivalent oxide thickness to SiO_2 of 12 Å. The leakage current density is 7.0×10^{-2} A/cm^2 at 1 V gate bias voltage. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1585116]

I. INTRODUCTION

Due to the limitation of physical thickness of SiO_2 gate dielectric film,[1] a gate dielectric with relative permittivity higher than that of SiO_2 is needed to meet the next generation complementary metal-oxide-semiconductor (CMOS) technology requirement. There are many potential candidates of high-*k* gate dielectrics, such as Ta_2O_5, $SrTiO_3$, Al_2O_3, ZrO_2, and HfO_2,[2–5] and among them, HfO_2 is one of the most attractive candidates due to its relatively higher stability on Si substrate and better reliability.[6,7]

The problem for HfO_2 in gate dielectric application is that it crystallizes at temperatures higher than 500 °C. Therefore, SiO_2 has been commonly used alloying with HfO_2 to form amorphous Hf silicate that is thermodynamically stable under high-temperature annealing up to more than 1000 °C. Even though the amorphous structure has been commonly accepted as the approach to select high-*k* gate dielectrics, epitaxial single-crystalline dielectric films are still of significant fundamental and technological interest. It is well known that epitaxial growth of metal oxide films on Si is a great technical challenge due to the easily formed amorphous silicon oxide layer on Si surface in an oxygen atmosphere preventing the intended oxide heteroepitaxy on Si substrate.[8] Nevertheless, epitaxial growth of yttrium-stabilized ZrO_2 (YSZ) and $SrTiO_3$ high-*k* gate dielectrics on bare Si has been successfully demonstrated.[9–11] However, to the best of our knowledge, there is no report of epitaxial HfO_2 on bare Si.

Single-crystal oxides grown by molecular-beam epitaxy methods can in principle be obtained, but the requirement of ultrahigh vacuum limits its application due to low wafer throughput. In this article, we report the deposit of thin epitaxial yttrium-stabilized HfO_2 (YSH) film on bare Si at relatively lower substrate temperature by pulsed laser deposition (PLD). Electric properties of the epitaxial films, mechanism for the epitaxial growth, and chemical reaction at the film/Si interface were studied.

II. EXPERIMENTAL PROCEDURE

Conditions for the epitaxial growth of HfO_2 films by PLD have been investigated by varying the growth conditions such as oxygen partial pressures, different targets (pure HfO_2 and YSH) and substrate temperatures. The thin YSH (with 10% of yttrium) epitaxial films on *p*-type (100) Si substrates with resistance of 5–25 Ω cm were deposited at conditions described subsequently. Si substrates were treated by a conventional HF-last process before film deposition leaving hydrogen terminal surface. The base vacuum of the PLD chamber was of 5×10^{-5} Pa. After heating up the substrate to 550 °C, the vacuum decreased to 2×10^{-4} Pa due to degassing. The wavelength of the excimer laser is 248 nm and the energy density is 6 J/cm^2 with a repetition rate of 2 Hz. In order to prevent the formation of SiO_2 interfacial layer during deposition, the films were deposited at 2×10^{-4} Pa without introducing any oxygen gas. The Pt dot electrode was formed on top of the films by subsequent deposition of Pt by PLD at 200 °C in the same chamber with a shadow mask of 0.20 mm^2. The so-formed MOS capacitors were evaluated by high-frequency $C-V$ and conductance–voltage ($G-V$) measurements using HP 4192A impedance analyzer. The leakage current of the MOS capacitor was characterized by $I-V$ measurement performed with Advantest TR8652 Digital Electrometer. The film microstructure and interfacial structure were studied by high-resolution transmission electron microscopy (HRTEM) with a JEOL 2010 microscope. The film surface roughness was evaluated by atomic force microscopy (AFM). The depth profile of the film was characterized by photoelectron spectroscopy (XPS) using a Physical Electronics Quantum 2000 XPS with a monochromatic Al K_α (1486.7-eV) source.

