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# Modification of band alignments and optimization of electrical properties of InGaZnO MOS capacitors with high-k $HfO_xN_y$ gate dielectrics

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ABSTRACT

High-*k* $HfO_xN_y$ and $HfO_2$ have been applied to amorphous InGaZnO (*a*-IGZO) metal–oxide–semiconductor (MOS) capacitors as high-k gate dielectrics by using radio-frequency sputtering at room temperature. Effects of nitrogen incorporation on the optical band gap, band alignment and electrical properties of $HfO_xN_y$/IGZO/Si gate stacks have been systematically investigated by spectroscopic ellipsometry (SE), UV–vis spectroscopy, x-ray photoemission spectroscopy (XPS) and electrical measurements. Experimental results have confirmed the successful incorporation of nitrogen into $HfO_2$ films and reduction in band gap with the incorporation of nitrogen for $HfO_xN_y$ thin films. Reduction in valence band offset and increase in conduction band offset have been observed for $HfO_xN_y$/IGZO gate stack. Electrical properties measurements for *a*-IGZO MOS capacitors based on $HfO_xN_y$ gate dielectrics have indicated that nitrogen incorporation leads to the improved interface quality, increased dielectric constant, reduced hysteresis voltage, and decreased leakage current density. Meanwhile, the leakage current mechanism under gate injection for MOS capacitors based on $HfO_2$ and $HfO_xN_y$ high-k gate dielectrics has been investigated systematically.

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## 1. Introduction

Thin-film transistors (TFTs) devices with amorphous oxide semiconductors (AOSs) recently have attracted much attention due to its high field effect mobility, low temperature deposition, transmission advantages and good chemical stability [1,2]. Among several promising AOS materials, amorphous InGaZnO (*a*-IGZO) is one of the most glaring candidates for its remarkably high electron mobility of 10 ~ 50 $cm^2\ V^{-1}\ s^{-1}$, small subthreshold voltage swing, good short-range uniformity, high electrical reliability and its ability to be deposited in amorphous form with a wide range of conductivities [3,4]. These types of *a*-IGZO TFTs can be used as flat panel displays, organic light-emitting diodes, integrate circuit and memory devices. However, these oxides TFTs typically require large operating voltage to improve the subthreshold swing (SS) and reduce the threshold voltage due to high carrier density [5–7]. Operating voltages can be reduced by developing high-k gate dielectric materials capable of large capacitance densities with low leakage currents that have good compatibility for the growth of the semiconductor channel, leading to low trap densities at the semiconductor/gate dielectric interface. And considering that the electrical stability strongly depends on the dielectric/channel interface properties in TFTs, a study in devices with different gate dielectrics is important. By far, much attention has been devoted to the investigation of the integration of high-k gate dielectric with *a*-IGZO channel materials. Due to the superior thermodynamic stability and suppressed impurity penetration, Hf-based high-k gate dielectrics have been regarded as the most promising gate dielectrics in *a*-IGZO TFTs [8]. However, there moderate dielectric, large frequency dispersion and hysteresis, and high leakage current

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make Hf-based gate dielectrics limited for future CMOS device scaling [9–11]. Inspired by the incorporation of nitrogen into the dielectric films to act as a diffusion barrier and thus suppress excessive interfacial layer growth, $HfO_xN_y$ films were successfully applied to prepare gate dielectric with a high dielectric constant and a suitable bandgap [10]. Based on our previous investigation, it can be noted that determination of the energy discontinuity in the valence band ($\Delta E_v$) and conduction band ($\Delta E_c$) of various dielectric/IGZO heterostructures plays an important role in fabricating IGZO TFTs, which is attributed to the fact that the injection of charge carriers into the dielectric depends strongly on the relative position of the energy levels [12]. Meanwhile, a band alignment diagram is a guide to choose appropriate constituent materials because it helps to predict the electronic structures and performances of the heterojunction devices such as band bending, electron transport in the interface, and built-in potential [12]. As an important parameter to determine the electrical performance of TFTs, the determination of the band alignment of high-k/IGZO heterostructures is needed for a complete TFT technology. Currently, there exist some investigations on the band alignment of high-k/IGZO heterostructures. However, there is no reports about the nitrogen incorporation dependent band offsets of $HfO_xN_y$/IGZO interface. Additionally, although the electrical characteristics and reliability of IGZO MOS Capacitors with $HfO_xN_y$ high-k gate dielectrics have been reported [5,11], the leakage current mechanisms of Al/$HfO_xN_y$/*a*-IGZO MOS capacitor have not been report systematically. In this work, the effect of nitrogen incorporation on the energy band gap of $HfO_xN_y$ gate dielectrics as well as the band offsets of $HfO_xN_y$/IGZO heterostructures has been investigated by x-ray photoelectron spectroscopy (XPS) measurements. The electrical parameters and the leakage current mechanisms of Al/$HfO_xN_y$/*a*-IGZO/Si MOS capacitors have been systematically discussed.

## 2. Experimental details

The substrates used for deposition of IGZO and $HfO_xN_y$ thin films were n-type silicon and quartz. The films deposited on quartz substrates were used to investigate the optical properties of IGZO and $HfO_xN_y$ thin films. The substrates were cleaned using an ultrasonic cleaning in acetone and ethanol for 10 min respectively to remove impurity element, then the silicon substrates were dipped in 1% buffered HF solution to remove any native oxide on the surface. Finally, the substrates were rinsed in deionized water and dried by high purity nitrogen before being placed into the sputtering system (JGP-DZS, Shenyang ZKY Technology Development Co., Ltd. Chinese Academy of Science). All of the samples were deposited at room temperature. The base vacuum and substrate-to-target distance were set at $3.8 \times 10^{-4}$ Pa and 60 mm for all film deposition. The working pressure, deposition power and Ar flow ratio were kept at 0.5 Pa, 40 W and 30 sccm for IGZO deposition, respectively. For $HfO_xN_y$ deposition, the working pressure, deposition power and Ar flow ratio were kept at 0.5 Pa, 60 W and 20 sccm, respectively. The different flow ratio of $N_2$/Ar mixture were obtained by changing the flow rate of $N_2$ from o to 3 sccm.

