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Ferroelectric Thin Film Bismuth Titanate Prepared From Acetate Precursors

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Abstract

Bismuth titanate ($Bi_4Ti_3O_{12}$) thin films were fabricated by spin coat deposition followed by rapid thermal processing (RTP). Acetate derived solutions for deposition were synthesized by blending bismuth acetate in aqueous acetic acid and then adding titanium acetate. A series of electrically insulating, semiconducting and conducting substrates were evaluated for $Bi_4Ti_3O_{12}$ film deposition. While X-ray diffraction and TEM analyses indicated that the initial perovskite crystallization temperature was 500°C or less for these $Bi_4Ti_3O_{12}$ films, a 700°C crystallization treatment was used to obtain single phase perovskite films. $Bi_4Ti_3O_{12}$ film crystallographic orientation was shown to depend on three factors: substrate surface morphology, the number of coating layers and thermal processing. While preferred c-direction orientation was observed for $Bi_4Ti_3O_{12}$ films deposited on silver foil substrates, preferred a-direction orientation was obtained for films deposited on both Si and Pt coated Si wafers. The films were dense, smooth, crack free and had grain sizes ranging from 20 nm to 100 nm. Film thickness and refractive index were determined using a combination of ellipsometry, waveguide refractometry and TEM measurements. Both low field dielectric and ferroelectric properties were measured for an 800 nm thick film deposited on a Pt coated MgO substrate. A remanent polarization of 38 $\mu C/cm^2$ and a coercive field of 98 kV/cm were measured for this film that was crystallized at 700°C.

Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$, abbreviated as BIT in this paper) is an important ferroelectric (FE) material. Single crystal BIT is a layered structure compound and has a very high Curie temperature (675°C). It possesses a pseudo-tetragonal structure as proposed by Aurivillus.[1] As temperature decreases below T_c, there is increasing lattice distortion[2] of (a/b), and the structure becomes monoclinic at room temperature as reported by Cummins and Cross.[3] However, ambient X-ray and neutron diffraction data are also consistent with a pseudo-orthorhombic structure[4] with a=0.5411nm, b=0.5448 nm, and c=32.83 nm. We will use the orthorhombic symmetry and notation for the rest of this paper. The interest in BIT for practical applications has focused on its ferroelectric properties and its electro-optical switching behavior. Single crystal BIT has two spontaneous polarization components with magnitudes of 50±5 $\mu C/cm^2$ in the b-direction (orthorhombic) and 4.0±0.1 $\mu C/cm^2$ in the c-direction, they can be reversed independently. Switching of Ps in the c-direction changes the birefringence and tilts the optical indicatrix of BIT in the b-c plane by approximately 10° which is attractive for electro-optic devices. In addition, the large spontaneous polarization in the b-direction makes BIT potentially useful for applications requiring large values of switched charge.

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Polycrystalline BIT has been readily fabricated by various processes. Preferentially oriented bulk BIT ceramics and thin films have received a great deal of attention for the development of both high temperature piezoelectric and integrated semiconductor devices. In the past few years, there have been attempts to make highly grain oriented bismuth titanate bulk ceramics.[5,6] There are a few reports of BIT thin film fabrication; for example, by pulsed laser deposition[7,8] solution chemistry,[9] and rf and reactive diode sputtering.[10] However, there has been no report of highly oriented thin films produced by wet chemical techniques. The purpose of this study is to investigate the evolution of perovskite BIT thin films from acetate precursors. Further, substrate technologies and associated film processing techniques which lead to preferential grain orientation in BIT thin films are discussed. The ferroelectric properties of a highly (200) oriented BIT film is also presented.

Experimental Procedure

Bismuth titanate thin films were deposited using spin coating and then crystallized using rapid thermal processing (RTP) on a variety of substrates: single crystal silicon, silver foils, glass, alumina, and Pt coated single crystal MgO substrates.

The acetate-derived precursor solutions were prepared by dissolving bismuth acetate [$Bi(COCCH_3)_3$, solid form] in an aqueous glacial acetic acid solution containing 20 vol% water at room temperature. A colorless solution was obtained, and titanium acetate [75% titanium bis(acetylacetonate) diispropoxide in isopropanol $Ti(CH_3COCHCOCH_3)_2$-$(OC_3H_7)_2$ was then added to the solution. The ratio of bismuth to titanium used in these solutions was slightly higher than the stoichiometric value of 4:3 in order to promote perovskite phase formation. A ratio of BiAca to TiAca of 1.492 was obtained by carefully weighing the initial precursors, which is approximately 12 mol% excess Bi compared to the stoichiometric value. The final precursor solution was visibly clear and had a yellowish tinge. A series of solutions were synthesized with concentrations ranging from 0.05 M to 0.3M to determine the effect of solution concentration on film quality. The solutions were stable over a period of several months.

