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Dielectric properties of vacuum deposited Bi_2Te_3 thin films

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Abstract

Multi-component alloys based on tellurium are used as switching materials, which induce the interest in studying these materials in the bulk and thin film states. Bi_2Te_3 films of various thicknesses were prepared and its structural, composition and surface morphological analysis were carried out. Thickness of the films was measured by an in built Quartz Crystal Monitor. From the X-ray diffraction patterns it is observed that the films possess polycrystalline rhombohedral structure. Using Scherer's formula the grain size (D) was calculated and it is found that the *D* value increases with increase of film thickness. The budding of micro crystallites were observed by the SEM analysis of Bi_2Te_3 thin film. The composition of the film is analyzed by EDAX and found that Bi:Te = 3:2. Thin film capacitors Al–Bi_2Te_3–Al were formed onto well-cleaned glass substrates by vacuum deposition method under a pressure of 10^{-5} Torr. The values of capacitance (*C*) and $\tan\delta$ were measured using a digital LCR meter at various frequencies (12 Hz–100 K Hz) and temperature (303–483 K). Knowing the value of C, d and area of the capacitor (*A*), the dielectric constant (ε') was calculated. The loss peak observed in $\tan\delta$ vs. frequency plot reveals the presence of relaxation effect. For a Debye process at higher temperatures and for given frequency, a maximum in $\tan\delta$ will occur at a temperature such that $2\pi f_{\text{relax}} = 1/\tau$. Cole–Cole plots over the audio frequency for two different temperatures are plotted and the relaxation time τ has been estimated and is found to

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be temperature dependent. The TCC and TCP values have been evaluated as 8.18×10^{-3} and 6.78×10^{-3} ppm/K, respectively for 100 KHz at 400 K. The high value of TCC suggests that these capacitors may be used as temperature sensors also.

Keywords: Bi_2Te_3 thin films; Thermal evaporation; Dielectric relaxation

1. Introduction

Thermoelectric materials are being actively investigated for direct conversion of thermal energy to electric energy and for electronic refrigeration. Thermoelectric energy conversion devices offer cooling and electricity generation capabilities in compact solid-state devices. The efficiency of these devices, however, has not been sufficiently high to propel this technology from niche applications to more ubiquitous refrigeration and waste heat conversion applications. The problem is fundamentally a materials limitation that is apparent in the basic materials figure-of-merit (Z). Binary compounds such as Bi_2Te_3 and its alloys are small gap semiconductors (0.16 eV) with layered crystalline structures and with a high thermoelectric figure of merit $Z = \alpha^2\sigma/\kappa$, where α is the thermo electrical power, σ and κ are the electrical and thermal conductivity. Their properties have been investigated in depth largely due to their great effectiveness as thermoelectric devices close to room temperature [1–4] and also for temperature control of laser diodes [5], optical recording systems [6], pressure gauges, hyper power sensors [7] and are known to find application ranging from photoconductive targets in TV cameras to IR spectroscopy [8,9]. The V_2–VI_3 ($V_2 =$ Bi, Sb: $VI_3 =$ Se, Te) binary compounds and their pseudo binary solid solutions are highly anisotropic and crystallize into homologous layered structure parallel to c-axis. Among these, alloys based on Bismuth Telluride (Bi_2Te_3), have been extensively investigated in bulk crystal form because of their excellent thermoelectric properties [10], whereas thin films of these alloys have received relatively little attention. However, the thin films have the potential to lead key technology in the micro fabrication of integrated thermoelectric devices. There have been various studies on the bulk and thin film characteristics of Bi_2Te_3 including optical and electrical properties [11–14], however there is no work on the dielectric and conduction studies of the Bismuth Telluride thin films. Thin films of Bi_2Te_3 with suitable good quality of thermoelectric properties have been produced by RF diode sputtering [15], molecular beam epitaxy [16], flash evaporation [17], MOCVD [18], ultra rapid quenching process [19], organic-assisted growth [20] and electrodeposition [21]. However, each one of these deposition methods has some drawbacks concerning mass production of relatively thick layers (around 100 micrometers). Hence, we have chosen relatively cheap vacuum evaporation technique and study the structural and dielectric properties which will allow the industrialist to reproduce and lead to growth of good quality thick layers. The purpose of this work is to report the preliminary results of the Bi_2Te_3 films obtained by simple evaporation technique and various microstructural and the dielectric properties and to focus the methodology for large scale applications.

