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# Characteristics of $Bi_4Ti_3O_{12}$ thin films on ITO/glass and Pt/Si substrates prepared by R.F. sputtering and rapid thermal annealing

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**Abstract** $Bi_4Ti_3O_{12}$ thin films are deposited on ITO/glass and Pt/Ti/Si(100) substrates by R.F. magnetron sputtering at room temperature. The films are then heated by a rapid thermal annealing (RTA) process conducted in oxygen atmosphere at temperatures ranging from 550–700°C. X-ray diffraction examination reveals that the crystalinity of the films grown on Pt/Ti/Si is better than that of the films grown on ITO/glass under the same fabrication conditions. SEM observation shows that the films grown on Pt/Ti/Si are denser than those grown on ITO/glass substrates. Interactive diffusion between the $Bi_4Ti_3O_{12}$ film and the ITO film increases with the increase of annealing temperature. The optical transmittance of the thin film annealed at 650°C is found to be almost 100% when the effect of the ITO film is excluded. The relative dielectric constants, leakage currents and polarization characteristics of the two films are compared and discussed.

**Keywords** $Bi_4Ti_3O_{12}$ · R.F. magnetron sputtering · RTA, ACTFEL · Perovskite

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## 1 Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$) thin film has attracted considerable attention due to the excellent electro-optic and ferroelectric properties induced by its uniform Bi-layered perovskite structure [1, 2]. The favorable properties of $Bi_4Ti_3O_{12}$ include a high dielectric constant, a high polarization charge density, high fatigue endurance, and a high transmittance, etc. Accordingly, bismuth titanate is an ideal material for non-volatile memories (NVRAM) or for the insulating layer of A.C. thin film electroluminescence (ACTFEL) devices. Various methods have been developed for the preparation of $Bi_4Ti_3O_{12}$ thin films, including chemical solution deposition [3], metalorganic chemical vapor deposition (MOCVD) [4], molecular beam epitaxy (MBE) [5], and R.F. sputtering [6]. For integrated circuit applications, the thin films should be grown on a silicon wafer. However, for ACTFEL devices, the films are grown on glass coated with a transparent electrode material such as ITO (indium-tin-oxide). R.F. sputtering is a suitable technique for the fabrication of uniform thin films covering large areas. However, in the traditional sputtering process, the substrate must be maintained at a high temperature for an extended period of time in order to promote the growth of a polycrystalline microstructure. Unfortunately, the characteristics of bismuth titanate are not entirely compatible with the requirements of the traditional R.F. sputtering process since the bismuth readily evaporates during the heating treatment because of its low melting point of 271°C. Furthermore, perovskite materials such as $BaTiO_3$, $SrTiO_3$, $PbTiO_3$ and $Bi_4Ti_3O_{12}$ interact readily with ITO [7], leading to a deterioration of the characteristics at high temperature. Additionally, the glass substrates cannot resist temperatures exceeding 500°C for long periods of time. To overcome these problems, the current study uses R.F. sputtering performed at room temperature to prepare $Bi_4Ti_3O_{12}$ thin films on Pt/Ti/Si

**Table 1** Deposition conditions of $Bi_4Ti_3O_{12}$ thin films

| Target | $Bi_4Ti_3O_{12}$ + 4 wt%$Bi_2O_3$ |
|---|---|
| Substrate | (1) 15 Ω/□ ITO/glass<br>(2) Pt/Ti/Si(100) |
| Deposition temperature | Room temperature |
| Atmosphere | High purity argon |
| Base pressure | $5*10^{-4}$ Pa |
| Working gas pressure | 1 Pa |
| Deposition time | 60 min |