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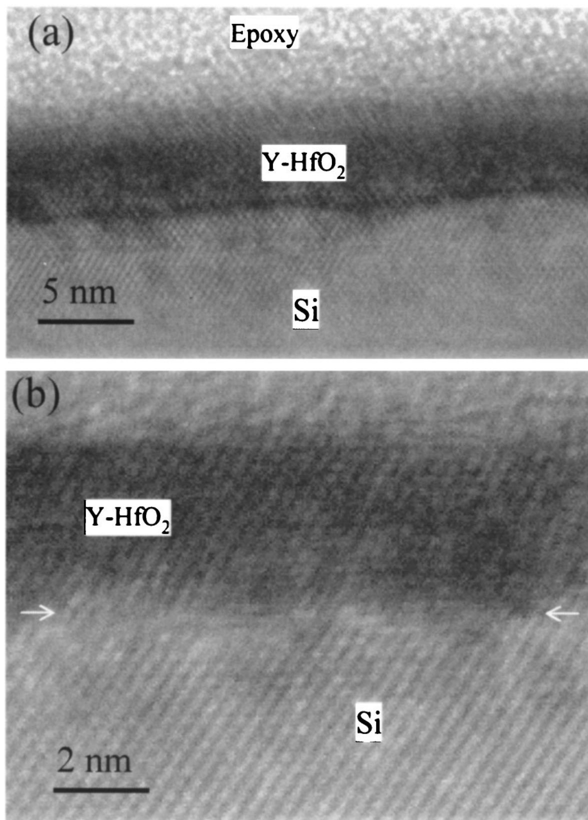

FIG. 1. HRTEM image of epitaxial YSH film on (100) Si observed along the direction of [110] of Si, (a) is a lower magnification image and (b) a higher magnification image.

III. RESULTS AND DISCUSSION

Figure 1 shows the cross-sectional HRTEM images of the as-grown 40-Å yttrium-stabilized HfO_2 film on Si substrate. Within all the TEM observation areas, there is no distinguishable grain boundary in the film and the film shows a fixed orientation relationship with the Si substrate. This characteristic suggests that the film is highly epitaxial. From the enlarged HRTEM image shown in Fig. 1(b), the orientation relationship between cubic HfO_2 and Si substrate can be determined as $(100)HfO_2//(100)Si$, and $[001]HfO_2//[001]Si$. One can also see that the interface is free from any SiO_2 amorphous layer. However, due to a large (5.7%) lattice mismatch between HfO_2 and Si, the interface is actually not atomically flat and sharp. This interface characteristic suggests that lattice strain and diffusion at the interface may occur. In addition, interfacial dislocations at the interface can also be identified by careful examination of the lattice image.

Figure 2 shows the $C-V$ and $G-V$ curves of the epitaxial YSH films on the MOS capacitor measured at 1 MHz. Due to the presence of oxygen deficiencies in the film, the as-grown samples show quite large leakage current (7.0×10^{-2} A/cm^2 at gate voltage of 1 V) as shown in the inset in Fig. 2. Thus, the $C-V$ measurements at different frequencies exhibited large discrepancy, especially for frequencies lower than 1 MHz, and only the result measured at 1 MHz is shown. The effective dielectric constant of the YSH film from the series capacitance analysis as shown in Fig. 2 is about 14, and the equivalent oxide thickness to SiO_2 is 12 Å.

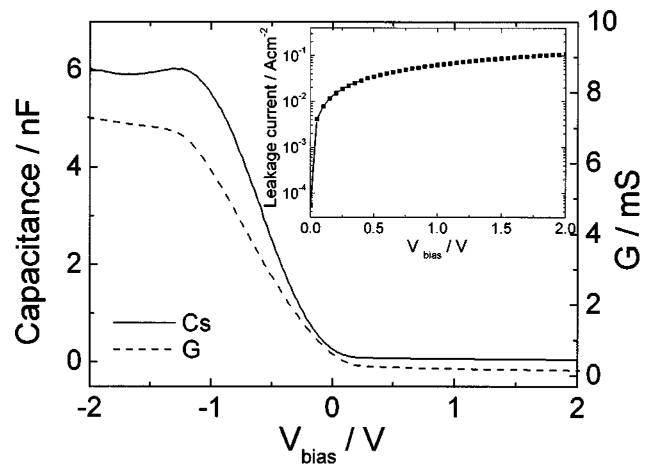

FIG. 2. High-frequency (1-MHz) $C-V$ and $G-V$ curves of the parallel plate capacitor of the as-grown 40-Å YSH epitaxial film. The inset is a characteristic $I-V$ curve of the epitaxial film.

