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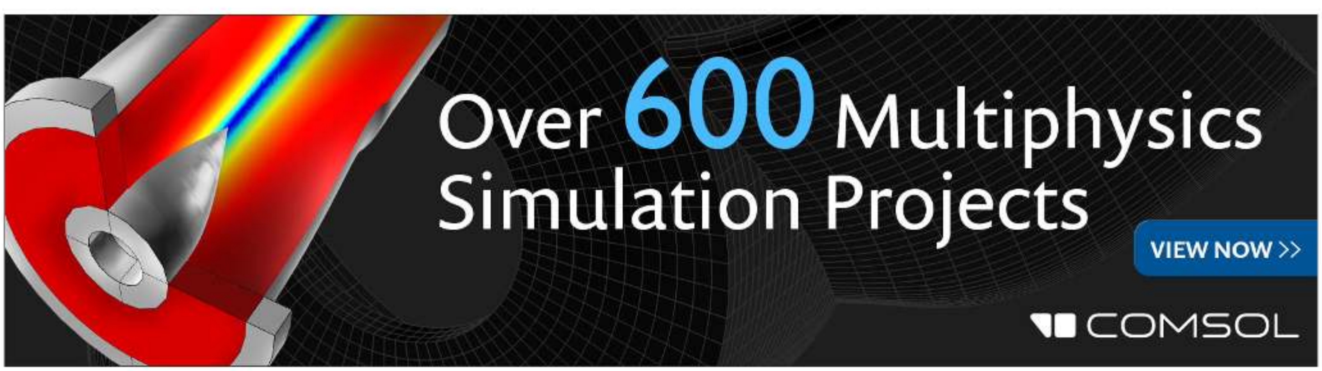

Growth of highly oriented HfO_2 thin films of monoclinic phase on yttrium-stabilized ZrO_2 and Si substrates by pulsed-laser deposition

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We report on the growth of highly oriented HfO_2 thin films of monoclinic phase stabilized by 5% Co doping on (001) yttrium-stabilized zirconia (YSZ) using pulsed-laser deposition at 700 °C at an oxygen partial pressure of 10^{-4} Torr. On the other hand, pure HfO_2 of such quality did not grow on YSZ in wide range of growth parameters. Rutherford backscattering-ion channeling in this film showed a 24% minimum yield (χ_{min}) indicating highly oriented film growth, while hardly any ion channeling was observed in the undoped sample. High-resolution transmission electron microscopy revealed a sharp interface, and no signature of Co clusters. Electron energy loss spectroscopy showed that Co is in the 2+ state. Attempts were also made to grow films on a (001) Si substrate, and the results showed a very low ion channeling yield (~8%). © *2005 American Institute of Physics*. [DOI: 10.1063/1.2142088]

For the development of next-generation complementary metal-oxide-semiconductor devices and the scaling down of their size, suitable high-*k* dielectric material[1–4] is a critical component as it is expected to take the place of the SiO_2 gate dielectric in order to maintain low leakage current density. Among many available high-*k* materials, Hafnia (HfO_2) is the most promising due to its relatively high dielectric constant (15–25), large band gap (5.5–5.8 eV), and good thermal and chemical stabilities.[5–7] Moreover, recent reports on ferromagnetism in pure HfO_2 thin films have opened up new possibilities of fabricating devices utilizing spin functionality.[8–10] In addition, HfO_2 films are attractive for many other possible applications,[11–13] such as a magnetic tunnel junction for memory chips, corrosion protective layer, carbon monoxide gas sensor, high reflectivity UV mirrors, etc.

Due to their large potential applications, a large number of studies[5–7,11,12] have been devoted to develop good-quality HfO_2 thin films and their characterizations. Pure HfO_2 films are usually insulators,[11] but often (depending on the deposition techniques and the parameters used) behave as an *n*-type semiconductor due to crystallographic defects and oxygen vacancies producing intermediate sates in the band gap.[7] Several thin-film deposition techniques, such as sputtering,[14–17] have been employed to grow HfO_2 films, however, in most of these cases, efforts have been made to produce good quality amorphous films. But, the growth of single-crystal HfO_2 thin films has not been studied much and is desirable for many of the applications mentioned above.

