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E-Beam Evaporated Glass and MgO Layers for Gas Panel Fabrication

Abstract: An electron-beam evaporation process has been developed that is capable of depositing stable, thick, borosilicate glass films (0.5–50 μm) on various substrates at a rate exceeding 0.5 μm/min. A very low stress of 4–10 $\times$ 10^7 N/m^2 in compression was obtained in freshly deposited glass films, and a further reduction below measurable levels of stress was observed after a thermal annealing at 500°C. The effects of evaporation parameter variation and thermal annealing on the film properties of the borosilicate glass layers, as well as the MgO secondary emission layers employed in the fabrication of gas discharge display panels, are presented.

Introduction

Some of the technology questions involved in fabricating ac gas panels have been considered in [1]. In the past it has been practical in panel fabrication to prepare a thick insulating dielectric film (15–30 μm) by a reflow process [2, 3] using a glass having a low melting point. Then a thin overcoat film (0.2–0.3 μm) of a high secondary emission material was evaporated onto the glass film. In the display industry the need for stable, thick dielectric films has been recognized [3]. However, stringent property requirements, such as low stress, high optical transparency, thickness uniformity, and high breakdown strength, have hampered the development of alternate processes.

Mindful of these strict requirements, we made intensive efforts in this laboratory to develop a short practical method for depositing thick, zero-stress dielectric films. What finally evolved was a high rate e-beam evaporation process [4], which provided, in addition to satisfying the above requirements, the advantages of minimizing panel contamination and breaking the thermal hierarchy [1].

The high rate e-beam evaporation process allows sequential evaporation of a borosilicate glass film and an MgO secondary emission film in a single pump-down of an evaporation system. These films are deposited only over the cell area of a panel through a mask to separate the dielectric and seal regions, thus allowing the breaking up of the thermal hierarchy. In addition to the obvious advantages, such as short processing time, reduced sample handling, and less contamination, another advantage gained with this process is the reduction of difficulties encountered in maintaining uniformity in the panel gap spacing, as experienced with panels made of unevenly distributed, reflowed dielectrics.

The uniform borosilicate glass films with very low stress, deposited by the e-beam evaporation process to a thickness of approximately 6.5 μm, result in panels that are equivalent in electrical characteristics [5] to those made of thick reflowed dielectric films. Stable MgO films having a high secondary emission are deposited sequentially over the glass films. Enhancement of the secondary electron yield is achieved by thermally annealing the MgO films in dry air during the panel sealing cycle.

Electron-beam evaporation

• *Evaporation techniques*

Evaporation techniques used in the preparation of thin dielectric films, up to 1 μm in thickness, are discussed in a recent review article [6]. For thicker films references are given in the article to techniques such as glazing, electrophoretic deposition, flame spraying, painting, and screen printing. For deposition of thin films of simple oxides, which are hard and stable, the e-beam evaporation technique can be used effectively [7–9]. However, deposition of multicomponent glasses by e-beam evaporation techniques yields, in general, poor-quality films

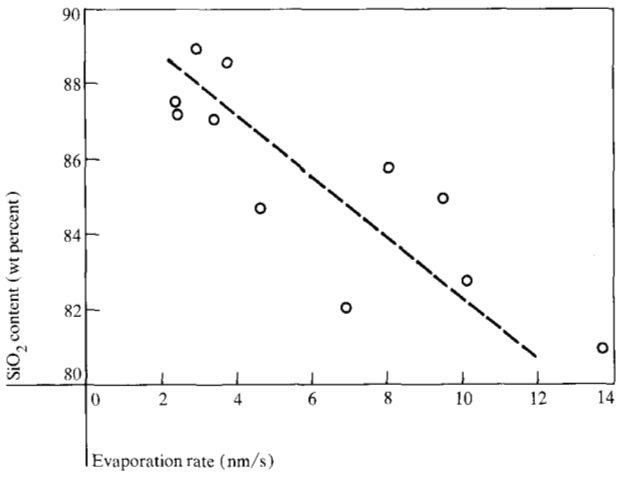

Figure 1 SiO_2 content in film vs evaporation rate.