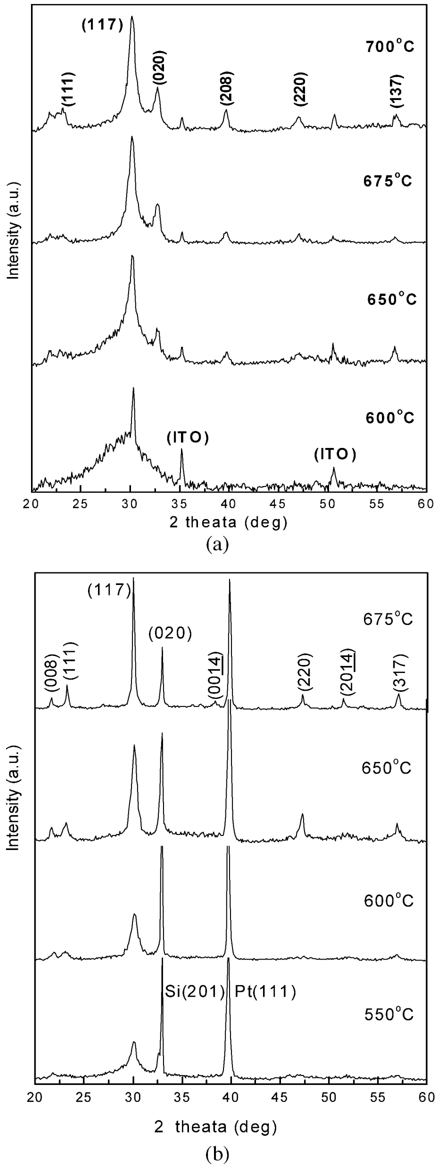
and ITO/glass substrates, respectively. The RTA process is then used to crystallize the resultant films. A $Bi_4Ti_3O_{12}$ ceramic target with an excess of 4 wt% $Bi_2O_3$ is adopted to compensate for the evaporation of bismuth during the heating of the films. The properties of $Bi_4Ti_3O_{12}$ films on the different substrates are investigated and compared in order to provide a reference for preliminary research into NVRAM and ACTFEL devices.

## 2 Experimental procedures

HOYA NA-40 glass coated with ITO and Pt/Ti/Si(P-type, 100, silicon wafer) were employed as substrates, respectively. The deposition conditions are summarized in Table 1. The resultant films were annealed at temperatures ranging from 550 to 700°C for 10 min in a rapid thermal annealing furnace in a pure oxygen atmosphere to form 500–600 nm thick polycrystalline $Bi_4Ti_3O_{12}$ films. Circular Al upper electrodes of 0.1 mm diameter were evaporated onto the surfaces of the films for the measurement of the electrical characteristics. The crystallization characteristics of the films were evaluated using a SIEMENS D5000 X-ray diffraction (XRD) spectrometer using Cu-K$\alpha$ radiation. The surfaces and cross-sectional morphologies of the films were observed using a field emission scanning electronic microscopy (FE-SEM), and the optical transmission spectra were acquired using an Ocean Optics USB2000 Photospectrometer over the visible wavelength. Meanwhile, an HP 4194 impedance analyzer was used to measure the capacitance-voltage (C-V) and loss factor (tan $\delta$) with a DC-bias ranging from −5 V to +5 V at various frequencies. The relative dielectric constant, $\varepsilon_r$, was derived from the capacitance at zero DC-bias from the relationship $C = \varepsilon_r \varepsilon_o (A/d)$. The I-V characteristics were measured using an HP4156B semiconductor parameter analyzer. The P-E hysteresis loops of the films deposited on the ITO/glass substrates were recorded at room temperature by an oscilloscope using a standard Sawyer-Tower circuit at 500 Hz.

## 3 Results and discussion

The XRD patterns of $Bi_4Ti_3O_{12}$ films annealed at different temperatures are shown in Fig. 1. An inspection of these patterns shows that the crystalline phase in the film depends strongly on the annealing temperature. The results indicate that the (117) diffraction peak becomes prominent at thermal treatment temperatures of above 675°C for the films deposited on Pt/Ti/Si substrate. However, there is no obvious change in the (117) peak for the films deposited on ITO/glass for annealing temperatures exceeding 650°C. Comparing the XRD patterns for the $Bi_4Ti_3O_{12}$ films deposited on the two kind of substrates and then annealed at



(a)

(b)

**Fig. 1** XRD patterns of $Bi_4Ti_3O_{12}$ thin films annealed at various temperatures for 10 min: (a) deposited on ITO/glass substrate, and (b) deposited on Pt/Ti/Si substrate a temperature of 675°C, it is clear that the main peak (117) of the film with a FWHM (full width at half maximum) of 0.24° deposited on Pt/Ti/Si is sharper than the peak of the film with a FWHM of 0.43° deposited on ITO/glass. This indicates that the crystalline characteristics of the $Bi_4Ti_3O_{12}$ films deposited on Pt/Ti/Si are superior to those of the films deposited on ITO/glass. Finally, it is noted that the peaks shift towards the higher $2\theta$ value as the annealing temperature increases. This implies that the distance between the $Bi_4Ti_3O_{12}$ crystal planes decreases as the temperature increases, i.e. the crystalline structure becomes denser as the annealing temperature increases. Hence, the present results demonstrate that the $Bi_4Ti_3O_{12}$ films deposited on Pt/Ti/Si have a lower crystallization temperature than the films deposited on ITO/glass.