In this letter, we report on the growth of highly oriented single-crystal HfO_2 thin films deposited by pulsed-laser deposition (PLD) on yttrium-stabilized zirconia (YSZ) substrates at relatively low temperatures. With the help of various characterization techniques, we demonstrate that the monoclinic HfO_2 phase stabilizes at lower temperatures with dilute Co doping (5 at. %). Moreover, we show that very high-quality HfO_2 films can be grown directly on (001) Si substrates without any YSZ buffer layer.

Using $Hf_{1-x}Co_xO_2$ (x=0.0–0.1) target prepared by standard solid state reaction route, thin films were grown by PLD on (001) YSZ (single-sided polished) or (001) Si single-crystal substrates (CrysTech, Germany) using a KrF excimer pulsed laser (Lambda Physik, λ=193 nm) operated at 10 Hz. The energy of the laser spot on the target was 2 J/cm^2. To optimize the single-crystal film growth, the substrate temperature was varied between 675 and 800 °C, and the oxygen partial pressure was varied in the range of 1×10^{-2}–1×10^{-6} Torr. Several characterization techniques, such as Rutherford backscattering (RBS) and ion channeling with 2 MeV He^+ ions, high resolution transmission electron microscopy (HRTEM), *Z*-contrast imaging, electron energy loss spectroscopy (EELS), and atomic force microscopy (AFM) were used to study these films.

Figure 1 shows the XRD plot of the 5% Co-doped HfO_2 samples obtained under optimized conditions, i.e., deposited at 700 °C under an oxygen partial pressure of 10^{-4} Torr. In the inset of Fig. 1, the data from 2% and 5% Co-doped films are compared with that obtained from an undoped (pure) HfO_2 thin film deposited under identical conditions. It is clearly seen that the Co-doped film is *c*-axis oriented with sharp (002) and (004) reflections, and they correspond to the monoclinic HfO_2 phase (a=5.12 Å, b=5.18 Å, and c =5.25 Å, $\alpha=\gamma=90°$, and $\beta=99°$, space group $P2_1/c$ at room temperature). In contrast, the corresponding peaks from the undoped HfO_2 film (as shown in the inset) are not well de-

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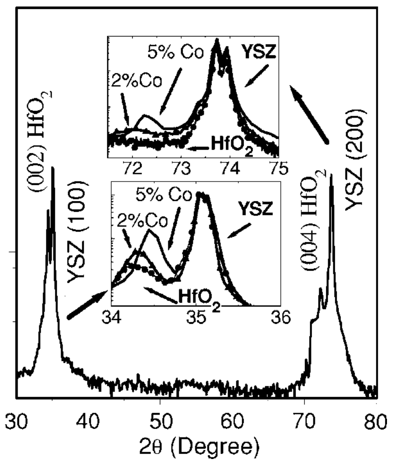

FIG. 1. XRD plot of the Co-doped HfO_2 thin film deposited on (001) YSZ substrate by PLD. In the inset, XRD reflections from undoped, 2% and 5% Co doped Hafnia are compared.

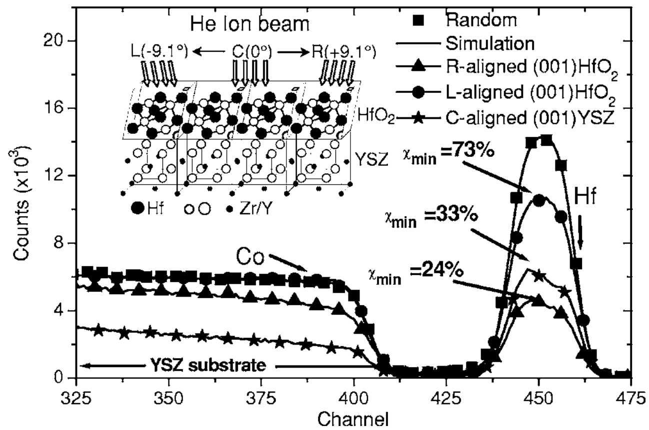

FIG. 2. RBS spectra taken under random and (001) axial channeling condition obtained from 5 at. % Co-doped HfO_2 film deposited on (001) YSZ substrate at 700 °C under oxygen partial pressure of 10^{-4} Torr. In the inset, schematic diagram of the alignment of ion beam with respect to the (001) directions of the film and substrate.

veloped and are very broad indicating poor crystallinity.