Table 1 Composition of borosilicate glass.

Composition	*Bulk* (wt %)	*Film* (wt %)
SiO_2	83.2 ± 1.0	82–89
B_2O_3	10.9 ± 0.2	8–15
Al_2O_3	2.54 ± 0.07	<0.09
Na_2O	2.21 ± 0.07	1.7–2.4

due to the glass decomposition and the nonuniform volatility of the glass components. As the desired thickness increases, the problem of nonstoichiometry and compositional change in e-beam evaporated glass films becomes more severe, with the deterioration of such film properties as density, strain, and optical transmission.

In attaining high-quality glass films, both the selection of a compatible glass system and the optimization of e-beam deposition parameters are critical. The porosity and strain in a deposited layer generally decrease with increased substrate temperature and decreased deposition rate [10]. However, at a substrate temperature as high as 400°C and deposition rates of 0.13 to 0.2 μm/min, even the simplest glasses, such as SiO_2, showed significant porosity, strain, and absorbed water [11]. Thus, justifiably, doubts have been expressed on the likelihood of producing high-quality glass films unless they are deposited at very high substrate temperatures that approach the annealing point of the mixed glass system [10]. In a practical application, however, the substrate temperature that has to be maintained in a vacuum system should not be excessively high, while the deposition rate should be high enough to result in a short processing time. Furthermore, the heating of the source of glass for evaporation should be uniform over a large, well-defined surface area to avoid glass decomposition and to ensure uniform evaporation.

• *Glass and MgO layer preparation*

The evaporation system we used consists of an Airco Temescal 2-inch electron-gun source with 270° beam deflection and an *x-y* sweep control unit, Temescal XYS-8, for automatic control of both longitudinal and lateral electron-beam sweeping. The source is driven by an 8-kW power supply, Temescal model CV-8. The substrate holder is equipped with heater elements and a height adjustor to vary the source-to-substrate distance. Other fixtures, such as metal mask, shutter, crystal thickness monitor, vacuum manipulator, and gas bleed-in valve, were placed through the top plate and the side ports of the evaporation chamber.

The e-beam evaporation starts with the production of a 2- to 10-cm^2 molten pool of borosilicate glass source material in a chamber evacuated to a pressure of approximately 1×10^{-4} Pa ($\approx 10^{-6}$ torr). Uniform heating over a large area is accomplished with the longitudinal and lateral electron-beam sweep control as well as the simultaneous control of the heating rate. Any bubbling or spitting, which is one of the limiting factors in conventional glass evaporation, is avoided with the establishment of a fast but steady evaporation rate. For the fabrication of the gas discharge display panels, a 6.5-μm-thick borosilicate film and a 0.2-μm-thick MgO film are sequentially deposited onto a metallized glass substrate in a single pump-down of an evaporation chamber. The substrates are heated at 4°C/min to 200°C, held at that temperature throughout the entire evaporation run, and then cooled down to room temperature at 4°C/min. The borosilicate glass film is deposited at a rate of 3–10 nm/second, measured at 25 cm from the source; the MgO film is deposited at 1–10 nm/second. It has been found that stable borosilicate layers of 50 μm or more can be prepared with very low stress by an extended evaporation.

Borosilicate glass layer

• *Analysis of composition*

A summary of data on the composition of the borosilicate glass is presented in Table 1 for bulk and for stable films. The composition of the bulk glass was obtained by wet chemical analysis and is in good agreement with that obtained by the electron microprobe technique. The compositions of the evaporated films were determined mainly by electron microprobe analysis. The data represent a range of compositions that are found in stable, low-stress films deposited on soda-lime glass substrates under various evaporation conditions. The boron oxide content in evaporated films was confirmed by wet chemical analysis.

