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Flexible metal–insulator–metal capacitor using plasma enhanced binary hafnium–zirconium–oxide as gate dielectric layer

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ABSTRACT

We have used a sol–gel spin-coating process to fabricate a new metal–insulator–metal capacitor comprising 10-nm thick binary hafnium–zirconium–oxide ($Hf_xZr_{1-x}O_2$) film on a flexible polyimide (PI) substrate. The surface morphology of this $Hf_xZr_{1-x}O_2$ film was investigated using atomic force microscopy and scanning electron microscopy, which confirmed that continuous and crack-free film growth had occurred on the PI. After oxygen plasma pre-treatment and subsequent annealing at 250 °C, the film on the PI substrate exhibited a low leakage current density of 3.22×10^{-8} A/cm^2 at -10 V and maximum capacitance densities of 10.36 fF/μm^2 at 10 kHz and 9.42 fF/μm^2 at 1 MHz. The as-deposited sol–gel film was oxidized when employing oxygen plasma at a relatively low temperature (~250 °C), thereby enhancing the electrical performance.

1. Introduction

Flexible substrates have attracted growing attention because they are considered to fabricate flexible electronic structures with their potential to bend, expand and manipulate electronic devices. The flexible devices have many performance advantages over conventional silicon based electronic devices as they are very lightweight, low processing temperature and low cost fabrication with large surface area [1,2]. Flexible circuits can be employed in a wide variety of applications, such as flexible flat-panel displays medical image sensors, photovoltaic, electronic paper, radio frequency identification tags, and flexible arrays of plastic microphones [3,4]. However, the additional number of steps and high-temperature processing to achieve high-performance flexible device, has limited the rate of implementation of semiconductor devices fabricated on flexible organic substrates.

The need for advanced materials is progressively focusing on composite systems that maintain or enhance the device performance. In some instances, the embedded system of binary high-*k* materials can not only replace the SiO_2 but suppress the leakage current with thin dielectric layer. To address the issue of leakage current, HfO_2 and ZrO_2 have been considered the most promising candidates for use as alternate gate dielectrics to replace SiO_2 [5]. However, pure HfO_2 or ZrO_2 suffers from mobility degradation, fixed-charged, and threshold voltage instabilities; whereby the development of combinatorial $Hf_xZr_{1-x}O_2$ thin film for future advanced gate dielectric application. It is recently reported that alloying zirconium into hafnium results to improve the film quality of high-*k* oxides without reducing their dielectric constants and increasing the leakage currents [6]. A composite system of these materials is very effective demand for a small system with scaled-down thickness [7,8]. In addition, to fabricate thin film of composite materials, a cost effective and elegantly simple way is sol–gel spin-coating technique [9]. The sol–gel method can mix various colloidal solvents and precursor compounds when metal halides are hydrolyzed under controlled conditions. The thin films are produced on a substrate by spin-coating or dip-coating, i.e., a small puddle of the fluid resin is placed at the center of a substrate, which is then spun at high speed. However, the dielectric films deposited at low temperature performs poorer properties and large current leakage due to numerous traps present inside the film. Thus, a challenge remains to develop a promising method to overcome these processing limitations. Reportedly, the oxygen (O_2) plasma treatment affects the performance of thin films deposited at low temperature through sol–gel process [9,10]. The electrical properties of such films can improve considerably after O_2 plasma exposure, with enhanced remnant polarization and decreased leakage current density.

In the current study we have developed a low temperature (ca. 250 °C) O_2 plasma enhanced method for preparing an $Hf_xZr_{1-x}O_2$ thin film-based MIM capacitor fabricated on a flexible organic PI substrate using sol–gel spin processing and insulating properties have been evaluated.

The insulating properties of MIM device prepared employing $Hf_xZr_{1-x}O_2$ film as a dielectric layer exhibited low leakage current density and maximum capacitance density. Therefore, we believed

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that $Hf_xZr_{1-x}O_2$ film would be a leading candidate for use in future flexible MOS devices as a stable gate dielectric.