Films were fabricated by depositing multiple spin coat layers and were then crystallized by rapid thermal processing. Before coating, the substrates were cleaned by alcohol or acetone and some were annealed at 400°C for 10 min. The precursor solution was deposited on a given substrate using a filtered syringe, and then spun on the substrate for 30 seconds at 3000 rpm. The film dried quickly at room temperature and was then crystallized at a fixed temperature in the range of 400°C to 800°C for 2 minutes. After the layer cooled, it was cleaned using an EFFA duster and the next layer was then deposited. The film was crystallized for 15 minutes after the last layer was deposited. Films ranging in thickness from 100 nm to 1000 nm were fabricated by this multilayer deposition process. Among the techniques used to characterize the BIT thin films were X-ray diffraction, differential thermal analysis (DTA), thermogravimetric analysis (TGA), atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and ellipsometry.

Electrical Measurements

Resistivity, low field dielectric constant, remanent polarization and coercive field were among the properties measured for a BIT film deposited on a Pt coated MgO substrate. The 100 nm thick Pt layer was rf magnetron sputter deposited at ambient temperature. While an HP 4192 impedance analyzer was used for the low field dielectric measurements, a Radiant Technologies RT66A ferroelectric tester was used to obtain ferroelectric hysteresis loops. Typically, low voltages (0.1 Vrms) were used to minimize ferroelectric domain contributions to the low field dielectric constants measured. Resistivity measurements (dc) were made by applying 20 volts and measuring the current two seconds after the voltage was applied. The details of the electrical fatigue measurements on this BIT film will be presented in the discussion section of this paper.

Results and Discussion

1. BIT Phase Formation

X-ray diffraction was used to monitor $Bi_4Ti_3O_{12}$ phase evolution as a function of crystallization temperature, as shown in Figure 1. All BIT films in Figure 1 were deposited on silicon (100) single crystal wafers. A native oxide (SiO_2) layer, approximately 5 nm thick, is estimated to be on the Si wafer surfaces. The results indicate that the structure of the film which was annealed at 400°C was essentially amorphous by X-ray diffraction analysis and the pattern contained a broad maxima around the highest intensity peak (117) of BIT. As temperature increases, the amorphous phase partially transforms into a highly crystalline perovskite phases, as evidenced by the sharp, high intensity diffraction peaks for the film crystallized at 500°C. The intensity of the major diffraction peaks of the BIT thin films further increases with increasing crystallization temperature, while the broad maxima decreases and eventually disappeared for the 700°C crystallization temperature. Since the perovskite diffraction peaks are so sharp, we attribute the broad maxima to a nanocrystalline pyrochlore phase. The sharp diffraction peaks for the film crystallized at 700°C indicated that the perovskite crystallinity was well defined at this temperature.

The X-ray diffraction patterns of Figure 1 demonstrate that the acetate-derived solution process results in substantial perovskite crystallization at 500°C. The crystallization temperature is less than previous reports of BIT materials fabricated by solid state reaction or molten salt synthesis. From X-ray diffraction and TEM measurements, no second phase was detected between the BIT film and the SiO_2//Si substrate. The SiO_2 layer was approximately 5 nm thick, which is below the detection limit for our instruments. Obviously, if BIT films can be deposited directly on Si with no oxide formation, this would be a great step forward for integrated ferroelectric applications. Whether these acetate-derived BIT films can be fabricated directly on Si with absolutely no interface oxide formation has yet to be determined. Our results indicated that little or no reaction occurred between BIT films and the following substrates: MgO, sapphire or Pt coated MgO.

2. Crystallographic orientation of BIT Thin Films

The crystallographic orientation of BIT thin films fabricated in this study was characterized by X-ray diffraction and TEM analysis. A highly c-oriented BIT film was obtained after deposition on a Ag foil substrate as shown by the X-ray diffraction pattern in Figure 2. No evidence of crystallite orientations other than

(00l) was observed. BIT films with multiple crystallite orientations are obtained after deposition on single crystal silicon substrates, as shown in Figure 3. Once again, the SiO_2 thickness is estimated to be approximately 5 nm. Similar crystallite orientation was found for the films deposited on either Si (100) or Si (111) substrates, as expected, if a thin native oxide layer is present on these substrates.

The degree of crystallographic orientation in a thin film is not always determined solely by the substrate lattice parameter. Surface nanotopography, cleanliness of the substrate, surface microchemistry and substrate lattice parameter are other factors that may affect BIT film structure. Silicon wafers have an almost atomistically smooth surface, whereas, the silver foil substrates have a rolled, grain textured surface. The surface roughness of a BIT film deposited on a (100) Si substrate was measured by AFM, as shown in Figure 4. The average surface roughness was approximately 10 nm. The top surface of a BIT film deposited on a silver foil substrate is shown in Figure 5. This film is far different morphologically than the BIT film deposited on Si. The grains are platelike, with the a-b plane of the BIT film being oriented parallel to the silver foil surface resulting in a high degree of c-orientation perpendicular to this surface. These results suggest that the microchemistry, lattice parameter and grain size of the underlying substrate strongly effects the crystallite morphology and orientation of BIT films. Our postulation is similar to that reported by Shu-Yau Wu and coworkers.[11]