In addition to the four major components listed in the table, optical emission analysis showed the following components to be present in the bulk borosilicate glass: K (1500 ppm), Mg (1000 ppm), Fe (1000 ppm), Zr (1000 ppm), Ca (500 ppm), Ti (500 ppm), Li (300 ppm), Ba (100 ppm), Ni (30 ppm), Cu (30 ppm) Mn (30 ppm), and Ga (17 ppm). The concentration of K was found to be the same both in the bulk glass and in the film.

The composition of the evaporated film differs consistently from the bulk glass by about 2.5 wt percent in Al_2O_3 content with little or no inclusion of this less volatile component in the film. Since the Na_2O content remains relatively constant, the difference is made up by variations in the SiO_2 and B_2O_3 contents, which depend on evaporation conditions. In Fig. 1 the decrease of the SiO_2 content in the evaporated films with increasing evaporation rate (as measured 25 cm away from the evaporation source) is shown. At a constant evaporation rate, the SiO_2 content increases slightly as the glass evaporation source is consumed but decreases when the O_2 partial pressure in the evaporation system is increased. Films evaporated at rates higher than 15 nm/s lifted off the substrates at room temperature even before any thermal cycling.

• *Stress analysis*

Stress in the deposited films was measured using the interference fringe technique [12]. The change of curvature of the circular wafer substrate, from its original state to that attained after the film deposition, was determined by comparing interference fringes. The substrates used primarily were 2.5-cm diameter, 0.25-mm-thick polished soda-lime glass wafers with a thermal expansion coefficient $\alpha_{(20-300°C)} = 93 \times 10^{-7}/°C$. The bulk borosilicate glass with a thermal expansion coefficient $\alpha_{(20-300°C)} = 27.5 \times 10^{-7}/°C$ was evaporated onto the glass wafers held at 200°C. All borosilicate glass films examined were approximately 6.5 μm in thickness.

All stress values reported here represent total stress measured at room temperature and include both the intrinsic stress produced during film deposition and the stress due to thermal expansion mismatch between the borosilicate glass film and the substrate. Freshly deposited borosilicate glass films are in compression, and their stress values generally are about 10^7 N/m^2. Figure 2 shows the effect on stress of varying evaporation rate as measured 25 cm away from the evaporation source at a normal incidence. Stress is minimized for evaporation rates within the 3 to 10 nm/s range. It has been found that the evaporation rate is the critical parameter with more direct effects on the film stress than the deposition rate.

Determination of the stress in borosilicate glass films, deposited simultaneously on two different types of soda-lime glass wafers, showed practically identical magnitudes of stress for both samples. Furthermore, the borosilicate glass films deposited on thin Corning 7059 glass wafers in the same evaporation run also had approximately the same magnitude of stress. Apparently, the stress in these borosilicate glass films is influenced very little by the variation in thermal expansion mismatch between the borosilicate glass films and the substrate. Here, it is believed that the ability of these borosilicate glass films to relieve stress by plastic deformation [13] is responsible for the observed, uniformly low stress.

