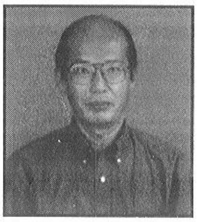
Photosensitive Glasses (Review)



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วัตถุประสงค์ : เพื่อปรับปรุงคุณสมบัติเชิงกลของผลิตภัณฑ์แก้วตกผลึก (Glass Ceramics)
การนำไปใช้ประโยชน์ : เป็นส่วนประกอบ (spacers) สำหรับจอภาพ (PDP: Plasma Display Panel) และส่วนประกอบในระบบการพิมพ์สำหรับ ink-jet printing

I. Introduction

There is one special glass group in which the additives less than 1 % act as a main role and provide the advanced functions to the glass. Photosensitive glass, which contains noble metal ions, such as Au+, Ag+, and Cu+, and optical sensitizer is included in this group.

The development of gold-ruby or copper-ruby glasses depends on the controlled nucleation and growth of metal particles from a glass matrix. When such colloidal colours in glasses are prepared, compounds of the colouring metal are added to the batch, and the metal initially dissolves as an ion. Also added to the batch are reducing agents such as the oxides of Sb, Sn, Se or Pb. When the glass containing these reducing agents is cooled, the gold or copper ions are reduced to neutral atoms, and a large number of metal nuclei may be formed. On subsequent reheating to an appropriate temperature range, growth of these nuclei takes place to a colloidal size.

In order for good colours to be formed, it is essential that the particles be present in small(colloidal) size and significant concentraions. This requires that a large number of nuclei be formed, both to prevent excessive particle growth and to provide the necessary concentration of scattering centers. A typical gold-ruby glass contains 0.01 to 0.1 wt% Au (Table 1, No.1 glass).

Table1. Typical compositions(wt %) of gold-ruby and photosensitive Glasses.

No.	SiO_2	Al_2O_3	Na_2O	ZnO	Sb_2O_3	CeO_2	Au
1	71.5	4	23	1	1.5	0.13	0.01
2	71.5	4	23	1	0.3	0.13	0.01

II. Photosensitive Glass

Photosensitive glass can be made by substituting an optical sensitizer(CeO_2) for the reducing ions present in normal ruby glass(Table 1, No.2 glass). These glasses are colourless and transparent when they are first made and cooled to room temeperature. Exposure to UV light in the absorption of photons by the sensitizing cerium ions converting the Ce^{3+} to Ce^{4+}.

While the glass remains at ambient temperature, the electrons are believed to be trapped close to the parent Ce ions. When the glass is subsequently heated, these electrons can migrate to nearby gold ions and

$$Ce^{3+} \xrightarrow{h\nu} Ce^{4+} + e^{-} \text{-----1)}$$

convert them to gold atoms, which then aggregate to form small metallic particles. This reaction might be expressed as follows thoroughly. The density of these particles can be controlled, by control of the incident radiation, from very small values in excess of 10^{12} per cm^3. A similar process takes place with glasses containing copper and silver, but in these

$$M^{+} + Ce^{3+} \xrightarrow{h\nu} M^{o} + Ce^{4+} \text{-----2)}$$

$$n(M^{o}) \rightarrow (M^{o})n \text{-----3)}$$

cases the metal ions need their own sensitizer

By using this process, one can make a permanent figures and pictures with own metal colors in a transparent glass matrix. Fig. 1 shows the absorption spectrum of gold-ruby and silver yellow glasses.

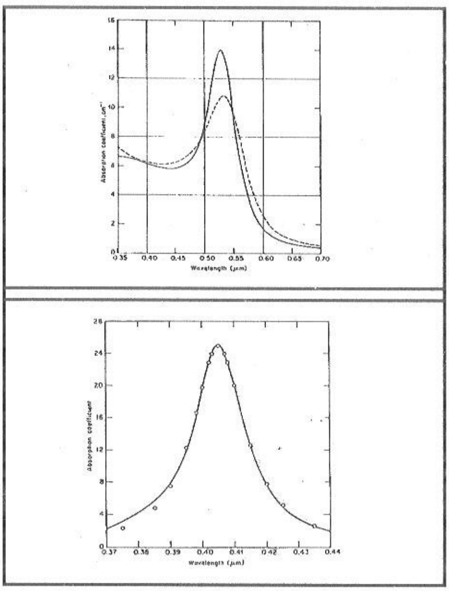


Fig. 1. Absorption spectrum of gold-ruby glass(a) and silver-yellow glass (b).

