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Solution-processed hafnium oxide dielectric thin films for thin-film transistors applications

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Abstract

Hafnium oxide (HfO_x) dielectric thin films were fabricated on heavily-doped silicon (100) substrates by a solution process. The precursor solution was prepared by dissolving $HfCl_4$ in ethanol. The annealing effects on the microstructural and electrical properties of HfO_x thin films were studied. The HfO_x thin film annealed at 500 °C exhibited the best insulating performance with a current density of 1×10^{-9} A/cm^2 at an electric field of 4.5 MV/cm. In order to demonstrate the possible application of HfO_x thin films in thin-film transistors (TFTs), the indium-zinc oxide (IZO) channel layer was fabricated by magnetron sputtering at room temperature. The IZO TFT based on 500 °C-annealed HfO_x can be operated under an operation voltage of 5 V, with a high field-effect mobility of 36.9 cm^2/V s, a threshold voltage of 1.8 V, a subthreshold swing of 0.38 V/dec, and an on/off current ratio of 10^9. The results demonstrate that HfO_x thin film prepared by the solution process is a promising gate dielectric for high-performance oxide electronic devices.

Keywords: Solution process; Hafnium oxide; Dielectric; Thin film transistor

1. Introduction

With the decrease of the size scale of the field effect transistor in integrated circuit, the thickness of SiO_2 was reduced to nanometer scale. The leakage current of SiO_2 is increased dramatically owing to the tunneling effect. A lot of researches have been conducted to study the high-*k* dielectric thin films to replace the SiO_2. Since high-*k* dielectrics possess potentials to increase the physical thickness of the dielectrics and to make the capacitance density unchanged, the fabrication of the high-*k* dielectrics with the required performance is the most hopeful way to replace the SiO_2. Another advantage is that they can be prepared by various methods such as metal anodic oxidation method, vacuum-based deposition, and solution-based techniques.

High-*k* dielectrics have been widely studied to replace the conventional SiO_2 layer in field-effect transistors (FETs). Compared with organic and polymer dielectric materials, the inorganic dielectrics such as aluminum oxide (AlO_x) [1,2], zirconium oxide (ZrO_x) [3–5], yttrium oxide (YO_x) [6–8], and hafnium oxide (HfO_x) [9–11], are proved to be more suitable for low-operating voltage thin-film transistors (TFTs) because of their large conduction band offset and excellent solvent resistance. Among these high-*k* dielectrics, HfO_x is considered as the most promising candidate due to its high dielectric constant ($k \sim 25$–30) and wide band gap (5.68 eV) with a large conduction band (CB) offset of 1.4 eV [12,13]. The CB offset is one of the key criteria in the selection of a gate dielectric. It must be over 1 eV to inhibit conduction by the Schottky emission of electrons or holes into the oxide bands, which guarantee adequately low leakage current.

Several techniques have been used to prepare the HfO_x thin films for TFTs, including atomic layer deposition (ALD) [14,15], photo-assisted pulsed layer deposition, evaporation with ion assisted deposition, metal organic chemical vapor deposition (MOCVD)

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[16–19], radio frequency sputtering (RFS) [20,21], and molecular beam epitaxy (MBE). Although the vacuum-based deposition methods have their own advantages, the high fabrication cost and large-area device uniformity restrict the areas of their applications. To fabricate the dielectric thin films with low cost, solution processes such as inkjet printing, dip-coating, and spin-coating techniques are proved to be promising. The solution-processability can lead to several advantages including printability, the possibility of large-area deposition, low-cost device fabrication, and compatibility with mechanically flexible substrates.

In this report, the HfO_x thin films were prepared by using a solution process and annealed at various temperatures. The physical properties, chemical composition, and the electrical properties of the HfO_x thin films were investigated. In order to validate the reliability of solution-processed HfO_x thin films as the gate dielectric, the indium zinc oxide (IZO) TFTs based on the optimized HfO_x dielectrics were fabricated by magnetron sputtering at room temperature.

2. Experiment

To deposit the HfO_x dielectric thin film, a solution was prepared by dissolving 0.1 M $HfCl_4$ (98%, Aldrich, USA) in ethanol. The solution was rigorously stirred for 1 h at room temperature, resulting in a transparent solution. The solution was filtered through a 0.2 μm membrane syringe filter and spin-coated at 3000 rpm for 30 s onto a p-Si substrate. After spin coating, the substrates were placed on a hotplate at 150 °C for 1 min. Finally, the substrates were annealed in the temperature range from 200 to 500 °C for 1 h in air. For convenience, the HfO_x thin films annealed at 200, 300, 400, and 500 °C will be referred, hereafter, as HfO_x-200, HfO_x-300, HfO_x-400, and HfO_x-500, respectively.