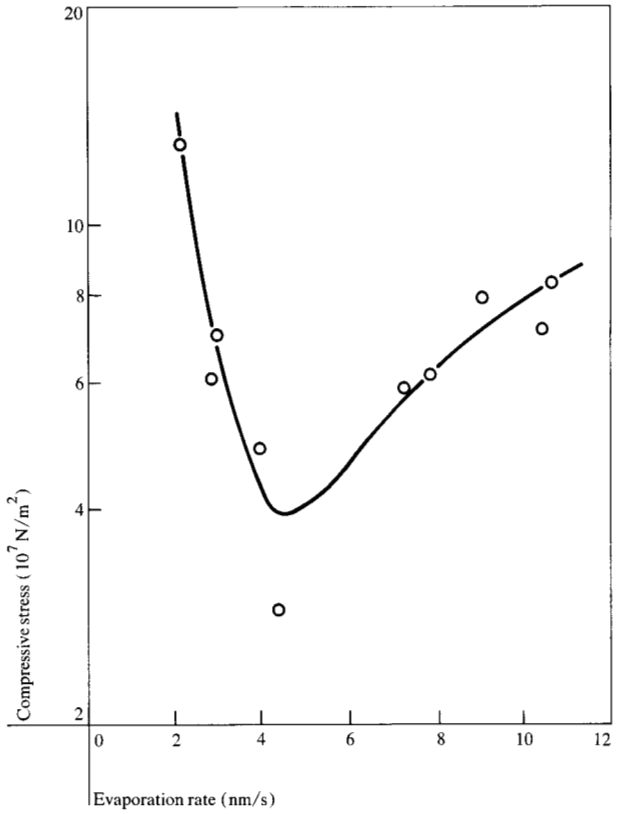

Figure 2 Stress vs evaporation rate.

Of considerable interest is the effect of thermal cycling of the films on stress. Depending on the temperature and duration of the cycling, stresses are largely annealed out of the glass films. Substrate curvatures are reduced to unmeasurably low levels in all of the glass samples, after a 500-°C, 30-minute annealing process in dry air or nitrogen.

• *Infrared spectra*

All infrared spectra were taken by transmission through approximately 0.8-μm-thick borosilicate glass films, e-beam deposited at 200°C on high resistivity, thick silicon wafers, using a Perkin-Elmer 521 double beam spectrophotometer. The presence of wafer and hydrogen bonded

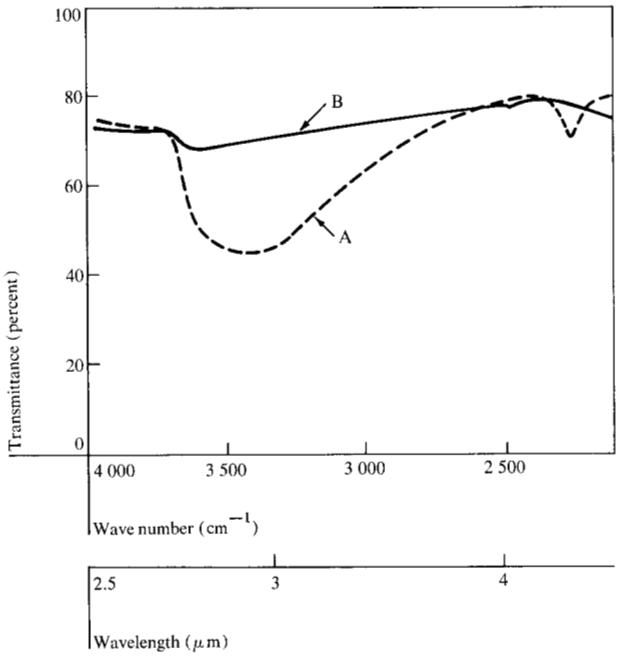

Figure 3 IR transmission of electron-beam evaporated borosilicate glass at 5×: curve A, before annealing; curve B, after annealing at 500°C for 30 minutes in dry air.

silanol (SiOH) surface groups in as-deposited film is shown in the 5× amplified spectrum of Fig. 3 by a broad, strong absorption band in the vicinity of 3400 cm^{-1} and the shoulder of another at 3650 cm^{-1}, respectively. In Fig. 4, in addition to the 1× spectra, the 5× spectra are shown covering the range between 1500 and 1800 cm^{-1}. The absorption bands at 3400 cm^{-1} in Fig. 3 and at 1630 cm^{-1} in Fig. 4 show the presence of a considerable amount of water in the glass film. By comparison, however, the sample that has been thermally annealed at 500°C for 30 minutes in dry air exhibits little or no absorbed water and only a slight amount of surface hydroxyl groups. As expected from the observations of similar phenomena in other dielectric films [11] following densification procedures, this 500-°C, 30-minute thermal cycle, which is the cycle used for sealing gas panels, is sufficient to remove all or most of the absorbed water and silanol groups present on the film and to densify the oxide structure so that new moisture is not reabsorbed.