2. Experiment

Plastic 25-μm thick DuPont Kapton® PI films were used as flexible substrates. They were cleaned ultrasonically with ethanol (Fluka; water content: <0.1%) for 30 min and deionized water and then high-pressure N_2 gas was used to remove the water and any remaining particles from the PI surface. Next, Cr (thickness: 10 nm; adhesion layer) and Au (thickness: 100 nm) were deposited for the gate electrode over the PI substrate using a thermal coater. To deposit $Hf_xZr_{1-x}O_2$ combinatorial thin film, a sol–gel solution was prepared by dissolving $HfCl_4$ (98%, Aldrich, USA) and $ZrCl_4$ (98%, Aldrich, USA) in ethanol as the solvent to yield a molar ratio of 2:1:1000; after adding a magnetic stirrer, the solution was heated under reflux while stirring for 30 min. The film was grown by spin-coating the sol–gel solution over PI at 3000 rpm for 30 s at room temperature using a Clean Track Model-MK8 (TEL, Japan) spin coater. The as-prepared samples were treated with O_2 plasma for 2 min in oxygen plasma reactor (Harrick Scientific Corp.), which supplied a plasma power of 30 W; subsequent annealing was performed in the presence of O_2 at 250 °C for 12 h (refer, OPT/A). Finally, 300-nm thick Al films were patterned as the top electrodes using shadow mask and a thermal coater.

The surface morphology of the $Hf_xZr_{1-x}O_2$ film over PI was evaluated using scanning electron microscopy (FE-SEM, JOEL JSM-5410, operated at 5 eV) and atomic force microscopy (AFM, Digital Instruments Nanoscope, D-5000) at a scan size of 2 μm and a scan rate of 1 Hz. We used ellipsometery techniques to measure the thickness of the $Hf_xZr_{1-x}O_2$ film. To characterize the leakage currents and capacitances of the films, we prepared them metal–insulator–metal (MIM) configuration represented in Fig. 1a. The leakage current density and electric field (*J*–*E*) measurements were performed using an Agilent-4156 probe station; the capacitance and voltage (*C*–*V*) was measured using an HP-4284A *C*–*V* analyzer. Fig. 1b displays a photograph of the flexible capacitor device on a ~25-μm thick PI substrate under a large surface strain, but without any cracks appearing on the surface.

3. Results and discussion

The combinatorial $Hf_xZr_{1-x}O_2$ film was prepared by spin-coating a sol–gel mother solution onto the Cr coated flexible PI substrate used for a gate insulator layer. Cr was used to make firm adhesion between PI and sol–gel derived $Hf_xZr_{1-x}O_2$ film. Fig. 2a and b presents top-view SEM images of the as-deposited, sol–gel spin-coated films after (a) baking at 80 °C and (b) annealing at 250 °C for 12 h. Many trap states were present over both films' surface, suggesting that they would directly affect the electrical performance of the device. When O_2 plasma pre-treatment was employed for 2 min on the as-grown sol–gel film and then annealing was performed at 250 °C for 12 h (abbreviated as OPT/A), a clean surface was generated. Fig. 2c displays the well-ordered, smooth and crack-free $Hf_xZr_{1-x}O_2$ film that was grown successfully on the PI substrate. The surface roughness of the insulator layer is another important factor affecting the performance of MOS devices. Here, we used tapping-mode AFM on a length scale of 2 μm × 2 μm to determine the surface roughness of the $Hf_xZr_{1-x}O_2$ film. Fig. 2d indicates the surface roughness of the film surface for the sample treated with OPT/A was 1.44 nm. We used an ellipsometery technique to measure the thickness of the film on PI. The average thickness of $Hf_xZr_{1-x}O_2$ film subjected to OPT/A-treatment was measured to be 10 nm.