In ACTFEL devices, a good transparency of the front insulating layer is a necessary requirement because the light generated from the phosphor layer must emit through the insulating layer. The optical transmission spectra of ITO/glass and $Bi_4Ti_3O_{12}$/ITO/glass annealed at various temperatures are shown in Fig. 2. It can be seen that the optical transmittance of the thin film of 600 nm thickness annealed at 650°C reaches approximately 100% for the wavelength of 600–650 nm when the effect of the ITO/glass layer is excluded. This is a powerful advantage of $Bi_4Ti_3O_{12}$ films compared to other insulating layer materials.

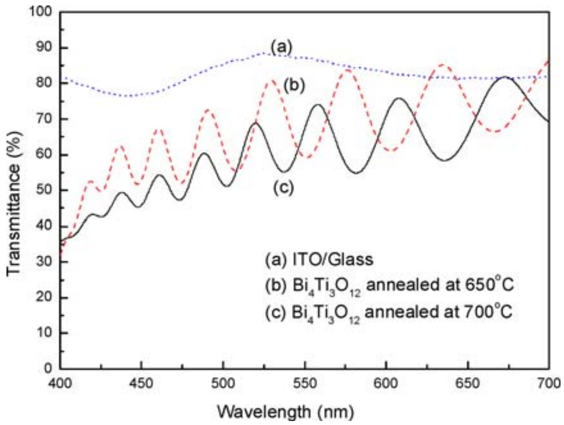


**Fig. 2** The transmittance spectra of $Bi_4Ti_3O_{12}$ films deposited on ITO/glass substrate

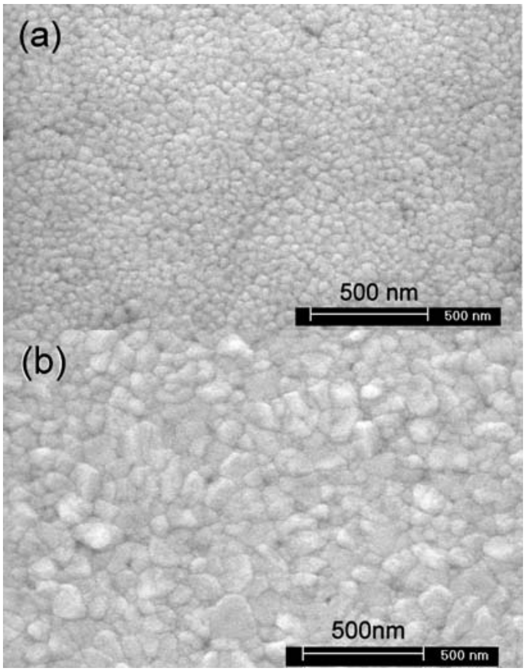


**Fig. 3** Surface morphologies of $Bi_4Ti_3O_{12}$ films deposited on: (a) ITO/glass substrate, annealed at 700°C, and (b) Pt/Ti/Si substrate, annealed at 650°C

Figure 3 shows the surface microstructures of the two $Bi_4Ti_3O_{12}$ films. The grain shape of the film grown on ITO/glass is granular (Fig. 3(a)), whereas that of the film grown on Pt/Ti/Si is plate-like (Fig. 3(b)). Additionally, the grain size of the former is approximately 30–40 nm, while that of the latter is 90–100 nm. Both films demonstrate excellent adhesion to the Pt/Ti/Si and ITO/glass substrates, i.e. no film is stripped from the substrate in either case. Figure 4 presents the results of the SEM cross-sectional analysis. It can be seen that the $Bi_4Ti_3O_{12}$ thin film grown on Pt/Ti/Si is approximately 17% thinner than that deposited on ITO/glass under the same fabrication conditions. This demonstrates that the $Bi_4Ti_3O_{12}$ thin film grown on Pt/Ti/Si has a higher density than that grown on ITO/glass. These results are consistent with those found in the XRD analysis. Besides, as indicated by the white circle in Fig. 4(a), inter-diffusion between the $Bi_4Ti_3O_{12}$ film and the ITO film causes the interface to be indistinct in some places.

