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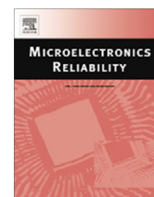

Plasma-enhanced flexible metal–insulator–metal capacitor using high-*k* ZrO_2 film as gate dielectric with improved reliability

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ABSTRACT

We demonstrate a new flexible metal–insulator–metal capacitor using 9.5-nm-thick ZrO_2 film on a plastic polyimide substrate based on a simple and low-cost sol–gel precursor spin-coating process. The surface morphology of the ZrO_2 film was investigated using scan electron microscope and atomic force microscope. The as-deposited ZrO_2 film under suitable treatment of oxygen (O_2) plasma and then subsequent annealing at 250 °C exhibits superior low leakage current density of 9.0×10^{-9} A/cm^2 at applied voltage of 5 V and maximum capacitance density of 13.3 fF/μm^2 at 1 MHz. The as-deposited sol–gel film was completely oxidized when we employed O_2 plasma at relatively low temperature and power (30 W), hence enhancing the electrical performance of the capacitor. The shift (Zr 3d from 184.1 eV to 184.64 eV) in X-ray photoelectron spectroscopy of the binding energy of the electrons towards higher binding energy; clearly indicates that the O_2 plasma reaction was most effective process for the complete oxidation of the sol–gel precursor at relatively low processing temperature.

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1. Introduction

Flexible electronic devices on plastic substrates have attracted growing attention. These new type of flexible devices have potential for development of electronic devices because of a wide variety of applications. Flexible electronic device assemblies have many advantages over silicon or glass based electronic devices that are inexpensive, lightweight, large aspect ratios, ease and modified processing of surface morphology, transparent to visible/UV and allowing the board to conform to a desired shape [1–3]. Many groups have been explored some practical methods to fabricate various devices on flexible substrates. John A. Rogers reported carbon nanotube thin-film integrated circuits on flexible plastic substrate [4]. Maher Al-Ibrahim indicated the polymer solar cells fabricated on flexible polyester foils [5]. However, yet no research have provided a suitable, simple method to fabricate a superior high-*k* film over flexible substrate.

Plastic substrates damaged at the high processing temperature during annealing or depositing the film, mainly this is because of their intrinsic low thermal compatibilities. This is the reason that conventional semiconductor process could not be employ to deposit high quality SiO_2, Si_3N_4 or poly-Si films directly on plastic substrates. Many techniques of thin film fabrication at medium temperature have been proposed to prepare insulating dielectric thin films such as atomic layer deposition (ALD) [6] and physical vapor deposition (PVD) [7,8] methods. In addition, there is a cost effective and elegantly simple way to obtain a very smooth, continuous and crack free ZrO_2 thin film at room temperature under normal pressure system instead of high vacuum system. That is sol–gel spin-coating technique [9,10]. Thin films produced on a piece of substrate by spin-coating or dip-coating when a small puddle of a fluid precursor on the center of a substrate and then spinning the substrate at high speed. Further, the oxygen (O_2) plasma is very important technique to improve the electrical characteristics of such sol–gel deposited film as it is directly interrelated to the performance of low process temperature based electronic devices [11].

In current study, we have developed a low temperature plasma enhanced method for preparing ZrO_2 thin film as high-*k* dielectric layer in metal–insulator–metal (MIM) structured capacitor on a flexible polyimide substrate. The sol–gel spin-coating technique has proposed for the flexible device fabrication and possesses the advantage over other standard plasma oxidized technology as it provides high oxidation speed with a wet film, relatively at lower treating temperature. The novelty of this work is the low-temperature plasma-assisted growth of ZrO_2 thin film on flexible polyimide (PI) substrate. To the best of our knowledge, they still lack of literature that reporting the reliable ZrO_2 film based device on plastic PI substrate with satisfactory electrical properties. In addition to the industrial processing of flexible electronic devices, O_2 plasma assisted sol–gel spin technique can be successfully

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accepted to the depositing of high-*k* nanocomposite materials on flexible substrate for future electronic device fabrication.