As shown in Fig. 4, the absorption band due to Si-O stretching is at a higher frequency for the thermally annealed film than that for the freshly deposited film. This shift of the absorption peak [10] from 1050 to 1080 cm^{-1}, along with a simultaneous narrowing of the band in the thermally annealed film, may be attributed to a reduction in the degree of oxygen deficiency in addition to some densification of the film and the annealing out of some bond strain. Further evidence for the reduction in the amount of oxygen deficiency in the film after thermal annealing comes from the loss in intensity of the Si_2O_3 absorption band [11] at 880 cm^{-1} in the annealed film.

- *Refractive index*

The refractive index of a freshly deposited borosilicate glass film is $n_\lambda = 1.4836$ and that of a film boiled in water for one hour is $n_\lambda = 1.4963$ at $\lambda = 546$ nm, measured using a VAMFO [14]. At $\lambda = 632.8$ nm the refractive index of a freshly deposited film is $n_\lambda = 1.473$, measured using an ellipsometer.

- *Dielectric strength*

The breakdown strength of a freshly deposited, 200-nm-thick borosilicate glass layer is observed to be 2.5 MV/cm. A significant improvement in the maximum value of the breakdown strength of the films is observed in films deposited on Cr-Cu-Cr base electrodes after annealing at 500°C for 30 minutes in air. The maximum breakdown strength for the annealed film is 6.2 MV/cm.

MgO layer

- *Bulk MgO*

The MgO single crystals used for the deposition of the high secondary emission layer were supplied by the Norton Research Corp [15]. Optical emission analysis of bulk MgO showed no impurities above the 100 ppm level and detected the following components: Si (60 ppm), Ca (60 ppm), Fe (60 ppm), Cr (50 ppm), Ti (30 ppm), Ni (30 ppm), Al (10 ppm), and Mn (10 ppm).

- *MgO films*

Electron microprobe analysis showed no major contaminants in the 200-nm-thick MgO films, deposited by e-beam evaporation at rates ranging between approximately 1 nm/s and 10 nm/s in a vacuum of 1.5–4 × 10^{-4} Pa (1–3 × 10^{-6} torr) into substrates held at 200°C. Particular attention was paid to detecting any Cu in the evaporated MgO films, because of possible contamination from the electron-gun crucible. However, it was below the detectable limit of the electron microprobe. Nuclear backscattering analysis showed a uniform distribution of oxygen throughout the MgO film.

The surface of the evaporated MgO films examined with an Auger electron spectrometer showed no traces of common surface contaminants such as carbon and sulfur. Study of the effect of storage in high vacuum revealed that the MgO films absorbed only a very small amount of carbon after 16 hours of storage at 10^{-7} Pa at room temperature. The absorption was spotty across the specimen surface and could be removed by primary beam exposure. Upon heating to 165°C and maintaining at that

temperature for 200 minutes, the MgO film picked up approximately 1 atomic percent of carbon, which could no longer be desorbed by high energy electrons.

Ion-induced secondary-electron emission measurements, made for 200-eV neon ions, showed that the secondary-electron emission coefficient was degraded from 0.45 to 0.30 as the initially clean, as-deposited MgO film was contaminated by trace amounts of carbon [16]. Thermal annealing of the clean MgO films through the panel sealing cycle of 30 minutes at 500°C resulted in an increase of the coefficient to 0.52 when annealed in dry air and a decrease down to 0.32 when annealed in an inert gas [17]. The observed changes in secondary-electron emission coefficient after thermal annealing are attributable to alterations of oxygen deficiency in the MgO films. In contrast to the oxygen deficiency produced in the MgO film during the inert gas annealing, it is argued that the additional oxygen supplied to the MgO surface during the air annealing could result in a large increase in density of filled states near the top of the valence band from which Auger electrons of increased energy can probably be emitted [18], and this increase in average energy modified favorably the dependence of the effective secondary-electron emission coefficient on the reduced electric field at the MgO cathode [19].

