Structural and electrical investigation of BLT films deposited at different times using electron beam evaporation technique

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Thin films $Bi_4Ti_3O_{12}$ (BLT) were deposited using electron beam evaporation on silicon substrate at several times, also on AlN/Si and SiO_2/Si substrates. Thin films morphology and thickness were measured via scanning electron microscopy (SEM). The crystallography was studied using X-ray diffraction (XRD) technique for films which have a (0010) preferred orientation in all substrate types. The capacitance values were contingent on frequency value in *C-V* measurement. The ferroelectric characterization was investigated for BLT film deposited on isolator layer (SiO_2 or AlN) for Al/$Bi_4Ti_3O_{12}$/SiO_2/Si devices. Memory effect value varied from 1 V to 3 V depending on the thin films isolator on substrate.

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La-substituted $Bi_4Ti_3O_{12}$ (BLT) polycrystalline films recently have interested due to use in ferroelectric random access memories (FRAMs) by reason of their big weariness endurance in addition to little deposition temperature[1,2]. Also, BLT has stable bipolar resistive switching (RS), and was ferroelectric materials[3].

BLT is piezoelectric and was investigated regarding both their important properties and device applications[4]. It is monoclinic ferroelectric with structure pseudo-orthorhombic whose unite cell *a*, *b* and *c* equal 0.545 nm, 0.541 nm and 3.283 nm respectively[5]. While in recent times, the BLT films are concerned epitaxial growth with c-axis-oriented films[6]. LIU et al[7] prepared bi-excess thin BLT films using radio frequency (RF) sputtering on Si substrates and Pt/Ti/SiO_2/Si, and they found the remnant polarization values were about from 0.8 μC/cm^2 to 4.8 μC/cm^2 depending on the annealing condition.

HWANGBO et al[8] have employed a metal naphthenate precursor aphthenate metal precursor and got the films optical band gap for BLT on substrate of MgO (100), where the band gap was improved between 3.53 eV and 3.67 eV with reducing the temperature of wishing (from 500 °C to 300 °C) and with reducing grain size. CHINCHAMALATPURE et al[9] have synthesized $BaTiO_3$/Si thin film using spin coating method and they studied their electrical and structural properties. The results showed that the deposited $BaTiO_3$ was good sufficient to be used as gate insulator. MANGLANI et al[10] have prepared $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin BLT film on substrate of Pt /Si (100) via sol gel spin coating technique at 600 °C during 2 h heating time.

Deposition of BLT films with metal organic chemical vapor deposition (MOCVD) technique was performed[11]. Also, KHEGAI et al[12] adjusted the composition for perovskite structure of BLT film by controlling the concentration. The FRAMs had characteristics of stability, better storage capacity, lesser operation voltage and good write and read speed[13]. The $PbZrTiO_3$ (PZT), BLT, $SrBi_2Ta_2O_9$, and (Ba, Sr)TiO_3 (BST) consider ferroelectric materials which have enhanced to increase storage capacity[4]. The BLT films have ferroelectric and optoelectronic characteristics with perovskite structure[4,14].

The thin BLT films were deposited by a variety of techniques like RF magnetron sputtering[15,16]. The thin ferroelectric BLT films were synthesized on several substrates of Pt/Ti/Si (100) via RF magnetron sputtering at 25 °C. Additionally, pulsed laser ablation technique was applied by KUMARI et al[17]. Electrical and structural description of the synthesized $Bi_2VO_{5.5}$/$Bi_4Ti_3O_{12}$ bilayer thin films was conducted. Molecular beam epitaxy was employed for deposition of BLT film[18]. There are many oxide films, such as TiO_2 deposited by electron beam evaporated[19], waver. We did not find any study of BLT deposition by E-beam evaporation except one recent work[5]. Among these techniques, electron beam elaboration is the most important one considering the features of electron beam evaporation constancy, reproducibility, high rate of deposition and the compositions of the films are managed. We can also find little work for not oxide films (for example ZnS) using electron beam

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technique[20,21] established polycrystalline hexagonal and cubic structures for ZnS films, respectively.

This paper is to study the probable BLT film by electron beam (E-gun deposition) without heating the substrate, using $Bi_{3.25}La_{0.75}Ti_3O_{12}$ target, on different substrate Si (100) Pt/Si and glass and characterize the optical, electrical (*C-V* and *I-V*) Al/BLT/Pt/Ti/SiO_2/Si (MIM) and Al/BLT/SiO_2/Si (MIS) crystallographers as well as structures properties.