We measured the quantitative leakage current and capacitance to evaluate the electric performance of the $Hf_xZr_{1-x}O_2$ film in the MIM configuration. Fig. 3a displays the *J*–*E* characteristics for the flexible MIM capacitors prepared under various sample treatment conditions. The as-deposited samples that were baked at 80 °C and annealed in the presence of O_2 at 250 °C for 12 h did not have sufficiently high thermal budgets and, thus, the their breakdown electric fields were relatively low and their leakage current densities were very high, i.e., 1.01×10^{-5} and 1.23×10^{-6} A/cm^2, respectively, at an applied voltage of −5 V. But, the superior low leakage current density was 3.22×10^{-8} A/cm^2 at −10 V for the sol–gel deposited $Hf_xZr_{1-x}O_2$ film subjected to OPT/A-treatment condition. The baking – only treated film exhibited the largest leakage current among these treated films because it had poor dielectric characteristics and numerous traps present within the film. A slight improvement in the electrical characteristics occurred for the annealing-only treated sample. The leakage current density decreased when the sample was treated with O_2 plasma for 2 min and then annealed at 250 °C for 12 h, indicating that the poorer leakage properties of the other two treated samples arose because of the existence of numerous traps over their film surfaces. The breakdown electric field (ca. 5.5 MV/cm) also increased when the sample was subjected to the OPT/A-treatment condition. The OPT/A-treated sample exhibited excellent electrical characteristics on the PI substrate because (i) the wet film underwent a high degree of oxidation under O_2 plasma treatment and (ii) subsequent annealing led to a reduction in the number of traps. The low leakage current of our flexible MIM capacitor is comparable with that of silicon-and glass-based capacitor devices [7,11].

The sol–gel mother solution was spin-coated over the PI substrate; the as-deposited film existed in the solid-state, presumably with a –HO–HfZr–O–HfZr–OR– structure based surface. It appeared that a homogeneous network of –O–HfZr–O–HfZr–O– bonds had not developed on the film surface and which is expected the combined organic impurities. There would be a direct interaction of active atoms and molecules in the plasma (O^+, O^-, O, O_2 and free electrons, etc.) with organic species available on the surface [9]. The power plasma induced the formation of some active oxygen species that reacted with model structure of HO–HfZr–O–HfZr–OR, resulting in partial oxidation. The imposing plasma gradually oxidized the as-deposited thin film, the film surface was near-complete oxidation to (–O–HfZr–O–)*n*; the organic part were completely removed.

To understand the carrier transport mechanisms of the OPT/A-treated hafnium–zirconium–oxide dielectric film, Fig. 3b presents a plot of ln(*J*) with respect to the square root of the applied electric

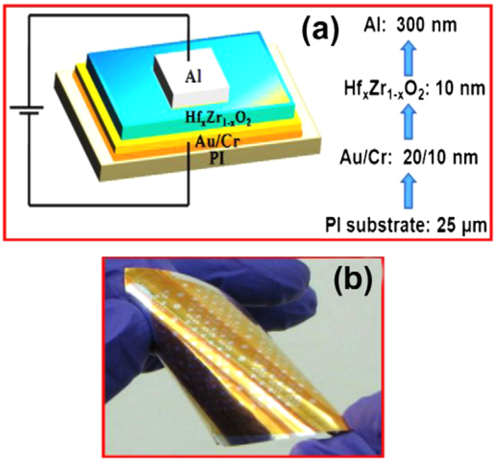

Fig. 1. (a) Schematic representation of an MIM capacitor featuring a binary $Hf_xZr_{1-x}O_2$ thin film on a PI substrate and (b) photograph of our MIM capacitor on the flexible ultra-thin PI substrate.