2. Experimental

The films were prepared by making use of a conventional vacuum coating unit (12A4, Hind Hivac, Bangalore, India) under a pressure of about 10^{-5} Torr. Pure aluminum (99.999%) was evaporated from a tungsten filament onto cleaned glass substrates through suitable masks to form the base electrode. Bi_2Te_3 (99.999%, Aldrich) powder was thermally evaporated under a vacuum of 2×10^{-5} Torr from a molybdenum boat by using a vacuum coating unit (Hind Hivac -12A4D) onto cleaned glass substrates and on aluminum electrodes for the structural and dielectric studies, respectively. The distance between the substrate and the source was always maintained at 0.15 m and the rate of evaporation was maintained constant around 2.5 Å per second throughout the deposition. Initially the substrates were not exposed to the vapor stream by using a shutter and after obtaining a constant rate of evaporation the shutter was opened and the substrates were exposed for the deposition. The thicknesses of the deposited films were monitored by a built-in quartz crystal thickness monitor. The thicknesses of the films were verified using a surfometer (Tencor alpha step100). The structure of the films were analyzed using X-ray diffraction (Rigaca, Japan, CuK_α radiation with $\lambda = 0.15418$ nm). The composition of the film was analyzed using a Philips Scanning electron microscope attached with EDAX for composition determination. Aluminum top electrodes were deposited onto the dielectric layer to form the MSM sandwich (Al–Bi_2Te_3–Al) structure. All the capacitors were stabilized by prolonged aging and repeated annealing cycles at about 403 K. The capacitance (C) and loss factor ($\tan\delta$) were measured in vacuum in the frequency range 12 Hz–100 Hz at various temperatures (303–483 K) using a digital LCR meter (LCR – 819, GW Instek, Good Will Instrument Company Ltd., Taiwan).

3. Results and discussion

3.1. Structural, composition and surface morphology

X-ray diffraction is a widely used technique for characterization of thin films because of its non destructive nature and for completeness of the structural information. In the present study, Bi_2Te_3 films deposited on the glass substrates are found to possess uniform thickness distribution. Fig. 1 shows the diffraction pattern of typical Bi_2Te_3 films of various thicknesses from 50 to 300 nm, respectively. In the case of Bi_2Te_3 film of thickness 50 nm there are no prominent peaks observed and the films are almost amorphous. But as the thickness increases peaks are observed and their orientation are labeled. All peaks in the patterns correspond to the reflections of rhombohedral phase R3 m. There is no difference in the XRD patterns of the films

