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Disappearance of aligning properties of deposited SiO_x films as caused by external factors

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Abstract. Thermal and degradation stability of SiO_x aligning films deposited by cathode reactive sputtering (CRS) in glow discharge plasma were investigated. It was shown that a heat treatment and other external factors initiate transformations on the surface of aligning film and provided new conditions at the interface. This leads to a change of slight axis orientation direction of LC molecules and appearance of various defects in the LC aligned structures. The technological ways to increase the aligning layer durability under influence of external factors were proposed.

Keywords: liquid crystal, molecular orientation, cathode reactive sputtering, aligned structures.

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1. Introduction

For the decision of high-quality LC-layer sealing problem in liquid crystal displays and light shutters, in the forefront raised was the task to use the hermetic with low hygroscopicity and high mechanical strength. For these two requirements, the glass frit composition (glass with low melting temperature) are fully satisfied.

However, the temperature of glazing and gluing these glass compositions together lies in the range from 360 up to 500 ºC. This fact practically does not allow to use them in the LCD technology because organic aligning layers (rubbed or UV cured poliimides) have the temperature range of destruction from 180 up to 230 ºC. Therefore, ploliimides can be substituted by the inorganic aligning layers. Recently, the technologies for creation of aligned nematic LC structures based on treatment of substrate surfaces by low energy ions, ion-plasma etching and sputtering were elaborated [1-8]. Among these methods, the special attention deserves the method of cathode reactive sputtering (CRS) of aligning layer by using a direct current (diode system of sputtering) [9, 10]. This method has a lot of advantages: simplicity of realization, reproducability of results and obtaining the aligned nematic liquid crystal (NLC) structures with the controllable parameters [11, 12].

As the developed CRS method for creation of aligning films is based on deposition of inorganic oxide films, the above mentioned types of hermetics can be effectively used for creation of LC modulators (including display devices) with high quality of sealing. This is especially important for devices operating under unfavourable conditions (increased humidity and temperature).

In this paper, the results of creation of thermostable aligning layers and investigation of their properties were shown. Use of such inorganic aligning layers gives the possibility to seal the LC devices with high reliable glass frit compositions.

2. Experimental setup

For investigation of aligning film defects related to the heat treatment of substrates exposed to thermal shock (heating from the room temperature up to the studied one for 5 min, exposed at the studied temperature for 10 min, cooling up to 300 ºC for 5 min and cooling to the room temperature for 3 min). Annealing was made in the oven of the type SNOL-044/12. Change of the substrate temperature with time was registered by the plotter КСП connected through the amplifier В2-15 to two series connected chromel-alumel (Ch-A) thermocouples, one of which had the ice melting point, and the second one was mounted on the substrate. The accuracy of temperature registration was 1 %. To except the temperature gradient during the heat treatment, the substrates were placed between two metallic plates.

For determination of optimal conditions and time for storage the substrates with deposited aligning films that providing high quality twist nematic (TN) LC

structure were divided into three parts. First part was stored in a closed volume (drying bottle with silica gel), the second one was stored under the room conditions (temperature was 20…25 ºC and humidity 50…70 %), and third one – at the room temperature in a closed volume with saturated water vapor (distilled water). After that, every day one substrate from these three parts was assembled with the as-prepared test substrate and filled with NLC. After aligning, the obtained NLC structures were investigated using a polarization microscope. The images of the typical defects of TN LC structures were recorded. The quality of TN LC structures obtained by two test of the as-prepared and assembled substrates was high, and defects or imperfections were absent.

To study the defects after thermal treatment of SiO_x aligning layers, four types of substrates were used. The first type was made of K8 glass, the second one – silica, the third and fourth ones were made of glass and had the ITO electrodes (substrates for watch displays) opened and covered by SiO_2, respectively. Deposition of SiO_x aligning layer was carried out by the CRS method as described in [10-13]. The parameters of the technological process were as follows: the applied cathode voltage U (from 2.5 up to 5 kV), current density J (from 1 to 5 mA/cm^2), oxygen concentration k_O (50 %). To study the preferable storage conditions of the prepared substrates with aligning layer, used were the substrates of the third and fourth types. The SiO_x aligning layer was on these substrates with the same parameters. In the course of deposition, three various values of oxygen concentrations k_O (0, 50 or 100 %) were used.

