

Extended Abstract of PSA-19 (review)

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Applications of surface analysis to Oxide Thin Film Devices

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(Received: May 29, 2019; Accepted: June 12, 2019)

Surface analysis has been applied to obtain electronic properties for ultrathin high-k dielectric gate oxide thin films, metal gate stack in CMOS, and transparent conductive oxide thin film transistors (TFTs) incorporating an oxide active channel layer. The band alignment in HfZr silicate gate dielectric thin films showed that the band gap, the valence band offset and the conduction band offset increased as the SiO₂ content increased, which yielded a substantially reduced gate leakage current density. The TiN/(LaO or ZrO)/SiO₂ metal gate stack structures in CMOS demonstrated that a flat band voltage (VFB) shift could be controlled in TiN/(LaO or ZrO)/SiO₂ gate stack structures. The electrical characteristics of GIZO TFTs mainly depend on the contents of indium (In) and gallium (Ga). The band gap energies of the GIZO thin films increased with the increase in their Gallium (Ga)/Indium (In) ratios. The barrier height of GIZO/Mo also increased by increasing in the Ga/In ratio, and then the threshold voltages positively shift. We also applied AES and REELS analyses to confirm the origin of intrinsic photoluminescence emission from subdomain graphene quantum dots

The rapid shrinkage of transistor feature sizes in complementary metal-oxide semiconductor (CMOS) technologies has forced the thickness of gate oxides to be reduced below the sub-nanometer scale. As a result, SiO₂ and/or SiON gate oxide materials are running out of atoms; this has hampered further scale down. The gate oxide thin films with a high dielectric constant (k) have been applied in CMOS technologies. For the last decades, we have studied on the thermal stability and the band alignment of the Hf-Al-O [1], HfO₂ [2], ZrO₂ [3], and HfZrO₄ [4] silicate dielectric thin films grown by atomic layer deposition (ALD) on p-Si (100) wafer by using surface analysis such as x-ray photoelectron spectroscopy (XPS) and reflection electron energy loss spectroscopy (REELS) measurements. The band alignment in HfZr silicate gate dielectric thin films showed that the band gap, the valence band offset and the conduction band offset increased as the SiO₂ content increased, which yielded a substantially reduced gate leakage current density [4].

Aggressive scaling down of CMOS also allows us to replace the conventional poly-silicon gate by a metal gate stack. The advantages of metal gates are low resistivity, a lack of charge depletion and no need for doping in poly-Si, which can penetrate into the gate dielectric. The ability to adjust threshold voltage

control for low voltage operation in metal gate devices via the work function of the gate materials remains a key factor. Among the various metal gate candidate materials, TiN has been widely used because it is chemically inert, has a low resistivity, and is compatible with current processing techniques. In general, the work function of the integrated metal-gate electrode/oxide/Si-sub structure is different from that of pure materials due to the formation of interfacial layers between each material. This phenomenon results in an effective work function (EWF), which is one of the most important parameters utilized in determining device performance. The EWF can change by varying the gate-electrode and oxide interface properties. The EWF of TiN/(LaO or ZrO)/SiO₂/Si has been investigated using ultra-violet photoelectron spectroscopy (UPS), and the work function depth profiling technique has been applied to measure the work function of the gate electrodes directly; furthermore, the work function was obtained from the cutoff energy of secondary electron energy distribution induced with the incident low energy (<2 keV) electron beam during Ar⁺ ion sputtering. These results demonstrated that a flat band voltage (VFB) shift could be controlled in TiN/(LaO or ZrO)/SiO₂ gate stack structures. The direct work function measurement

technique allowed us to make direct estimate of flat band voltages (VFB). As a function of composition ratio of La or Zr to Ti in the region of a TiN/(LaO or ZrO)/SiO₂/Si stack, direct work function modulation driven by La and Zr doping was in good agreement with the work functions obtained from UPS and the cutoff value of secondary electron emission by AES [5].

Oxide thin film transistors (TFTs) incorporating an oxide active channel layer have been studied for transparent electronics on the strengths of their high mobility, good uniformity, and large band gap. Due to their special conduction mechanism, high carrier mobility can be realized even in the amorphous phase. The ZnO, In₂O₃, and SnO₂ are typical valence compounds with a conduction band derived from spherically symmetric ns orbitals with a (n-1)d¹⁰ns⁰(n > 4) electronic configuration. The spatial spread of this vacant s-orbital enables direct overlap between neighboring heavy-metal cations. Amorphous oxides with heavy-metal cations, such as indium zinc oxide (IZO), zinc tin oxide (ZTO) and gallium indium zinc oxide (GIZO), have been researched for application as a channel layer of oxide TFTs. Indium tin oxide (ITO) thin films fabricated by a sol-gel method are transformed from a conductor to a semiconductor by simply adding Al into the composition to enlarge the band gap and transition to an amorphous phase. The optimized composition of a solution-processed aluminum indium tin oxide (AITO) thin film channel layer in a TFT shows high mobility, a high on-to-off current ratio, and a low subthreshold swing, thus making it applicable to the backplane of active matrix organic light emitting diode and active matrix liquid crystal displays [6]. The electrical characteristics of indium zinc tin oxide (IZTO) TFTs mainly depend on the contents of tin (Sn) and zinc (Zn). The electron mobility of thin film transistors with higher Sn/Zn composition ratio was dramatically improved due to a shorter zinc-zinc separation distance. The thin film transistor with the composition of In:Zn:Sn = 20:48:32 exhibits a high mobility of 30.6 cm²V⁻¹s⁻¹ and a high on-off current ratio of 10⁹ [7]. The band gap energies of the GIZO thin films deposited by RF magnetron sputtering on SiO₂/p-Si increased from 3.03 eV to 3.43 eV with the increase in their Gallium (Ga)/Indium (In)

ratios of 0.83, 1.05, and 1.34. The barrier height of GIZO/Mo also increased by increasing in the Ga/In ratio, and then the threshold voltages positively shift. From the transfer curves of the GIZO thin films, the mobility shows the decreasing tendency by the increase in the ratio of Ga/In. As a result, it is suggested that the increase in the density of defect density in the GIZO thin film plays a dominant role in the decrease in its mobility [8].

We also applied AES and REELS analyses to confirm the origin of intrinsic photoluminescence emission from subdomain graphene quantum dots [9].

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