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Structural and electrical properties of $(Zr,Ti)_{0.85}(Ca,Sr)_{0.15}O_{1.85}$ thin films grown on $Cu/Ti/SiO_2/Si$ substrate using RF magnetron sputtering

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$(Zr,Ti)_{0.85}(Ca,Sr)_{0.15}O_{1.85}$ (ZTCS) films grown on Cu electrode at room temperature showed a crystalline cubic stabilized ZrO_2 structure when large sputtering powers (≥ 75 W) were used. The smoothest film, grown at sputtering power of 75 W, showed the lowest leakage current (4.0×10^{-6} A/cm^2 at 0.75 MV/cm) and highest breakdown voltage (2.7 MV/cm) among all the films prepared, indicating that surface roughness considerably influences the electrical properties of the ZTCS film. A dielectric constant (k) of 21.5 and a tan δ of 0.007 were obtained at 100 kHz, and a similar k of 19.4 with a high quality factor of 52 at 2.0 GHz. Moreover, a high capacitance density (78 nF/cm^2) and a small TCC (256 ppm/°C at 100 kHz) were obtained. Such a ZTCS film therefore satisfies the requirements of the International Technology Roadmap for Semiconductors for capacitors grown on organic substrates for 2016.

Key words: Dielectric, Thin Film, Embedded Capacitor.

Introduction

With the development of mobile devices, the size reduction of passive devices such as resistors, inductors, and capacitors has now become essential [1, 2]. In particular, since the capacitor occupies a large area in the electronic device, research into capacitor size reduction has increased. Miniaturization of capacitors can be achieved by their embedment in printed circuit boards (PCBs). Furthermore, embedded capacitors have less parasitic inductance than surface mount capacitors [3-6]. Therefore, it is necessary to develop embedded capacitors that enable further miniaturization and performance enhancement of electronic devices. In order to synthesize a capacitor inside a PCB, the dielectric thin film must be grown at low temperatures (≤ 300 °C). Moreover, according to the International Technology Roadmap for Semiconductors (ITRS) for a capacitor grown on an organic substrate for the future (by 2016), the device should have a high capacitance of 5.0 nF/cm^2 with a high quality factor (Q) of 50 at radio frequency and a breakdown voltage greater than 100 V [7]. Therefore, it is necessary to develop new dielectric thin films which have a large dielectric constant (k) with a low tan δ, are good insulators, and have a low growth temperature.

Cubic stabilized ZrO_2 (CSZ) ceramics have been referred to as the oxygen conductors because they contain many oxygen vacancies [8]. As a result, these ceramics have been investigated for applications in electrolytes, oxygen sensors, solid-state batteries, and solid oxide fuel cells [9-13]. However, the dielectric properties of these CSZ materials are rarely investigated. Recently, crystalline $(Zr,Ti)_{0.85}(Ca,Sr)_{0.15}O_{1.85}$ (ZTCS) films, which have a CSZ crystal structure, have been grown on $Pt/Ti/SiO_2/Si$ at RT and showed good dielectric properties: a k of 30.4 with a tan δ of 0.007 at 100 kHz, Q of 225 at 1.0 GHz, TCC of −60.7 ppm/°C at 100 kHz, and a breakdown electric field of 1.85 MV/cm [14]. Therefore, it is considered that ZTCS films are a good candidate for use in embedded capacitors in PCBs. Because Cu is generally used as the electrode metal in PCBs, ZTCS films should be grown on the Cu electrode for the application of an embedded capacitor in PCBs. However, Cu ions easily diffuse into the film and oxidize, which is undesirable for their application in embedded capacitors. Therefore, in this work, ZTCS films were grown on $Cu/Ti/SiO_2/Si$ (Cu-Si) at RT under an Ar atmosphere at various sputtering power values, and their microstructure and electrical properties were investigated to evaluate their potential for use in embedded capacitors.