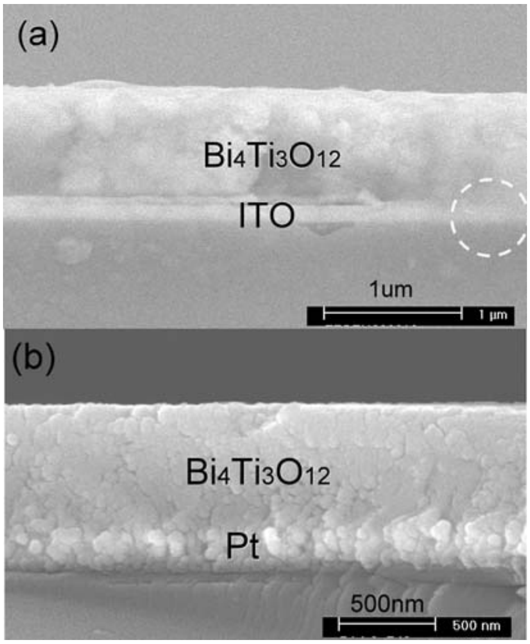


**Fig. 4** Cross-sections of $Bi_4Ti_3O_{12}$ films deposited on different substrates and annealed at 675°C: (a) on ITO/glass substrate, and (b) on Pt/Ti/Si substrate

Figure 5 plots the current density as a function of the applied field for the two $Bi_4Ti_3O_{12}$ films. The leakage current density of the film deposited on ITO/glass remains stable at approximately $10^{-5}$ A/cm$^2$ and is an order of magnitude smaller than that of the film deposited on Pt/Ti/Si. This could be a result of the larger grain size and pinholes within the films. Even though the current leakage current is slightly higher than that reported in related studies [8], no breakdown phenomenon occurs for both films under a 400 kV/cm field.

The variation of relative dielectric constant of the $Bi_4Ti_3O_{12}$ films grown on ITO/glass and Pt/Ti/Si substrates under various annealing temperatures are illustrated in Fig. 6. The results show that the relative dielectric constant increases with increased annealing temperature. This is because a higher annealing temperature causes the $Bi_4Ti_3O_{12}$ film to be denser and thinner. The relative dielectric constant attains a maximum value of 305 at an annealing temperature of 700°C for the films deposited on ITO/glass and a maximum value of 295 at an annealing temperature of 650°C for the films grown on Pt/Ti/Si at a frequency of 1 kHz. Furthermore, it is observed that the dielectric constant reduces for films annealed at temperatures higher than 650°C on Pt/Ti/Si substrates and at temperatures higher than 700°C for ITO/glass substrate. The phenomenon can be attributed to the occurrence of inter-diffusion [9] between the $Bi_4Ti_3O_{12}$ film and the Pt/Ti/Si and ITO films, respectively. The loss factors of the films deposited on ITO/glass range from 0.02 to 0.05, and are clearly superior to those of films grown on Pt/Ti/Si at a frequency of 1 kHz, which vary from 0.1 to 0.15. This result could be due to the greater number of pinholes at the grain boundary in the films deposited on Pt/Ti/Si, as shown in Figs. 3 and 4.