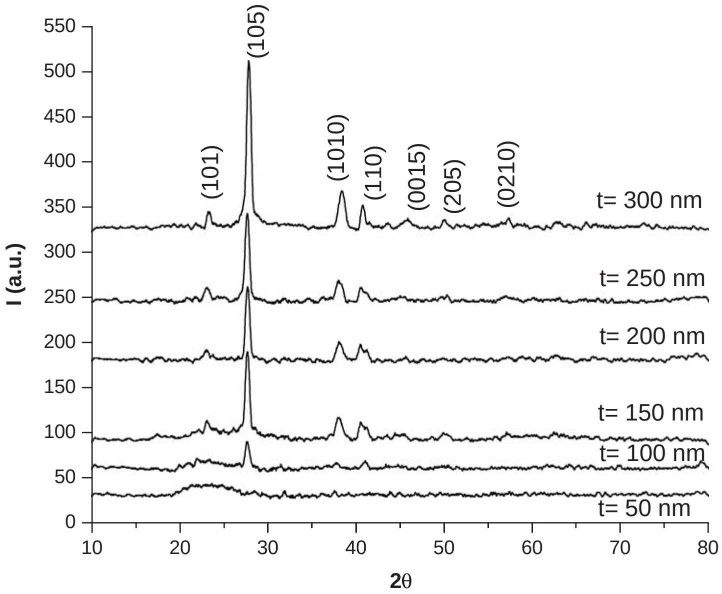

Fig. 1. X-ray diffractogram of thermally grown Bi_2Te_3 film of various thicknesses.

of various thicknesses except the decrease in the magnitude of the peaks. At higher thicknesses, since the peaks having high intensity, the peaks for the lower thickness films seems to be small. It is observed at $2\theta = 27.82\text{Å}$ which corresponds to (0015) plane. From the X-ray pattern of Bi_2Te_3 film of various thickness it is observed that the film of 250 and 300 nm posses many peaks at $2\theta = 2.32$, 45.8, 49.9, 57.2 etc, indicating that the films are in rhombohedral and polycrystalline in nature. The lattice parameters deduce from the diffraction angles are found to be $a = 4.39$ Å and $c = 34.28$ Å which are almost coinciding with the standard (JCPDS 15-0863). The grain size of the deposited films was calculated using Scherrer's formula [22]. The grain size is found to increase with increase in thickness and the values are 3.23 and 16.70 Å for the film of thickness 360 and 2500 Å, respectively.

The surface morphology and crystallinity of the deposited thin films on amorphous substrate are found to be strongly dependent on the growth parameters. The SEM micrographs are shown in Fig. 2 (a) and (b) for typical Bi_2Te_3 thin film of thickness around 250 nm. Fig 2a clearly indicates the formation of the crystalline films and the cross-sectional view (Fig. 2b) shows uniform formation of the film except the scattering of particles observed due to cutting of the film across. It is observed that all crystallites are not symmetrical in shape and showing a rhombohedral inclined platelet. The crystallites are not randomly oriented towards their c-axis which is perpendicular to the substrate plane. The results of EDAX spectra of a representative Bi_2Te_3 films of lower most and higher most thicknesses on a glass substrate are shown in Fig 2(c) and (d). From the EDAX analysis (Table 1) it was found that as the thickness increases, the films reach the stoichiometric