To investigate the optical properties of IGZO and $HfO_xN_y$ thin films, 95 nm *a*-IGZO and 60 nm $HfO_xN_y$ thin films were deposited on n-silicon and quartz substrates. The physical thickness of the films was estimated by spectroscopic ellipsometery (SC630, SANCO Co, Shanghai) with rotating analyzer type and thin film analysis apparatus (USA, F20-UVX). The measurements were done in air at room temperature in the wavelength range of 280–1100 nm with a step of 10 nm at an incident angle of 65° and 75°. And Cauchy-Urbach model was used to obtain the thicknesses and optical constants. UV-VIS-NIR spectrophotometer (UV-3600) with wavelength ranging from 190 to 900 nm were used to investigate the optical transmission spectra and band gap energies of samples.

To obtain the band offsets of $HfO_xN_y$/IGZO interface, four sets of samples were prepared for XPS measurements: a 120 nm thick IGZO layer grown on Si substrate to measure the valence band maximum (VBM), In 3d and Ga 3d core-level (CL) of bulk IGZO; a 6 nm thick $HfO_2$ and $HfO_xN_y$ (flow rate of $N_2$ to 0 and 3 sccm) layer grown on IGZO substrate to determine N 1s and VBM of $HfO_xN_y$ thin films. The film composition and chemical bonding states were investigated by x-ray photoelectron spectroscopy (XPS) using an ESCALAB 250Xi system, equipped with an Al Ka radiation source (1486.6 eV). The XPS spectra were collected by hemispherical analyzer with pass energy of 20 eV and 0.1 eV/step for high-resolution scans. The C 1s line with a binding energy of 284.8 eV was used as a reference to eliminate the charging effect [13,14]. The software (XPSPEAK Version 4.1) was used for XPS fitting. Spectral deconvolution was performed by Shirley background subtraction using a Voigt function convoluting the Gaussian and Lorentzian functions. The XPS spectrometer energy scale was calibrated using Cu 2p3/2, Ag 3d5/2, and Au 4f7/2 photoelectron lines located at 932.65, 368.19, and 84.0 eV, respectively.

In order to explore the electrical characteristics of InGaZnO MOS Capacitors with $HfO_2$ and $HfO_xN_y$ high-k gate dielectrics, Al/$HfO_2$($HfO_xN_y$)/*a*-IGZO/Si/Al MOS capacitors (two samples for $N_2$ flow rate of 0 and 3 sccm) were prepared for leakage current and leakage current mechanisms analysis. 120 nm IGZO films were deposited on n-type silicon. Subsequently, $HfO_2$ and $HfO_xN_y$ film (34 nm) was prepared on *a*-IGZO with $N_2$ flow rate of 0 and 3 sccm. Al top electrode were sputtered through a shadow mask with a diameter of 200 μm, the back Al film were deposited after the back surface oxide stripping to decrease contact resistance. A semiconductor device analyzer (Agilent B1500A) combined with Cascade Probe Station was used for *C-V* and *I-V* measurement at room temperature. Short circuit and open circuit calibration were performed before real measurements.

## 3. Results and discussion

A 6 nm thick $HfO_2$ and $HfO_xN_y$ ($N_2$ flow rate of 0 and 3 sccm) layer grown on IGZO substrate was prepared for XPS measurements to determine the N 1s core-level spectra. Fig. 1(a) shows the N 1s XPS spectra of $HfO_2$. $HfO_2$ sample without nitrogen incorporation shows no peaks for N 1s, indicating that the dielectric film is pure $HfO_2$. The inset of Fig. 1(a) shows N 1s photoelectron spectra of $HfO_xN_y$ film with $N_2$ flow rate of 3 sccm. The apparent N 1s peak indicates the incorporation of nitrogen into the $HfO_2$ film. A curve-fitting analysis shows that N 1s XPS spectra have four peaks located at 396.8 eV, 397.8 eV, 399.2 eV and 402.8 eV. The binding energy located at 402.8 eV is attributed to the N–O bond, the N–O bond may be formed by the O atoms connected to the interstitial N atoms or the substituted N atoms connected to interstitial O atoms [15,16]. The N 1s peak of 396.8 eV and 397.8 eV were assigned to N-Hf and N-Ga bonds in the film, respectively [15,17]. Besides, N 1s peaks located at 399.2 eV was attributed to the interstitial nitrogen [18,19]. To further confirm the nitrogen incorporation into $HfO_2$ film, Hf 4d core-level XPS spectra has also been paid attention, as shown in Fig. 1(b). Compared with the reported values of 214.1 and 224.6 eV for Hf 4d5/2 and Hf 4d3/2 peaks of $HfO_2$ with a spin-orbit split separation of 10.5 eV [20], the binding energies corresponding to Hf 4d, shown in Fig. 1(b), demonstrate an apparent shift for $HfO_xN_y$ samples. The shift of Hf 4d peaks attributed to the nitrogen may originate from the formation of Hf–N bonds in the $HfO_xN_y$ films.

To investigate the effect of the nitrogen incorporation on the interface chemistry of $HfO_2$/IGZO, O 1s core-level spectra have been paid attention, as shown in Fig. 2. For $HfO_2$/IGZO, each O 1s

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