Experimental and Discussion

ZTCS films were grown on Cu-Si substrates by rf-magnetron sputtering at RT using a 2.0-inch-diameter $(Ca_{0.7}Sr_{0.3})(Ti_{0.2}Zr_{0.8})O_3$ target. The target was synthesized at 1400 °C for 3 hrs by using the conventional solid-state

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method. Deposition was carried out in an Ar atmosphere with a total pressure of 5 mTorr. Various sputtering powers ranging between 25 and 100 W were used for the growth of the films. The crystal structure of the films was examined by X-ray diffraction (XRD; D/Max-2500/PC, Rigaku, Tokyo, Japan). Microstructure and surface roughness of the films were investigated using scanning electron microscopy (SEM; Hitachi S-4800, Hitachi High-Tech, Tokyo, Japan) and atomic force microscopy (AFM; Dimension 3100 Nanoman, Veeco, Santa Barbara, CA), respectively. The film interface was investigated using Auger electron spectroscopy (AES; Physical Electronic PHI 680 Auger electron spectroscope, ULVAC-PHI, Inc., Chigasaki, Japan). Pt was deposited on the films by conventional dc sputtering to form a top electrode of a metal-insulator-metal (MIM) capacitor. The top electrode was patterned using a shadow mask to form a 380-μm-diameter disk. The leakage current of the films was measured using a programmable electrometer (Keithley 6517, Keithley Instruments, Inc., Cleveland, USA). The capacitance and dissipation factor of the films were measured using an LCR meter (Agilent 4285A, Agilent Technologies, Palo Alto, USA). To measure their dielectric properties in the rf range, Al was deposited on the films as the top electrode by using rf magnetron sputtering. The Al electrode was patterned to form a circular patched-capacitor structure by photolithography. The complex reflection coefficient of the films was measured from 0.5 to 5 GHz by using a vector network analyzer (Agilent (HP) 8510C Network Analyzer, Agilent Technologies, Palo Alto, CA). The k and tan δ values of the films were calculated from two reflection coefficients of capacitors having different inner diameters but equal outer diameters [15, 16].

Fig. 1(a) shows a cross-sectional SEM image of a ZTCS film grown on a Cu electrode at RT under Ar atmosphere with a sputtering power of 75 W. A 240-nm-thick ZTCS film was well formed on the Cu electrode exhibiting a continuous interface. Fig. 1(b) shows an Auger depth profile of the ZTCS film grown on a Cu electrode under Ar atmosphere. No diffusion of Cu ions, nor Zr, Ti, Ca, Sr, and O ions, into the ZTCS film or the bottom Cu electrode was detected, indicating the formation of a chemically sharp interface between the ZTCS film and Cu electrode.

Figs. 2(a-d) show XRD patterns of ZTCS films grown at RT using various sputtering powers. For the film grown using a sputtering power of 25 W, peaks for the crystalline ZTCS phase were not observed, indicating the formation of a primarily amorphous ZTCS phase. Peaks for the crystalline ZTCS phase, which has a CSZ structure, appeared for the film grown using a sputtering power of 50 W (see Fig. 2(b)). The intensities of these peaks increased with increasing sputtering power and the (111) and (200) peaks of the ZTCS phase were clearly observed with a relatively large intensity for the films grown using the sputtering power of 75 and 100 W, as shown in Figs. 2(c) and 2(d). Therefore, although a $(Ca_{0.7}Sr_{0.3})(Ti_{0.2}Zr_{0.8})O_3$ target was used for sputtering, the crystalline ZTCS phase was well developed in the films grown with a sputtering powers larger than 25 W. However, since the intensities of these peaks were smaller than those of the ZTCS films grown on a Pt electrode at RT, [14] the crystallinity of the ZTCS film grown on a Cu electrode could be lower than that of the ZTCS film grown on a Pt electrode. In addition, it is worth a mention that the perovskite $(Ca_{0.7}Sr_{0.3})$

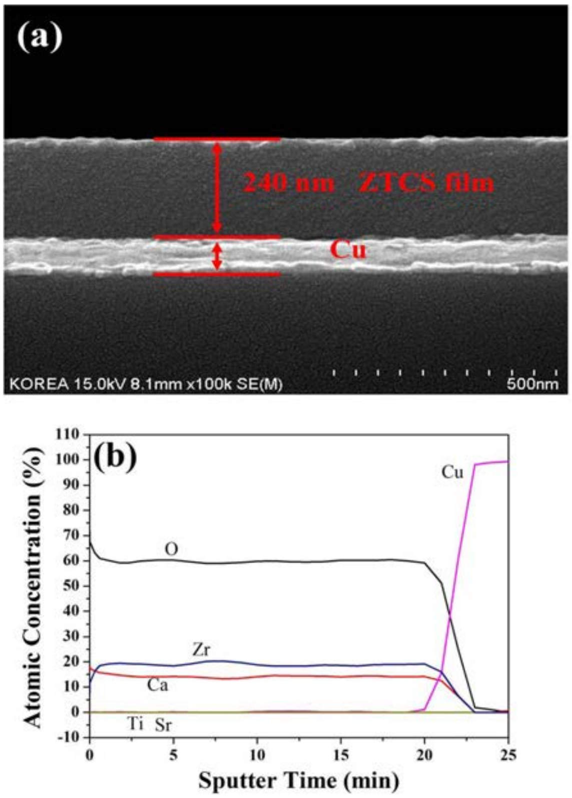

Fig. 1. (a) Cross-sectional SEM image and (b) Auger depth profile of a ZTCS film grown on a Cu electrode at RT under Ar atmosphere.

