# PROPERTIES AND STABILITY OF BISMUTH DOPED TIN OXIDE THIN FILMS DEPOSITED ON VARIOUS TYPES OF GLASS SUBSTRATES

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## ABSTRACT

This work reports on deposition of transparent semi-insulating tin oxide thin films deposited by spray-pyrolysis over large area glass substrates. The precursors used are based on diluted chloride solutions. Bi-doped high resistivity tin oxide thin films are required in the fabrication process of an analog grey scale ferroelectric liquid crystal matrix display. Various parameters have been optimized in order to achieve good reproducibility and uniformity of the electrical and optical properties. Deposition temperature and the properties of the glass substrates have been found as the most critical variables which affect the deposition rate and the quality of the deposited films. The different substrates used, borosilicates and soda-lime glasses, lead to different electrical properties. A further investigation on the stability of the film properties versus different kind of aging procedures have been conducted. Preliminary results of the operation of the complete display making use of our films are shown.

## INTRODUCTION

The work described in this paper is finalized to use a transparent high resistivity layer to develop an analog gray shades passive matrix display using surface stabilized ferroelectric liquid crystal (SSFLC). Such a display can provide small cost solutions for TV and various multimedia applications. The construction is made by coupling a high resistivity plate to a conventional Indium-Tin-Oxide plate. The transparent high resistivity layer is electrically connected by metal stripes and the voltage drop between them provides continuous grey levels through continuous changes in the switched area[1]. This work is supported by the ESPRIT project "PROFELICITA" in the development of a range of analog grey scale ferroelectric liquid crystal displays. Among various possibilities examined, the addition of Bismuth to the intrinsically n-type doped tin-oxide results to an increase of the electrical surface resistivity up to tens of $M\Omega/\square$ required for our application, without degrading significantly the optical transmittance of the device. Furtherly high resistivity $SnO_2$:Bi have been chosen for the possibility of being deposited over large areas with good uniformity and the relatively small cost of the deposition equipment. The films are deposited by spray-pyrolysis[2,3] using a novel deposition system that improves uniformity over large areas[4]. In this paper we report the electrical and morphological properties of Bismuth-doped Tin Oxide thin films, deposited on different kinds of glass substrates. A careful investigation has been made concerning the stability of these films versus the various steps of the ferroelectric liquid crystal display fabrication procedure. Finally preliminary results from our complete device are shown in the last paragraph.

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## FILM DEPOSITION AND PROPERTIES

Figure 1 shows the spray-pyrolysis deposition chamber. It consists of a flat rotating hot plate that can house substrates up to 18 cm in diameter and a diffusor, consisting of a pyrex glass ring, surrounds this hot plate. The aerosol is injected radially in the deposition chamber through the many small holes that are regularly arranged in the inner surface of the glass ring, close by the hot plate. During the deposition the chamber is covered by a pyrex glass plate that enables the aerosol to saturate the volume over the hot plate, thus resulting in a good uniformity of the film thickness over the substrate area. Further details on the deposition system configuration can be found in a previous paper[4]. A dilute solution of stannic chloride and bismuth chloride is properly atomized using nitrogen as a carrier gas. The diluted solution in isopropyl-alcohol is prepared in large quantities such as 500 ml. It is further diluted in DI water immediately before the start of the run.

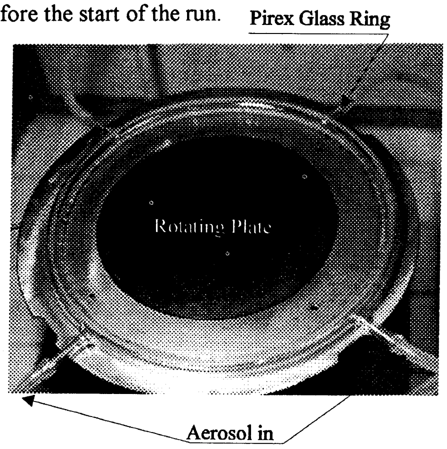

Fig. 1) Photograph of the deposition chamber. The pyrex diffusor has many holes located in the inner surface of the glass ring.