III. Chemically Machinable Photosensitive Glass

The phenomena of photosensitivity has been used commercially in a number of applications. One of these involves the use of the small metal

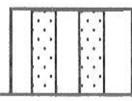
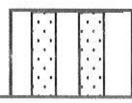
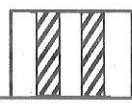
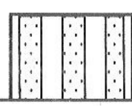
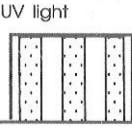
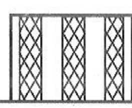
Step	Patterns	Reaction
(1).Glass melting & forming		Au^{+}, Ag^{+}, Cu^{+}, Ce^{3+} Containing Li_2O-SiO_2 glass
(2).UV Irradiation	UV_light_Mask 	Photochemical reaction $M^{+} + Ce^{3+} \xrightarrow{h\nu} M^{o} + Ce^{4+}$
(3). 1st Heat treatment	Coloration 	Colloid formation $n(M^{o}) \rightarrow (M^{o})n$
(4). 2nd Heat treatment	glass crystal 	Crystallization of $Li_2O\cdot SiO_2$ crystal, M^{o}acts as Nucleus(heterogeneous)
(5). HF etching	glass hole 	Chemically machining $Li_2O\cdot SiO_2$ crystal dissolved out Crystal/glass ≈ 20 ~ 50
(6).UV irradiation	UV light 	Photochemical reaction same as (2)
(7).Crystallization	Crystal 	Crystallization $Li_2O\cdot 2SiO_2$, β-Quartz high strength, hardness, high thermal expansion 800 holes/cm^2

Fig.2. Process of chemically machinable photosensitive glass.

Table 2. Composition (wt%) of chemically machinable photosensitive glasses studied.

No.	SiO_2	Al_2O_3	Li_2O	K_2O	ZnO	Na_2O	CeO_2	Ag
1	80	5	10	4	1	-	.03	0.96
2	80	2	11.2	3.8	3	-	.03	.096
3	82	5	10	4	1	1	.03	.048

Particles as heterogeneous nuclei for further crystal growth of other compositions. In particular, lithium silicate glasses are suitable for the precipitation of a crystalline phase, $Li_2O{\cdot}SiO_2$, which is much more soluble in HF solution than the surrounding glass. This has made it possible to prepare a glass which can be chemically machined. The photosensitive glass is exposed to UV light pattern which forms metal nuclei and is then heated to temperature at which the $Li_2O{\cdot}SiO_2$ crystal grow to form a pattern in the glassy matrix. Exposure to HF solution dissolves out these crystalline parts of the glass and provides a method of forming desired structures, such as fine grid of holes, which can not be obtained in other ways. With this technique, array of holes with densities as large as $5x10^4/cm^2$ can be produced.

Here, the processing, properties and applications of chemically machinable photosensitive glass and glass-ceramics are reviewed.

3.1. Outlines of Processing

The outline of processing of chemically machinable photosensitive glass is shown in Fig. 2.

(1). Melting and Forming

The lithium silicate glass containing a noble metal ion and optical sensitizer is initially melted under milder reducing condition and is formed to thin plate(1~ 2mm thick). These glasses are colourless and transparent.

(2). Exposure to UV light

The photosensitive glass is exposed to UV light using a negative mask with desired pattern. In this process, the photochemical reaction might occur.

$$M^+ + Ce^{3+} \xrightarrow{h\nu} M^o + Ce^{4+} \quad ----4)$$

(3). 1st heat-treatment

Metal atoms or nuclei aggregate to form a small metallic particles (colloid). Exposure part of glass turns to its own metallic colour.

$$n(M^o) \xrightarrow{KT} (M^o)n \quad ----5)$$

(4). 2nd heat- treatment

$Li_2O{\cdot}SiO_2$ crystal grows to form a pattern in a glassy matrix. The crystalline part turns to its own metallic colour. Metal colloids act as heterogeneous nuclei for the crystallization of $Li_2O{\cdot}SiO_2$

(5). HF etching

The crystalline part dissolves out and provides the structures in this process. The ratio of etching rate of crystalline and glassy phases becomes to be about 40-50.

(6). 2nd exposure to UV light

Whole area of glass is exposed to UV light same as (2).

(7). Final heat-treatment

According to heat-treatment schedule, the photosensitive glass can be heat-treated, and $Li_2O{\cdot}2SiO_2$ and β-Quartz crystals precipitate and grow.

1. **Glass composition**

Basically, the composition of glass is lithium silicate glass. However, a small amount of Al_2O_3, K_2O and ZnO is contained to improve the chemical durability and other properties of glass. It should be noted that K_2O has an important role to precipitate $Li_2O{\cdot}SiO_2$ crystals.

When the glass does not contain K_2O, $Li_2O{\cdot}2SiO_2$ crystal precipitates but not $Li_2O{\cdot}SiO_2$ crystal. Table 2 shows the typical composition of chemically machinable photosensitive glass. From DTA results, it is noted that the peak position of crystallization shifts to lower temperature and the shape of peaks become to be sharp by UV irradiation.

2. **UV-irradiation**

The intensity of UV light also affects the precipitation and crystal growth of metallic particles. In this experiments, 500W Xe-lamp with D2 filter was used to exposure of UV light from the distance of 50cm at room temperature (D2 filter:5mm thick). Longer than 30sec exposure, the amount of crystal precipitated reached to the constant value. Then, the exposure time of 5 min. was used for the later experiment.

3. **Crystallization**

Heat treatment schedules for each glasses were determined by DTA results. Heat treatment schedules and crystalline phases precipitated are summarized in Table 3.