Different substrates types were employed in this paper for investigating the structural and electrical properties. BLT films were deposited on Si (100) for 10 min, 20 min and 30 min, and we studied the quality crystalline for this film as a function of elaboration time. BLT films were elaborated on SiO_2/Si (100) and AlN/Si (100) for 30 min, where the AlN film was deposited using direct current (DC) magnetron sputtering[22] with a prefer orientation (002) at 36.058° with about 850 nm thickness, while the amorphous SiO_2 was deposited by thermal evaporation with 500 nm thickness.

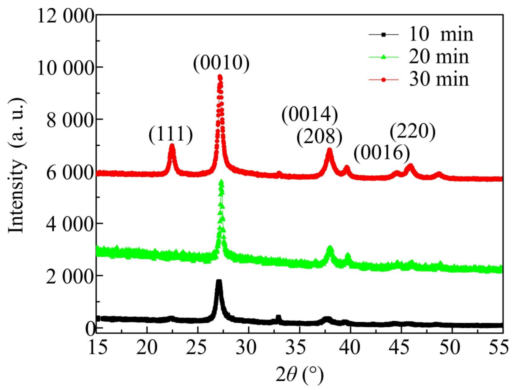
Elettrorava electron beam-physical vapor deposition (EB-PVD) system (made in Italy) was employed to deposit the BLT films (from 10 min to 30 min), where a brief characterization of the method will be provided here. $Bi_{3.25}La_{0.75}Ti_3O_{12}$ target (5 mm in diameter) was employed as evaporating source. In the vacuum chamber, high power electron beam (filament made in tungsten) was bombarded the crucible from the graphite. It used turbo pumps to obtain chamber vacuum below 9×10^{-6} mbar. Thickness and morphology of thin films were evaluated ex-situ utilizing scanning electron microscope (SEM, TSCAN model). The crystalline properties of the films were performed utilizing X-ray diffraction (XRD, Stoe Transmission X-ray) with θ-2θ scan configuration.

On the other hand, electrical characteristics were measured (*C-V* and *I-V*) by the 4192A-HP analyzer of the impedance, Keithley (237) supply measurement unit and QuadTech (1920 LCR) meter. The metallic spot contacts were procedured by synthesizing aluminum (circular with area of 0.48 mm^2) on films[23], the electrical characterization has done for both structures, the first for MIS (Al/BLT/Si) structure and the second for BLT film on isolators (Al/BLT/SiO_2/Si) and Al/BLT/AlN/Si.

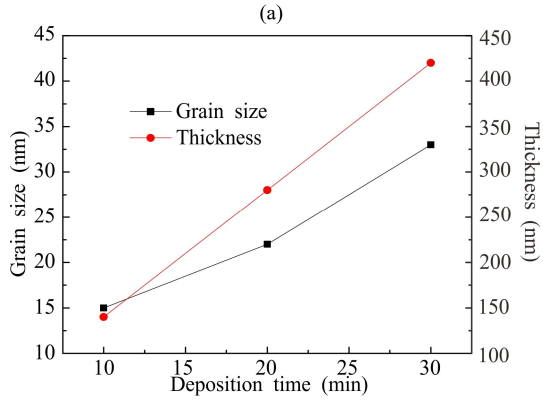
Fig.1(a) shows XRD patterns of BLT thin films elaborated on silicon orientation (100) substrate at different time, which changed from 10 min to 30 min.

These structures of films have preferential orientation of (0010) corresponding to 27.15° for orthorhombic phase and (111) corresponding to 22.45° orientation and (0014) corresponding to 37.94° orientation (well according with the number of PDF: 50-300) utilizing Crystallographica Search-Match software. These results are similar to HWANGBO et al[8] and recent work[5].

Fig.1(b) presents the thickness evolution and size of the grain with the deposition time (10 min, 20 min and 30 min), which shows the thickness increasing from 140 nm to 420 nm as a function of the deposition time (10—30 min). The grain size for (0010) peaks of BLT thin films is estimated via Scherrer's formula[24] and it was found to increase with augmenting the thickness (Fig.1(b)). The grain size estimated for $Bi_4Ti_3O_{12}$/Si (100) from 15 nm to 33 nm with the thickness increasing from 140 nm to 420 nm corresponding to deposition time from 10 min to 30 min. The effect of the thickness on the electrical and structural properties of ZnS[25] and ZnO[23] thin films was studied. The quality of the crystalline was improved, i.e., big grains expanded with increasing the film thickness[26].



