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The effect of deposition temperature and chamber pressure on the electrical and physical properties of the $MgTiO_3$ thin films

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ABSTRACT

The effects of deposition temperature and pressure on the properties of $MgTiO_3$ the films were investigated. $MgTiO_3$ thin films were grown on Si(1 0 0) substrate by radio frequency (RF) magnetron sputtering. The microstructure and the surface morphology of $MgTiO_3$ thin film have been studied by X-ray diffraction (XRD) and atomic force microscopy (AFM). The XRD showed that the deposited films exhibited a polycrystalline microstructure. The grain size of the film increased with an increase in the substrate temperature. The electrical properties were measured using *C–V* and current–voltage (*I–V*) measurements on metal–insulator–semiconductor (MIS) capacitor structures. At a Ar/O_2 ratio of 100/0, RF power of 400 W and substrate temperature of 350 °C, the $MgTiO_3$ films with 5.62 μm thickness possess a dielectric constant of 15.91 (f = 10 MHz), a leakage current density of 9.1×10^{-10} A/mm^2 was obtained at 500 kV/cm. The leakage current decreased with decrease chamber pressure and substrate temperature.

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1. Introduction

In recent years, thin films such $BaTiO_3$ [1,2], $SrTiO_3$, $(Ba,Sr)TiO_3$, $Pb(Zr,Ti)O_3$ and $(Ba,Pb)(Zr,Ti)O_3$ with a high relative dielectric constant have been considered for use as storage capacitors in dynamic random access memories (DRAMs), such a dielectric material should have a low leakage current and a high dielectric constant, and it is desirable that it has a paraelectric phase to avoid fatigue due to ferroelectric domain switching. Until very recently, a significant, global research and development effort has been implemented to identify and qualify suitable high-*k* dielectric materials. In complementary metal-oxide semiconductor technology, using high-*k* materials is a formidable task to achieve further gains in productivity and performance for device scaling due to direct tunneling currents and boron penetration in SiO_2 below ∼1.5 nm. Similar problems are anticipated with the dynamic random access memory storage capacitor dielectrics. For the next generation of ultra-large scale integrated dynamic random access memory, it is widely believed that dielectric materials with high dielectric constant such as $SrTiO_3$, Ta_2O_5, and $(Ba,Sr)TiO_3$ will be needed for storage capacitors. The use of such thin films that are fabricated with high dielectric constant materials makes it possible to reduce the size of storage capacitors, and to simplify the memory cell structure for higher integration density. These prepared thin films are also capable in reducing the dimension of a device in communication integration density. Besides, thin-film technology has become a major requirement for integration since integrated circuits have been applied in microwave communication system, such as mobile phones, global positioning systems (GPS), and satellite communications, the demand for monolithic microwave integrated circuit technologies (MMIC) has been increasing [3,4]. For miniaturization of integrated circuitry, microwave dielectric components need improved characteristics, smaller size, and compatibility with existing circuits. Requirements for these dielectric resonators are a combination of a high dielectric constant ($\varepsilon_r > 15$) for possible size miniaturization (size of a dielectric resonator $\sim 1/\varepsilon_r$), a low dielectric loss ($Q > 5000$ at 7–9 GHz, where $Q = 1/\tan\delta$) for a stable resonant frequency, and a near-zero temperature coefficient of resonant frequency (τ_f) for temperature stable circuits [5–8].

The ilmenite titanates, $M^{2+}TiO_3$ (where M^{2+} = Ni, Mg and Mn) series, have attracted much attention for their high *Q* values and low dielectric constant due to the isolation of the TiO_6 octahedral by the MO_6 octahedron layer and cation vacancy layer in comparison with the perovskite titanates. In the ilmenite structure, each TiO_6 octahedral layer is sandwiched by two layers of MO_6 octahedron being a modified α-Al_2O_3 structure. $MgTiO_3$ has an ilmenite structure which is a rhombohedral crystal system ($R^{\bar{3}}$). $MgTiO_3$ has been widely used in microwave ceramic capacitors and resonators because of its high dielectric constant, high *Q* values and thermal stability [9–11]. The $MgTiO_3$ exhibits the microwave dielec-