2. Experiment

Plastic 25 μm-thick DuPont Kapton® polyimide (PI) films were used as flexible substrates for device fabrication. The PI films were immersed in ethanol (Fluka; water content: <0.1%) and employed an ultrasonic cleaner to clean the PI films for 10 min. The rinsing process was very important because the remaining particles would induce impurities over PI surface. Next, chromium (20 nm-thick) and gold (100 nm-thick) films for bottom electrode were deposited on PI substrate by thermal evaporator. The chromium layer between PI substrate and gold layer was used for obtained excellent adhesion, single gold layer contacted with PI substrate existed poor adhesion and peeled off the substrate easily. The sol–gel solution was prepared by the precursor of $ZrCl_4$ (98%, Aldrich, USA) with most suitable concentration between 0.01 and 0.06 g dissolved into 10 ml of ethanol. The magnetic stirrer was put into the solution and was refluxed under stirring for 15 min. The thin film growth was carried out when sol–gel solution was coated on Au/Cr-coated PI by spin-coater at 3000 rpm for 30 s. The as-prepared thin films were treated with oxygen (O_2) plasma power (30 W) for 2 min in O_2 plasma reactor and subsequent annealing treatment was performed at 250 °C (hereafter referred as OP-A) for evaporating the solvent. The duration of the annealing treatment was 12 h. Beside OP-A condition, we also used different sequences of treatment steps to further investigate the efficiency of O_2 plasma treatment. The sol–gel films performed only annealing treatment at 250 °C (referred as AT) and annealing followed oxygen plasma treatment (referred as A-OP). Finally, 300 nm-thick aluminum films as top electrodes were deposited by thermal evaporator for making sandwich-like configuration, i.e., metal–insulator–metal (MIM) structure to evaluate the electrical characteristics.

The surface morphology of the ZrO_2 film over PI was evaluated using scan electron microscope (FE-SEM, JOEL JSM-5410, operated at 5.0 kV) and atomic force microscope (AFM, Veeco Dimension 5000 Scanning Probe Microscope) at scale size of 5 μm × 5 μm and scan rate of 1 Hz. The thickness was measured using ellipsometry techniques. We used X-ray photoelectron spectroscopy (XPS) to analyze the bonding elements under various treatment conditions. The leakage current density and capacitance density of the film were characterized in MIM configuration as represented in Fig. 1a. And, Fig. 1b displays a photograph of the flexible capacitors bent at a 5 mm radius of curvature and fold near 360° angles, but without any cracks appearing on the surface. The photograph shown in Fig. 1b indicates the excellent bendability of capacitor on the PI substrate.

3. Results and discussion

Fig. 1c displays the SEM result revealed a well ordered, smooth and crack free ZrO_2 film subjected to OP-A treatment condition was successfully grown on the PI substrate. When O_2 plasma of pretreatment was employed for 2 min on the as-grown sol–gel film and then subsequent annealing was performed at 250 °C for 12 h then, the clean surface was generated. The surface roughness of the insulator layer is another important parameter, which affect the performance of the MOS devices. The AFM image shown in Fig. 1d indicates the roughness of the surface was to be 0.8 nm subjected to OP-A treated film on scale size of 5 μm × 5 μm. Thus, the ZrO_2 film over PI substrate had occurred uniform surface morphology after OP-A treatment condition. The average thickness of ZrO_2 film was measured to be 9.5 nm. Fig. 2a shows the leakage current density versus electric field (*J*–*E*) characteristics for the flexible MIM capacitor when the samples carried out with different sequences of oxygen plasma treatment. The AT-treated sample did not acquire sufficiently high thermal budgets and thus, the breakdown electric field of the AT sample was relatively very low. In our efforts on using sol–gel method to fabricate excellent ZrO_2 thin films for gate dielectric layer, the leakage current density depended on the annealing temperature [10]. As increased the annealing