The IZO channel layer with a thickness of 50 nm was deposited by sputtering from an IZO ceramic target (In:Zn=2:5 in molar ratio) in a gas mixture with 20% Ar in O_2. Finally, Al source and drain electrodes, with a thickness of 100 nm, were deposited on the channel layer by thermal evaporation. The schematic structure of IZO/HfO_x TFTs is shown in Fig. 1. In this report, the channel length and width were 100 and 1000 μm, respectively.

The transmittances of the HfO_x thin films on sapphire substrates were measured by an UV–vis spectrophotometer (UV-2550, SHIMADZU). The surface morphologies of the HfO_x thin films were investigated by an atomic force microscope (AFM, SPA-400). The chemical compositions of HfO_x thin films were analyzed by x-ray photoelectron spectroscopy (XPS, ESCALAB 250). The thicknesses of various HfO_x thin films were measured by ellipsometry (ESS01, Sofn Instrument). The electrical and dielectric properties of the HfO_x capacitors and as-fabricated TFT devices were investigated by a semiconductor parameter analyzer (Keithley 2634B) and an impedance analyzer (Agilent 4294A), respectively.

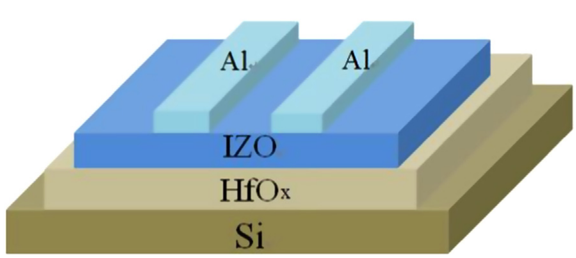

Fig. 1. Schematic structure of IZO TFT with HfO_x gate dielectric.

3. Results and discussion

The transmittances of the HfO_x thin films on sapphire substrates are shown in Fig. 2. It is found that the transmittances of all thin films are over 80% in the visible range. The high transmittances of the HfO_x thin films indicate the potential applications in transparent electronics. The transmittance of HfO_x thin film was found to be decreased with increasing annealing temperature. It means that the samples annealed at higher temperatures are more absorbable. The decrease in transmittance may be attributed to the slight increase of surface roughness or the elimination of interstitial oxygen at higher annealing temperatures [22].

The band gap energy of the semiconductor channel layer is an important parameter in the TFT. The electrical properties of the channel layer are sensitive to the photons with energies larger than its band gap (E_g). The band gap of the HfO_x thin films was extracted by plotting $(\alpha h\nu)^2$ against the photo energy $h\nu$ and extrapolating to the energy axis. The calculation method for the band gap energy of the HfO_x thin films is shown in the inset of Fig. 2. The E_g determined from the obtained absorption spectrum is around 5.51, 5.8, 5.81, 5.82 eV for HfO_x-200, HfO_x-300, HfO_x-400, and HfO_x-500 thin films, respectively. This value is much higher than the photon energy of the visible light, thus the HfO_x thin films are insensitive to the visible light.

Generally, a desirable criterion for insulating material applied as gate dielectric in electronic devices is that the surface morphology should be as smooth as possible. Fig. 3(a)–(d) shows the surface morphologies of the HfO_x thin films on Si substrates. The surfaces of HfO_x-200, HfO_x-300, HfO_x-400, and HfO_x-500 were smooth with the root mean square (rms) roughness values of 0.17, 0.19, 0.28, and 0.29 nm, respectively. The smooth surface of dielectric thin film can suppress the formation of interface charge traps, reduce carrier scattering centers and obtain high field-effect

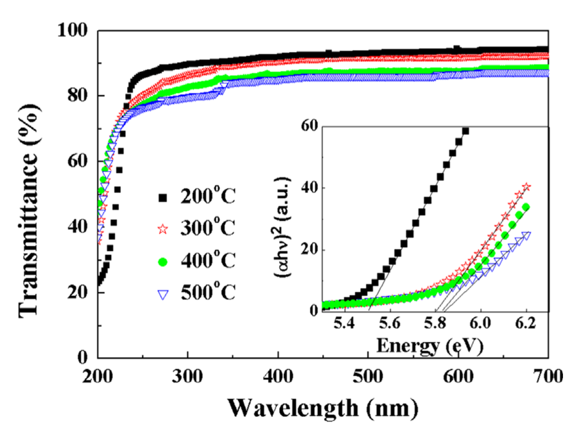

Fig. 2. Transmittances of HfO_x thin films annealed at different temperatures.