3. Results and discussion

3.1. Defects of alignment after the heat treatment

Our analysis showed that defects of alignment after the heat treatment differ and can be divided into four kinds according to the influence of the following factors:

a) the heat treatment;
b) substrate properties;
c) evaporation of glass frit decomposition products;
d) low temperature glue decomposition (tapes of PVB, BF and others).

At the annealing temperature in the range of 400 to 520 ºC, aligning layers on silica, K8 glass and SiO_2-covered ITO electrodes (fourth type of substrates) created defectless high quality TN LC structures. It means that the SiO_x aligning layer remains thermally stable up to 520 ºC for the enough wide ranges of deposition technological parameters.

Imperfect TN LC structures were obtained on the substrates of the third type (glass with opened ITO electrodes) when the annealing temperature was higher than 450 ºC. These structures had a lot of defects such as disclination lines surrounded by the squares of 0.1 to 1 mm^2 located on the substrate surface in the area free of ITO electrodes. The photos of these defects are shown in Fig. 1.

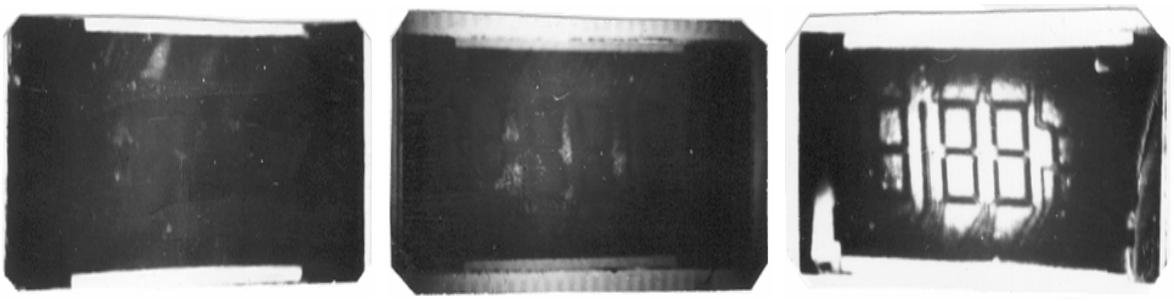
However, the TN LC structures between ITO electrodes was perfect after annealing of the substrates up to the temperature 515 ºC.

The reason of defect appearance on glass surface is the processes of glass lixiviation causing chemical interaction (for example, free sodium) with the deposited SiO_x film or mechanical destruction of aligning layer under the action of high annealing temperature. As was experimentally shown, the temperature of such defect appearance is in the range from 440 to 480 ºC and even sometimes up to 500 ºC and depending on the type of glass substrates.

As shown in Fig. 2, with increasing the cathode voltage the temperature of defect appearance was increasing, too. The reason of such behavior is the higher temperature of ion treatment of substrate in the deposition process because of the greater ion energy.

3.2. Defects related to the influence of glass frit

Defects caused by the influence of evaporation of glass frit decomposition product on aligning layers at heat treatment have a sufficient difference in comparison with the considered above. In this case, the destruction of aligning layers was observed on the surface of ITO electrodes. The photo of these defects is shown in Fig. 3. It was noticed that defects appeared, when the annealing temperature was by 20 to 40 ºC higher than that of glass



a) b) c)

Fig. 1. Defects of aligning at various annealing temperatures: 460 (a), 480 (b), and 500 ºC (c).

frit melting. In Fig. 4 shown was the experimental dependences of maximal annealing temperature providing the absence of defects on the temperature of glass frit melting (for three types of glass frit with the values of melting temperature 380, 400 and 437 ºC).

The analysis of ITO electrode defect appearance reasons allows to assume that destruction of alignment layer on ITO electrodes is the result of chemical interaction of fusible components of glass frit (for example, compounds of lead) directly with the transparent conducting film that has general formula In_2O_3:Sn, followed with a complete destruction of aligning layer. The TN LC structure quality in the area free of ITO electrodes remains high.

For the substrates of fourth type (made of glass and having the ITO electrodes covered with SiO_2), these defects did not appear up to 520 ºC annealing temperature. It is natural to assume that for excluding the defect appearance, it is necessary to provide the precision temperature control during gluing the substrates together with glass frit sealing. Thus, the increase of the gluing together temperature to 500…515 ºC must be provided in the case when it is theoretically and practically grounded.