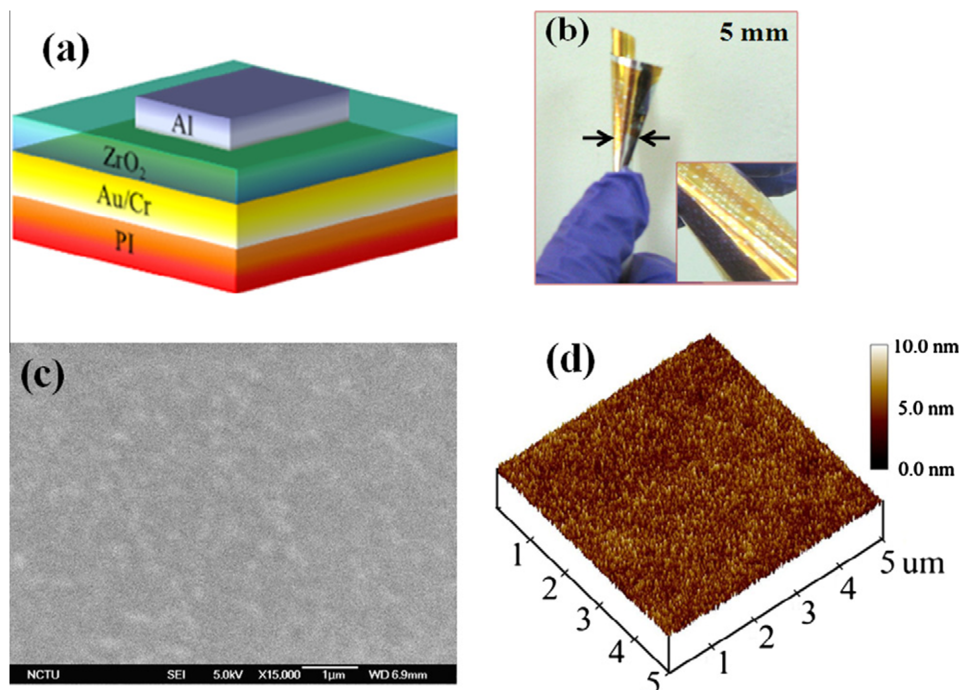


Fig. 1. (a) The schematic illustration of a MIM capacitor structure on flexible PI substrate, (b) photographs view of our flexible capacitor bent at 5 mm radius of curvature; inset: shows flat view, and (c) and (d) show top view SEM and AFM images of OP-A sample, the roughness of the surface was to be 0.8 nm on scale size of 5 μm × 5 μm.