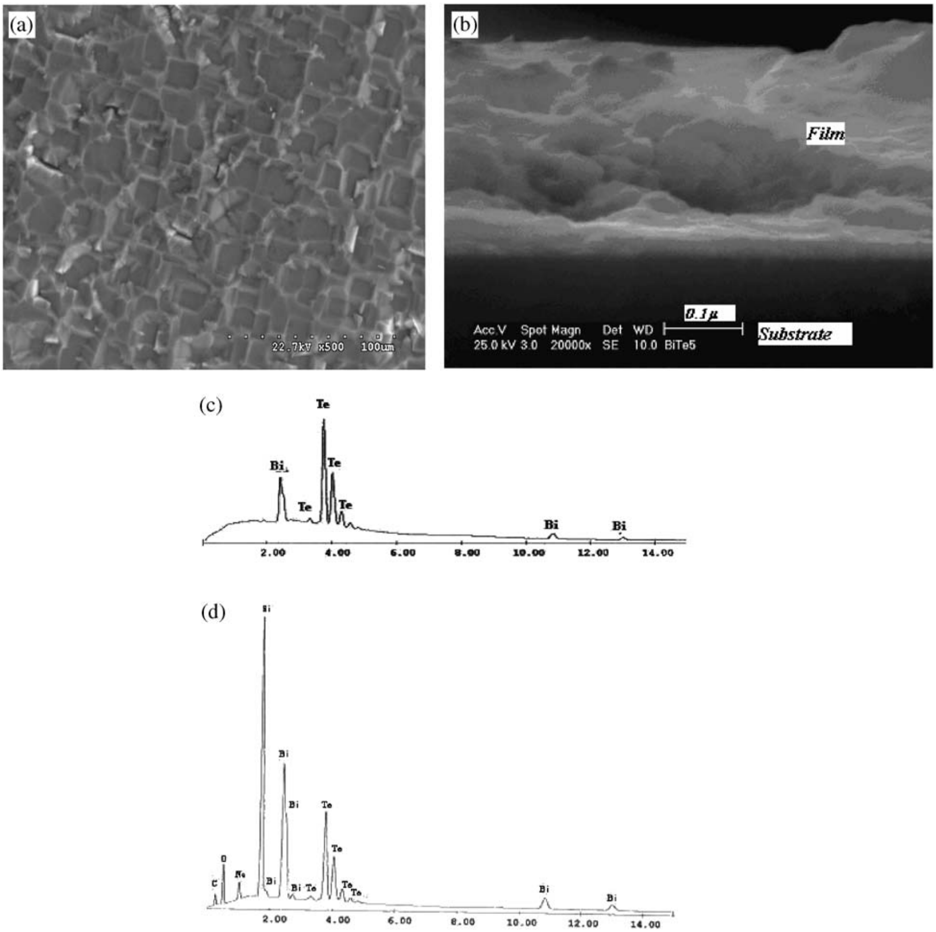

Fig. 2. (a) Surface morphology of Bi_2Te_3 thin film of thickness 250 nm, (b) SEM observation of the cross-section of Bi_2Te_3 thin film of thickness 250 nm, (c) EDAX pattern of Bi_2Te_3 film of thickness 50 nm, (d) EDAX pattern of Bi_2Te_3 film of thickness 250 nm.

Table 1
EDAX analysis results

Thickness (nm)	Composition	
	Bi	Te
50	30.45	69.55
100	45.65	54.35
150	48.84	51.16
200	52.38	47.62
250	52.61	47.39
300	52.61	47.39

composition. But still it is found that the films have little deficit of tellurium contents (52.61 Bi and 47.39 Te %), while the other identified peaks in the spectra correspond to the substrate.

3.2. Aging and annealing

During aging or self-annealing, structural changes and a redistribution of atoms takes place in the same way as in the case of annealing of thin films. The rapid changes in the internal field of the capacitors may be responsible for the large reduction of capacitance during the initial period of aging. The stabilization of these capacitors could be increased if the aging is carried out by repeated annealing cycles. The variations of capacitance with frequency for different annealing cycles are shown in Fig. 3. The capacitor has been annealed for three cycles (each at 373 K for 1 h) and has been found that the capacitance decreases with repeated annealing cycles. Freshly prepared films may contain many defects such as voids, grain boundaries, etc. Annealing of these films reduces the defects, which may lower the concentration of charge carriers and thereby enhances the resistivity of the film, which in turn reduces the capacitance. Similar behavior is observed for all the thicknesses and for our further studies, only one representative film of about 250 nm thickness is chosen.

3.3. Dielectric constant

Since the capacitance, dielectric constant and dielectric loss are important parameters in the selection of materials for device application, the dielectric study has been carried out on the stoichiometric film (250 nm) at different frequencies and temperatures to study their effect on capacitance, dielectric constant and dielectric loss. Fig. 4 shows the dependence of capacitance (C) on frequency at different temperatures for Bi_2Te_3 of thickness 250 nm.It is seen that the capacitance decreases

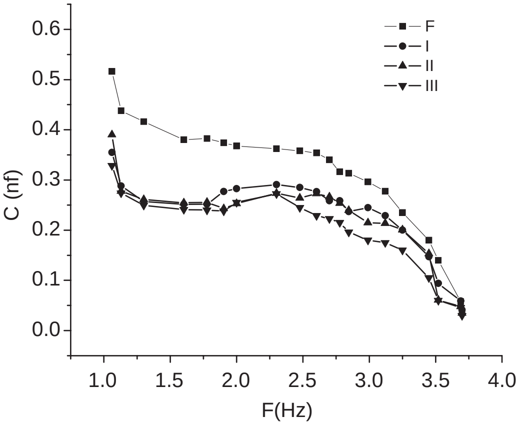

Fig. 3. Variation of capacitance with frequency for different annealing cycles for Bi_2Te_3 film.