The films were deposited on Corning 7059 glass substrates and on soda-lime glass substrates with and without a $SiO_2$ buffer layer. Films without Bi were also deposited at two different deposition temperatures, in order to compare doped and undoped film results. Figure 2 shows the values of the surface resistivity for various films deposited at 310 °C and 340 °C. The thickness of the films has been estimated to be in the range 1000-1500 Å. Values of surface resistivity for Bi doped films deposited at 340 °C are out of range of the measuring instrument, >1000 MΩ/□. A downward parabolic-like temperature dependence of the deposition temperature has been usually found with our $SnO_2$:Bi films, with a minimum around 310 °C[4]. This minimum resistance value can be varied according to the water concentration of the solution and adapted to the required surface resistivity. In the case of undoped $SnO_2$ the resistivity shows a gradual decrease by raising the deposition temperature. This result is fully consistent with previously published results[5]. The difference in the resistivity obtained between the Corning substrates and the soda-lime glass may be related to diffusion of impurities which also affect nucleation and growth of the films, that also results in the observed change in the grain size of the polycrystalline films. Figure 3 are SEM micrographs showing the morphology of polycrystalline films of a) $SnO_2$ and b) $SnO_2$:Bi films deposited on Corning substrates. It is evident on both cases a microcristalline structure, with a grain size an order of magnitude smaller in the $SnO_2$:Bi films. A slight growth of grain size on increasing the film deposition temperature has been systematically observed in our experiments; the Lifshitz-Slezov model of the growth mechanism of polycrystalline films provides good agreement with this experimental evidence [6]. The increase in surface resistivity in the higher temperature deposition range in the $SnO_2$:Bi films is related to a pronounced increase in Bismuth concentration, as evident from a compositional analysis of Bismuth and Tin previously reported[4] with a Bismuth-Tin weight ratio ~0.3-0.4. Various measurements already published[4,5] and the strong mismatch between Bi and Sn ion size supports the hypotesis that grain boundaries act as segregation regions for Bismuth where it easily oxidizes, being the

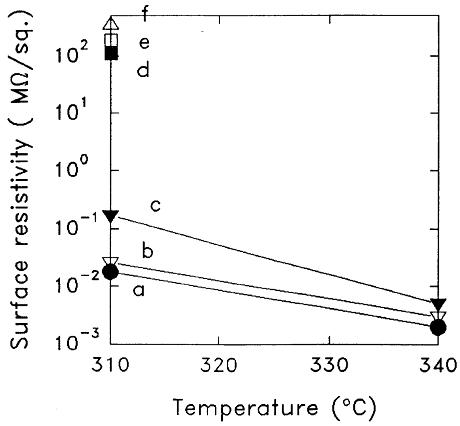

Fig.2). Surface resistivity for various films deposited at 310 °C and 340 °C. a) $SnO_2$films deposited on Corning 7059. b) $SnO_2$ films deposied on soda-lime glass with a buffer layer of $SiO_2$. c) $SnO_2$ deposited on soda lime glass. d) $SnO_2$:Bi on buffered soda-lime glass e) $SnO_2$:Bi on Corning glass f)$SnO_2$:Bi on soda-lime substrate.

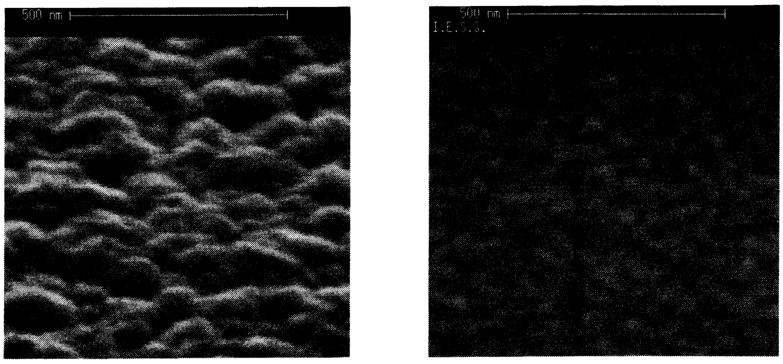

Fig. 3. SEM micrographs of a) $SnO_2$ films and b) f) $SnO_2$:Bi films deposited on Corning substrates at 310 °C .