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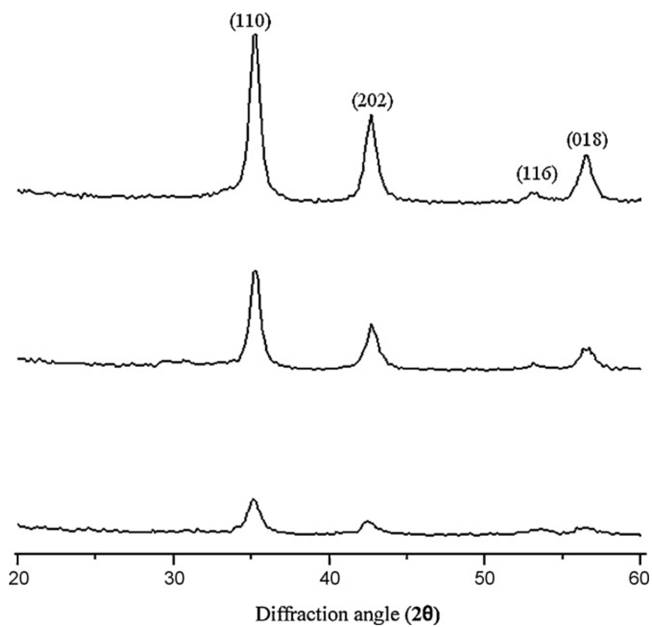

Fig. 1. X-ray diffraction patterns of the $MgTiO_3$ thin film deposited at different pressure: (a) 2 mTorr, (b) 6 mTorr, and (c) 8 mTorr.

tric properties with a good quality factor $Q \sim 21,800$ at 8 GHz, a dielectric constant $\varepsilon_r \sim 17$, and a temperature coefficient of resonant frequency $\tau_f \sim -50$ [12]. Many experiments were performed to study the preparation and properties of $MgTiO_3$ [13–15]. However, most studies on $MgTiO_3$ have limited in bulk ceramic form. Few studies on $MgTiO_3$ thin film have been reported [16–18].

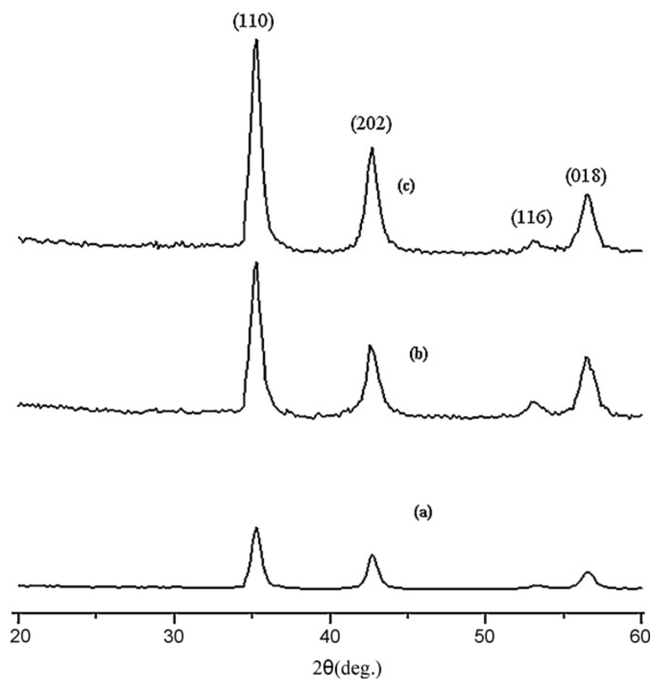

Fig. 3. X-ray diffraction patterns of the $MgTiO_3$ thin film deposited at 400 W, Ar/O_2: 100/0, sputtering time: 3 h and different substrate temperature: (a) 150 °C, (b) 250 °C, and (c) 350 °C.