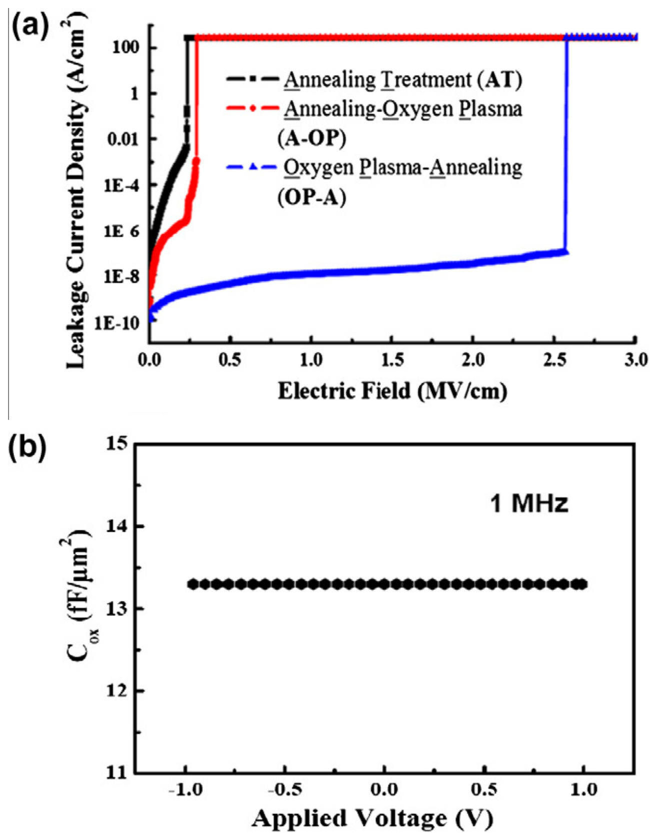


Fig. 2. (a) Leakage current density measured at various applied voltages for the flexible MIM capacitor with different sequences of treatment steps and (b) capacitance density versus applied voltage for OP-A only treatment condition.

temperature of the ZrO_2 thin films, sufficient thermal budgets recovered the traps and defects in the ZrO_2 films by active oxygen atoms and compact the films which show lower leakage current density. According to the conventional process of oxygen plasma treatment [11], the A-OP sample was fabricated to explore the effect of plasma treatment. This investigation indicates the poor leakage current density ($\sim 2 \times 10^{-6}$ A/cm^2 at 1 V) and meager breakdown electric field (~0.25 MV/cm) when we performed annealing process at 250 °C for 12 h and then carried out the oxygen plasma process. But, many researches indicated the plasma treatment would impact the performance of devices, but the efficiency of plasma power was limited.

Fig. 2a shows the strong evidence that insufficient annealing temperature and limited treatment induced the poor electric properties of the ZrO_2 films. Further, a significant improvement in leakage current density was found for sample treated under OP-A condition; the leakage current density of 9.0×10^{-9} A/cm^2 at applied 5 V and breakdown field was up to 2.5 MV/cm. However, the OP-A sample displays excellent electrical performance compared than the AT and A-OP treatment conditions because the ZrO_2 films obtained high degree of oxidation. The low leakage current density for our flexible capacitor device is comparable to the silicon-based capacitor device [12]. Fig. 2b shows the capacitance versus voltage (C–V) characteristics of our capacitor device. Here, we have only measured the capacitance density for the OP-A-treated ZrO_2 film; the maximum capacitance density was measured of 13.3 fF/μm^2 at 1 MHz. In addition, according to the capacitance and thickness data, the estimated dielectric constant was 14.8. However, the k value for ZrO_2 thin film based flexible capacitor is still higher than that of SiO_2 (k = 3.8). The value of calculated dielectric constant is low than pure ZrO_2. This is because of the Lorenz's local field theory as decreased as the film thickness is very low (~10 nm) [13].

When the sol–gel solution was coated on the gold bottom electrode without baking, the film was at a wet state, by means the distance of each zirconia atoms on the surface was far as depicted in model structure of Fig. 3a. We used a plasma oxidation growth mechanism at low temperature to examine the influence of O_2 plasma on the as-deposited zirconia film. The sol–gel solution comprising $ZrCl_4$ dissolved into ethanol and then coated over the flexible Au/Cr/PI substrate. Fig. 3b displays the chemical reaction of oxygen plasma on the as-deposited sol–gel film. It was expected that there would be a direct interaction of active atoms and molecules in the plasma (O^+, O^-, O, O_2, free electrons, etc.) [2] with organic species available on the surface. The power plasma induced the formation of some active oxygen species that reacted with the zirconic film, resulting in partial oxidation to zirconium sol–gel film. The O_2 plasma treatment gradually oxidized the as-deposited thin film. In the final step Fig. 3c, the film surface was near-complete oxidation to ZrO_2 using plasma oxidation; the organic parts were completely removed. This effect of oxidation through O_2 plasma treatment of the as-grown film was influenced the upper surface of the film and the oxidation occurred at low temperature than conventional high-temperature annealing on thin film. The process allows high-performance electronic devices to be fabricated on plastic PI substrate via low power plasma technology.

