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Low temperature hermetic laser-assisted glass frit encapsulation of soda-lime glass substrates

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ABSTRACT

Room temperature and low temperature (120 °C) laser-assisted glass frit bonding of soda-lime glass substrates are accomplished in this work. The locally laser melted bonding showed hermeticity with helium leak rate of $< 5\times10^{-8}$ atm cm^3 s^{-1}, maintaining its leak rate even after standard climatic cycle tests. Small size devices were bonded at room temperature while larger areas were sealed at the process temperature of 120 °C. The sealing parameters were optimized through response surface methodology that makes the process capable for further development regardless of device size.

1. Introduction

Hermetic encapsulation is one of most common requirements for several electrical device technologies such as microelectromechanical system (MEMS) [1], organic light emitting diode (OLED) [2] or photovoltaic (PV) cells [3]. Generally, protection from environmental external (*i.e.* oxygen and moisture) and internal elements (*i.e.* leakage of components of the device) are the major benefit of a hermetic sealing. Commonly, hermetic encapsulation is referred to as sealing with extremely low helium penetration. The most common method of fine leak measurement is according to 1014.13 method of MIL-STD-883 standard, in which encapsulations with helium leak rates lower than 5×10^{-8} atm cm^3 s^{-1} are considered hermetic [4].

In this context, glass frit encapsulation is one of the most interesting candidates to achieve hermetic sealing [5]. Glass frits are generally produced in a form of glass pastes that are a mixture of glass powder (grain size of < 15 μm), solvents, binders, and fillers; the latter can be tailored to match the final thermal coefficient of expansion (CTE) of the paste to various substrates (*e.g.* glass, metal, semiconductors) [1]. To reach high quality bonding, the CTE of the sealing glass frit and the substrates should be close. The glass frit bonding steps are: (a) glass frit deposition on the substrate(s) (commonly, through screen-printing); (b) thermal treatment (pre-firing) of the paste to remove the volatile additives and reach a sintered bonding layer; (c) bonding (sealing) process. The bonding is formed when the intermediate frit layer is heated to its sealing temperature. Various compositions of the glass frit offer wide range of sealing temperatures and CTEs [6,7].

The most common method for glass frit bonding is thermo-compression in which the bonding is formed by applying pressure and temperature [8]. Generally, the sealing temperature of glass frits are higher than 380 °C and to reach the bonding through thermo-compression method, the substrates should be held at the sealing temperature for several minutes inside a furnace. Therefore, application of thermo-compression method is limited to encapsulation of electrical devices that can withstand temperature up to sealing condition of the frit. Alternatively, the bonding process can be achieved through local melting of the glass frit *via* laser radiation. Laser-assisted bonding uses laser beam to locally heat, melt, and join substrates. The only limitation of this process is that at least one of the substrates should be transparent at the wavelength of the laser. This method can be used for bonding of various intermediate layers such as glass frits, metals, and polymers. Laser-assisted technique was previously reported for wide range of substrates as well as bonding materials including borosilicate glass (Pyrex) to Si bonding with Al and Au [9], metal layers of Cr, Ta, Au [10] and Ti [10,11] to seal borosilicate glasses, and even direct (with no intermediate layer) welding of Pyrex glass to Si [12]. Moreover, organic adhesives such as benzocyclobutene (BCB) are reported to weld Si to glass using a laser-assisted process [13–15]. Laser-assisted glass frit bonding of glass substrates is being investigated by several authors [16–24]; Table 1 illustrates a summary of these reports.

In Table 1, process temperature indicates an external heating source which is usually added to the laser-assisted method for bonding of glass

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Table 1
Summary of previously reported laser assisted glass-glass sealing.

Substrates/CTE	Laser wavelength/nm	Process temperature/°C	Scan velocity/mm s^{-1}	Device size/mm^2	Reference
Borosilicate/3.2×10^{-6} K^{-1}	810	25	20	32×32	[17]
Borosilicate/3.2×10^{-6} K^{-1}	808	25	2–16	30×20	[24,25]
Soda-lime/9×10^{-6} K^{-1}	810	100–200	2	32×32	[17,22]
Soda-lime/9×10^{-6} K^{-1}	808	25–100	20	Not closed area	[21]
Soda-lime/9×10^{-6} K^{-1}	1070	330	40	18.5×8.5	[18]
Soda-lime/9×10^{-6} K^{-1}	1070	390	40	140×13	[23]

substrates to minimize thermal shocks during the laser irradiation (*i.e.* crack, delamination, etc.). As shown in Table 1, glasses with lower CTE can be bonded at room temperature, while high CTE substrates can be joined at higher temperatures (>100 °C). Moreover, the process temperatures are higher as the size of the device increases. Soda-lime glasses are the most inexpensive glass substrates in this topic and therefore more desirable for large-scale productions. The focus of research is now on low temperature sealing of large area devices constructed with low-cost materials.