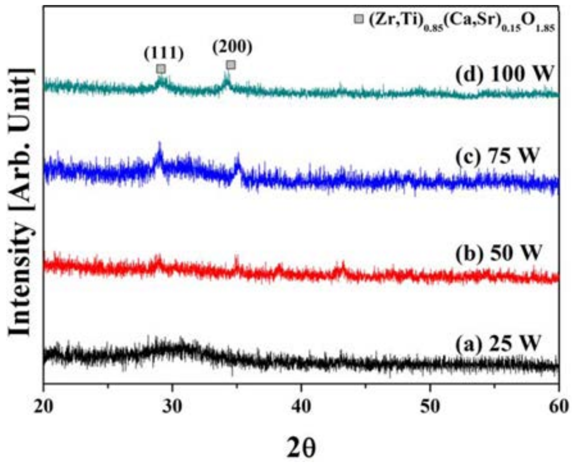

Fig. 2. XRD patterns of ZTCS films grown at RT under Ar atmosphere using various sputtering powers: (a) 25 W, (b) 50 W, (c) 75 W, and (d) 100 W.

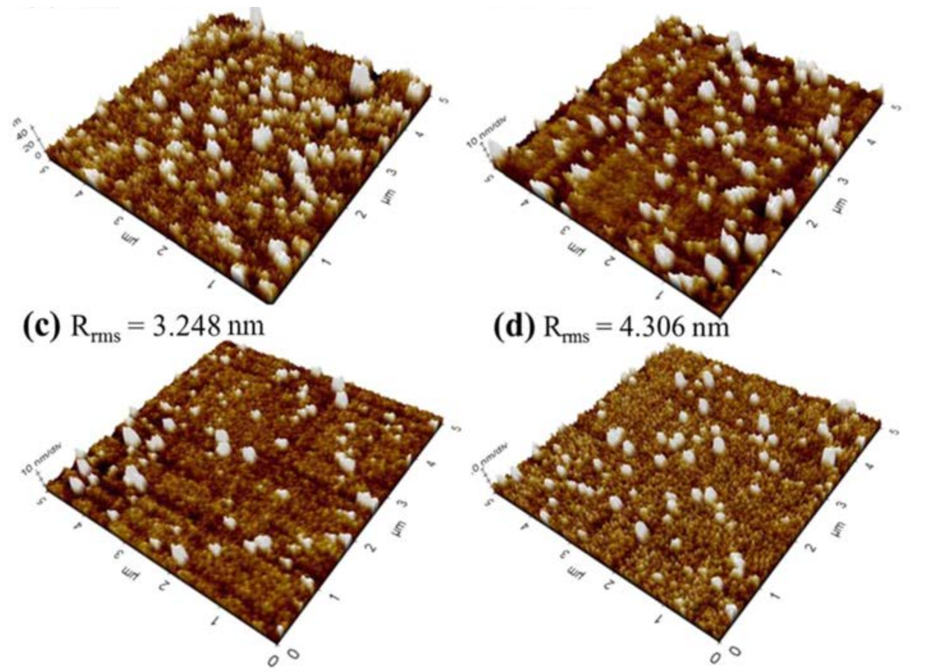

Fig. 3. AFM images of ZTCS films grown under Ar atmosphere using various sputtering powers: (a) 25 W, (b) 50 W, (c) 75 W, and (d) 100 W.

$(Ti_{0.2}Zr_{0.8})O_3$ phase was not formed in these films, although a $(Ca_{0.7}Sr_{0.3})(Ti_{0.2}Zr_{0.8})O_3$ sputtering target was used for the growth of the films. According to a previous study, when a $CaZrO_3$ target was used for the growth of the films using pulsed laser deposition, an orthorhombic perovskite $CaZrO_3$ phase was formed only if they were grown under high oxygen pressure [14, 17]. However, for films grown under low oxygen pressure, the CSZ phase was formed [17]. Similar results were observed for ZTCS films grown on a Pt electrode [14]. For the growth of ZTCS films on a Cu electrode, the films must be grown under an Ar atmosphere without oxygen in order to prevent the oxidation of the Cu electrode. Therefore, it is considered that a film having a CSZ structure, such as the ZTCS phase, is expected to form on the Cu electrode.