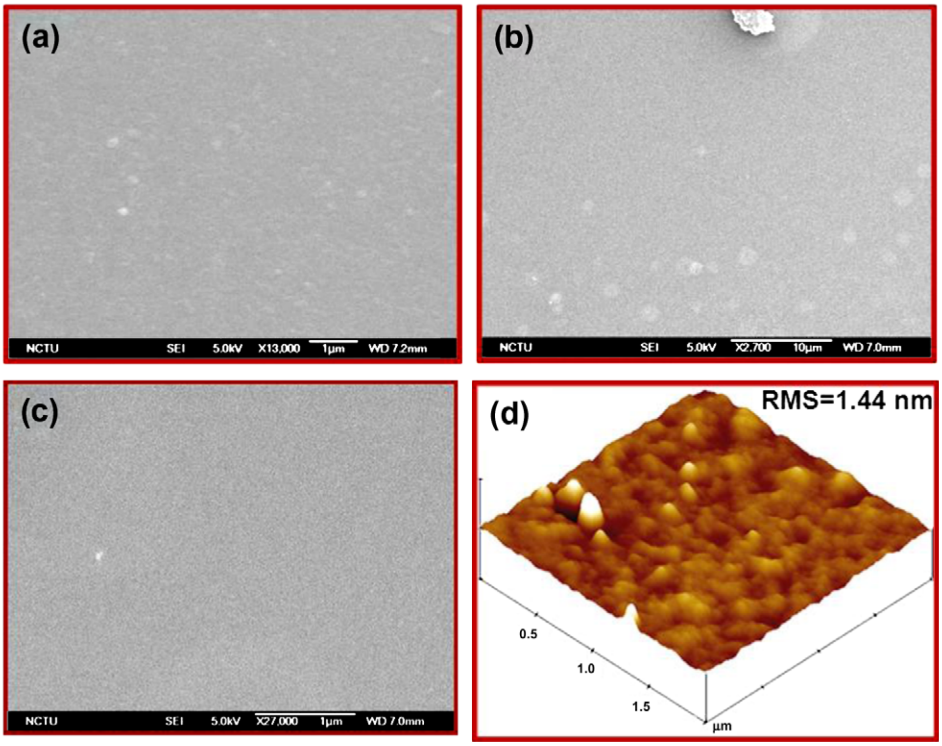

Fig. 2. (a–c) Top-view SEM images of as-deposited $Hf_xZr_{1-x}O_2$ films on Cr/PI substrates after (a) baking, (b) annealing at 250 °C for 12 h, (c) sequential O_2 plasma treatment and annealing at 250 °C for 12 h (OPT/A) and (d) tapping-mode AFM image of the film subject to OPT/A-treatment.

field ($E^{1/2}$). For standard Schottky–Richardson (SR) emission, the plot of ln(*J*) versus $E^{1/2}$ should be linear; can be expressed as [12].

$$J = A^{*}T^{2}\exp\left[\frac{-q\left(\phi_B - \sqrt{qE/4\pi\varepsilon_r\varepsilon_0}\right)}{KT}\right] \qquad (1)$$

where A^* is the effective Rechardson constant, $q\phi_B$ is the Schottky barrier height, ε_0 is the permittivity in a vacuum, and and ε_r is the dynamic dielectric constant. SR emission induced by the thermionic effect is caused by electron dominates the conduction mechanism [13]. The conversion of the current transport mechanism from trap-assisted tunneling for the as-deposited and annealing-only samples to SR emission for the OPT/A sample demonstrates theoretically that the sol–gel hafnium film was oxidized and traps were completely terminated. Fig. 3c presents plots of ln(*J*/*E*) versus $E^{1/2}$ for the baking and annealing only-treated $Hf_xZr_{1-x}O_2$ films; the inset displays a schematic energy band diagram that elucidates the leakage transport mechanisms. It is believed that the Poole–Frenkel (PF) emission is due to field-enhanced thermal excitation of trapped electrons in the bulk of the insulator. The conduction process at higher voltages is likely due to the PF emission, which is described by the equation [14].

$$J = CE\exp\left(\frac{-q\phi_t}{kT}\right)\exp\left[\frac{1}{rkT}\sqrt{\frac{q^3}{\pi\varepsilon_0 K_T}}\sqrt{E}\right] \qquad (2)$$