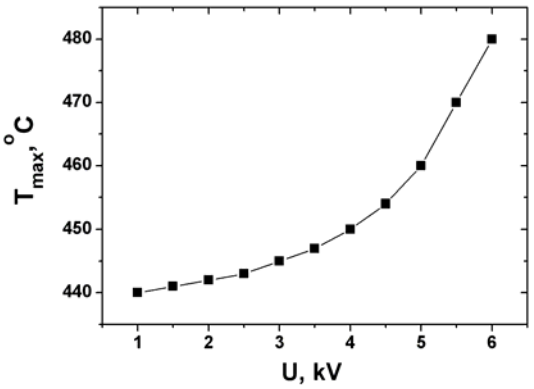


Fig. 2. Dependence of maximal temperature of substrate annealing (defectless orientation of TNLC) on the cathode voltage during SiO_x aligning layer deposition.

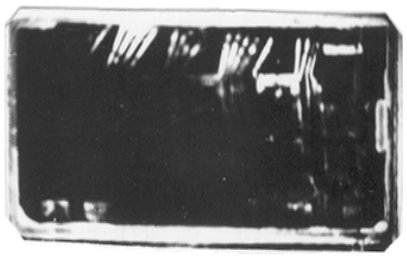


Fig. 3. Appearance of defects of the SiO_2 aligning layer covering the ITO electrodes by frit glass vapor (480 ºC gluing) action.

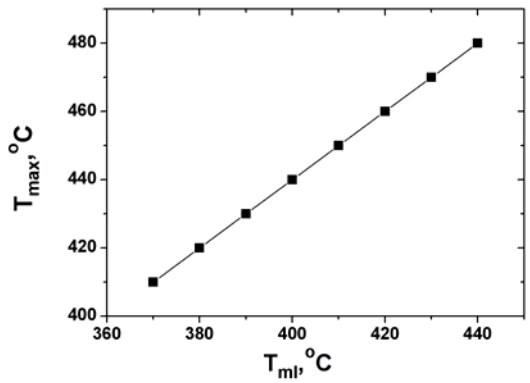


Fig. 4. Experimental dependences of maximal annealing temperature providing the absence of defects on the temperature of glass frit melting.

3.3. Defects related to low temperature glues

Defects of such type are mainly localized on a surface free of ITO electrodes and look similar to defects of glass lixiviation, but they are more closely packed. Defects similar to these appeared over all the area covered by SiO_2. Appearance of defects is caused by sedimentation of PVB and BF glues decomposition products on a surface of glass free of ITO electrodes or covered with SiO_2. It should be noted that the examined defects appeared when superheating the glue or increasing the gluing time (at T = 80…100 ºC for 45 to 60 min).

Photos of typical defects caused by low temperature glue decomposition products on the aligning layers are shown in Fig. 5.

3.4. Influence of ionic treatment on a glass frit and ITO electrodes

Using the SiO_x aligning layer demands to take into account the influence of an ionic treatment on the properties of glass frit. High temperatures of substrate surface in the process of SiO_x aligning layer deposition in a combination with ionic bombardment can result in destruction of glass frit partially or completely. Dependences of substrate surface temperature on technological parameters (cathode voltage, discharge power, concentrations of oxygen and argon, deposition

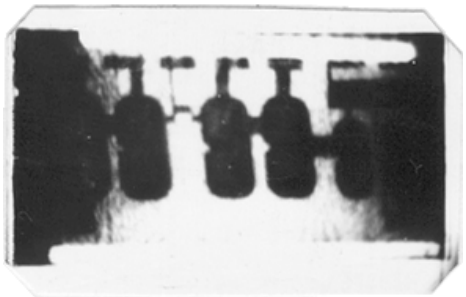


Fig. 5. Typical defects caused by the influence of low temperature glue PVB and BF decomposition products on the aligning layer.

angle) of SiO_x aligning layer deposition were investigated. Some of these dependences are shown in Figs 6-8. The analysis of the dependences in Figs 6 to 8 allows to draw the following conclusions.

The substrate surface temperature in the course of deposition of alignment layer strongly depends on the oxygen concentration, deposition angle and applied cathode voltage. As were experimentally found, a glass frit during deposition becomes plastic at the temperature of 360 to 370 ºC and comparatively destroyed at the cathode voltages more than 4 kV. These circumstances put the following limitations on the deposition angle, cathode voltage and oxygen concentration: $\alpha \le 15^{\circ}$, $U \le 4$ kV, $k_O \le 50$ %.