Contour and quasi-simultaneous methods are normally used for laser-assisted bonding of glass substrates [26]. Contour bonding uses the movement of laser along the sandwiched bonding line between the two substrates simultaneously joining the substrates – Fig. 1a. Quasi-simultaneous sealing method uses fast scan of the entire bonding material for several loops to achieve the required temperature of bonding – Fig. 1b. Therefore, the first method is suitable for large area sealing, while the second method is only possible for small areas ($<50\times50$ mm^2) since it requires fast rate scanning equipment to obtain a uniform temperature along the entire glass frit [21].

Laser-assisted sealing is a versatile method to seal different types of substrates without submitting the entire device to the sealing temperature of the bonding material. Several factors, such as glass frit sintering condition, wavelength of the laser, laser spot diameter, bonding material, among others, influence the sealing quality. In present work, glass frit laser-assisted encapsulation of soda-lime glass substrates with both above described methods is reported. Smaller area devices were laser welded with quasi-simultaneous method at room temperature, while larger area devices were bonded with contour technique at process temperatures as low as 120 °C.

2. Material and methods

2.1. Materials

Glass substrates were 2.2 mm thick soda-lime coated with FTO (fluorine doped tin oxide; SnO_2:F – NSG TEC™ 15 from Pilkington). The glass frit was a low melting temperature paste (from Dyesol) which is a mixture of lead zinc silicate, barium silicate and silver with CTE of *ca.* 9×10^{-6} K^{-1} suitable for soda-lime glass sealing. The particle size distribution and thermogravimetric analysis (TGA) of the glass paste are presented in Fig. 2.

The TGA was carried out with *NETZECH TG 209 F1* instrument for temperature range from 25 °C to 600 °C under air atmosphere; the heating rate was 20 °C min^{-1} and air flowrate was 50 mL min^{-1}. The particle size was measured using a coulter counter (*Beckman LS 230*) and the glass frit samples were dispersed in distillated water.

TG analysis and particle size are the main factors determining the sintering and deposition (screen printing) conditions of the glass paste. The TGA showed two major weight losses; the step at 120 °C is related to solvent removal while the step between 180 °C to 380 °C is related to the removal of binders and fillers – Fig. 2a. The particle size of the paste was analyzed to find the suitable screen-printer mesh size for its deposition; the particles size range from 40 nm to 195 nm, with mean and mode of 99 nm and 70 nm, respectively – Fig. 2b.

2.2. Sample preparation

Glass paste was screen-printed on the glass substrates with screens of 200 metallic mesh. Glass substrates were ultrasonically washed with distillated water and detergent before deposition of glass paste. Various cavity shapes (*e.g.* circle, square, rectangle, etc.) were printed on glass substrates. Two sealing cavity shapes were selected for the present work – Fig. 3: small circle shape (diameter 35 mm) and large square shape (70 mm×70 mm); the width of the sealing line for both shapes are 1 mm.

The printed samples were then sintered inside a furnace. The sintering process (pre-firing) was optimized for the glass frit based on the TGA. The sintering process is composed of three steps: solvent removal, binder burn out and glazing. The optimized pre-firing condition is presented in Fig. 4. Samples were briefly levelled at room temperature for 10 min before starting the sintering process. The sintering was achieved using a furnace with heating rate of 10 °C min^{-1}, while there was no control of the cooling down step.

The sintering process of the glass paste plays a critical role not only on the adhesion of the paste to the substrates but also on the quality of sealing after laser bonding process. Binder burn out step removes all of the additives of the paste that results in pin-hole free

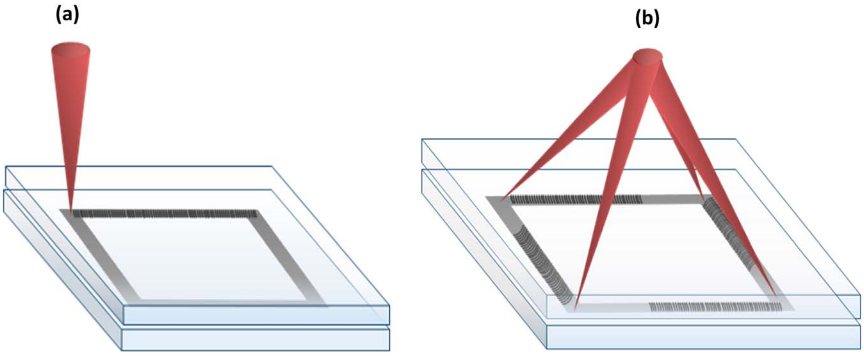

Fig. 1. The most common laser sealing methods for glass-glass bonding; (a) contour and (b) quasi-simultaneous.