SrHfO₃ as gate dielectric for future CMOS technology

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Abstract

Thin epitaxial films of the high-κ perovskite SrHfO₃ were grown by molecular beam epitaxy on Si(100) and investigated by ellipsometry and X-ray photoelectron spectroscopy to determine its band gap and valence band offset. Conducting AFM shows a good correlation between topography and current mapping, pointing to direct tunneling conduction. Long channels MOSFETs with low equivalent oxide thickness (EOT) were fabricated and their channel mobility measured. Mobility enhancement can be achieved by post processing annealing in various gases but at the cost of interfacial regrowth. An alternative approach is to increase mobility without changing EOT by electrically stressing the gate dielectric at ~150 °C.

Keywords: high-κ gate dielectrics; perovskites; MOSFETs; band gap and band offset; channel mobility

1. Introduction

Among all high-κ gate dielectric oxides proposed and investigated for the next generations of CMOS devices, the perovskite SrHfO₃ (SHO) could be a valuable candidate because of its good physical and electrical properties. Its epitaxial growth on Si(100) wafers by molecular beam epitaxy (MBE) is possible and the fabrication of working MOSFETs with equivalent oxide thickness EOT < 1 nm was recently demonstrated [1]. Only few studies of this material are found in the literature [2-5] in contrast to SrTiO₃. We present results of the optical band gap measured by spectroscopic ellipsometry, of the valence band offset derived from X-ray photoelectron spectroscopy (XPS) and electrical characterization of capacitors and FETs. Two approaches for increasing the channel mobility are presented: post processing annealing and electrical stress intended to reduce the density of interface charges and fixed charges.
2. Experimental details

The 10 unit cells thick SHO films were grown on 2 inch Si(100) wafers by MBE using one unit cell of SrO (~0.5 nm) as template layer. The deposition process [6] was optimized to achieve good quality epitaxial thin films with no or little interfacial SiO_x or (Sr,Hf)SiO_x. The films were characterized by X-ray diffraction, spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS) and conducting atomic force microscopy (c-AFM). Electrical data were taken on capacitors and non-self-aligned long-channel FETs fabricated with Pt gate electrodes. High implanted source and drain contacts without metallization were used to permit post-processing annealing experiments. These were performed in an UHV chamber partially filled with different high purity gases, at temperatures between 300 and 500°C and at a typical pressure of 30 Torr.

3. Results and discussion

In spite of a 6% lattice mismatch with Si, the SHO films grow epitaxially with a good crystallinity as assessed from in-situ RHEED imaging during deposition and from XRD after deposition. The thickness measured by X-ray reflectometry, 4.2 ± 0.5 nm, is in good agreement with the nominal value. The optical absorption coefficient $\alpha(E)$ of a SHO/SrO/p-Si film was derived from spectroscopic ellipsometry measurements taken up to 8 eV. The optical band gap of 6.07 eV is derived from the position of the absorption edge defined in the plot $(\alpha(E) \times E)^{1/2}$ vs. $E$ (Fig. 1), as usually done for allowed transitions in indirect band gap materials [7].

First-principle calculations of the electronic structure of cubic SHO by two groups [3, 8] predicted lower indirect band gap values around 3.6-3.7 eV. This discrepancy between theoretical and experimental data, also reported for SrTiO$_3$, seems to be typical of the local density approximation used in density functional calculations for oxides [3].

The XPS valence band spectrum of a similar film is shown in Fig. 2 after correction for the substrate contribution. The maximum of the valence band (VB), extracted by linear extrapolation, is 3.5 eV. After subtracting the Si valence band level, including the band bending, the resulting VB offset of SHO with respect to Si is found to be -3.0 ± 0.1 eV. From the band gap onset value of 6.1 eV found above for SHO, a minimum conduction band (CB) offset of about 2.0 eV can be estimated. By comparison, XPS data on epi-SrTiO$_3$ films give a VB offset of -2.1 to -2.3 eV [9]. Using a band gap value of 3.4 eV, the relevant CB offset is thus only 0 to 0.2 eV, an unsuitable barrier to inhibit Schottky emission of electrons. In contrast, our data on SHO show that this material is particularly suited as a gate dielectric for n- and p-FETs with potentially low gate leakage current.

![Fig. 1. Absorption coefficient $\alpha$ plotted as $(\alpha(E) \times E)^{1/2}$ against energy $E = h\nu$ for a 4.2-nm SHO/SrO/p-Si film.](image1)

![Fig. 2. Valence band spectrum of SrHfO$_3$ film on p-Si](image2)

The epitaxial SHO/SrO/p-Si films have a low surface rms roughness of ~0.16 nm (over 0.8×0.8μm$^2$) as measured in dry air by c-AFM. Topographic and current images were measured simultaneously in contact mode for positive tip-substrate bias voltages. Local variations in oxide
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