We have also determined the variation of grain orientation with the number of coating layers as determined by XRD and TEM analyses, as shown in Figure 3. There is no significant preferential orientation for the films deposited on silicon for the first layer. As the number of coating layers increases, up to 5 layers, the diffraction intensities in the (001), (200) and (111) directions increased. With further increase in the number of deposition layers, the orientation in the (200) direction increased, while the volume fraction of crystallites with (001) type orientations decreased. The variation in crystallite orientation with the number of deposition layers is shown in Figure 6, for which, plots of Lotgering orientation factors in the (001) and (200) directions as a function of number of coating layers are presented. The maximum c-direction orientation occurs for the 5 layer film. When the number of coating layers were greater than 10, the (200) orientation was dominant. The Lotgering orientation factor for the (200) direction was 42%, which indicates that almost half the BIT grains in this film had this orientation.

The preferential orientation in the (200) direction (corresponding to the b-axis in the monoclinic BIT cell) of the BIT thin film is very attractive because the largest value of spontaneous polarization lies in the monoclinic a-c plane and in the orthorhombic a-direction. As the degree of (200) orientation increases, a higher remanent polarization should be achieved in BIT films. For the oriented polycrystal, if the a-c or b-c plane is parallel to the substrate, the a nd b directions can be reversed by an applied electric field, and a large change in dynamic polarization will be measured. This phenomena may be attractive for next generation, high density memories or optical display applications. The basic principle of operation for the metal ferroelectric semiconductor (MFST) device is to control the surface conductance of a bulk semiconductor (silicon) and to perform the memory function.[13] Therefore, a high remanent polarization is desired to obtain a sufficient modulation.

3. Characterization of BIT Thin Films

3.1 Morphology

The BIT thin films fabricated in this study were for the most part transparent. A systematic change in interference color was observed for BIT films deposited on Si wafers as a function of thickness. The BIT films appeared shiny when deposited on other substrates, such as, glass, MgO, Ag, and sapphire. Large uniform areas and crack-free films were observed using optical microscopy, SEM and AFM. The films were dense and contained no apparent porosity by these techniques. The average particle size increased for 20 nm to 400 nm, as the number of coating layers increased from 1 to 10, for BIT films deposited using 0.09 M solutions. Figure 7 shows both particle size and film surface roughness increases with increased number of coating layers. This was attributed to the increase in grain size of the BIT films with increasing film thickness. We caution that particle size determined by AFM analysis does not always correspond directly to grain size, this is the reason for the distinction between particle and grain size. Our microscopic analysis indicates that for these BIT films that particle size and grain size are indeed similar.

It must be emphasized that the surface condition of the substrate affects the nanomorphology of the film. Since the Si wafer is extremely smooth, homogeneous nucleation rates are comparable to heterogeneous nucleation rates and a fine particle size (less than 100 nm) is obtained. However, the BIT film deposited on the Ag foil exhibited a distinctly different surface morphology. The particle size was extremely large ($\approx 1\ \mu m$) compared to the size of the BIT grains for the films deposited on Si substrates. Pores were also observed in films with a reduced number of deposition layers. These observations suggest that an epitaxial type finish for the underlying substrate is most appropriate for production of high quality ferroelectric thin films.

3.2 Thickness

The thickness of the various BIT thin films was indicated by the interference color, as previously noted. Film thickness was measured by both a manual ellipsometer and by TEM analysis. Film thickness - refractive index relationships were determined using the ellipsometer software analysis. Figure 8 shows the film thickness as a function of both the number of deposition layers and the concentration of solution. Linear relationships were observed in both cases, within the accuracies indicated on the plots. These thickness measurements were further confirmed by TEM analysis for a select group of these films. While a thickness of approximately 270 nm was measured from TEM analysis for a 10 layer film, deposited from 0.1 M solution on a Si substrate and crystallized at 700°C, a thickness of 255 nm was obtained from the ellipsometer measurements. The accuracy of the ellipsometer measurements is approximately ± 40 nm. The variation of thickness as function of crystallization temperature did not significantly change. Thus, ultimate BIT film thickness can be controlled by either the number of deposition layers or the concentration of the precursor solution.

4. Property Evaluation of BIT Thin Films

4.1 Refractive Index

The refractive indices of the films were measured using both a Gaertner model L1117 manual ellipsometer and a waveguide refractometry technique. The average refractive index for the BIT films was determined to be 2.60±0.1 using ellipsometry. Iterative fits to the raw data obtained using waveguide refractometry

failed to completely describe the angular positions of reflectivity minima corresponding to waveguide modes within the BIT film/MgO system. Approximate limits on the probable refractive index, however, do suggest an average refractive index in the 2.6 range for this sample. It is important to note that the inability to obtain a fit to the raw data indicates that the film may not possess macroscopically uniform optical properties defined by a single refractive index. Although a change in refractive index with film thickness may be used to describe the observed behavior, a unique fit to the raw data can not be obtained in this case due to the corresponding increase in adjustable parameters describing the unknown films. Within the assumptions used to model the thin film/substrate system, both techniques give results which are in fair agreement with the single crystal values of refractive index that are on the order of 2.68