where *C* is a constant, *q*, *k*, *T*, and *E* represent the electronic charge, the Boltzmann constant, the temperature, and the electric field, respectively, ϵ_0 denotes the permittivity of free space, K_T is the high-frequency dielectric constant (square of the refractive index), and ϕ_t is the energy barrier separating the traps from the conduction band. The coefficient *r* is introduced to take into account the influence of the trapping or acceptor centers ($1 \leqslant r \leqslant 2$). As a result, the plot of ln(*J*/*E*) as a function of $E^{1/2}$ in Fig. 3c reveals that the as-deposited baking- and annealing-only samples possessed huge numbers of traps, which decreased the band gap in the $Hf_xZr_{1-x}O_2$ films because the thermal budget was insufficient to form dense and trap-free dielectric layers. The traps within the $Hf_xZr_{1-x}O_2$ film were not reduced after baking-only treatment; the device featured a high leakage current and a low breakdown electric field. For annealing-only sample, the traps inside the films had been reduced and the current transport mechanism was improved from trap-assisted tunneling to FP emission, but this improvement remained less obvious and resulted in poorer dielectric properties. Under treatment with O_2 plasma, the PF emission was gradually restrained. These findings confirm that the number of traps was minimized within low temperature deposited binary hafnium–zirconium–oxide film after the plasma treatment.

Fig. 4a displays the high frequency *C*–*V* characteristics of the MIM capacitor under different treatment conditions. The maximum capacitance densities at applied frequency of 10 kHz, were measured of 1.26 fF/μm^2 (as-dep), 2.06 fF/μm^2 (annealing-only) and 10.36 fF/μm^2 for OPT/A-treatment. Fig. 4b shows *C*–*V* curves of the $Hf_xZr_{1-x}O_2$ film at applied frequency of 1 MHz. The maximum capacitance density for as-deposited film was of 0.39 fF/μm^2, for annealing-only was of 3.20 fF/μm^2 and for OPT/A-treated film was found to be 9.42 fF/μm^2 at 1 MHz. According to recent publication [15], the trapping states in the high-*k* film severely affect the capacitance property. The polarization ability of the $Hf_xZr_{1-x}O_2$ film depends on the degree of oxidation, the more oxidized $Hf_xZr_{1-x}O_2$ film reveals higher capacitance value and lower leakage current. If the trapping states exist in the $Hf_xZr_{1-x}O_2$ film, the polarization ability will be diminished, and therefore decrease the capacitance. Again, it can be concluded that the effects of the O_2 plasma pre-treatment is adopted in low temperature processing to enhance the capacitance properties at different applied frequencies to the flexible MIM capacitor devices. Further, the highest maximum capacitance for this low temperature deposited $Hf_xZr_{1-x}O_2$ film then OPT/A pre-treatment on the PI would allow its

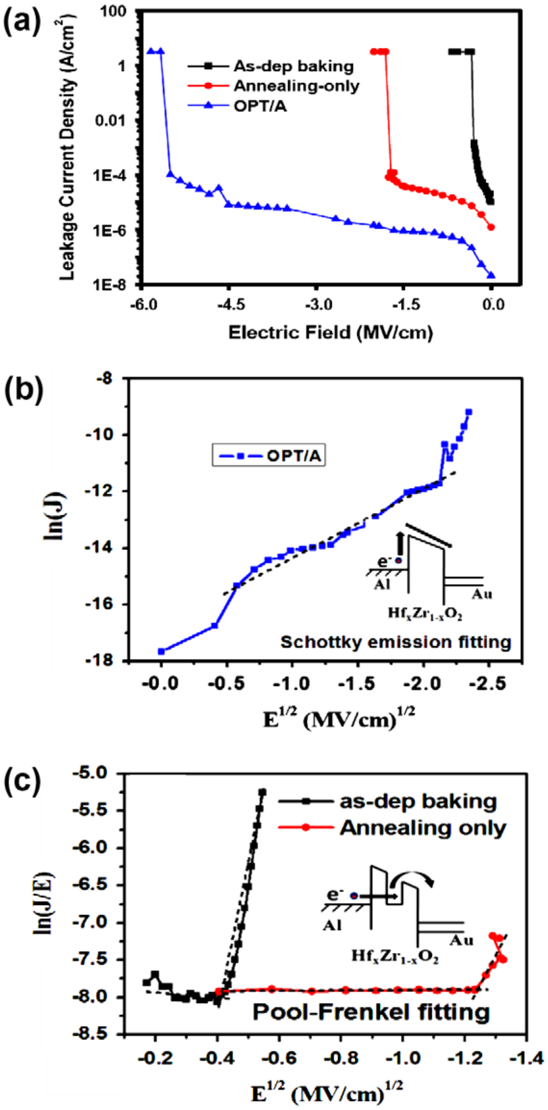

Fig. 3. (a) Plots of leakage current density versus electric field under an applied negative voltage for samples prepared using all three treatment conditions, (b) plot of ln(*J*) versus the square root of electric field ($E^{1/2}$) for the OPT/A-treated sample and (c) plot of ln(*J*/*E*) versus ($E^{1/2}$) for the two samples. The corresponding schematic energy band diagrams are presented to explain the SR and PF emissions.

future flexible electronic devices to be operated in the low voltage regime.