In this work, $MgTiO_3$ thin films on n-type silicon substrates were prepared by RF magnetron sputtering. The $MgTiO_3$ target was fabricated and used for deposition. The $MgTiO_3$ thin films were deposited at chamber pressure from 2 mTorr to 8 mTorr, sub-

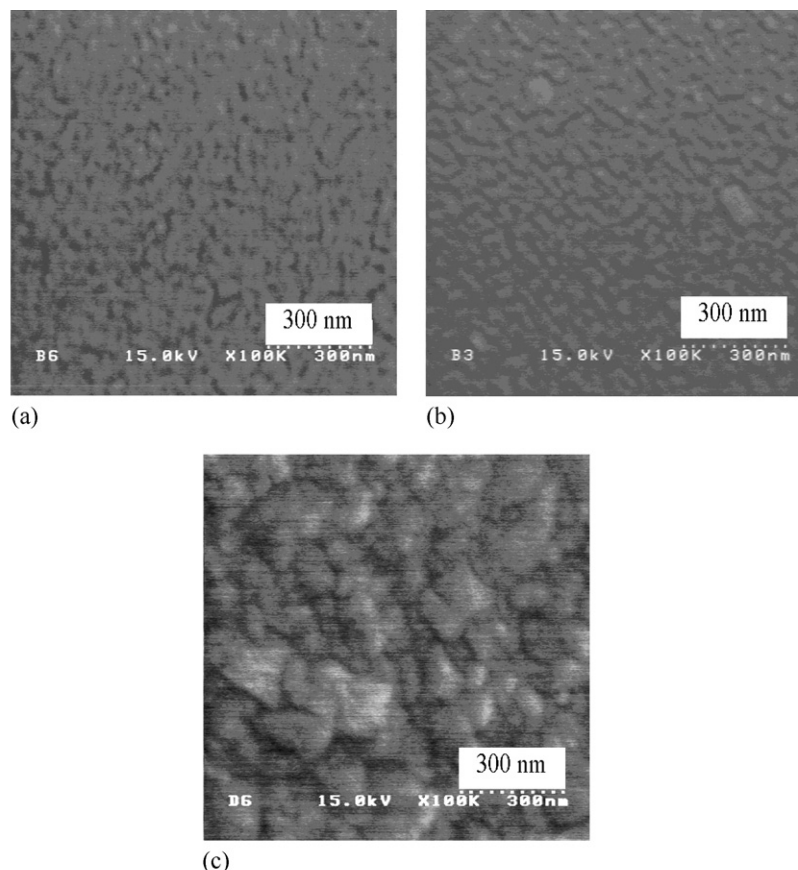

Fig. 2. SEM photograph of the $MgTiO_3$ films deposited at a substrate temperature of 400 °C and various chamber pressure: (a) 2 mTorr, (b) 4 mTorr, and (c) 8 mTorr.

strate temperatures from 150 °C to 350 °C. We have investigated the dependence of the structure and electrical properties as a function of chamber pressure and substrate temperature.

2. Experimental procedures

The target composition of $MgTiO_3$ was synthesized via a conventional solid-state reaction. Starting powders of high-purity oxide powders (>99.9%): MgO and TiO_2, were weighed and placed in polypropylene containers with milling media for 8 h in distilled water. The mixture was dried at 100 °C, and then thoroughly milled before it was calcined at 1100 °C for 4 h. The calcined powder was sintered at 1400 °C for 4 h. The sintered powder was ground and sieved through 100-mesh screen to produce $MgTiO_3$ target powder. Finally, this solid-state reaction was repeated twice to obtain the $MgTiO_3$ phase and was examined by X-ray diffraction (XRD), which revealed that all of the targets represented a rhombohedral phase. The sintered powder was then pressed into disks having 3-in. diameters and 6-mm thicknesses, to be used as $MgTiO_3$ targets.

A three-target magnetron sputtering system was used to sputter $MgTiO_3$ thin films from a 3-in. diameter, $MgTiO_3$ powder target. The substrate was placed above the target in an on-axis, sputtering-up arrangement, with a substrate-target distance of ∼5 cm. Three targets are placed on a circle, sitting on magnetron pedestals on the floor of the chamber. A diffusion pump was used to evacuate the pressure to 10^{-6} Torr. The sputtering gas Ar with a purity 99.99% was introduced to the chamber. A 3-channel mass flow controller was used to independently control the injection rates of Ar.

$MgTiO_3$ thin-film deposition was prepared using RF magnetron sputtering, as previously described. The target was cleaned by sintering with RF power of 50 W for 15 min with pure Ar atmosphere, at the same time the substrate was covered with the shield. The following sputter conditions were used in this work: chamber pressure of 2–8 mTorr which was maintained by an argon, different substrate temperature (150–350 °C) and sputtering time for 3 h then the deposited films were annealed at 400 °C for 2 h.

