Effect of ZnO on dielectric properties of Li-Al-Si photoetchable glasses as an interposer

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Abstract: In current three-dimensional (3D) radio frequency (RF) package field, the silicon interposer can’t entirely meet the needs of the package because of its non-negligible dielectric loss. Similarly, the application of through Glass vias (TGV) has restriction for the same reason. Therefore, this paper focuses on reducing dielectric loss of photoetchable glass (PEG), as well as the performance of TGV technology of PEG for packaging. The PEG was reduced in the dielectric loss by the addition of ZnO. The reduction in dielectric loss is due to changes in structure. The structure of PEG was analyzed through the XRD and the Raman spectroscopy. The dielectric performance was verified by the Impedance Analyzer. The result indicated dielectric loss obviously decreased to 0.0035 by ZnO doped and the reason primarily attributed to the decrease number of the Non-Oxygen-Bridge in the glass network and the structure is more stable. Through thermal processes and etching, the average diameter obtained around 75μm by TGV, and the aperture ratio of up to 25: 1, TGV density can reach 10000 / cm².

1. Introduction
With the development of integrated circuit, the silicon interposer has been occupied an important position in the packaging field [1]. However, silicon interposer has some problem, which is dielectric loss rather large at high frequency. As we all know, the interposer materials include quartz, glass, high resistance silicon and GaAs. Interposer materials need excellent performance of dielectric properties at high frequency. PEG is a new interposer material [2], which can be fabricated by graphic exposure and chemical etching, has attracted much attention [3]. However, the PEG have the same problem with silicon interposer. The decrease of PEG dielectric loss is key technology.

To reduce the dielectric loss of glass, many specialists have been published a large number of papers in high impact journals [4] [5] [6] [7]. J. Zhang et al. studied the Li2O-Al2O3-SiO2-xLa2O3 (where x is 0%~1%) glass system. They discussed the effect with rare-earth element on dielectric properties of glass with respect to frequency and temperature [4]. B. Deb discovered that the dielectric constant increased, due to non-bridging oxygen bonds increased with amount of Mo increased [5]. G. H. Zhang discovered that when replacing K2O by Na2O while keeping the concentrations of other components constant, the electric conductivity first decreases and then increase in CaO-MgO-Al2O3-SiO2 system or the mixed-alkali effect occurs [6]. H. Savabieh et al. studied the Li2O-SiO2-Al2O3-TiO2-BaO-ZnO glass system. They discovered that an increase of dielectric constant due to increase of density and dielectric loss was...
mainly influenced by the structure [7].

In this paper, doped with various proportions ZnO to reduce the dielectric loss. The change of crystal phase analyzed by XRD after doped ZnO. The change in the dielectric properties was measured by an impedance analyzer. Explain the change of the network of glass by Raman.

2. Materials and Methods

The PEG was based on the Li-Al-Si system. The specific formula was (77-X)%wt. SiO₂, 10%wt. Li₂O, 5%wt. Na₂O, 5%wt. K₂O, 1%wt. Al₂O₃, X%wt. ZnO (where the X was 2,3,4,5), 0.2%wt. Sb₂O₃, 0.04%wt Ce₂O₃ [8]. Because PEG contains Li⁺, K⁺ and other alkali metal ions, after treatment, it can from an easily etched lithium metasilicate (Li₂SiO₃) crystal. When the temperature of the glass liquid rise to 1500°C, the glass liquid will be symmetrical and clear. Through the annealing process was obtained the original glass sample. The glass samples with size of 20mm × 30mm × 0.5mm and a surface roughness of 30-40nm was obtained by cutting and polishing. Samples were exposed to UV of 310nm in wavelength and 7J/cm² in dose. Subsequently, annealing at 565°C. Afterwards, the samples were soaked in 10% HF solution in an ultrasonic bath at room temperature for chemical etching [9].

The glass materials were analyzed by XRD (Cu Kα radiation, Rigaku, Japan, with a scanning angle from 0° to 80° with a step of 0.02°.), Raman Spectroscopy, and Impedance Analyzer (E4991B, Agilent, from 0 GHz to 1 GHz.).