And, the dielectric constants of the $Hf_xZr_{1-x}O_2$ film subjected to OPT/A-treatment condition, calculated from the capacitance and physical thickness measured by ellipsometery; were approximately 14.3 and 12.8 for 10 kHz and 1 MHz, respectively. However, the addition of these elements actually lowers the dielectric constant of pure HfO_2 or ZrO_2 films. The addition of metal elements had made to improve the electrical properties such as the breakdown voltage and leakage currents compared to pure HfO_2 or ZrO_2 films. The observation of the calculated value of *k* is lower, but consistent with the previous results for calculated dielectric constant of $Hf_xZr_{1-x}O_2$ film from atomic layer deposition [7]. The calculated value of *k* is sharply decreased as the film thickness was very low (~10 nm) by means of Lorenz's local field theory [16]. The mixed $Hf_xZr_{1-x}O_2$ dielectric materials with dielectric constants of about 14 or above, replace the conventional SiO_2-based low-*k* dielectric materials with dielectric constants of about four or below.

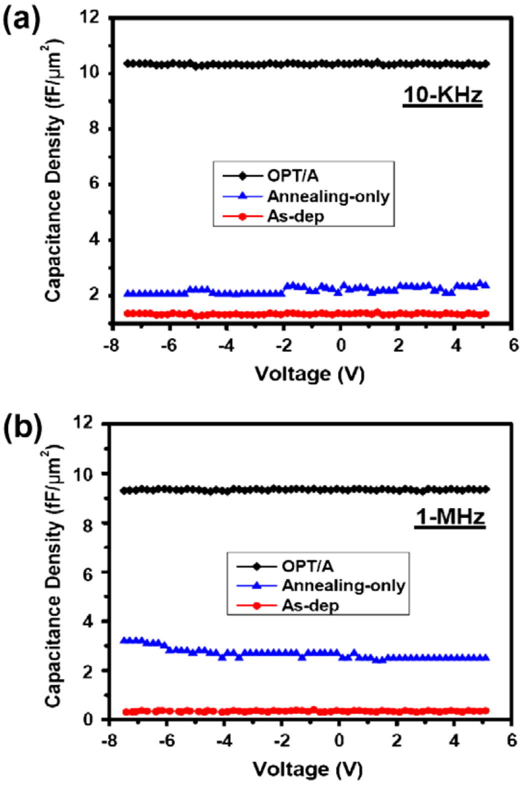

Fig. 4. Plot of capacitance density (*C*) as a function of the applied voltage (*V*) under as-deposited, annealed and OPT/A-treatment conditions at applied frequency of (a) 10 kHz and (b) at 1 MHz.

4. Conclusion

We have investigated the intrinsic dielectric and surface properties of sol–gel deposited $Hf_xZr_{1-x}O_2$ film on the flexible PI substrate. MIM-structured device prepared using $Hf_xZr_{1-x}O_2$ film as a dielectric layer exhibited low leakage current density of 3.22×10^{-8} A/cm^2 at -10 V and maximum capacitance density of 10.36 fF/μm^2 at 10 kHz and 9.42 fF/μm^2 at 1 MHz. The surface properties and electrical performance of this film verified the effectiveness of applying low temperature plasma processing to the fabrication of future soft devices. It is expected that amorphous combinatorial $Hf_xZr_{1-x}O_2$ would be a leading candidate for use in future flexible metal–oxide–semiconductor imaging devices as a stable gate dielectric fabricated through processing at low temperature.

Acknowledgments

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