However, a parallel capacitance analysis yields a dielectric constant smaller than 1. The large discrepancy between the series and parallel analysis revealed a large dissipation of the capacitor (dissipation factor is calculated to be 5.1 at 1 MHz from the admittance). Since the as-grown film/Si interface may contain Hf–Si bonds and interfacial dislocations, the interface trap density and flat-band voltage are expected to be much higher than acceptable values, as suggested by Fig. 2. However, for a very thin YSH film, it is difficult to optimize the annealing condition in oxygen ambient, since the resistance to oxygen diffusion for HfO_2 film is very low. Therefore, a layer of SiO_2 will normally be formed at Si interface after thermal annealing in oxygen ambient. The effort to find an optimized annealing condition without forming SiO_2 interfacial layer was not successful and it deserves further studies.

In order to study the epitaxial growth mechanism, some comparison experiments were carried out. Pure HfO_2 ceramic target was used to grow HfO_2 films under the same condition for the epitaxial growth of YSH films. TEM observations of the pure HfO_2 films revealed that the films are polycrystalline even though there is no SiO_2 layer present at the interface. Figure 3 shows a TEM image of a few HfO_2

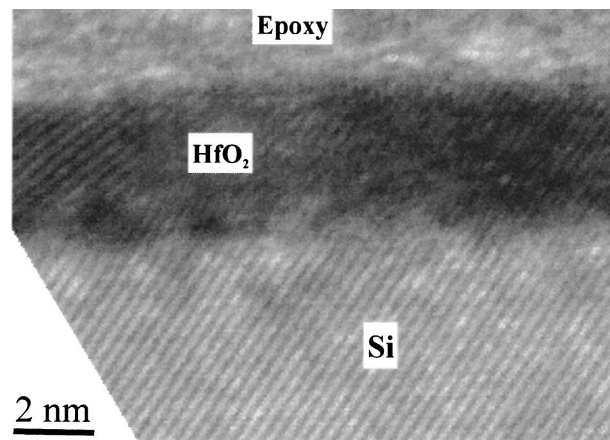

FIG. 3. HRTEM image of a polycrystalline HfO_2 film on Si.

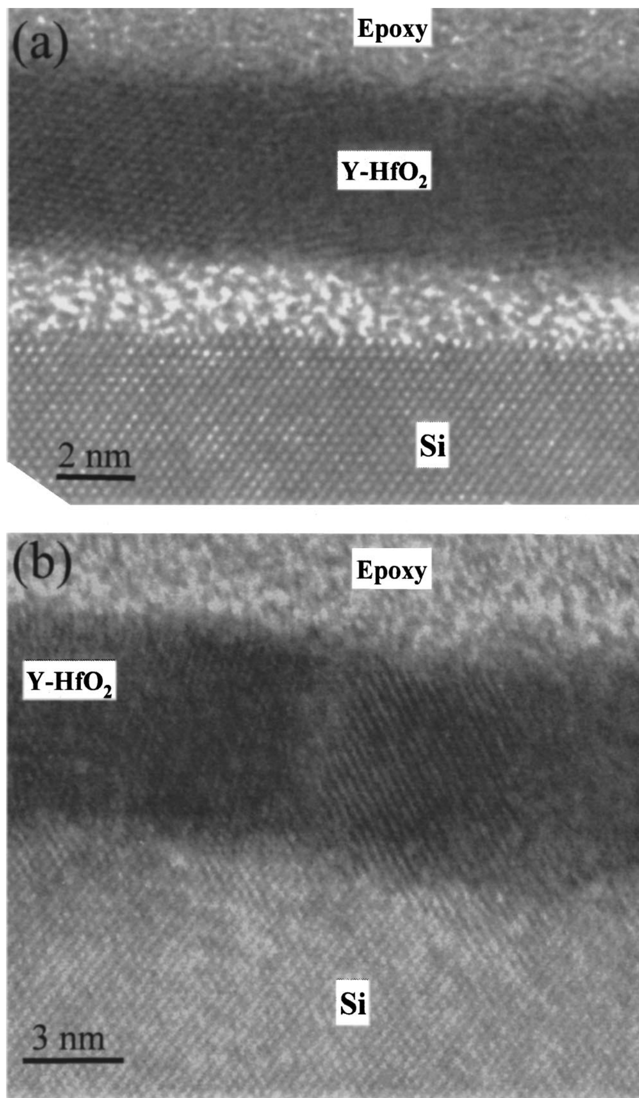

FIG. 4. HRTEM image of polycrystalline YSH film on Si, (a) grown at 600 °C and (b) grown at 450 °C.