To determine the optimal conditions and time for storage the substrates with deposited aligning films used was the method described in Section 2.4.

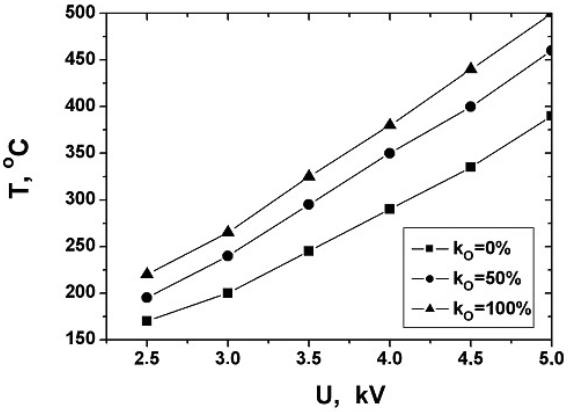


Fig. 6. Dependence of the substrate surface temperature during deposition on the cathode voltage for three various oxygen concentrations.

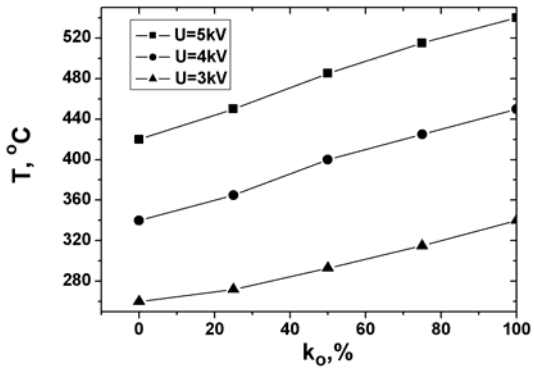


Fig. 7. Dependence of the substrate surface temperature during deposition on the oxygen concentration for three various cathode voltages.

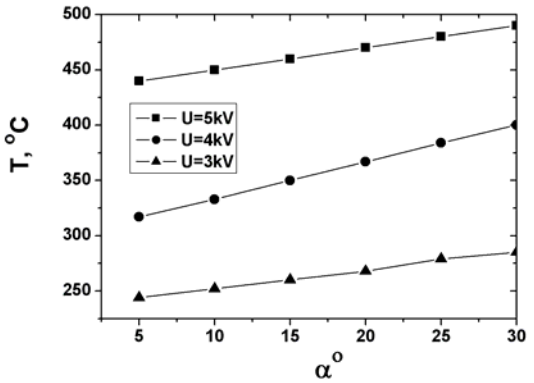


Fig. 8. Dependence of the substrate surface temperature during deposition on the deposition angle for three various cathode voltages.

3.5. Influence of storage method on degradation of aligning layers

After deposition of SiO_x aligning layers at various oxygen concentrations, the substrates were stored in a closed volume (drying bottle with silica gel) for six days. After that they were assembled and filled with NLC to create TN structures. The results of investigation of TN structures were shown in Fig. 9.

The analysis of results showed that the degradation stability of aligning layers deposited in the atmosphere of oxygen 50 and 100 % is higher than in the atmosphere of pure argon. It is possibly caused by predominance in the SiO_x alignment layer of lower silicon oxides, which much less shadow the surface of glass against moisture (the defects appear on glass mainly) and, at the same time, they very effective hydrate.

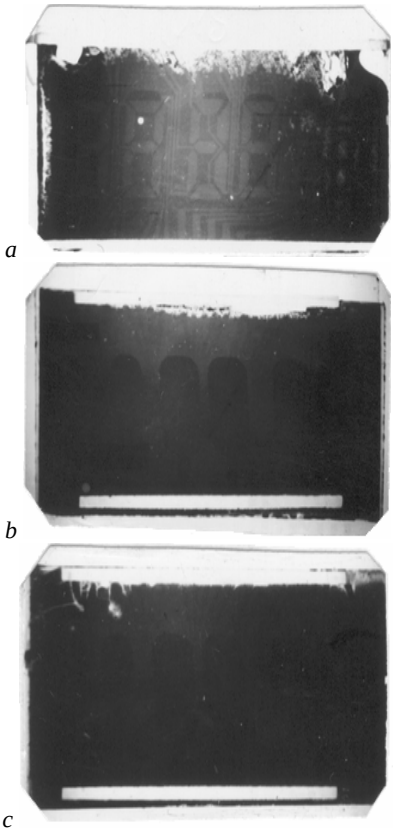


Fig. 9. Degradation of the SiO_x aligning layer after six days of storage in dry atmosphere, which was deposited in: pure argon (a), mixture of 50 % oxygen and 50 % argon (b), pure oxygen (c).