The film structure was analyzed by X-ray diffraction (Rigaku D/Max III.V) at 30 kV and 20 mA with Cu Kα radiation. The thin film grown on n-type Si(1 0 0) substrates was analyzed by ultrahigh resolution scanning electron microscope (SEM, Hitachi S4100). The morphology of the film surface was determined using an atomic force microscope (AFM, Digital Instrument DI3000) and scanning electron microscopy. The thickness of the $MgTiO_3$ films was measured with an alpha step (Tenco α-step 500).

The electrical characteristics were evaluated by capacitance–voltage (*C*–*V*) and current–voltage (*I*–*V*) measurements on metal–insulator–semiconductor (MIS) capacitor structures. The sample structures were fabricated by symmetrically depositing Al electrodes on $MgTiO_3$ film and on the other side of a Si wafer. The

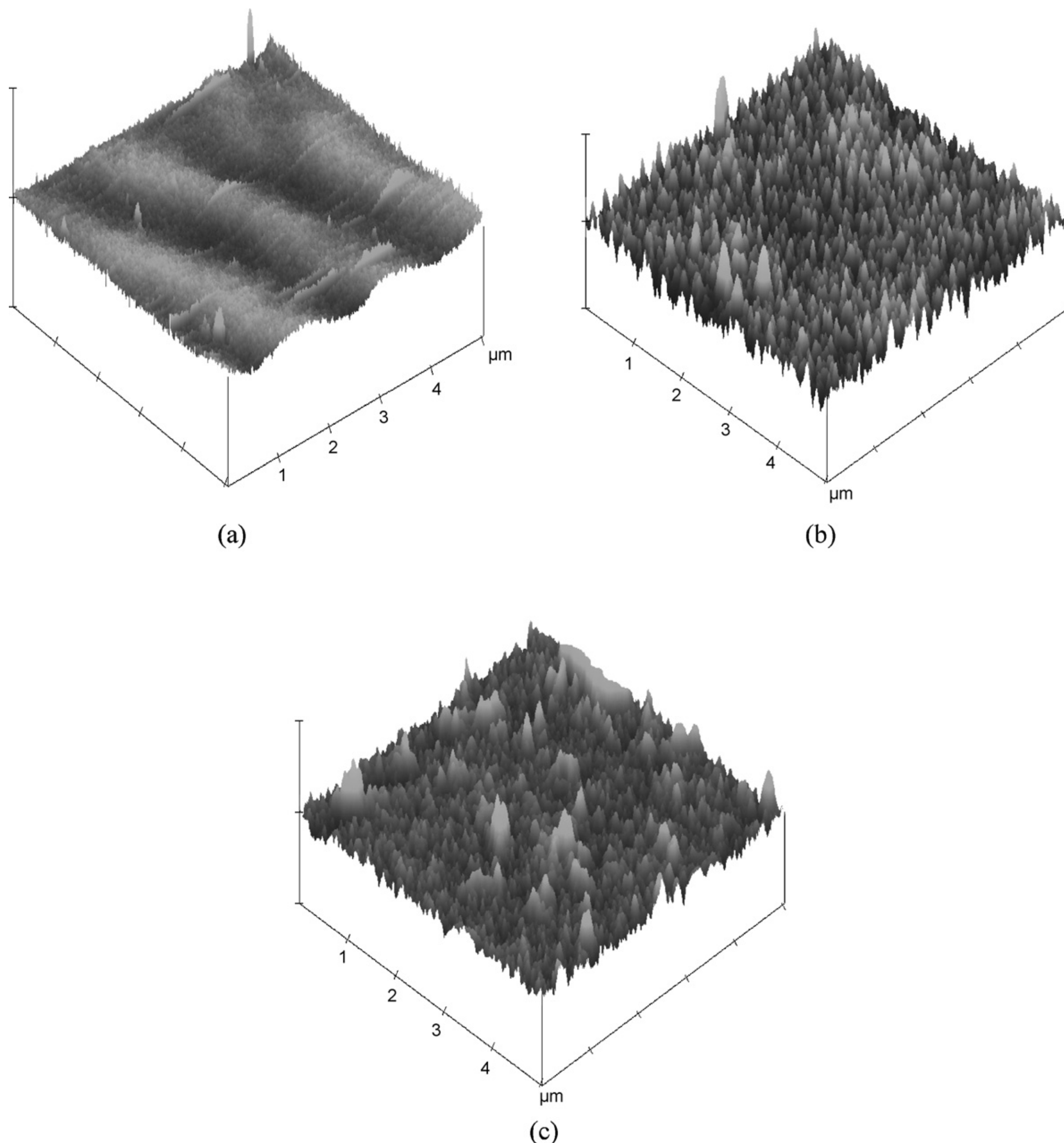

Fig. 4. AFM surface morphology of $MgTiO_3$ films at substrate temperature: 400 °C, Ar/O_2: 100/0 and chamber for (a) 2 mTorr, rms: 1.473 nm; (b) 4 mTorr, rms: 5.33 nm; and (c) 8 mTorr, rms: 10.34 nm.

C–V and *I–V* characteristics of the MIS capacitors were obtained by using an HP4192 impedance Analyzer and HP4156 Parameter Analyzer.

3. Results and discussion

3.1. Crystal structure of films

Fig. 1 shows the XRD pattern of $MgTiO_3$ films deposited at different chamber pressure with substrate temperatures of 350 °C, sputtering time of 3 h, Ar/O_2 ratio of 100/0 for 3 h. It reveals that the $MgTiO_3$ films were polycrystalline was obtained at chamber pressure from 2 mTorr to 8 mTorr. The