3. Results and Discussion

The PEG was based on Li-Al-Si system doped ZnO. Analyzed PEG of doped various mass fractions of ZnO by XRD. The XRD is mainly use qualitatively and quantitatively analyzed phase of materials. Subsequently, the PEG was annealing at 565 °C. Obviously, the XRD results demonstrated the Li₂SiO₃ phase [10]. The XRD results of the PEG doped with 2%, 3%, 4%, 5 % ZnO show in Fig. 1. The results obvious that the mainly crystal phase have no change.

![Fig.1 XRD of the glass doped 2%, 3%, 4%, 5% of ZnO](image)

The dielectric constant and dielectric loss of the various glasses is presented in Fig. 2. It is quite obvious that photoetchable glass doped ZnO of dielectric constant and dielectric loss lower than undoped samples. Dielectric constant of PEG which doped with 2% ZnO is minimum. Dielectric loss of PEG which doped with 2% ZnO is minimum. The dielectric properties of glass depended on internal and external factors: grain size, porosity, lattice vibration, oxygen vacancy and chemical homogeneity [11].
Fig 2. Dielectric constant and dielectric loss of PEG with 2%-5% of ZnO

As the frequency increases to 50 MHz, dielectric constant decreases due to the polarizability of the glass decreases. When the frequency increases to 100 MHz, the dielectric constant of glass tends to stable. Thereafter, the dielectric constant have unobvious change with frequency. In the range of 1 MHz to 100 MHz, the doping ZnO glass loss tends to increase, because in this frequency range, the glass has a loss of relaxation and gradually increases. The loss of relaxation of the glass doped with ZnO tends to decrease near the frequency of 100 MHz, indicating that at this frequency, the glass conductance loss is reduced, the relaxation loss is reduced, and the conductance loss is gradually reduced by relaxation loss. As the frequency increases, the dielectric loss of glass gradually increases.

Fig. 3 Raman of PEG with 2%, 3%, 4%, 5% of ZnO

To clarify the relationship between dielectric and Raman spectra, the Raman spectra of PEG doped with 2%, 3%, 4%, 5% ZnO show in Fig. 3 [12]. Raman gain in glass has been actively investigated for high gain dielectric loss. By adding metal oxide ZnO, the metal ions enter the grid of the vitreous body to prevent the entry of alkali ions and weaken the vibration of different structures in glass. In the Raman spectra of silica glass, the Q0-Q4 group (where Q is the number of bridging oxygen bonds), the peaks at approximately 850 cm⁻¹, 880 cm⁻¹, 1000–950 cm⁻¹, 1050 cm⁻¹ and 1150 cm⁻¹ correspond to Q0, Q1, Q2, Q3, and Q4, respectively [13]. Subsequently, the ZnO destroy the tetrahedral oxygen bridge structure and lead to structural stability [14]. According to the literature [11], the structural vibration mode of glass affect performance that doped ZnO. The Si–O–Si asymmetric stretching vibration at 1100 cm⁻¹ displayed Raman activity [15]. The weakened of stretching vibration of Si-O-Si bonds lead to the negative deviation of shift at 1100 cm⁻¹ in glass network [16]. The vibration could produce changes in the polarization degree, causing a Raman shift with the incident photon energy exchange. It shows that
due to ZnO doping, the asymmetric stretching ratio of Si–O–Si in the glass network is reduced. The dielectric loss of glass is closely related to the network vibration of glass. The increase in the number of oxygen bridges makes the glass network more stable. Therefore, the structural vibration of the glass is weakened, and its dielectric loss is reduced.

Using HF etching, the SEM microscopic results in Fig. 4. Doping the ZnO not affect the etching effect. Through thermal processes and etching, the average diameter obtained via TGV is around 75μm. The original thickness of the glass is 503μm, as show in Fig. 4, the thickness of the glass after etching is 497μm, the aperture ratio of up to 13: 1.

4. Conclusions
In the Li-Al-Si glass system, by the addition of ZnO into the glass results the asymmetric structure vibration weakened and lead to the glass dielectric loss was reduced. ZnO lead to the glass network was stable. The dielectric loss of the doped glass is obviously reduced and is highly stability at high frequency. Consequently, relaxation time of ionic polarization becomes long and cause relaxation loss, from analysis of Raman spectra. The dielectric constant of PEG at room temperature and from 50MHz to 1GHz frequency can be as low as 4.7, and dielectric loss can be as low as 0.0035, respectively.

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