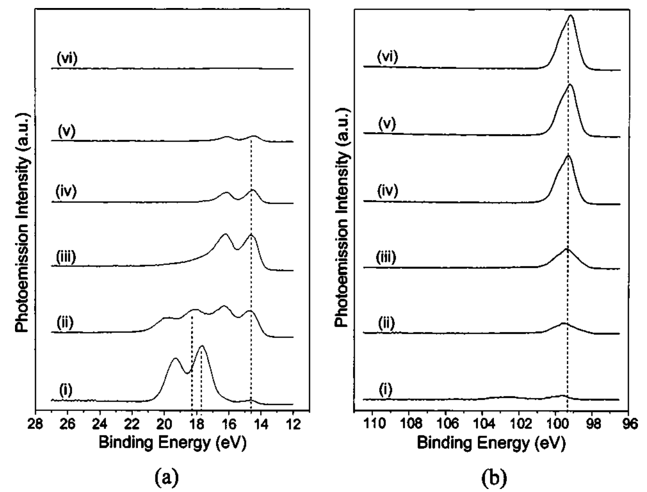

FIG. 5. XPS depth profile of epitaxial YSH film on Si: (a) Hf $4f$ peak, (b) Si $2p$ peak. The sequence of the spectra are as follows: (i) film surface, (ii) after a 150-s sputtering, (iii) after a 270-s sputtering, (iv) after a 750-s sputtering, (v) after a 1110-s sputtering, and (vi) after a 1600-s sputtering.

grains with different orientations in the film. Polycrystalline HfO_2 film on bare Si grown by PLD has been reported by Ikeda and co-workers.[12] However, due to the large stress at the interface and the possible phase transformation from cubic to tetragonal structures in the film, it is difficult to grow pure HfO_2 epitaxial films on Si. This is due to the well-known instability of HfO_2 cubic structure that undergoes martensitic phase transformation to tetragonal and monoclinic structures under stress.

Substrate temperature was found to be a critical parameter for the epitaxial growth of YSH films. TEM observations revealed that a higher substrate temperature at 600 °C caused SiO_2 formation on Si surface before film deposition and therefore prevented the epitaxial growth of the films [see Fig. 4(a)]. On the other hand, the films grown at a lower substrate temperature of 450 °C also resulted in polycrystalline structure even the interface is free from SiO_2 layer [Fig. 4(b)]. This can be understood by considering the different mobility of adatoms at the Si surface under different temperatures. Higher substrate temperatures result in higher atom mobility and allows the atoms to move into low-energy lattice sites and thus leads to a layer-by-layer growth. Lower substrate temperatures result in lower atom mobility; thus, the adatoms do not have sufficient kinetic energy to overcome the energy barrier to reach the epitaxial lattice sites and the film growth is basically via island growth mechanism forming columnar grains with different orientations. Again one can see that the film/Si interface is rough, suggesting interfacial diffusion and reaction.

The process window for YSH epitaxial growth on bare Si in our case is very narrow. We believe this is due to the relatively lower vacuum in our system as compared to a UHV system. Due to the residue oxygen gas in the chamber, there is a temperature limit above which SiO_2 will be formed on Si surface. For a UHV system in which SiO_2 and SiO can be vaporized at high temperature, the epitaxial growth can be realized over a broad range of temperatures. This suggests that the quality of YSH epitaxial films may be improved by growing the films in a UHV system at higher temperatures. The oxygen content in the YSH films is another issue since it is very difficult to be optimized. However, a well-controlled and optimized SiO_2 layer of less than 10 Å can result in a compromised effect between a decreased gate stack capacitance and improved interfacial quality to Si, since no high-k system has yet shown an interfacial quality equal to that of SiO_2.[13]

The advantages of the YSH epitaxial films over the HfO_2 polycrystalline films have been studied in terms of surface flatness. AFM analysis revealed that the surface rms roughness for the YSH epitaxial film is 2.5 Å, and 5.4 Å for pure HfO_2 film. Therefore, the surface flatness for epitaxial YSH films is better than that of polycrystalline HfO_2 films.