intensity of the peaks decreased with increasing chamber pressure. It may be assumed that these results are due to a decrease of crystallinity which resulted from a drop in the kinetic energy of the sputtered atoms due to a shorter mean free path and the consequent reduction of surface mobility of the atoms on the substrate surface with increasing chamber pressure. As the chamber pressure was decreased, the intensities of $MgTiO_3$ films (1 1 0), (2 0 2), (1 1 6) and (0 1 8) peaks were enhanced. The intensities of (1 1 0) and (2 0 2) peaks were relatively higher than those of other peaks of $MgTiO_3$ films, indicating that highly (1 1 0)-oriented $MgTiO_3$ films were obtained on n-type Si(1 0 0) substrates.

Fig. 2 shows the surface microstructures of the $MgTiO_3$ films deposited at n-type Si(1 0 0) substrates with different chamber pressure. SEM observations reveal that the films deposited at low pressure exhibit a dense microstructure with any apparent porosity (as shown in Fig. 2(a)). As chamber pressure increased to 8 mTorr, not only the films become more and more porous but also their features significantly increase in size. At 8 mTorr, the films have a highly porous structure and are composed of very large features (as shown in Fig. 2(c)). These results shown that denser films can be obtained at low gas pressure due to a longer mean free path and the consequent to add of surface mobility of the atoms on the substrate surface with decreasing chamber pressure. The SEM indicated the gain size increase with increasing chamber pressure.