In No.1 and No.3 glasses, only $Li_2O{\cdot}SiO_2$ crystal can precipitate, but $Li_2O{\cdot}2SiO_2$ crystal also precipitates in No.2 glass. The nucleation and crystallization behavior has been investigated in more detail using No.1 glass. Increase in nucleating temperature(1st heat treatment temperature) results in increase in the amount of $Li_2O{\cdot}2SiO_2$ crystals. In 2nd heating process, $Li_2O{\cdot}2SiO_2$ and β-Quartz crystals begin to precipitate at around 800°C. Therefore, the 1st and 2nd heating temperature should be below 500°C and 800°C, respectively.

Table 3.Crystalline phases and etching rate.

Glass No.	Heat treatment 1st	2nd	Crystalline phase (XRD)	Etching rate(mm/Hr) Glass	Crystalline	Ratio(C/G)
1	480-1	610-1	LS	0.01	0.48	48
2	480-1	610-1	L2S, LS	0.025	0.52	21
3	490-1	590-1	LS	0.01	0.44	44

4.6% HF solution at RT, °C-Hr, LS=$Li_2O{\cdot}SiO_2$, L2S=$Li_2O{\cdot}2SiO_2$

4. **HF etching**

Exposure to HF solution(4.6% HF solution, RT) dissolves out these crystalline part of glass, and etching rate was measured for both crystalline and glassy phases. And the ratio of etching rate can be determined from these results.

Glass No. 1 and 3, in which $Li_2O{\cdot}SiO_2$ crystal precipitates and contain much Al_2O_3, show the large ratio of etching rate. Although the etching rate of crystalline part is large, that of glassy phase is greater resulting in less ratio in No.2 glass. The relation between heat treatment temperature and crystalline phases precipitated, and the ratio of etching rate is investigated in more detail using No. 1 glass. These results indicate that the ratio of etching rate is greater as $Li_2O{\cdot}SiO_2$, crystal precipitates. Fig. 3 shows the example of chemically machined glass.

Table 4. Effect of heat treatment on the etching rate of No. 1 glass.

No.	Heat treatment 1st (°C-hr)	2nd	$\alpha(x10^{-7}K^{-1})$	Crystalline Phases	Etching rate (mm/Hr)	
1	-	-	76.6	-	0.01	-
2	480-1	560-1	81.1	LS(w)	0.015	1.5
3	"	600-1	83.8	LS, L2S(w)	0.4	40
4	"	650-1	85.6	LS, L2S(w)	0.46	46
5	"	700-1	85.6	LS, L2S(w)	0.45	45
6	"	750-1	80.0	LS, L2S	0.33	33
7	"	800-1	103.7	LS, L2S, β-Q	0.33	33
8	"	850-1	99.7	L2S, β-Q	0.18	18
9	"	910-1	93.8	L2S, β-Q	0.14	14

4.6% HF solution at RT, LS:$Li_2O{\cdot}SiO_2$, L2S:$Li_2O{\cdot}2SiO_2$, β-Q:β-Quartz

IV. Applications

As mentioned already, a fine holes with the density as large as 800 holes/cm^2 - 1mm thick, can be obtained by this technique. And also the final glass-ceramics(after 3rd heat treatment) has a very high strength, high-hardness and high thermal expansion coefficient. And this glass ceramics provides a good abraded flexural strength of above 200Mpa (200MNm^{-2}) and the thermal expansion coefficient of 120x10^{-7}K^{-1}, matching for ferrites and metals.

Numerous applications of this glass and glass-ceramics have been developed, some of which requires high resolution. They include magnetic recording head pads, fluidics devices, cellular faceplates for gas-discharge displays(PDP), charge plates for ink-jet printing, housing, bushings and substrates for opt-electronics devices, etc.

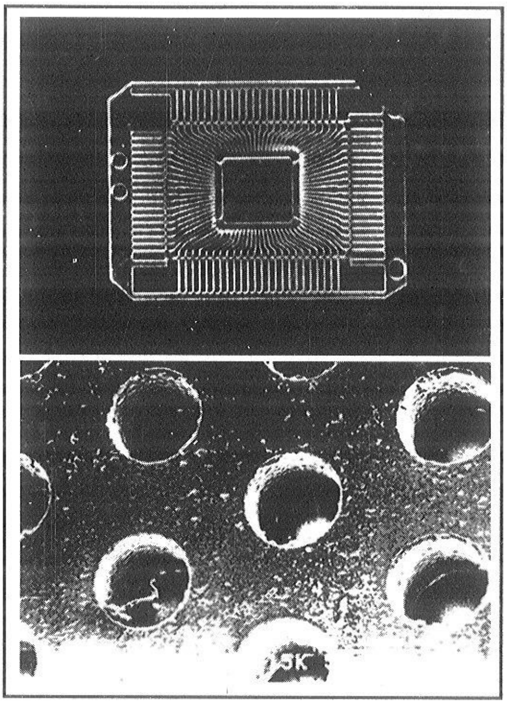


Fig. 3. Typical chemically machinable photosensitive glass ceramics.

V. Summary

The processing of photosensitive and chemically machinable photosensitive glasses were reviewed. The glass and glass-ceramics would have many possibilities in the present industrial technologies. The author would like to expect the further development of this material for new applications.