The surface orientations of 200-nm-thick MgO films, prepared by e-beam evaporation onto 6.5-μm-thick borosilicate glass films on soda-lime glass substrates, were determined by the reflection high-energy electron diffraction technique [20]. The patterns obtained for films deposited at 200°C show that the surface structure has a ⟨111⟩ preferred orientation. Upon annealing in dry air at 500°C for 30 minutes, the preferred orientation remains unchanged. The patterns obtained for films deposited at 200°C and then annealed in dry nitrogen at 500°C for 30 minutes show that the ⟨111⟩ orientation developed at 200°C disappears upon annealing and some degree of ⟨100⟩ preferred orientation develops. These results suggest that oxygen adsorption inhibits surface diffusion and, hence, the dissolution of the orientation during annealing. The patterns also show an appreciable grain growth after the annealing as indicated by the sharpening of the diffraction rings. Detailed discussions of high-energy electron diffraction and infrared analyses of e-beam evaporated MgO films are presented in [20].

Conclusion

A high rate e-beam evaporation process has been developed that is capable of depositing stable borosilicate glass films up to 50 μm in thickness on various substrates. Application of the process to the fabrication of the gas discharge display panel has resulted in panels with long life, stable electrical characteristics, high brightness, and high resolution [5].

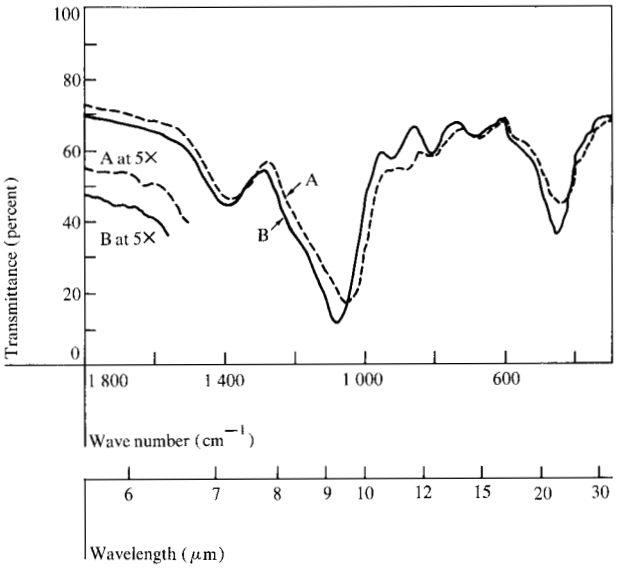

Figure 4 IR transmission spectra of electron-beam evaporated borosilicate glass at 1× with additional 5× spectra above 1500 cm^{-1}: curve A, before annealing and curve B, after annealing at 500°C for 30 minutes in dry air.

For gas panel fabrication, the panel parts are prepared by the sequential evaporation of a borosilicate glass layer and an MgO secondary emission layer in a single pump-down of an evaporation system. The thermal annealing of the gas panel parts with the evaporated dielectric layers is carried out in dry air during the panel sealing operation which further stabilizes and strengthens the dielectric layers and also improves the secondary-electron yield of the MgO layer.

The high rate e-beam evaporation process can be applied to many other areas where stable dielectric layers are needed. The process may also be applied to produce a stress-balanced coating composite by depositing a borosilicate layer between a substrate and a top layer that is poorly matched in its thermal expansion characteristics. The process is well suited for a large scale, in-line operation.

Acknowledgment

The authors acknowledge W. Pliskin for IR analysis, W. Reuter for microprobe and chemical analyses, J. Ziegler for nuclear backscattering analysis, N. Chou for secondary emission and Auger analyses, O. Aboelfotoh for electron diffraction analysis, and C. Osburn and S. Tan for dielectric strength measurements. The authors thank A. Reisman, M. Berkenblit, and T. B. Light for helpful discussions and suggestions during the course of this work.

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Received July 22, 1977; revised December 2, 1977

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