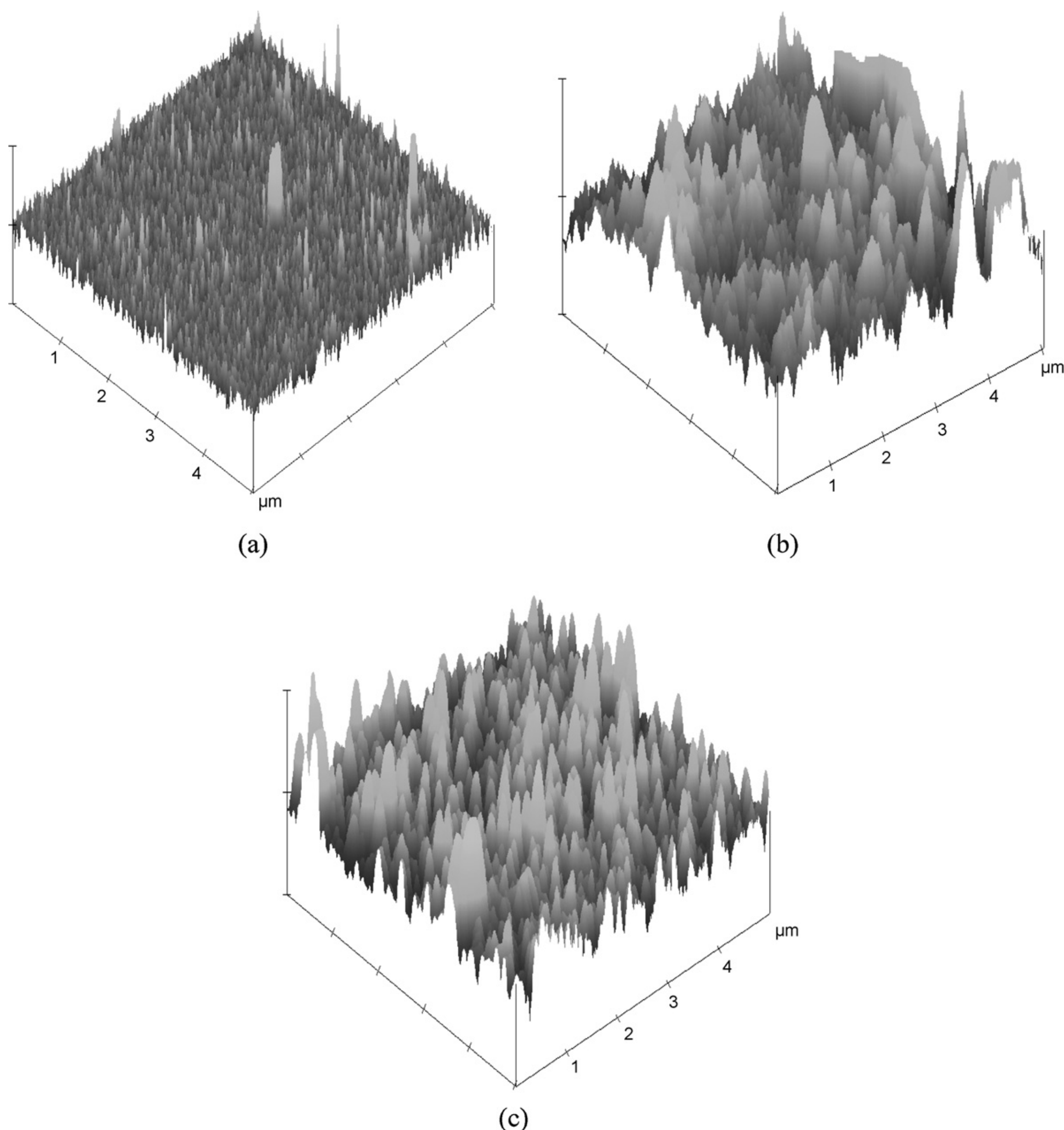

Fig. 5. AFM surface morphology of $MgTiO_3$ films at Ar/O2: 100/0, sputtering time 3 h, RF power: 400 W and substrate temperature: (a) 150 °C, rms: 6.73 nm; (b) 250 °C, rms: 9.34 nm; and (c) 350 °C, rms: 10.96 nm.

Dense and uniform grain growth ceramic films were obtained at chamber pressure of 2 mTorr.

Fig. 3 shows the XRD pattern of the target material and $MgTiO_3$ films deposited at different substrate temperatures (150–350 °C) with a sputtering time of 3 h, Ar/O_2 ratio of 100/0, RF power of 400 W, sputtering pressure of 2 mTorr and annealed at 400 °C for 2 h. It indicates that the $MgTiO_3$ films (1 1 0), (2 0 2), (1 1 6) and (0 1 8) peaks tend to be enhanced gradually with increasing substrate temperatures. The XRD and SEM results indicate that the depositing at higher RF power and substrate temperature induced crystallization of the $MgTiO_3$ thin films.

The influences of the chamber pressure and substrate temperature on the morphologies of the $MgTiO_3$ films were examined by atomic force microscopy using tapping mode amplitude modulation. Fig. 4 shows the surface morphologies of the films deposited at the chamber pressure range of 2–8 mTorr. The average roughness of films decreased with decreasing chamber pressure due to a longer mean free path and the consequent to add of surface mobility of the atoms on the substrate surface with decreasing chamber pressure. The average roughness of each film was 10.34 nm, 5.33 nm and 2.47 nm under 8 mTorr, 4 mTorr and 2 mTorr. Fig. 5 shows the surface morphology of the films deposited at 150–350 °C with a RF power of 400 W. The root-mean-square (rms) roughness varied from 6.73 nm to 10.96 nm as the substrate temperature increased from 150 °C to 350 °C. It indicates that the root-mean-square roughness of the films increased as the substrate temperature increased. Therefore, improvement in crystallinity of the $MgTiO_3$ films was accompanied by the increased in surface roughness.