The surface roughness of the ZTCS films grown under an Ar atmosphere using various sputtering powers was studied using AFM, as shown in Figs. 3(a-d). For the film grown using the low sputtering power of 25 W, a rough surface with a root mean square surface roughness (R_{rms}) of 6.1 nm developed. For this film, the sputtered particles might not have sufficient energy to move on the surface after the deposition, resulting in the amorphous phase with a large R_{rms} value. The R_{rms} value of the films decreased with increasing sputtering power and the film grown using a sputtering power of 75 W exhibited a relatively small R_{rms} value of 3.2 nm probably owing to the formation of a ZTCS film with good crystallinity. However, it slightly increased to 4.3 nm for the film grown with a sputtering power of 100 W, which could be due to an increased grain size [18].

The leakage current densities of the ZTCS films grown using various sputtering powers were also studied, as shown in Fig. 4. A large leakage current density was obtained from the film grown using a sputtering power of 25 W and it slightly decreased for the films grown using sputtering powers of 50 and 100 W. Moreover, the film grown using a sputtering power of 75 W exhibited the lowest leakage current density of 4.0×10^{-6} A/cm^2 at 0.75 MV/cm with a high breakdown field of 2.7 MV/cm. Therefore, the variation of the leakage current density of the ZTCS films is similar to that of the R_{rms} value of the films (see the inset of Fig. 4). Since the interface between the Pt top electrode and the ZTCS film could be influenced by the surface roughness of the film, better electrical properties are expected for films with a smooth surface, as shown in Fig. 4. These results indicate that the surface roughness considerably influenced electrical properties of the ZTCS film such as leakage current and breakdown voltage. In addition, since the thickness

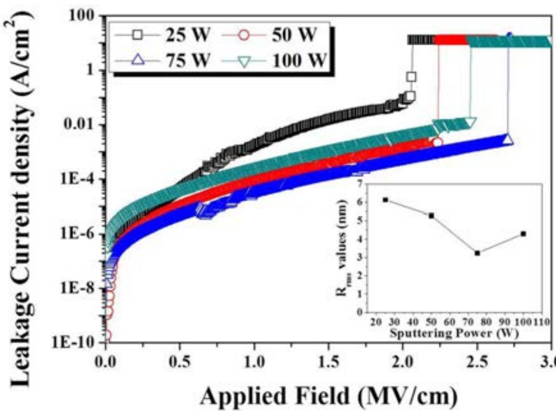

Fig. 4. Leakage current densities of ZTCS films grown under Ar atmosphere using various sputtering powers. Inset shows the variation of the R_{rms} value of the films with respect to the sputtering power.