4.2 Dielectric properties

A reasonably saturated, dielectric hysteresis loop was obtained for a 760 nm thick BIT film deposited on a Pt coated MgO substrate, as shown in Figure 9. While a 20 volt peak signal was used to electrically switch the ferroelectric film, 11.5 ms was required to obtain the hysteresis loop. The bottom electrode was fabricated by RF magnetron sputtering a 100 nm thick Pt film on a MgO substrate (Atomergic Corporation) with an epitaxial finish. The top Pt electrodes were also deposited by RF magnetron sputter deposition and had an area of 1.55×10^{-3} cm^2. A remanent polarization of 38 μC/cm^2 and a coercive field of 98 kV/cm were measured. These properties compare favorably to previous work.[14,15] Measured dc resistivities were essentially polarity independent and were on the order of 4×10^8 ohm-cm. The percentage of electrode dots tested that gave good electrical properties was not large, as only 15% of the dots tested were not electrical shorts. For the highly c-oriented BIT film deposited on silver foil, a low voltage (0.1 Vrms), 10 kHz dielectric constant of 108 was obtained. This value is approximately that measured for BIT single crystals in the c-direction. A higher dielectric constant of approximately 550 and a dissipation factor of 0.037 was measured for the BIT film of Figure 9 that contained multiple crystallite orientations.

4.3 Fatigue Measurements

The electrical fatigue performance of the BIT film deposited on a Pt//MgO substrate was considerably better than that obtained for a PZT 40/60 film with Pt electrodes. For both films, a 250 kV/cm, sinusoidal field was used to fatigue the specimens. After 1.2×10^8 cycles, the polarization of the PZT 40/60 film decreased from 24.5 to 10 μC/cm^2; whereas, the remanent polarization of the BIT film decreased from 26.9 to 25.3 μC/cm^2. The difference in remanent polarization compared to the BIT film electrode dot tested in Figure 9 indicates that there is presently some variability in our processing.

IV. Conclusions

Single phase $Bi_4Ti_3O_{12}$ thin films were fabricated from acetate-derived solutions. Substantial perovskite crystallization occurred for temperatures as low as 500°C. From precursors that were clear and relatively stable with time, BIT films that were dense, homogeneous and crack-free were fabricated. The crystallographic orientation of BIT thin films were shown to depend on the type of substrate used and the condition of the surface of the substrate. Preferentially (200)

oriented films were obtained by multiple layer deposition on single crystal silicon wafers. BIT films that were highly (002) oriented were fabricated on silver foil substrates. The refractive index measured for the BIT thin films in this study is approximately 2.6±0.1, which is close to single crystal values. The thickness of the films varied linearly both with the concentration of the precursor solution and the number of coating layers. A remanent polarization of 38 $\mu C/cm^2$ and a coercive field of 98 kV/cm were measured for a BIT film deposited on Pt//MgO substrates and crystallized at 700°C.

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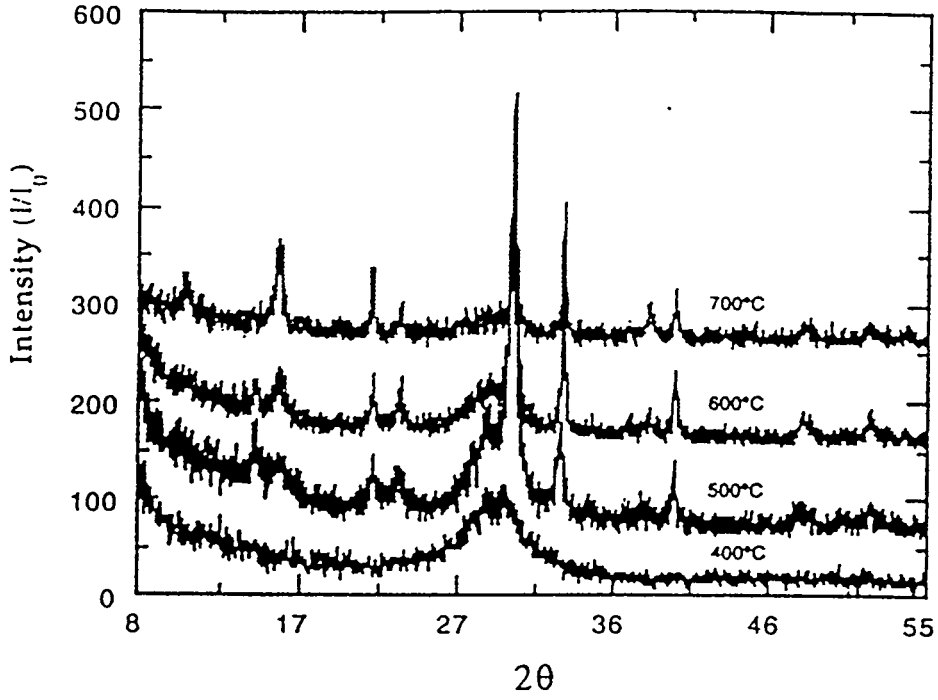


Figure 1: X-ray diffraction patterns depicting BIT thin film phase evolution as a function of temperature. All four films were deposited on Si (100) wafer sections, consisted of 4 layers and were approximately 120 nm thick.

