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**Corrosion of Glass Bonded Silver Electrodes on Lead Zirconate
Titanate in Aqueous Media**

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ABSTRACT

The effect of various solutions on silver electrode adhesion strength on lead zirconate titanate has been studied through a series of soak tests, thick film adhesion pull tests, and SEM/EDS/XRD characterization. The work was sponsored by Piezo Kinetics Incorporated (PKI) in an attempt to identify why only certain silver electrodes peeled after contact with their dicing fluid mixture. This study determined that PKI utilizes a glass frit which serves as the permanent adhesive to bond the silver to the PZT. It was hypothesized that a chemical reaction is occurring between the dicing fluid mixture and this glass frit.

It was found that the following solutions cause peeling of the electrode: hydrochloric acid, sodium hydroxide, DiamafloTM (a component of the dicing fluid mixture), and the dicing fluid. A unique censored and separated Weibull approach was used to analyze the corrosion process, and failure loads corresponding to a 10% failure probability were used to compare all the samples. The tensile pull test data showed no distinct correlation between intrinsic adhesion strength and peeling probability after soaking. In fact, all electrode and PZT combinations exhibited very strong adhesion before soaking. However, adhesion strength after corrosion was shown to be comprised up to 90% in some conditions.

SEM characterization of the electrodes before soaking showed that electrode microstructures with a Bi-based glass frit sintered to a higher density and contained smaller pores as compared to electrodes using a Pb-based glass frit. It is hypothesized that the denser silver layer may act as a barrier, shielding the glass components from contact with the dicing fluid. SEM and EDS also showed the presence of fine precipitates on the surface and bottom of the peeled electrodes. Most of these precipitates contained lead, bismuth, oxygen, silver or chlorine. XRD identified strong matches to silver chloride and bismuth oxide, but could not identify the precipitates containing lead. It is expected that these solutions corrode the glass bonding agents through ion-exchange or network dissolution. Without the glass, the electrodes exhibit poor adhesion strength and peel easily.

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LITERATURE SURVEY

This study investigates the source of adhesion between the silver electrode and the PZT substrates. Therefore, it is first beneficial to review the different types of adhesion and bonding available in materials. Following this introduction, there will be a more detailed survey addressing industry standard techniques for bonding metals to ceramics, specifically glass-bonded electrode systems. With PKI's bonding technique identified, failure mechanisms and corrosion of glass-frit bonded systems will also be covered. Since there are obvious challenges on how to measure the intrinsic electrode adhesion strength, various methods used to measure the mechanical strength of electrodes on substrates will also be addressed.

Principles of Adhesion

At a fundamental level, this study investigates the bonds formed between the electrode and PZT surface and why they fail. It is difficult to identify the exact type of bond present between the two materials, so indirect methods must be used to make the correlation. It is the goal of this study to identify what is responsible for the loss of adhesion between the electrode and PZT. Adhesion between two materials involves the interaction of atoms or molecules at their interface. This cohesive force can be categorized by the type of interaction and includes: physical, chemical, and mechanical bonding processes [6]. Each of these interaction processes carries an associated bonding strength.

Physical bonding, such as Van der Waals, is always present in materials despite its weak contribution to the overall adhesion force. Other intermolecular forces include dispersion forces (called London Forces), dipole-dipole interactions and hydrogen bonding. The magnitudes of these forces ($\sim 0.1-1$ eV/atom) stem from interatomic interactions that are a function of atomic radii and separation [7]. The Lennard-Jones potential [7] is one of the most common approximations of this interaction energy and is given as: $V(r) = \epsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right]$ where σ is equal to radius of repulsive core or the distance at which the inter-particle potential is zero. The strength of attraction (depth of potential well) is denoted by ϵ and the distance between atoms, r . While intermolecular forces are relatively short range and weak, they are still important in describing molecular interactions between solid-solid interfaces.

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

In addition to physical bonding, chemical bonding plays an even larger role in adhesion between materials [6]. Chemical bonding involves the formation of ionic, covalent or metallic bonds across an atomic interface. The bond strength per atom is much larger than that observed in physical bonding processes, with magnitudes between 1–10 eV/atom. However, the strength of the chemical bonding depends significantly on bond character and wetting, which influences the likelihood of these strong chemical bonds forming [6].

One consequence, or benefit, of chemical bonding may be the formation of at least one new phase at the interface between base materials. This event, called reactive bonding, can promote strong adhesion between dissimilar materials or it can reduce adhesion, because the bond strength becomes related to the properties of the interface and new phases that have formed. This process is controlled by the solid state diffusion and reaction kinetics of the two interface materials [8]. Species with high diffusion coefficients will establish a large concentration gradient into the other solid, and again depending on the properties of the new phases, these may improve or decrease the adhesive force between the two base materials.