X-ray photoelectron spectroscopy (XPS) was performed to examine the chemical composition of the samples. Fig. 4 shows the comparison of the high resolution XPS spectra for Zr 3d bonding for samples at different sequences of oxygen plasma treatment. The high-resolution spectra were measured at three different positions of AT, OP-A and A-OP samples, respectively. The shift in binding energy of Zr 3d from 184.1 eV of the AT sample to 184.64 eV of the OP-A sample was clearly obtained. This observation relates to the oxidization of the Zr atom toward blue shift [14,15] and hence

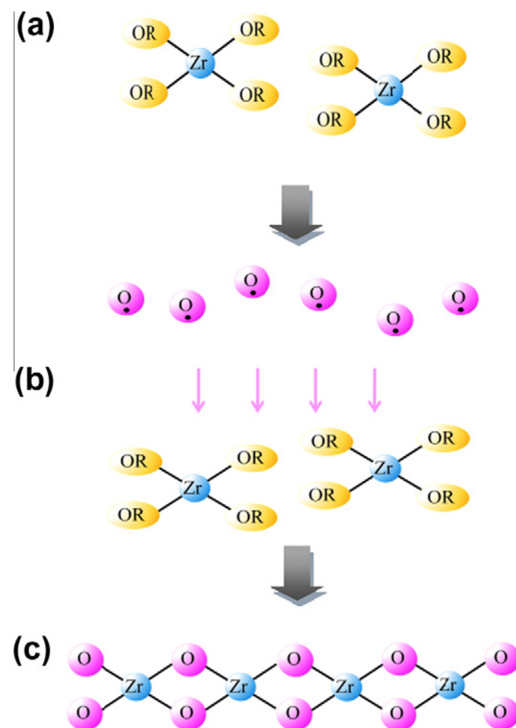


Fig. 3. Schematic representation of the O_2 plasma growth mechanism for sol–gel-derived spin-coated ZrO_2 film.

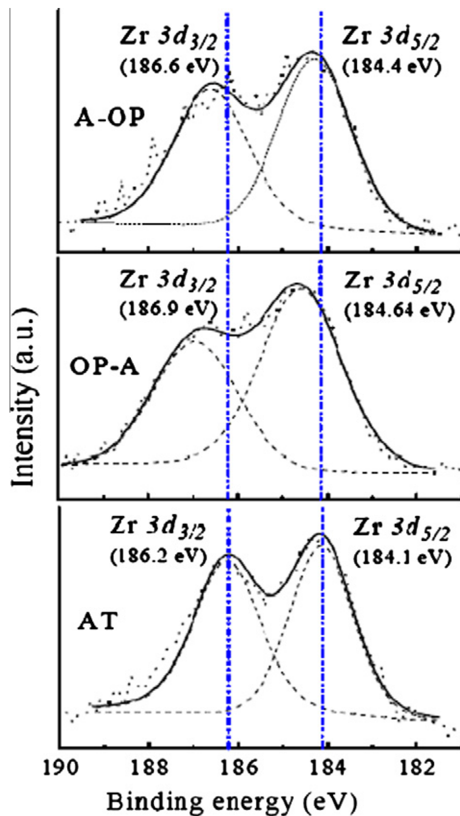
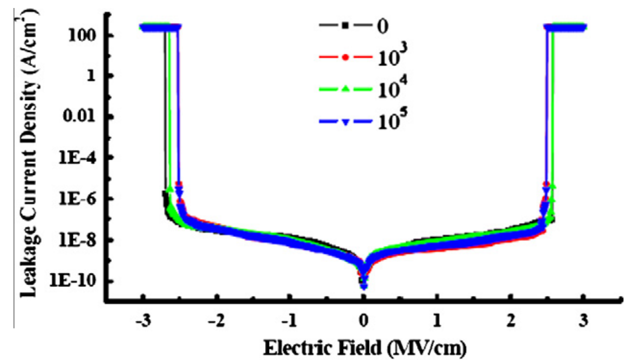