After storage of substrates in moist conditions the aligning properties of SiO_x aligning layer deposited on glass are completely and very quickly destroyed (see Fig. 10).

As the degradation of SiO_x aligning layer is mainly determined by the presence of moisture, laboratory rooms in which the relative humidity from 40 to 80 % are useless for the long term storage of substrates after deposition. Nevertheless, at maintenance of some microclimate conditions of room (T = 20 ºC, humidity 40 %) it is possible to guarantee the safe keeping of deposited substrates for a few days. Fig. 11 represents the TN LC structures, obtained between the substrates which were kept in the above laboratory conditions for thirteen days.

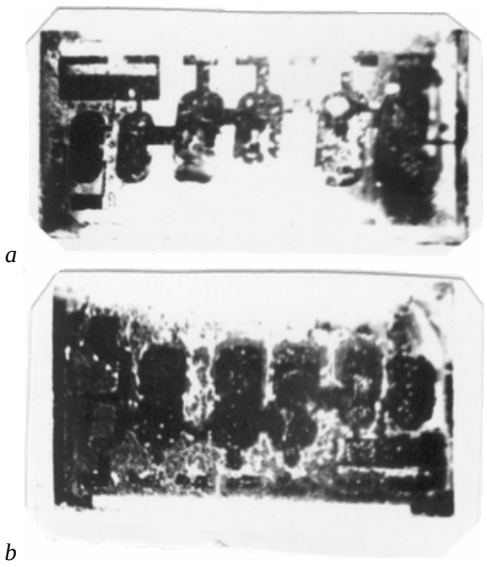


Fig. 10. Degradation of the SiO_x aligning layer deposited on glass after storage in moist conditions for one (a) and two (b) days.

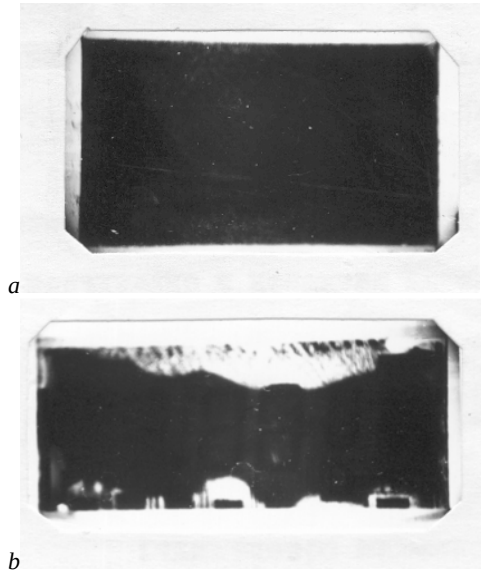


Fig. 11. Degradation of the SiO_x aligning layer after storage under room conditions for thirteen days: a) ITO electrodes covered by SiO_2, b) opened ITO electrodes.

4. Conclusions

Thus, the results of researches allow to ground the choose of the following technological regimes for deposition of SiO_x aligning layer for glass frit sealing:

- cathode voltage is 4 kV (mainly, is limited to thermal stability of glass frit and possibilities of the high-voltage power supply of the industrial plants for CRS);
- cathode current density is 5 mA/cm^2 (it is limited to the substrate heating temperature at the oxygen concentration 50 %);
- oxygen concentration in the operating mixture of gases is 50 % (it is limited to the substrate heating temperature and requirements to the modern vacuum technological equipment);
- deposition angle is 15º (it is determined by the requirement of high aligning properties, substrate heating temperature and rate of SiO_x alignment layer deposition);
- main factor determining the degradation of SiO_x aligning layers on storage is moisture. At the same time, to hydrogenate not SiO_x alignment layer but surface of free glass;
- SiO_x aligning layer deposited on uncovered SiO_2 substrates can be storaged for 1-4 days under the room conditions, and they are able to demonstrate the perfect orientation, or 10 days in dry conditions;
- SiO_x aligning layer deposited onto uncovered SiO_2 substrates are considerably less exposed to the influence of moisture.

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