Gibbs free energy of $Bi_2O_3$ formation $\Delta G = -493$ KJmol compared to $\Delta G = -520$ KJmol for $SnO_2$[7]. In this situation the tunneling across grain boundaries may be the dominant effect on the carriers transport, as already reported by Kojima et al [8]. $SnO_2$:Bi films with thicknesses of 1000-1500 Å show a mean value of the optical transmittance equal to 0.8, measured in the wavelength range from 0.4 and 1.0 µm.

After deposition films are exposed to various thermal, photolithographic and deposition steps which contribute to build an SSFLC display device. Further steps, like harsh thermal treatments were added in the fabrication process. This further steps accelerate aging processes in order to study the film stability. One of the main concerns in using such a high resistivity films is related to resistance variations which can degrade the performance of the final device. The influence of oxygen surface species on semiconductor oxides has been clearly identified in studying mechanism of gas sensing[9]. Physisorbtion of oxygen and various species which get in touch with the film during the various process steps lead systematically to a variation of the resistance between metal tracks. Despite most of the steps performed during the device fabrication are wet processes, which could dramatically increase the conductivity of our films, the total variations observed in the films deposited on Corning and buffered soda-lime substrates are relatively small and can be accounted for using different starting values of surface resistivity films. Metal track made of Silver over Cromium, serving as column electrodes were patterned on the high resistance film. Figure 4 shows measurements of track to track, "t-t" resistance, in two different cells on Corning and buffered soda-lime substrates versus two main steps required for the fabrication of the device and a further aging thermal treatment. Unreproducible results were obtained in the non-buffered soda-lime substrates and consequently were not considered for device fabrication. The initial value of the t-t resistance measured immediately after the stripes photolitography is a close to the calculated value, which is directly related to the original surface resistivity measurement. A nylon film, employed to align the FLC, is spin-coated on top of the metal tracks. The nylon film deposition requires a prebake at 90 °C for 20 minutes and a recrystallization annealing which is performed at a temperature of 160 °C for 4 hours. The two steps produce a factor of two increase in the resistance. The resistance is then further increased by a 17 hours aging thermal treatment at 120 °C. The steps were performed in atmospheric pressure and in vacuum oven without appreciable differences.

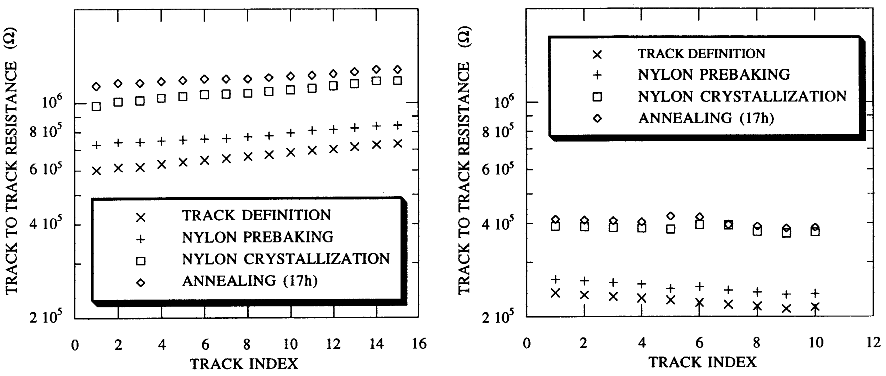

Fig. 4. Track to track resistance measured on (left) Corning glass and (right) on $SiO_2$ buffered soda-lime substrate.