Fig. 4. Zr 3d XPS spectra of the sol–gel thin films after different sequences of oxygen plasma treatment. Dotted curves, dashed curves and solid curves represent the experimental results, the fitted peaks, and the summarized results of the fitted data.

accordingly, it can be concluded that XPS confirms the fabrication of zirconia film by our sol–gel procedure. Here, we pointed out the most important thing of aging effect of the O_2 plasma, i.e., the surface modification of the zirconia thin film was investigated. XPS results suggested that the O_2 plasma treatment introduced some polar groups (such as O=Zr—O) to film surface. It seemed that there exists an optimum treatment condition for ZrO_2 films prepared by sol–gel processes and treated by oxygen plasma.

Fig. 5 illustrates the leakage current density versus voltage characteristics for the ZrO_2 films subjected to OP-A only treatment condition. The film had low leakage current density in different bending times for both applied negative and positive biased voltages. The bending setups indicate the number of bend times and sample under bend test depicted and viewed in photo of Fig. 5. The sample without any bending treatment, the leakage current was measured to consider the initial MIM-capacitor properties and revealed the electrical characteristic of ZrO_2 film had available performance. The electrical characteristics of ZrO_2 films under O_2 plasma treatment are analogous to it under 500–600 °C annealing temperature. The liquid condition of sol–gel films in spin-coating process revealed the high oxidative capability compared to solid films because the distance of each Zr atoms in liquid was longer than it in solid condition because activated oxygen gained more probability to oxide Zr atoms. The measurements of the electrical characteristics under bend test for 10^3, 10^4 and 10^5 times were carried out; we obtained the curves without any change and strong adhesion between Zr and Au films via Cr. This result indicates the use of spin-coating process for ZrO_2 films provides superior electrical performance and reliability for MIM structure. Thus, it can be concluded from this work the performance of the flexible based devices is comparable to that of silicon and glass-based devices even after bending the device up to 10^5 times. It was an attractive result because of the highest process temperature is only 250 °C in annealing processes of the fabricate ZrO_2 films, the electrical characteristic will not improve. The effect of oxygen plasma in our experiments supports a useful method to fabricate ZrO_2 films as a stable insulator layer with improved reliability during low temperature processing as necessary for soft devices.



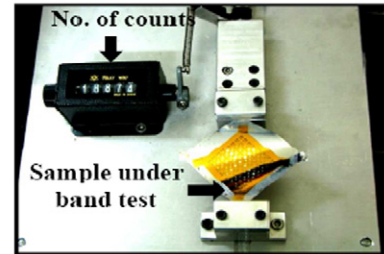


Fig. 5. Leakage current density measured at various applied voltages for the flexible MIM capacitor subjected to OP-A only treatment under different bending times. The bending setup indicates the number of bend times and sample under bend test.

4. Conclusion

The integration of metal–insulation–metal capacitor device comprising high-*k* ZrO_2 thin film on a flexible polyimide substrate via sol–gel spin-coating is successfully demonstrated. The surface morphology of the ZrO_2 film was investigated using scan electron microscope and atomic force microscope. The flat and smooth thin film using sol–gel process to fabricate ZrO_2 film on a flexible PI substrate is achieved under low temperature manufacturing process. The material properties and electrical performance of this ZrO_2 film verify the effectiveness of low power (30 W) O_2 plasma treatment. Prior to use in advanced flexible devices; the electrical behavior was analyzed under bend test, revealed that our flexible capacitor functioned independent of the number of bend times. We believe that sol–gel deposited high-*k* ZrO_2 film is a leading candidate for application in future flexible devices as a stable high-*k* dielectric layer fabricated at low process temperature.

Acknowledgments

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