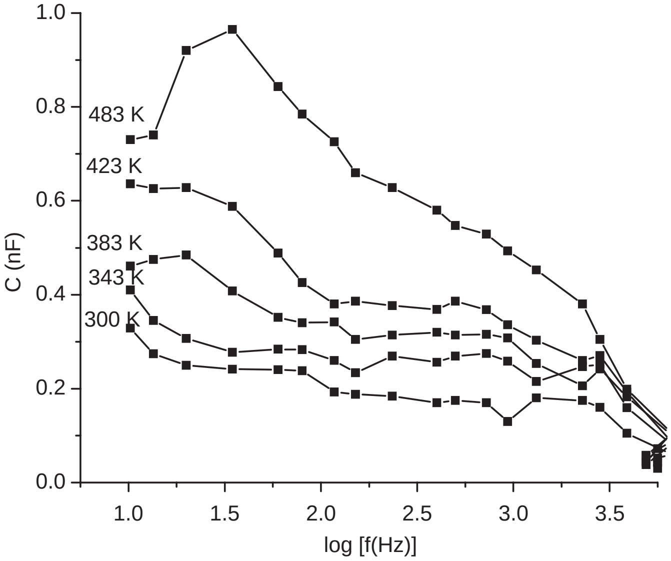

Fig. 4. Variation of capacitance C vs. Log f for different annealing cycles for Bi_2Te_3 film.

with increase in frequency at all temperatures. The observed nature of the capacitance is due to the inability of the dipoles to orientate in a rapidly varying electric field [23].

The dielectric constant of a solid is a property, which depends on the presence of atoms and molecules and their arrangements. From the known values of capacitance (C), thickness (t), free space permittivity (ε_0), and area of the semiconductor layer (A), the value of dielectric constant (ε') for different thickness of the films have been calculated using the relation [24],

$$C_{\mathrm{d}} = \varepsilon'\varepsilon_0 A$$

At higher temperatures ε' increases drastically with decrease in frequency and stabilizes a little and again shows a large variation at low-frequency region (Fig. 5).

Fig. 6 shows the variation of $\tan\delta$ (dielectric loss) with frequency at different temperatures. If the electric polarization in a dielectric is unable to follow the varying electric field, dielectric loss occurs. An applied field will alter this energy difference thus producing a net polarization, which lags behind the applied field because the tunneling transition rates are finite. This part of the polarization, which is not in phase with the applied field, is termed as dielectric loss. The gradual rise of $\tan\delta$, up to a frequency of 600 Hz and then a rapid increase may be due to the leading resistance and the inductance. It is interesting to note that the peak shifts towards higher frequency region with the increase of temperature. This shift of the relaxations peak towards the higher frequency region with the increase of temperature is found to be in agreement with the Debye theory of dipole orientation [25]. The presence of prominent loss peak manifests a dielectric relaxation effect in