The relative shift of the (002) peak to a higher 2θ value for Co-doped HfO_2 films indicates the incorporation of Co into the Hf lattice, which clearly helps in the stabilization of the highly oriented monoclinic HfO_2 phase at the considerably low temperature of 700 °C. The ionic radii of Hf^{4+} is 0.83 Å, while those of Co^{2+} and Co^{3+} are 0.65 Å and 0.55 Å, respectively. This Co incorporation will reduce the bulk lattice parameters and bring it down toward 5.12 Å of YSZ. This should reduce the compressive strain and, hence, reduce the out-of-plane d value, as is indeed observed. The full width at half maximum of the rocking curve obtained from (002) peak of the doped sample is ~0.22° (close to that of the YSZ substrate) indicating good crystallinity. The mechanism of phase stabilization after cobalt doping of HfO_2 may be similar to that for stabilization of ZrO_2 by Y doping.[18] Thus, substitution of Hf^{4+} by a low charge state, such as Co^{2+} or Co^{3+}, should create oxygen vacancies in the proximity of the dopant for local charge neutrality. The interacting lattice distortions and the corresponding ordering effects could then cause the phase stabilization.

The RBS spectra recorded under random orientation, and after alignment along the (001) axis of either the film or the YSZ substrate are shown in Fig. 2. The RBS spectrum from undoped sample (not shown) clearly shows that the composition of pure HfO_2 film (210 nm thick) is quite stoichiometric. However, ion-channeling measurement showed very poor axial channeling yield (80%) indicating highly disordered film.

On the other hand, the axial channeling yield ($\chi_{\min}$) along the (001) axis of the 5 at.% Co-doped film (taken from the direction R indicated in the schematic diagram), as shown by solid triangular line in Fig. 2, was dramatically lower (only 24% as opposed to 80% for undoped film) indicating improved cryatalline quality of the film after Co doping and is consistent with the XRD results.

The channeling spectrum obtained by aligning the ion beam along the (001) direction (direction C in schematic diagram) of the substrate (line with solid star) is also given in Fig. 2. As seen from the figure, when the film is aligned along the (001) axis of the film (direction R in schematic diagram), channeling yield (solid triangular line) in the film was lowest (24%), but the substrate yield became poor (about 80%). On the other hand, when the ion beam is aligned along the (001) axis (direction C in schematic diagram) of the YSZ substrate, the film yield became poor (33%) and the substrate yield became relatively better. The variation of yields is due to the fact that the (001) axis of the film is not aligned along the (001) axis of the substrate. In fact, they are tilted by 9.1° with respect to each other. This tilt angle of 9.1°, required to realize the minimum yield from the film, matches well with the angle $[\beta = 99°(90° + 9°)]$ of the monoclinic distortion of Hafnia as confirmed by XRD analysis.

In order to see whether the tilted growth of the film is in one direction, or simultaneously grown in the other three directions, channeling measurements were performed by tilting the sample in the other three directions with respect to the c axis of the substrate. For comparison, one channeling spectrum (obtained from direction L as shown in the schematic diagram) is depicted in Fig. 2 (line with solid circle). It clearly shows a very poor channeling yield ($\chi_{\min} = 73\%$) from the film, in comparison to 24% obtained before from the direction R. Similar poor channeling results were obtained from the other two directions. These suggest that the film with monoclinic distortion was most likely grown as one directional variant.

The HRTEM image in Fig. 3(a) clearly shows the sharp interface of the Co-doped HfO_2 film and YSZ substrate. No evidence of Co cluster formation was observed in the film. Selected area electron diffraction confirmed the monoclinic structure of HfO_2, supporting the observation made in the ion channeling and XRD analyses.

The electron energy loss spectrum in Fig. 3(b) shows the $L_{2,3}$ edge riding on the background signal. It may be noted that the signal-to-noise ratio is small due to the presence of a small amount of Co in the film. By measuring the ratio of the $L_{2,3}$ white lines using Gauss peak fitting, the main valence state of 2+ signals of Co was found in the film. No significant variations were observed in EELS while performing line scans, which indicates a homogeneous distribution of Co ions in the lattice.