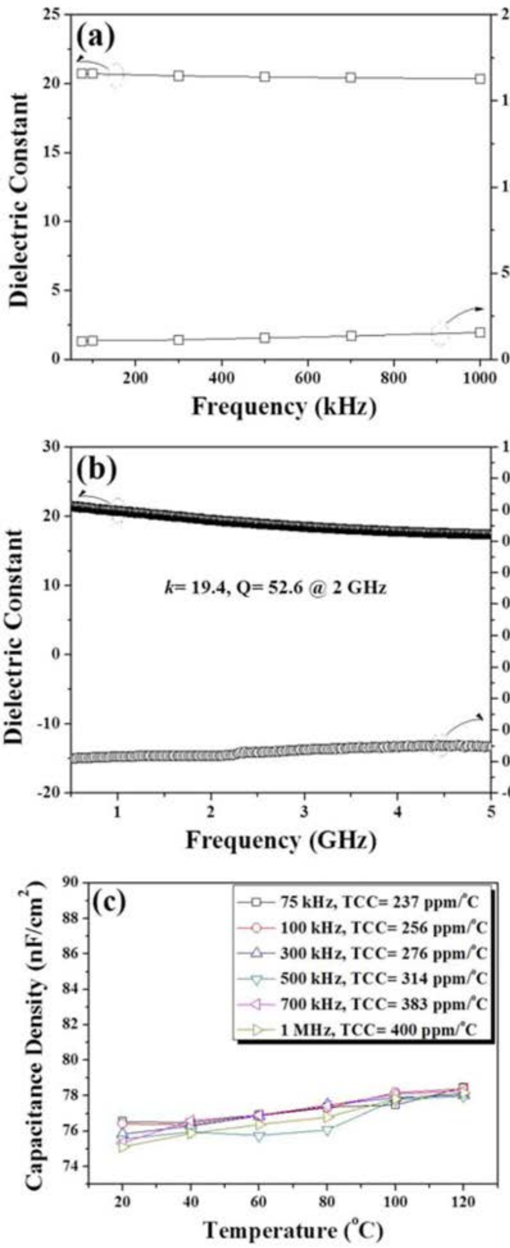

Fig. 5. k value and dissipation factor measured at (a) low frequencies (75 kHz-1.0 MHz), (b) radio frequencies (1.0-5.0 GHz), and (c) variation in capacitance density measured at various frequencies as a function of temperature for the ZTCS films grown using a sputtering power of 75 W. Inset of Fig. 5(a) shows a variation of the capacitance density of this film with respect to the applied voltage measured at 100 kHz.

of this film is 240 nm, the breakdown voltage of this film is about 64.8 V. According to the ITRS, the breakdown voltage is required to be greater than 100 V [7]. This requirement can be easily satisfied when the thickness of the ZTCS film is increased to 375 nm.

Fig. 5(a) shows the k value and dissipation factor as a function of frequency for the ZTCS film deposited using a sputtering power of 75 W, which showed a low leakage current with a large breakdown voltage. The k value of this film is approximately 21 at 100 kHz with a negligible variation with frequency. Moreover, this film has a low dissipation factor of 1.0% at 75 kHz-1.0 MHz. The k value of this film is slightly lower than that of the ZTCS film grown on a Pt electrode at RT (27.5), [14] probably owing to the lower crystallinity of the ZTCS film grown on a Cu electrode. This indicates that the crystallinity of the ZTCS film influences its dielectric properties. The inset of Fig. 5(a) shows there is a negligible variation of the capacitance density of this film with respect to the applied voltage measured at 100 kHz, at which a high capacitance density of 76 nF/cm^2 was observed. In order to satisfy the breakdown voltage requirement, the thickness of the ZTCS film must be increased to 375 nm. The capacitance density of the film decreases with increasing film thickness. A capacitance density of 48.6 nF/cm^2 is calculated for a 375 nm-thick ZTCS film, which is significantly higher than the required value of 5.0 nF/cm^2. Therefore, it is considered that the ZTCS film grown on a Cu electrode at RT satisfies the ITRS requirements in terms of both the capacitance density and breakdown voltage.

The k and tan δ values of the ZTCS film grown using a sputtering power of 75 W were also measured in the rf ranges, as shown in Fig. 5(b). The k and tan δ values of this film were measured to be 19.4 and 0.019 at 2.0 GHz, respectively, which are similar to those measured at lower frequencies. Moreover, this film shows a high Q value of 52 at 2.0 GHz, which satisfies the ITRS for the Q value for a capacitor on an organic substrate to be greater than 50 by 2016. The TCC of this film was also measured at various frequencies, as shown in Fig. 5(c). The TCC of this film was 237 ppm/°C at 75 kHz and slightly increased with increasing frequency to 400 ppm/°C at 1.0 MHz. According to ITRS, the TCC value for a capacitor grown on an organic substrate should be less than 300 ppm/°C by 2016, indicating that the TCC value of this ZTCS film satisfies the ITRS requirement at low frequencies (< 500 kHz) but was slightly larger at high frequencies.

Conclusions

A crystalline ZTCS film was successfully grown on a Cu-Si substrate at RT by rf sputtering using a $(Ca_{0.7}Sr_{0.3})(Ti_{0.2}Zr_{0.8})O_3$ ceramic target. Crystallinity and surface roughness of the ZTCS film were affected by the sputtering power. A crystalline ZTCS film with a small R_{rms} value of 3.2 nm, which was grown under a sputtering power of 75 W, showed a low leakage current density (4.0×10^{-6} A/cm^2 at 0.75 MV/cm) and a high breakdown voltage (2.7 MV/cm). Therefore, the microstructural properties such as surface roughness and crystallinity considerably influenced the electrical properties of the ZTCS film. The k value of this film was 21.5 with a low tan δ value of 0.007 at 100 kHz; a similar k value of 19.4 with a high Q value of 52 was obtained for this film at 2.0 GHz. Moreover, this film showed a high capacitance density of 78 nF/cm^2 with a small TCC value of 256 ppm/°C at 100 kHz. Therefore, the ZTCS film grown on a Cu electrode is a good candidate for use as an embedded capacitor in PCBs.

Acknowledgments

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