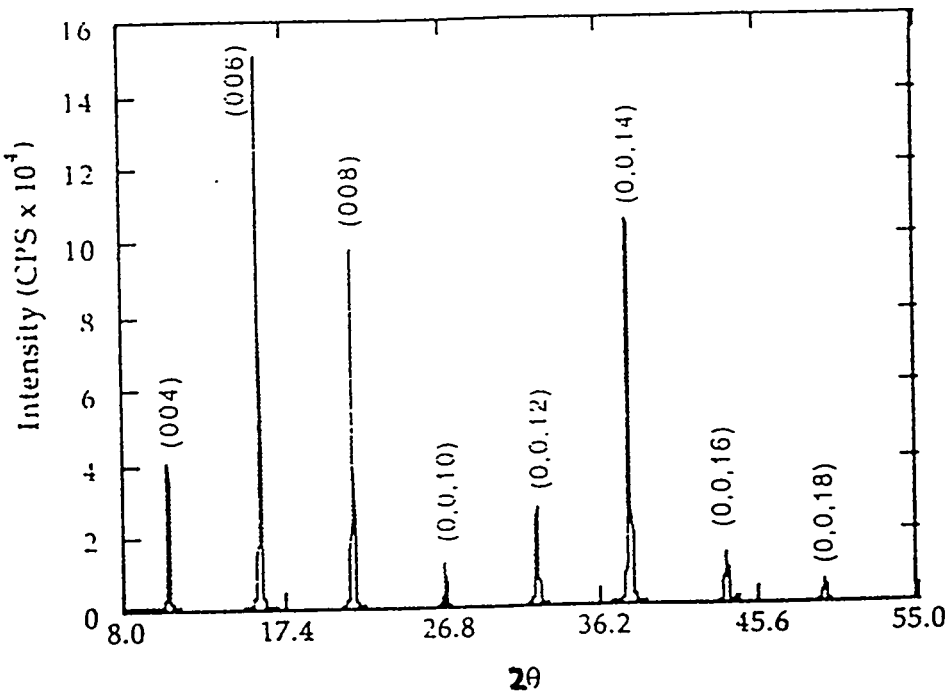


Figure 2: X-ray diffraction pattern of a BIT thin film crystallized at 700°C.