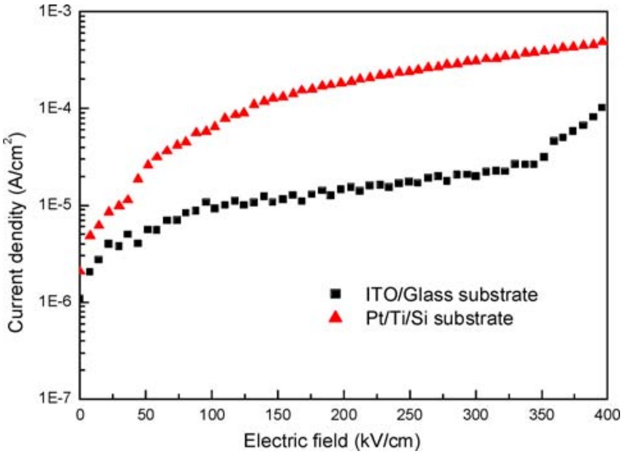
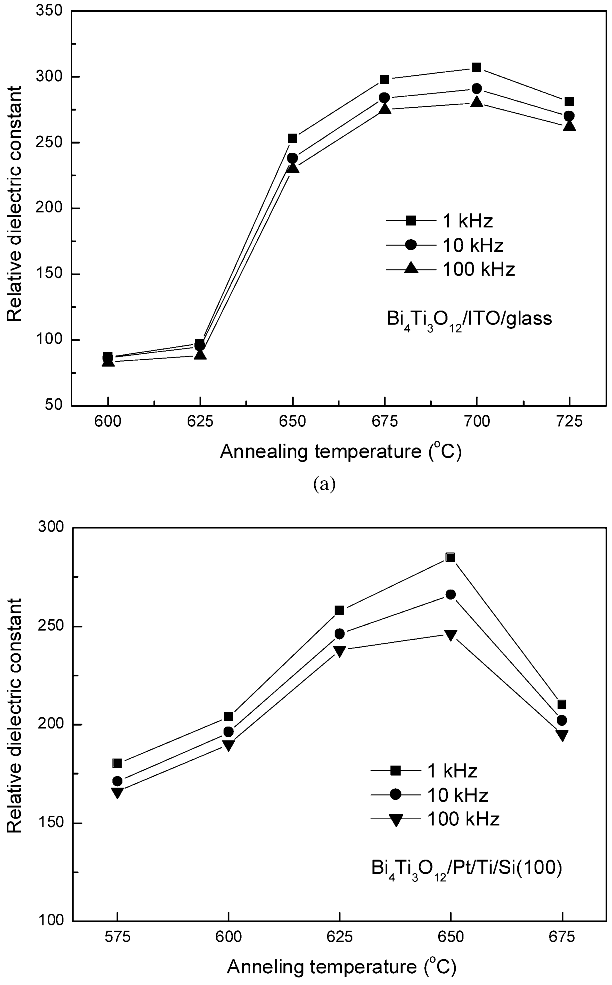


**Fig. 5** . Variation of current density with applied electric field for $Bi_4Ti_3O_{12}$ films



(a)

(b)

**Fig. 6** Variation of relative dielectric constant with different annealing temperatures for $Bi_4Ti_3O_{12}$ films: (a) deposited on ITO/glass substrate, and (b) deposited on Pt/Ti/Si substrate

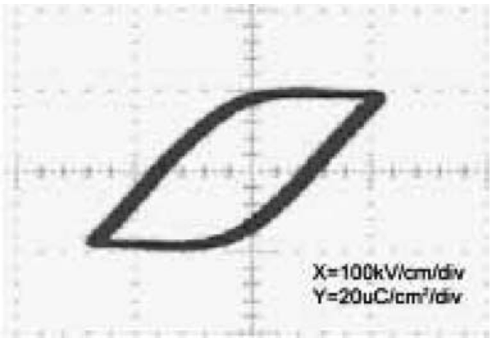


**Fig. 7** P-E hysteresis loop of $Bi_4Ti_3O_{12}$ film grown on ITO/glass substrate

The typical polarization characteristics of a thin film deposited on ITO/glass and then heat treated at 700°C is shown in Fig. 7. The remnant polarization (Pr, charge storage density) is approximately 18 $\mu$C/cm$^2$ for film on ITO/glass substrate and 10–12 $\mu$C/cm$^2$ for that on Pt/Ti/Si substrate. The coercive field (Ec) is approximately 50 kV/cm for film on the ITO/glass substrate and 120 kV/cm for that on Pt/Ti/Si substrate, respectively. The differences in the ferroelectric characteristics of the two films can be ascribed to the different grain sizes and grain shape [10], which are caused by their different substrates.

## 4 Conclusion

In this study, (117) preferred oriented polycrystalline $Bi_4Ti_3O_{12}$ thin films are successfully fabricated on ITO/glass and Pt/Ti/Si substrates by R.F. magnetron sputtering and then heated using a rapid thermal annealing process. The crystallization temperature of the films deposited on Pt/Ti/Si substrate is lower than that of films deposited on ITO/glass substrate. However, the existence of pinholes within the grain boundary and larger grain sizes of the films on Pt/Ti/Si will cause the loss factor and leakage current of these films to be greater than the equivalent properties of the films deposited on ITO/glass substrate. The present results have demonstrated that other than the fabrication method, the substrate is a significant factor determining the characteristics of the films. The excellent ferroelectric characteristics of $Bi_4Ti_3O_{12}$ films render it a suitable candidate material for random access memory and ACTFEL devices.

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