Increasing the strength of diffusion welded joint silicon-copper: criteria of choice of an interlayer

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Abstract. The issues of increasing the strength of the silicon-copper welded joint are considered and the criteria for choosing intermediate layers are formulated.

In modern instrumentation, a promising direction is the use of silicon as a sensitive element for highly sensitive sensors of temperature, pressure, heat flow, etc. In the production of precision products, one of the main tasks is to create a reliable connection of monocrystalline silicon with highly heat conductive metals, and if the connection of monocrystalline silicon with aluminum is well represented in the literature, the diffusion welding of Si with copper is practically not studied.

Diffusion welding refers to methods of joining materials in the solid state, where the formation of the joint is carried out due to diffusion processes in the contact zone of the compositions to be joined.

Existing explanations of the formation of joints in diffusion welding in vacuum (DWV) are based mainly on ideas about the need to increase the energy of the surface atoms involved in the interaction or on submissions on the possibility of the interaction of materials only on juvenile surfaces arising from the removal of oxide films or on ideas about the decisive role of diffusion processes in the joint area.

In most cases, the assessment of the quality of the welded joint of Si with metals is made by indirect characteristics: mechanical strength on separation or shear. The strength characteristics of the welded joint of Si with metals can not serve as a criterion for optimizing the process of DWV, because they do not fully characterize the basic requirements for the connection: the continuity of the bulk interaction and low electrical and thermal resistance. In general, there is no correlation between these characteristics of the compound and its strength. It is known that in strength tests of semiconductors, the determining factor is the state of the semiconductor surface and the scale factor.

In many cases, the use of intermediate layers is the only or preferred option for obtaining diffusion compounds that meet the necessary requirements. Intermediate layers are introduced, in particular, to prevent formation of brittle phases that are formed along the contact surface, reducing the temperature of the weld between the joined materials and of course layers – joints (dampers) to reduce stresses caused by difference of coefficients of linear thermal expansion of the welded materials.

The processes occurring in the material–interlayer–material system are complex and in each practical case are determined by the properties of all materials involved in the interaction, their purity and thickness of the interlayer.
As interlayers, alloys or pure metals are applied to both or one of the joined surfaces by galvanic or chemical deposition, thermal deposition in vacuum, in the form of foil or rolled powder. Intermediate layers can be classified according to their purpose:

1. Compensators of the stresses arising at creation of connections from materials with various coefficients of linear thermal expansion (CLTE);
2. Activators of the joined surfaces due to higher plastic characteristics of the interlayer than that of the base metal;
3. Interlayers – intensifiers of the mass transfer process by increasing the diffusion coefficients;
4. Barrier layers that prevent the formation of undesirable phase structures, such as eutectic, intermetallides, carbides, during the diffusion connection of heterogeneous materials;
5. Interlayers lowering process temperature and pressure, used in the form of foil, electroplating, nickel plating, etc.;
6. Interlayers that increase the corrosion resistance of the compound by reducing the jumps of the electrochemical potential in the transition zone.

The above allows us to put forward the first criterion for choosing an interlayer for diffusion welding of monocrystalline silicon with copper. The interlayer should be a compensator of stresses arising when connecting materials with different coefficients of linear thermal expansion (CLTE): Si (2.3), Cu (16.6).

When obtaining a compound from dissimilar metals using intermediate layers of other materials, the strength of the diffusion compound in the absence of brittle phases depends on the mechanical properties of the base and intermediate materials. When connecting materials of increased hardness and brittleness, soft interlayers are used, which are activators of interaction due to higher plastic characteristics, Ni, Cu, Ag, Au are most often used, which allows to designate the second criterion for choosing an interlayer for diffusion welding of monocrystalline silicon with copper.

In the development of new compounds of great importance are phase diagrams of state, reflecting the interaction of components, the formation of solid solutions, the stabilization of certain phases, the formation of intermediate compounds and phase equilibria.

![Figure 1](image1.png)

**Figure 1.** Character of properties change for the alloys of elements with different diagrams of states.

The metals that give the alloy with unrestricted solubility are well-connected to each other by diffusion welding. In the transition zone, due to mutual diffusion, homogeneous solid solutions are formed, i.e. the metal in the junction zone will be single-phase, which will favorably affect the
properties. In a continuous series of solid solutions, the properties of the alloys should change from the properties of the metals forming them smoothly without jumps (figure 1a). A characteristic property of homogeneous solid solutions is their increased strength compared to the strength of both components while maintaining high plasticity and heat resistance. Therefore, such compounds after the completion of all stages of the process are destroyed, as a rule, by the less durable of the welded materials.

A large group of metals in the interaction can form mechanical mixtures in the welding zone – eutectics during crystallization from the liquid state or eutectoids (a structural component of metal alloys similar to eutectic, but unlike it formed not from the liquid but from the solid phase, therefore having a thinner, dispersed structure of two or more phases) during secondary crystallization.