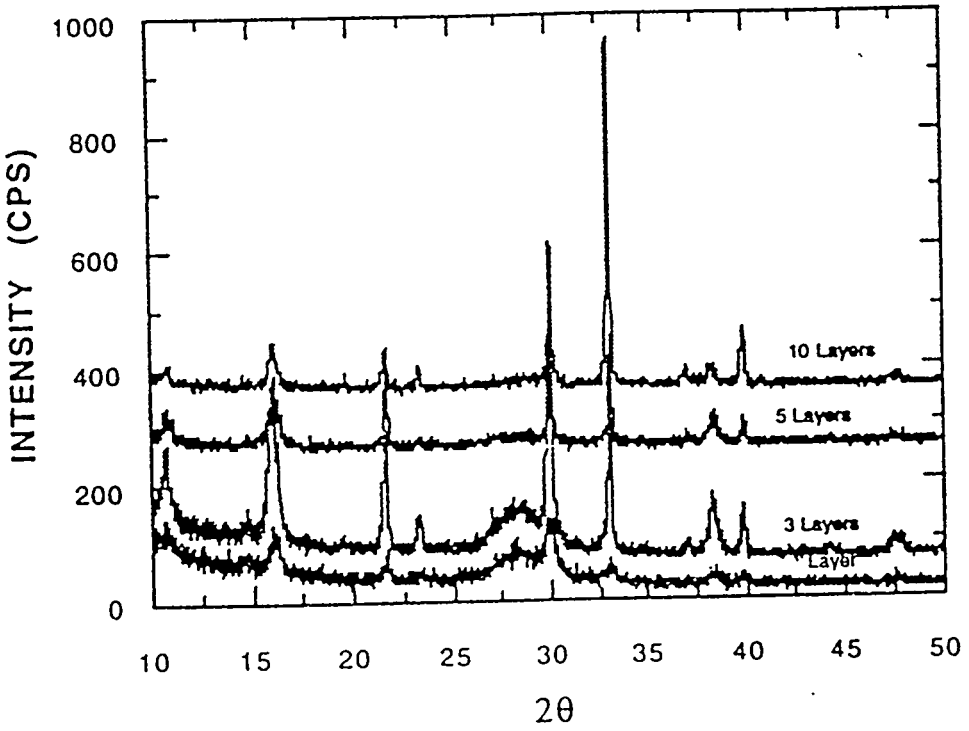
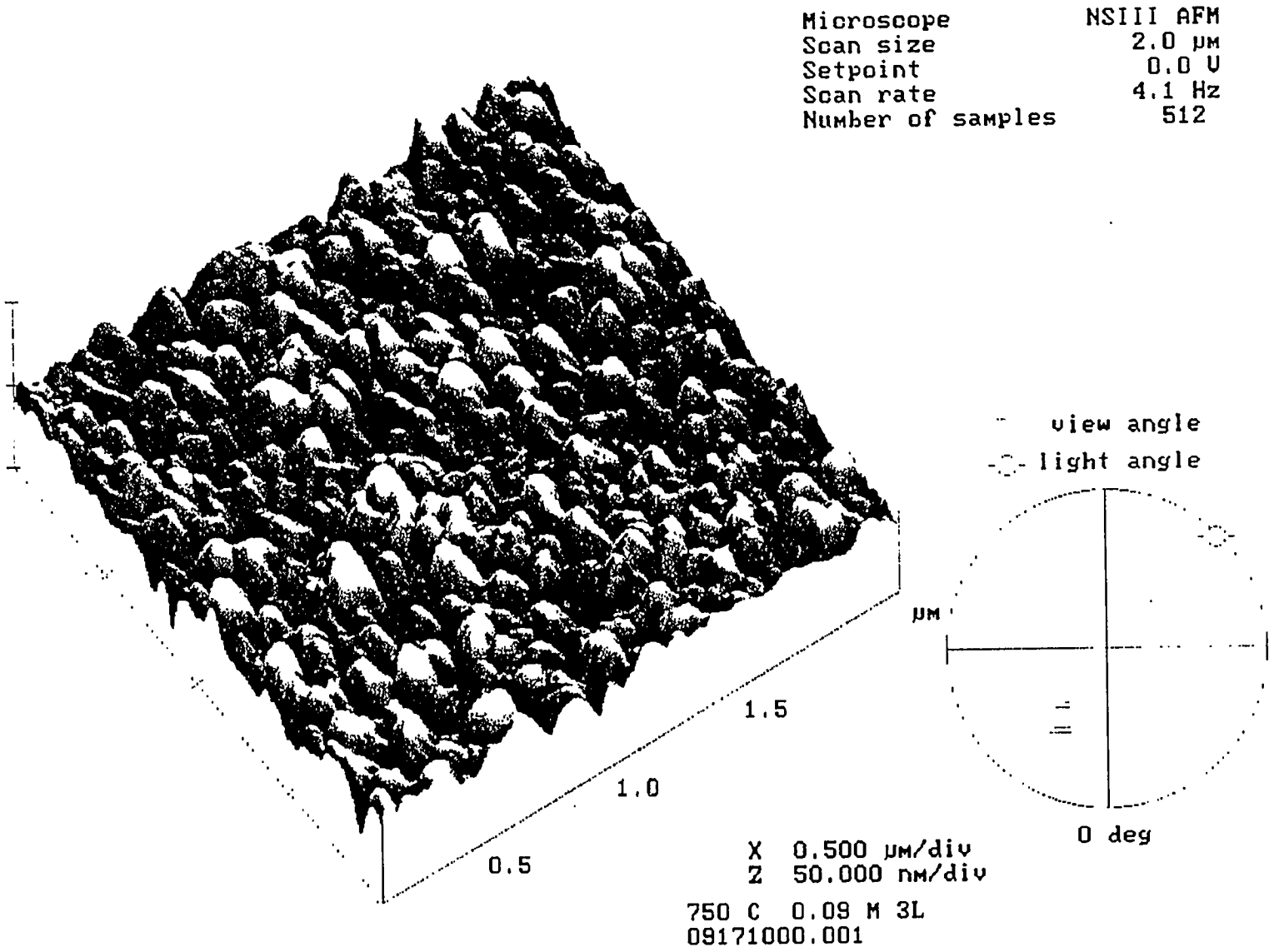


Figure 3: X-ray diffraction patterns of BIT thin films of 4 different thickness: 300 Å, 900Å, 1500Å, and 3000 Å.

Figure 4: Atomic Force microscope image of a BIT thin film deposited on a Si (100) substrate.



AFM image shows morphology of BIT thin film deposited on silicon substrate.

Figure 5: SEM micrograph of a BIT thin film deposited on a silver foil.