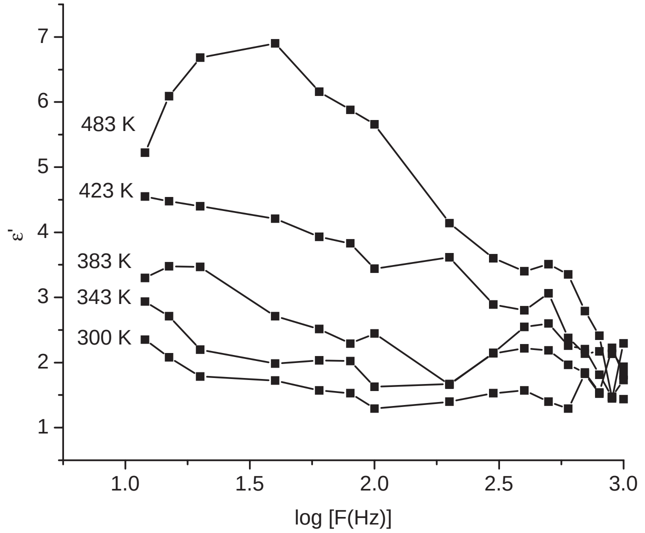

Fig. 5. Variations of ε′ with frequency at various temperatures for Bi_2Te_3 film.

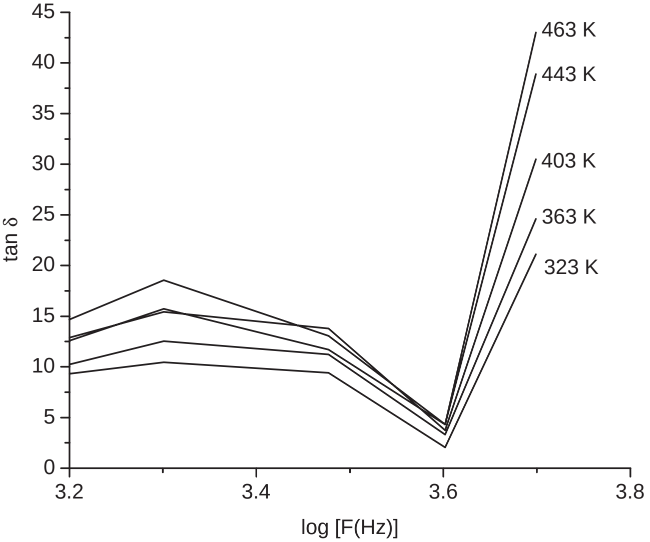

Fig. 6. The variation of tan δ with frequency at different temperature ($t = 250\,\text{nm}$) for Bi_2Te_3 film.

these films. The loss factor is seen to increase with increase of temperature and shows a maximum at each temperature, which shift towards a higher frequency as the temperature is increased [26,27]. For a Debye process at high temperature and for given frequency, a maximum in $\tan\delta$ will occur at a temperature such that $2\pi f_{\text{relax}} = 1/\tau$, τ is the relaxation time. Accordingly, f_{relax} will be greater when τ is less. The raise in temperature causes a reduction in the mean time of study of ionic dipoles [28] which in turn causes τ to decrease and f_{relax} to occur in the higher frequency range, as observed in the present study.

Cole–Cole plots of ε'' versus ε' at different frequency ranges for various temperature are shown in Fig. 7. According to the single Debye model for dipoles characterized by a single relaxation time the plot ε'' versus ε' over the entire frequency range will always be a semi circle. In evaporated solid films, the arrangement of nearest neighbour atoms is not exactly the same for all dipoles. Hence the dipoles cannot be characterized by a single relaxation time as in the simple Debye model. They will have a spread of relaxation time, the points lie on an arc of a circle which tends to become a semicircle with increasing temperature with its centre below the ε' axis. The value of spreading factor β at 323 K is determined as 0.244 and it decreases to 0.157 at 453 K. Thus the spreading factor is found to be temperature dependent and its value tends to zero at higher temperature. Knowing β, τ_a can be determined using the relation [29] $v/u = (\omega\tau_a)^{1-\beta}$, where v is the distance on the Cole–Cole diagram between ε_s and the experimental point, u is the distance between that point and ε_∞ and ω is the angular frequency. The values of β and τ_a obtained for two different temperatures are: $\beta = 0.244$ and 0.157 and $\tau_a = 5.01 \times 10^{-4}$ and 2.42×10^{-5} s for 323 and 453 K, respectively. In the capacitance–temperature plot (Fig. 8) it is observed that the capacitance increases with temperatures at all frequencies. The temperature coefficient of capacitance (TCC) for a film of thickness 2500 Å was estimated to be as 8.18×10^{-3} ppm/K for the temperature 450 K and at 100 Hz.