XPS has been commonly used in the study of thin film chemical structure and interfacial reaction of HfO_2 and Hf silicate on Si.[14–21] In order to study the interfacial reaction and diffusion that may occur at the interface of the epitaxial YSH film on Si, the as-grown film was subjected to XPS analysis. Figure 5 shows the depth profile XPS binding en-

ergy of Hf $4f$ and Si $2p$ peaks as the film was progressively milled by Ar^+ *in situ* sputtering. One can see from Fig. 5(a) that with increasing depth, the peak position of Hf $4f$ shifted from HfO_2 (17.6 eV) to elemental Hf (~14.6 eV). The presence of elemental Hf peak inside the film illustrates the existence of oxygen vacancies. The dominated elemental Hf peak at the interfacial area suggests more oxygen deficiencies during the early stage of film growth as well as Hf-silicide formation since the Hf–Si binding energy is very close to that of the elemental Hf peak.[14–16]

Since the film is only about 40 Å, the XPS spectra from surface may also contain information from the interfacial area due to the penetration effect. The Si $2p$ peak at ~102.8 eV in spectrum (i) as shown in Fig. 5(b) illustrates Hf-silicate formation close to the interfacial area.[14] The shifting to a higher binding energy of Hf $4f$ peak from spectrum (i) to (ii), as can be clearly seen in Fig. 5(a), also evidences the presence of Hf-silicate at the interfacial area.[14,16] It can also be identified from Fig. 5(b) that there is a shift of Si $2p$ peak from 99.3 eV to higher energy end in the first three spectra. This fact and the appearance of elemental Hf $4f$ peak when approaching the film/Si interface suggest that the Hf silicide or Hf–Si bonds may be formed at the interfacial area, even though there is no evidence from TEM observation. The formation of Hf silicide or Hf–Si bonds can be understood by considering the fact of insufficient oxidation of Hf atoms at the beginning of film growth on bare Si surface, leading to the reaction of Hf with Si. The Hf-silicate formation is believed to be due to the further oxidation of Hf silicide that has been formed at the interface. Therefore, it is reasonable to expect that with sufficient oxygen during film growth, the Hf-silicide formation can be suppressed at the early stage of film growth or can be eliminated during subsequent growth.

Wang and co-workers have reported the epitaxial growth of YSZ on Si.[10,11] A dynamic growth model for the first few atomic layers has been proposed in which the reaction of Zr with SiO_2 and the desorption of SiO were thought to be essential for the epitaxial growth. At the beginning, the coming Zr atoms react with the preformed SiO_2 and the product of SiO is desorbed, leading to the epitaxial growth of ZrO_2 film. However, the YSH epitaxy in our case is expected to follow a different mechanism; that is, the film was epitaxially deposited on the crystalline Si surface directly, without the reaction between Hf atoms and SiO_2. This assumption is based on two facts. First, the epitaxial growth was at substrate temperature of 550 °C, which was much lower than the temperature of 730 °C for the YSZ epitaxial growth.[10,11] At such a low temperature, the oxidation of hydrogen-terminated Si surface at vacuum of 2×10^{-4} Pa was difficult. The film growth condition of 550 °C and 2×10^{-4} Pa is actually close to the lower limit to form SiO_2, as reported by Seiple and co-workers.[22] Secondly, it is difficult to expect desorption of SiO at a temperature of 550 °C (if any). Therefore, we believe that the epitaxial deposition of YSH on bare Si is by direct growth, without the formation of amorphous SiO_2 layer. In fact, the formation of Hf–Si bonds suggested by the XPS result also supports this direct growth mechanism.

IV. CONCLUSION

Epitaxial YSH thin films have been deposited on p-type (100) Si substrates by pulsed laser deposition at a low substrate temperature of 550 °C. The orientation relationship between the epitaxial film and Si is $(100)\mathrm{Si}//(100)\mathrm{HfO_2}$ and $[001]\mathrm{Si}//[001]\mathrm{HfO_2}$. The effective dielectric constant of an as-grown 40-Å YSH epitaxial film was characterized to be about 14, and the equivalent oxide thickness is 12 Å. The leakage current density is 7.0×10^{-2} A/cm^2 at 1 V gate bias voltage. A direct growth mechanism of epitaxial YSH thin films on Si is proposed.

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