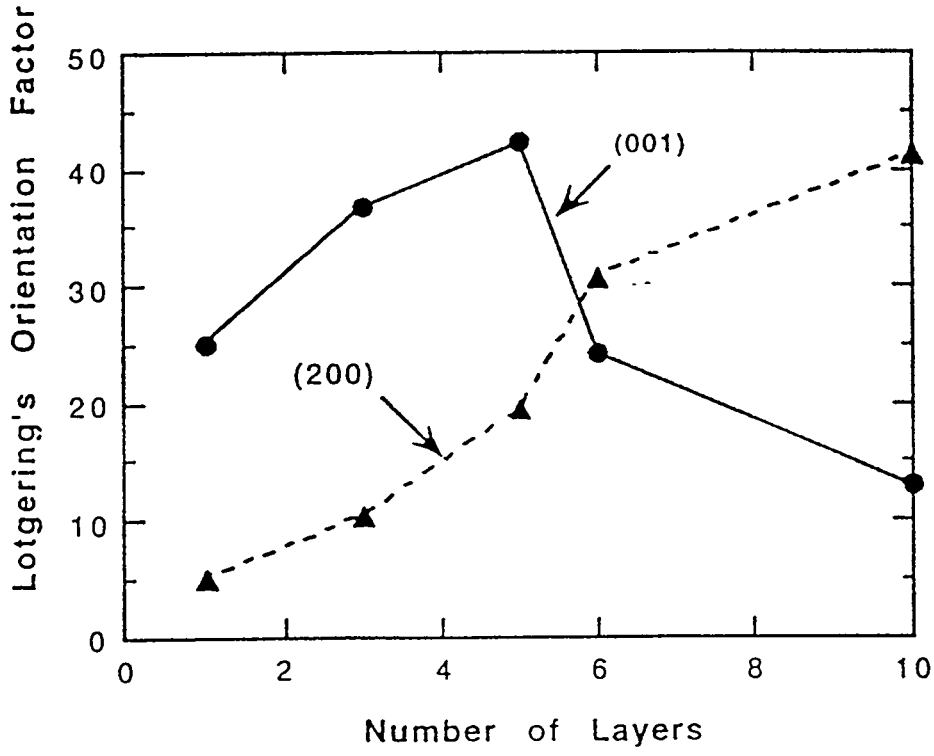


Figure 6: The Lotgering orientation factors for the (001) and (200) directions as a function of the number of deposition layers for a series of BIT films deposited on (100) Si wafer substrates.

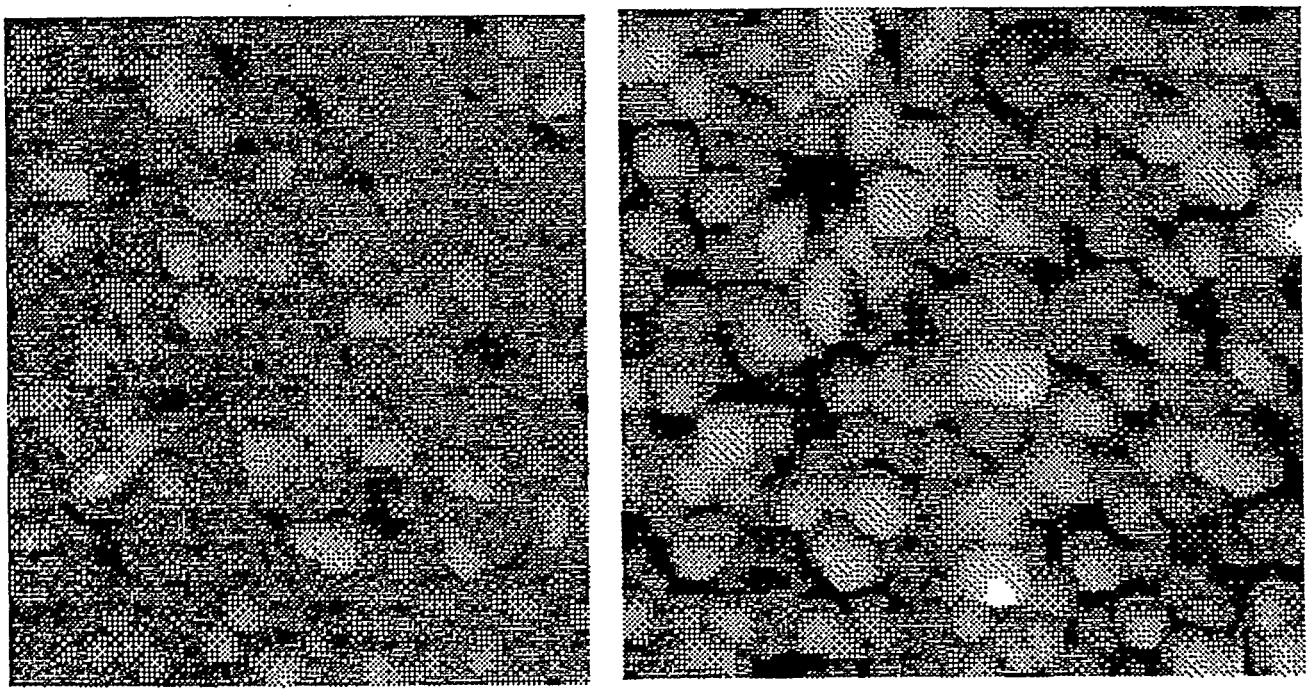


Figure 7: Atomic force microscopy images depicting particle size for two different BIT film thickness: 1600Å and 2500Å.