Similarly the temperature coefficient of permittivity (TCP) was calculated from the plot of ε' vs. T shown in Fig. 9, and it is determined as 6.78×10^{-3} ppm/K at 400 K and at 100 Hz. Since the capacitance of a capacitor is proportional to the permittivity of the capacitor dielectric, it is possible to relate TCC to TCP by the equation,

$$\mathrm{TCC} = \mathrm{TCP} + \alpha,$$

where α is the linear expansion coefficient of the capacitor dielectric and is evaluated as 1.4×10^{-3} ppm/K for the Bi_2Te_3 film. Making use of the relation [30,31],

$$F_m = F_0 \exp(-E/KT)$$

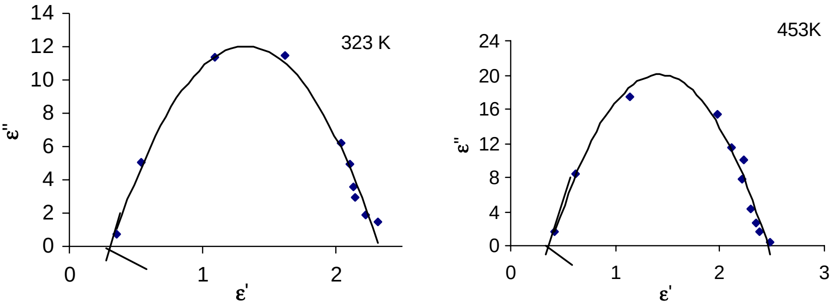

Fig. 7. Cole–Cole plots at different temperatures for Bi_2Te_3 film.

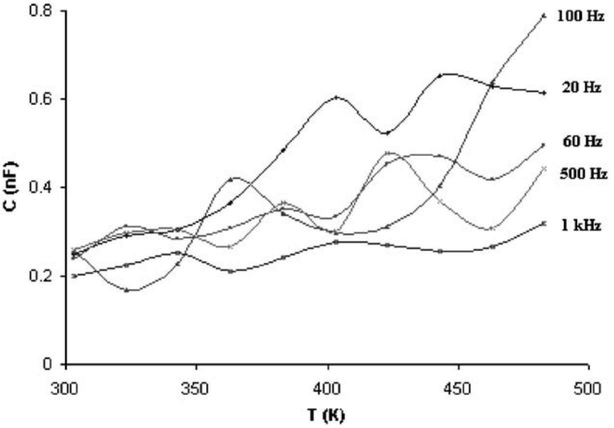

Fig. 8. Variation of capacitance (C) with temperature (T) at different frequencies for Bi_2Te_3 film.

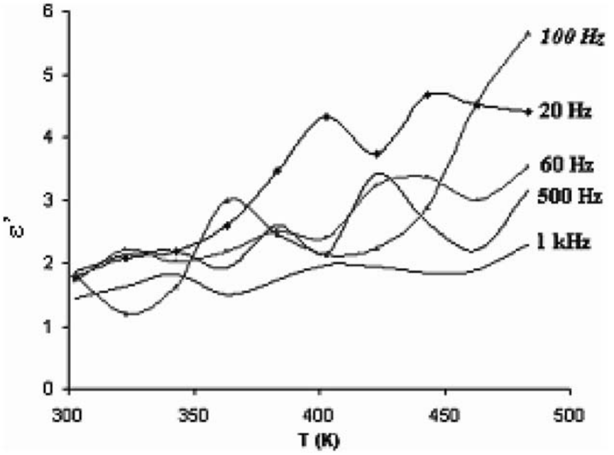

Fig. 9. Variation of dielectric constant ε' with temperature at different frequencies for Bi_2Te_3 film.

a plot was made, Fig. 10 of the logarithm of the frequency F_m at which $\tan\delta$ is a maximum against the inverse absolute temperature. The slope of this curve yields activation energy of 0.423 eV. The relaxation frequency here is the frequency at which $\tan\,\delta$ is maximum. The variation of $\log\omega$ with $1/T$ for two constant capacitances is shown in Fig. 11. The two plots are found to be linear and parallel and the activation energy was found to be 0.29 and 0.39 eV, respectively.