(a)



(b)

Fig.1 (a) XRD pattern for BLT thin films deposited on Si (100) substrate; (b) Grain size and thickness evolution for 10 min, 20 min and 30 min deposition time

Fig.2 shows the BLT films deposited on AlN and SiO_2 film have prefer orientation (0010). The BLT/AlN film has better crystallinty (peaks intensity and grain size of BLT/SiO_2). The grain sizes for (0010) peaks of BLT films were found to be 17 nm and 30 nm for BLT films deposited on SiO_2/Si and AlN/Si, respectively.

The substrate effect was reported by LIU et al[7] and previous work[27]. The thick AlN deposited on Si (100) and on molecular-beam epitaxy (MBE) grown AlN/Si (111) films were deposited by DC magnetron sputtering with a good quality crystalline with (002) ordination. Whereas, the synthesized AlN/Si (100) has equal crystalline quality to the MBE grown AlN. Also, RAHMANE et al[22] have examined that the ZnO/AlN film synthesized which is very dependent on the quality crystalline of the substrate (AlN film) and offers an epitaxial growth, where these films were described by selected area of electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) photos.

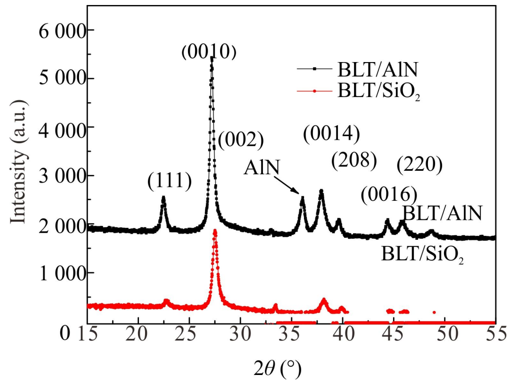


Fig.2 Patterns of XRD for BLT thin film elaborated on AlN/Si and SiO_2/Si substrates for 30 min

One can show thin BLT film cross-section elaborated at 10 min (Fig.3) using SEM, where the thickness was about 140 nm. The development of thickness with the deposition time highlights a linearly augmenting behavior in Fig.1(b), and the deposition rate is calculated to be 14 nm/min. In previous work, similar behaviors were described[25], where thin ZnS films/Si (100) were doposited by ultrasonic spray pyrolysis.

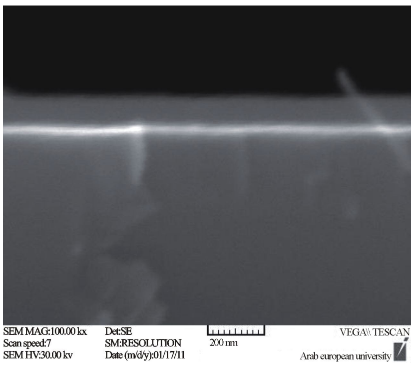


Fig.3 SEM for BLT/Si thin films elaborated for 10 min

We found in Fig.3 that the size of the crystallite increased with increasing of the thickness for (0010) orientation. This evolution enhancement with the thickness was reported in Na_2WO_4 films utilizing ultrasonic spray pyrolysis[28].

Properties of the current-voltage of Al/BLT/Si were perpendicular to films for various thickness values (from 140 nm to 280 nm) as shown in Fig.4. All curves' general direction shows the current of the semiconductor conduction heterostructure[23]. We investigated usual *I-V* properties of Al/ZnO/Si heterostructure below reverse bias for varied film thickness. It can be observed that value of the current is important at thickness of the top film with conduction controlled primarily using grain boundaries offered inside ZnO.

ALNAMA et al[25] investigated ZnS/Si heterostructure below bias of reverse for diverse film thickness. Fig.4 shows usual *I-V* properties of Al/BLT/p-Si below forward bias for various thicknesses of the film as indicated, where the region of little voltage from 0 to 2.5 V of recombination was created as electrons of the excitation from the band of valence to the band of conduction correlated with holes that existed at valence band. Ahead of 2.5 V, current of tunneling get part and it could examine an enhance as exponential in the current scale (diffusion of current) at upper voltage of forward as a function of conduction controlled now via diffusion. In the reverse bias apiece from the film deposited at 20 min, the generation current process occurred at an enlarged values of voltage (> 4 V), after which the current of diffusion obtains over[29].