3.2. Electrical properties

The bias stability of MIS capacitors was analyzed in terms of capacitance–voltage (*C*–*V*) and leakage current characteristics to establish their reliability for microwave applications. Fig. 6 shows that *I*–*V* curves of the $MgTiO_3$ films deposited on n-type Si(1 0 0) substrate at different chamber pressure. It indicates that the $MgTiO_3$ films MIS capacitors have very low leakage current ($I < 10^{-7}$ A at 500 kV/cm). The *I*–*V* cures of the $MgTiO_3$ films deposited on n-type Si(1 0 0) substrate at different substrate temperature with a RF power of 400 W are illustrated in Fig. 7. The leakage current increased with increasing chamber pressure and substrate temperature. With increasing chamber pressure from 2 mTorr to 8 mTorr and substrate temperature from 150 °C to 350 °C, the leakage current increased from 1.429×10^{-7} A/cm^2 to 1.25×10^{-5} A/cm^2 and 6.6×10^{-11} A/cm^2 to 9.12×10^{-10} A/cm^2 at 5 kV/cm, respectively. The increase of leakage current with chamber pressure and substrate temperature is attributed to the increase of the surface roughness of the film. A similar result was observed by Bhattacharya et al. [18].

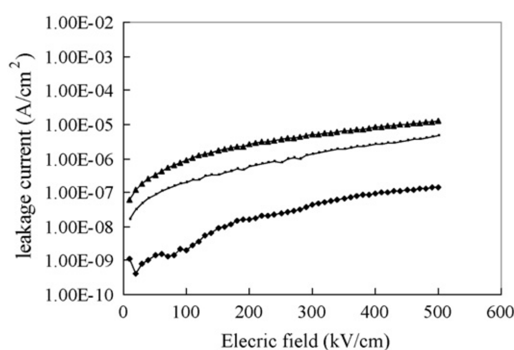

Fig. 6. The *I*–*V* curves of the $MgTiO_3$ films deposited on n-type Si(1 0 0) substrate at different chamber pressure.

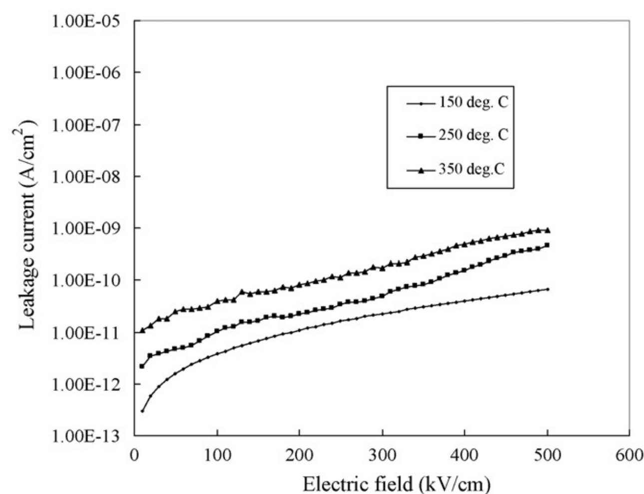

Fig. 7. The *I*–*V* cures of the $MgTiO_3$ films deposited on n-type Si(1 0 0) substrate at different substrate temperature with a RF power of 400 W for sputtering time of 3 h.