One final bonding process worth mentioning is the mechanical bond. There are several variations on the topic, but all involve a material penetrating into the substrate and becoming mechanically interlocked at some level. To increase the strength of this physical bond, one of the materials is usually required to be able to flow and penetrate into grain boundaries, pores, etc. Thus, glass is a prime example that uses this principle and is commonly used in the design of seals and adhesive bonds. Mechanical bonding can also be enhanced by increasing the surface roughness of the substrate.

Ceramic-Metal Bonding Techniques

There are several techniques available for joining ceramics and metals. These include mechanical fasteners, friction welding, adhesive bonding, and brazing [9]. The first two methods can be dismissed when considering the performance requirements and applications for PZT/electrodes, as they are not relevant. Brazing is a technique commonly used in the electron device industry to create a vacuum seal between the metal and ceramic. It involves a technique called metallization, wherein a

special alloy is used to coat a non-metallic object. Then, a filler metal is melted and distributed between another metal and the coated object. The filler metal acts as the bonding agent between the two metal surfaces. This technique is also impractical in light of the special electrical properties desired in the final product for PKI. That leaves adhesive bonding as the remaining technique, which is discussed below.

The adhesive bonding technique utilizes a physical adhesive that essentially joins the two materials together. A solder glass frit is commonly used in the piezoelectric and solar power industries [10]. It has long been recognized that glass is able to bond well to a wide variety of metals and alloys, and as such, can be used to facilitate the bond between metals and non-metals. The glass forms a mechanical and chemical bond to the substrate, penetrating into the surface defects and grain boundaries. This generates a strong, low-temperature ceramic-to-metal seal that has been introduced into many new applications. Studies have shown that the chemistry of the electrode material has a large influence on the wettability and adhesion to the underlying substrate [11]. Different electrode compositions and their effect on adhesion are outlined in the next section.

Glass Frit Bonding

Glass frit bonding is a fusion technique in which the glass is melted in contact with the metal and ceramic parts [12]. The conductive metal powder, glass components and organics are homogeneously mixed into a paste. Organics are used to improve wetting on the substrate and disperse the powders. During firing, the viscous glass melt is able to flow into and onto the surface of the parts, where it wets the surface and reacts to form an interface. The glass frit migrates to the ceramic substrate and forms a pillar-like structure, which provides the mechanical strength needed to join the two materials [13]. The glass frit bonds both mechanically and chemically to the ceramic and the silver film [13].

Types of Glass Frit Bonding

According to Wang et al [11], three types of bonding can occur between the metal and ceramic depending on the chemistry of the electrode: glass bonding, reaction bonding, and flux bonding. In glass-bonded systems, typically containing 2–10 wt. % lead borosilicate glass, the glass migrates to the ceramic-metal interface and forms a chemical bond to the metal film in

addition to the mechanical bond to the ceramic [11]. In reaction-bonded systems, adhesion is created using a variety of dopants, typically oxides of copper or cadmium used in the range of 0.1–1 wt. % [11]. These additives can form intermediate compounds with the base ceramic during firing. One drawback of this technique is that it requires higher firing temperatures than non-reactive glass bonding to create the bond. Flux bonding incorporates 1–5 wt. % of an oxide, which can form a liquid phase with the ceramic. For instance, Bi₂O₃ is a common flux agent used on alumina substrates because of the eutectic liquid formation of Bi₂O₃-Al₂O₃ at 820 °C [14]. Combinations of the three techniques are also employed successfully, depending on the application. Since PKI utilizes a bismuth-based and a lead-based glass frit with external dopants, the combination of glass bonding and reaction bonding will be discussed in more detail.

Glass Frit Structure and Function

As the silver electrodes used by PKI contain either a Bi-based or Pb-based glass, it is beneficial to consider the function and structure of the glass frits, in addition to their interaction behavior with the silver powder and substrate. Kim et al. and Ko et al. [10, 15] studied the characteristics and effectiveness of these Bi-based and Pb-based glass frits, respectively, as binders for silver powder on silicon wafers.

The glass frit acts as a permanent adhesive i.e., the glass bonds the silver particles to the substrate and also promotes sintering of the silver powder during the firing schedule. This approach significantly improves the bond strength between the electrode film and substrate when compared to a pure silver film [10]. When considering liquid phase sintering, it is logical that the silver microstructure densifies more easily with the addition of the glass sintering aid. The glass frit was found to be well distributed in the silver grains when fired at 600 °C [10, 15].

REFERENCES

1. Follow the citation format from the most prestigious Journal in your discipline.
2. If you can't find a good description of the proper citation format, then use the Journal of the American Ceramic Society format.
3. For an excellent example of how to build figures, tables, citations, use of SI units, etc., see: J. Am. Ceram. Soc., 83(12) 3235-3238(2000)