4. Conclusion

Without sacrificing the simplicity and versatility of vacuum evaporation method, good quality, stoichiometric films were prepared. All the films are found to possess

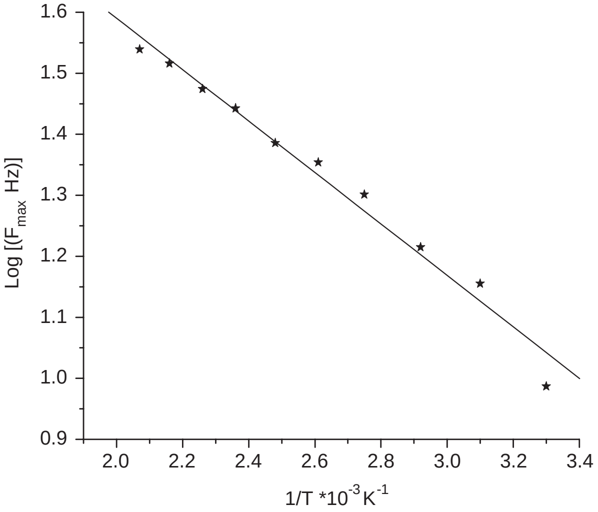

Fig. 10. Plot of $\log F_{\max}$ vs. the inverse absolute temperature of Bi_2Te_3 film.

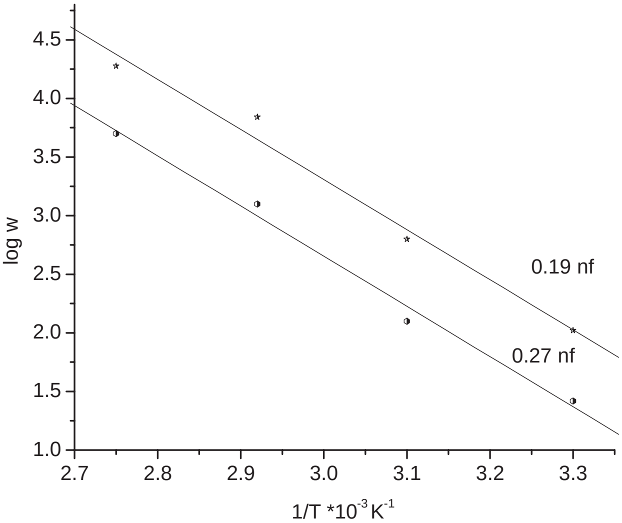

Fig. 11. Plot of $\log \omega$ vs. $1/T$ for constant capacitance of Bi_2Te_3 film.

rhombohedral structure. Al–Bi_2Te_3–Al thin film capacitors were fabricated are stabilized by annealing. The value of the dielectric constant varies from 0.65 to 2.86 in the thickness range 50–300 nm. The capacitor was found to decrease with increasing frequency and this is attributed to the increasing inability of the dipoles to become oriented in a rapidly varying electric field. The increase in capacitor towards low frequency suggests the possibility that charge carriers are blocked at the electrodes. The increase of capacitors with temperature in the film is due to expansion of the lattice and also to the excitation of charge carriers at the sites of defects. The variation of conductivity as a function of temperature and frequency reveals that the conduction mechanism in the Bi_2Te_3 film is mostly due to electronic hopping. The activation energy decreases with increase in frequency and with film thickness. The various observations made in this study clearly demonstrate the dielectric relaxation phenomenon arising from the dipolar reorientation in Bi_2Te_3 films.

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