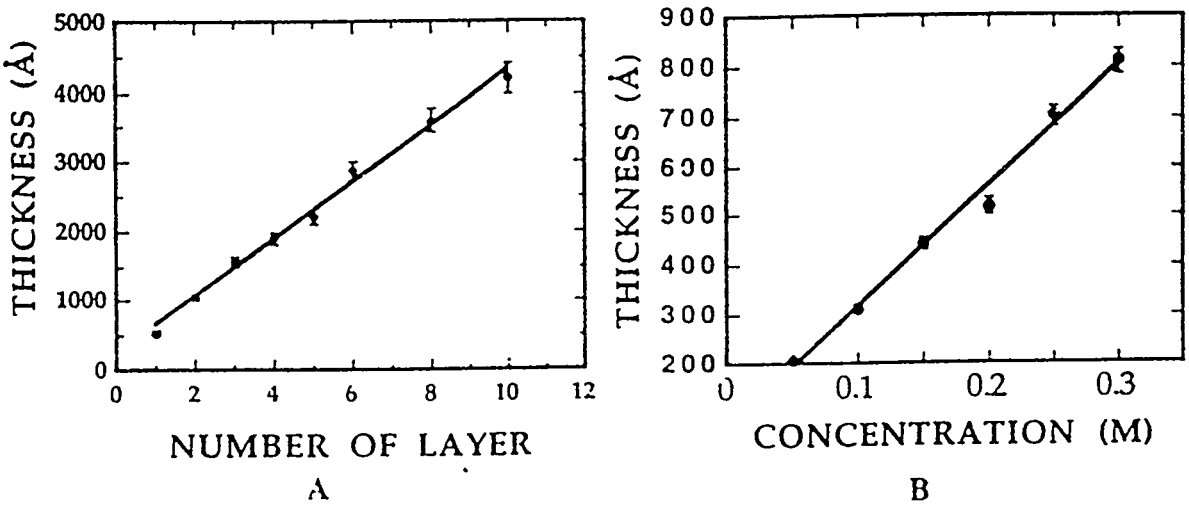


Figure 8: BIT film thickness as a function of the following parameters: (A) number of coating layers and (B) precursor solution concentration.

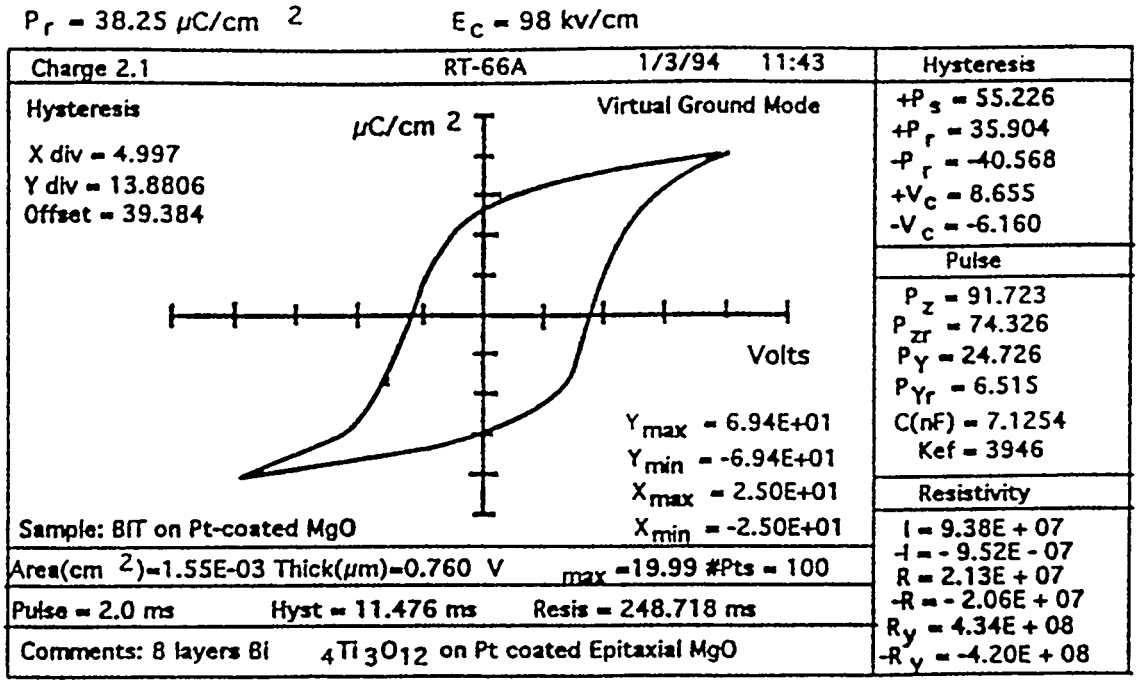


Figure 9: Dielectric hysteresis loop for a 0.76 μm thick BIT film deposited on a Pt coated MgO (100) single crystal substrate.