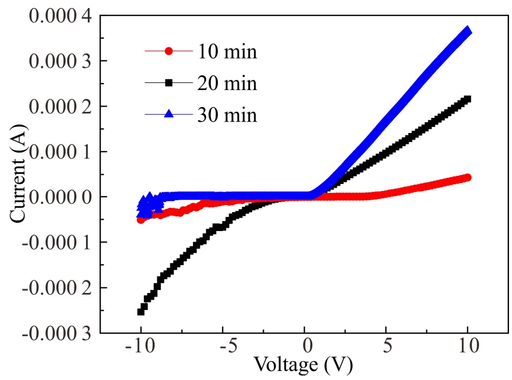


Fig.4 *I-V* measurement of Al/BLT/Si for different thicknesses of film

In common, the forward current is produced because the majority carriers flow, where the applied voltage of bias decreases width of reduction layer and the built-in potential like the majority carriers gets inserted (Fig.4). It is famous that crystal quality enhancement (bigger grain) is related to important and sharper characteristic of *I-V* for 30 min, which accorded with previous work[25] for studied *I-V*. Al/n-ZnS/Si films were obtained perpendicular to films for some values of deposition time (from 10 min to 70 min).

ALNAMA et al[25] investigated 25 mV in 1 MHz frequency with bias of forward correlated to electrode of the Al gate. The interface of computer was utilized to assist precise data achievement through the characteristic process.

Fig.5 shows four indicated curves of *C-V* for BLT films get at functional frequency (1 MHz) associating to deposition of the time varied from 10 min to 30 min as indicated by the legends. The properties were verified in an extensive voltage of bias from −35 V to 35 V, as could be observed with clearly perfect depletion, inversion layers, and accumulation indicating n-type carriers' conduction.

Fig.4 shows increase in the capacitance values (from about 2 pF to 3.1 pF) with increasing the deposition time corresponding to increase in the thickness (from 120 nm to 420 nm), which was contrary to ALNAMA et al[25] in

C-V study for ZnS/Si films. ABDALLAH et al[24] in a metal-insulator-semiconductor design studied that the films have good quality with a great ratio between maximum and minimum capacitance values. Moreover, the enhancement in the film crystallinity with augmenting thickness has effected in decreased capacity.

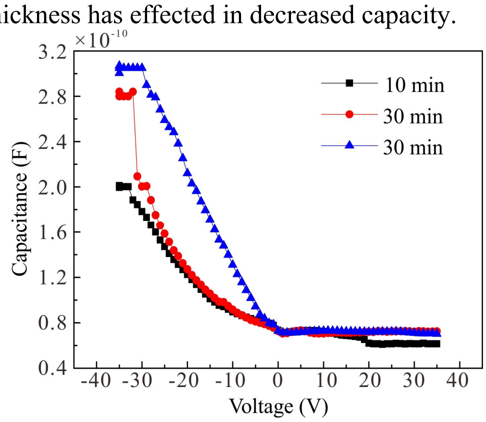


Fig.5 Typical *C-V* properties of Al/BLT/Si under sweeping the voltage of bias backward (The frequency is 1 MHz for thickness of diverse film)

Fig.6 shows the capacitance versus bias voltage between 1 MHz and 100 kHz frequencies. For thickness of the BLT/Si film of 420 nm (30 min), it presents the interface presence traps offsetting the *C-V* curve. This manner was identified in previous work[24] for capacitance versus bias voltage between 1 MHz and 150 kHz frequencies for thickness of the AlN/Si film of 200 nm.

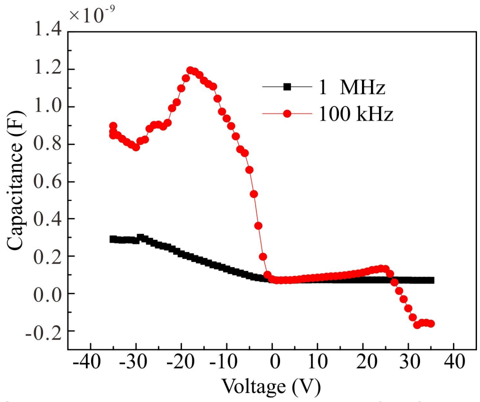


Fig.6 Capacitance versus bias voltage for frequencies of 100 kHz and 1 MHz with thickness of the BLT/Si film (420 nm at 30 min), indicating the interface traps presence offsetting the *C-V* curve

Fig.7(a) presents the *C-V* characteristics of Al/BLT/SiO_2/Si structure of capacitor of 10 min for sweeping the voltage of bias backward and forward down to 1 MHz frequency for 140 nm thickness of the film (10 min deposition time). It has memory effect value of about 1 V.

Fig.7(b) presents measurements of the *C-V* of Al/$Bi_4Ti_3O_{12}$/AlN/Si capacitor of 30 min of sweeping the voltage of bias backward and forward at 1 MHz frequency for film thickness at 420 nm (30 min deposition time). It has memory effect value of about 3 V.