Fig. 8 shows the dielectric constant and tangent loss. The dielectric constant of the $MgTiO_3$ films decreased with increasing chamber pressure. The dielectric constant is influenced by grain size and crystallinity. From XRD patterns, the intensity of $MgTiO_3$ peak (1 1 0) decreased with increasing chamber pressure. As the deposition pressure was increased from 2 mTorr to 8 mTorr, the value of *k* decreased from 17 to 11.8. With a higher deposition pressure, the energies of the charged reactive species generated by the plasma from the precursor molecules in the deposition chamber decrease, leading to the formation of less dense films. Less dense films are generally thought to have lower *k* values. Tangent loss proceeds by two mechanisms: resistive loss and relaxation loss. In resistive loss case, energy is dissipated by mobile charges, and the tangent loss depends on the magnitude of leakage current; in relaxation loss case, energy is dissipated by relaxation of dipoles, and the tangent loss is proportional to the dielectric constant. Comparing Figs. 6 and 8 reveal that the trend of the tangent loss against of chamber pressure is similar to that of leakage current. Hence, the resistive loss dominates the tangent loss. Therefore, the loss tangent increases as the resistance decreases or leakage current increases. As chamber pressure decreased, the dissipation factors decreased owing to the uniform thin-film morphology. As mentioned above, $MgTiO_3$ thin films with better microstructures could be fabricated with reduced leakage current.

The dielectric constants and dissipation factor of the $MgTiO_3$ films deposited at various temperatures are plotted as a function of sputtering temperature in Fig. 9. The dielectric constant and dissipation factor of the $MgTiO_3$ films increased with sputtering temperature. XRD, SEM and AFM results showed that the

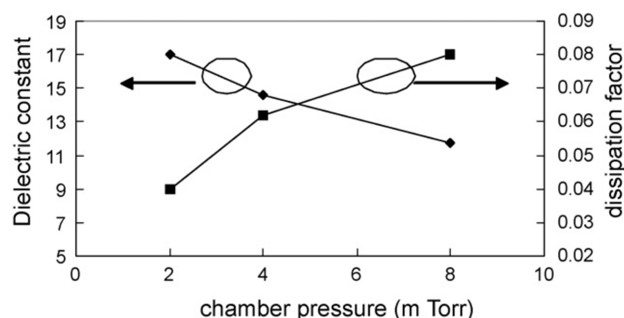

Fig. 8. The dielectric constants of the $MgTiO_3$ films deposited at various chamber pressure for 3 h, Ar/O_2 ratio of 100/0 with a RF power of 400 W.

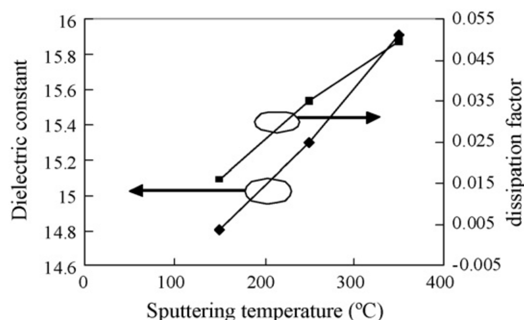

Fig. 9. The dielectric constants of the $MgTiO_3$ films deposited at various sputtering temperature for 3 h, Ar/O_2 ratio of 100/0 with a RF power of 400 W.

increase in dielectric constant with increasing substrate temperature is attributed to the increase in the grain size and crystallinity of the thin film. It is well known that as the grain size increase, the dielectric increase and as the porosity in the film increased, the dielectric constant decreases. The dielectric constant of the film at 10 MHz is 15.85 which is similar to the bulk ceramic [12].

4. Conclusions

Crystalline $MgTiO_3$ thin films grown on n-type Si(1 0 0) substrate by RF magnetron sputtering at various chamber pressure (2–8 mTorr) and substrate temperatures (150–350 °C) were investigated. The quality of $MgTiO_3$ films was found to strongly depend on substrate temperature and chamber pressure. As the chamber pressure decreased and substrate temperature increased, the crystallinity of the $MgTiO_3$ thin films improved. In addition, the surface roughnesses of the thin films decreased with increasing substrate temperature were observed by AFM. The optimum conditions for the growth of $MgTiO_3$ thin films in this study were a substrate temperature of 400 °C and RF power of 400 W. The MIS structure was introduced in the measurement of *C*–*V* and *I*–*V* curves for the $MgTiO_3$ thin films. A high dielectric constant of 16.2 (f = 10 MHz) and a low dissipation factor of 0.04 were obtained for the prepared films. All the characteristics of the prepared $MgTiO_3$ thin film suggest the suitability of them for microwave and integrated circuit application.

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