## SSFLC DISPLAY WITH ANALOG GREY SCALES

As previously described the $SnO_2$:Bi films are used as high resistance transparent electrodes in order to obtain gradation in surface stabilized ferroelectric liquid crystal panel displays[1]. The display operates by controlling the liquid crystal area switched between adjacent metal tracks, hence this grey scale technique can be named switching area control (SAC). The main role is played by the high resistivity of the $SnO_2$:Bi coating layer which induces a gradient of the electric field from one powered metal track to the other. Once a certain row electrode has been selected the switching area on that row, besides the metal tracks of the columns, is controlled by modulating the amplitude or the position of the data voltages applied to the tracks, during the writing pulse of the selection waveform applied to that row. In this way the electric field gradient is responsible for domain creation and switching process growing gradually from the metal tracks. Fig. 5 shows 4 pictures of an area of the display of about 10 $mm^2$ between two crossed linear polarizers. The dark lines represent the column tracks, Fig 5a and 5d show black and white states,while Fig. 5b and 5c are intermediate grey shades, obtained by means of four different data voltages applied to the columns. According to this approach a single pixel can be defined as the transparent space on a row electrode besides a single column metal track either up to half way to neighboring tracks or up to them. Such a former configuration does not imply neither loss in resolution nor an augmented complexity in the connections with respect to a standard display with same number of row and column electrodes. In the latter configuration all odd tracks are connected to a data independent waveform and this implies a reduction of resolution by 50%, even though a better control of the switching areas is guaranteed. An interesting characteristic of SAC technique combined with bistability of FLC's is that the gradual switching area is made up of fully switched domains hence the grey shades are stable and non volatile even after unplugging the display. In other words each pixel can memorize any grey shade, so that an image can be stored in the display at any time and even after disconnecting the power supply.

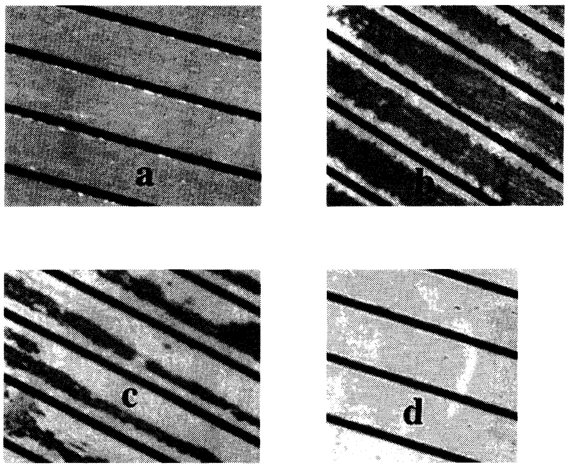

Fig. 5. Four different grey shades in an analog SSFLC display using $SnO_2$:Bi as high resistance transparent film: (a) black, (b) and (c) intermediate greys, (d) white [1].

## CONCLUSIONS

Bismuth doped high resistivity tin oxide has been deposited by spray-pyrolysis on various type of glass substrates. The film deposited on Corning glass and on soda-lime glass buffered with $SiO_2$ are suitable for fabrication of analog passive matrix display using ferroelectric liquid crystals. The stability of the electrical properties have been investigated. Different grey shades in an analog FLC display have been shown.

## ACKNOWLEDGMENT

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## REFERENCES

[1] P. Maltese, F. Campoli, A. D' Alessandro, V. Foglietti, A. Galbato, A. Galloppa, G. Rafaelli and M. Wnek, FLC 95 Proceedings of the International Ferroelectric Liquid Crystal Conference, Cambridge 1995, Ferroelectrics, in press.
[2] J.C. Manifacier, L. Szepessy, J.F. Bresse and M. Perotin, Mater. Res. Bull. **14**, 163 (1979).
[3] P. Grosse, F.J. Schmitte, G. Frank and H. Kostlin, Thin Solid Films **90**, 309 (1988).
[4] V. Foglietti, A. Galbato, A. Bearzotti, A. Galloppa and P. Maltese, in Polycrystalline thin films, Mater. Res. Soc. Proc., MRS (1995), in press.
[5] A. De Acutis, M.C. Rossi, M. Barbetti, in Flat Panel Display Materials , Mater. Res. Soc. Proc., MRS Vol. 345, 235 (1994).
[6] I.M. Lifshitz and V.V. Slezov, J. Phys. Chem. Solids, **19**, 35 (1961).
[7] The data are taken from TAPP, thermochemical and physical properties, ES microware.
[8] M. Kojima, H. Kato, A. Imai and A. Yoshida, J. Appl. Phys., **64**, 1902 (1988).
[9] P.T. Moseley, D.E. Williams, in Techniques and mechanism in gas sensing, edited by P.T. Moseley, J.O.W. Norris and D.E. Williams, Adam Hilger(1991)ISBN 0-7503-0074-4.