The relative dielectric constant (ε_r) measured on patterned Co-doped HfO_2 films was about 18.0. AFM analysis showed that the surface of the film was quite smooth. The characterizations of magnetic properties are under progress.

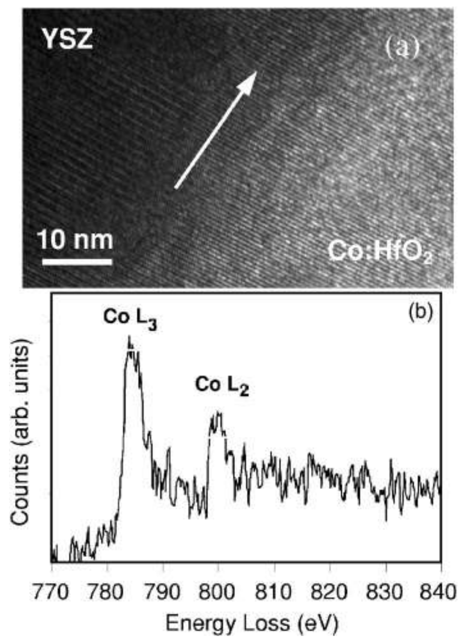

FIG. 3. (a) The HRTEM image of the 5 at. % Co-doped HfO_2 film shows high crystalline quality interface of the film. (b) The high-resolution electron energy loss spectrum shows the Co $L_{2,3}$ edges.

Such study is interesting as there is a possibility to introduce ferromagnetism in this film by Co ions as observed in many other oxides, such as SnO_2, TiO_2, and ZnO.[19–22]

Attempts were made to grow HfO_2 layer with 5–10 at.% Co doping on (001) Si substrate under identical deposition condition. Initial data showed promising results. A sample doped with about 6.5 at.% Co revealed a very good channeling yield of about 8% as shown in Fig. 4. This indicates that the single-crystal quality of this film (thickness 230 nm) is much better (three times) than the one obtained on the YSZ substrate discussed above. It should be noted that, like on a YSZ substrate, the single-crystalline pure HfO_2 film did not grow on the Si substrate.

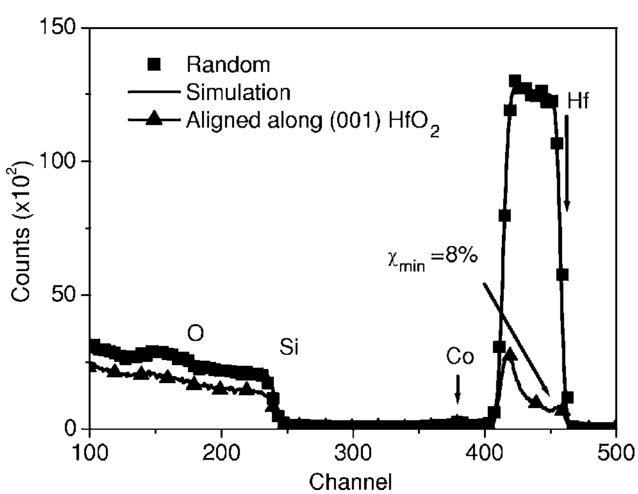

FIG. 4. RBS spectra taken under random and (001) axial channeling conditions for 6.5% Co-doped HfO_2 film deposited on (001) Si substrate by PLD at 700 °C under oxygen partial pressure of 10^{-4} Torr.

We have shown, in detail, the results of highly oriented growth of HfO_2 thin films on YSZ substrates by PLD deposition at the relatively low temperature of 700 °C and oxygen partial pressure of 10^{-4} Torr. Highly oriented growth (only one directional variant) of the monoclinic phase was realized by Co doping. Ion channeling yield, χ_{min}, from the film grown on the YSZ substrate, was found to be 24%. This indicates good single-crystal quality and is supported by the very sharp XRD peaks and HRTEM analysis. However, pure HfO_2 films hardly gave any channeling and showed very broad XRD peaks. EELS showed that almost all Co atoms were mostly 2+ state; suggesting they substituted Hf atoms. Preliminary results on the growth of this film directly on a (001) Si substrate showed a three times lower channeling yield (8%); indicating the growth of a very high-quality single-crystal HfO_2 thin film.

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