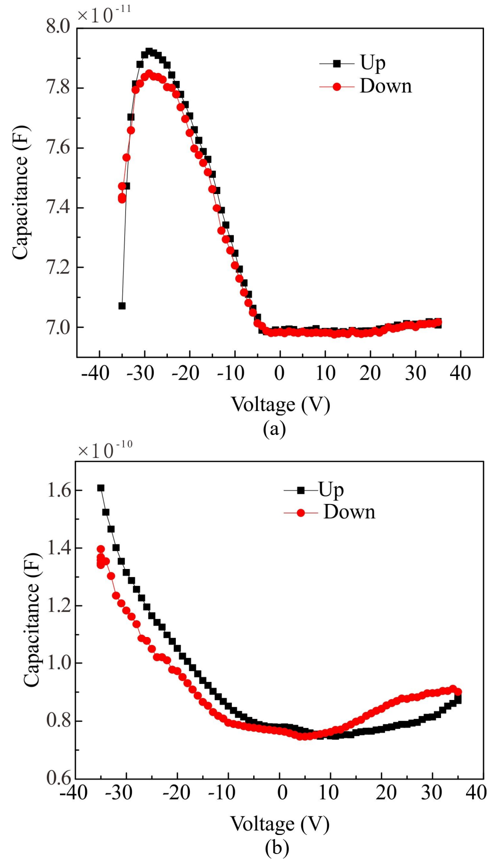


Fig.7 Typical *C-V* measurements of (a) Al/BLT/SiO_2/Si and (b) Al/$Bi_4Ti_3O_{12}$/AlN/Si under sweeping the voltage of bias forward and backward at frequency of 1 MHz for the film at 140 nm and 420 nm, respectively

The characteristics of *C-V* were performed by applying a small signal of 0.5 V (alternating current), with a differing electric field (DC). The DC voltage was removed between positive (35 V) to negative bias (–35 V) in steps of 0.1 V with a removal rate of 0.1 V/s and set back another time. KUMARI et al[30] found the butterfly curve shape, and verified the nature of ferroelectric for the BVBT BL film (Au/BVO/BTO/Si (100)) and the capacitance explains physically powerful voltage reliance. The two loops matched to the field buttoning voltage in reverse and forward directions, while the reversal of polarization gets place. The irregularity that is noticed in *C-V* curve proposes that the electrodes are irregular and the film contains moving charges or ions accumulated at the boundary (interface) between the electrode and the film. There is a discrepancy between values of the capacitance for the two peaks, possibly because of many defect stages of energy in the film.

CHEN et al[31] for BLT on Al_2O_3/Si (utilized in support of one-transistor ferroelectric like memory) reported that the hysteresis curves of *C-V* shown in their results are linked to characteristics of the ferroelectric for BLT film due to Al_2O_3 gate dielectric has insignificant hysteresis. The reduced value of capacitance at positive gate bias in the FeMOS structure is because the little series capacitance in silicon depletion area. The phenomenon is various from that in the metal/ferroelectric/metal (MFM) structure due to the insignificant depletion width in metal. A threshold voltage move of 1.6 V is calculated for BLT on Al_2O_3/Si that is the same as that in MFM capacitor. The same voltage shift proposes that the electric memory characteristics of BLT on Al_2O_3/Si are at least even or the same better than that on Pt, because of the further voltage drop in Al_2O_3 gate dielectric and decreased electric field in BLT[31].

BLT films were deposited using electron beam evaporation, when deposition time increased as the thickness increased. A usual study of the control of thickness for several (special physical) thin BLT films properties was achieved. The crystalline of quality was improved, i.e., big grains size increased with the increasing thickness. All films synthesized on Si (100) at different thicknesses and synthesized on SiO_2/Si (100) and AlN/Si (100) have prefer orientation deduced by XRD technique. Morphology and thickness were studied for films by SEM.

The capacity increased with film thickness increased, accompanied with the increase of the size of grain for BLT on Si (100) substrate. The size of grain to BLT film synthesized on AlN crystalline orientated (002) was better than that for the film deposited on amorphous SiO_2.

There is an important relation between the electrical behaviors and substrates quality and nature (amorphous or crystalline) in BLT, and consequently the correlation between the crystallographic proprieties and ferroelectric behaviors was studied. The memory window was maximal value for BLT film deposited on isolator AlN buffer layer (about 3 V).

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Ethics declarations

Conflicts of interest

The authors declare no conflict of interest.

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