In the formation of such mixtures for the formation of welded joints, it is important whether the elements have limited mutual solubility in the solid state or form mixtures without limited solid solutions. The possibility of limited mutual diffusion is important in diffusion welding, it can be an additional factor in improving the properties of welded joints. The increase in the thickness of the eutectoid layer is accompanied by a decrease in the plastic and strength properties of the compound. This is probably due to the fact that the eutectoid works in the compound as a brittle interlayer.

Diffusion welding of metals that do not form solid solutions according to state diagrams is associated with certain difficulties, since the absence of mutual, at least limited solubility of the welded metals in the solid state practically eliminates the diffusion processes at the interface.

A stronger chemical bond between the atoms of the components in intermetallic compounds causes the appearance of a different lattice than that of the components. At the same time, intermetallides are characterized by high strength and sharply reduce the plastic characteristics of the compound.

The main importance for the properties of the welded joint is the formation of a layer of crystals of a new chemical compound, sometimes with properties different from the properties of the welded components. This heterogeneity of properties can be harmful to the performance of the product, especially if the boundary between the zone of the chemical compound and the welded metals in the absence of signs of at least a small limited solubility is sharp (figure 1c).

The considered material allows us to formulate one more criterion in the design of the interlayer for obtaining a strong welded connection of monocrystalline silicon with copper: the interlayer must form solid solutions with unlimited solubility or eutectic with a zone of limited solubility, which will ensure smooth change of properties in the welded connection.

Thus, the list of criteria for choosing interlayers for obtaining a strong welded connection of monocrystalline silicon with copper is as follows:
1. The interlayer should be a compensator of stresses arising when connecting materials with different coefficients of linear thermal expansion (CLTE): Si (2.3), Cu (16.6);
2. The interlayer must have higher plastic characteristics than the basic materials for the activation of the joined surfaces;
3. The interlayer should form a solid solution with unlimited solubility or a eutectic with a zone of limited solubility with the materials to be connected.

In the development of new compounds of great importance are phase diagrams of state, reflecting the interaction of components, the formation of solid solutions, the stabilization of certain phases, the formation of intermediate compounds and phase equilibria.

In the Cu–Si system, only the η phase melts congruently at a temperature of 859 °C and a content of 24.083 % (at.) Si. The remaining phases are formed either by peritectic reactions – β, δ, or by peritectoid reactions – K, γ and ε. All these phases have different regions of homogeneity.

At temperatures of 620 and 570 °C, peritectoid transformations occur with the formation of phases η' and η", and at temperatures of 558 and 467 °C, eutectoid transformations of phases η and η' occur. The solubility of Si in Cu is maximum at the peritectoid conversion temperature of 842 °C and is 11.25 %. The solubility of Cu in Si is negligible, it is shown in table 1.

Based on the literature review, we chose Ag and Ni. Based on the formulated criteria, let us consider the possibility of using these metals as an intermediate layer.
Figure 2. Phase diagram of Cu–Si system.

Table 1. Solubility of Cu in Si as a function of temperature.

| Temperature, °C | 1300  | 1200  | 1000  | 800   | 500   |
|-----------------|-------|-------|-------|-------|-------|
| Solubility of Cu, % (at.) | $2.8 \cdot 10^{-3}$ | $2.0 \cdot 10^{-3}$ | $5.5 \cdot 10^{-4}$ | $8.5 \cdot 10^{-5}$ | $5.3 \cdot 10^{-6}$ |

The results of the analysis of phase diagrams of Ni–Si [111], Cu–Ni [111], Ag–Si [111], Ag–Cu [111] allow us to conclude that nickel and silver can be used as an intermediate layer when welding silicon with copper, since both elements satisfy the criterion – the interlayer must form solid solutions with unlimited solubility or eutectic with a zone of limited solubility, which will ensure smooth change of properties in the welded joint.

For nickel:
- Cu–Ni state diagram is characterized by the formation of a continuous series of solid solutions (Cu, Ni) with a face-centered cubic structure during crystallization;
- maximum solubility of Si in Ni reaches 15.8 % (at.) at 1143 °C (eutectic temperature).

For silver:
- Ag–Cu state diagram refers to eutectic type systems with limited solubility of components in each other, for eutectic temperature values of 778–779 °C are given, and for eutectic concentration – values of 39.8; 39.9; 40.4; 40.9 % (at.) Cu;
- Ag–Si state diagram, belongs to the eutectic type of diagrams, eutectic is formed at a temperature of 830 °C and a content of 11.3 % (at.) Si.

Now it is necessary to answer the question of how these metals relate to other requirements that must satisfy the interlayer.
To reduce the silicon–copper contact stresses caused by a significant difference in the CLTE of the welded materials: Si – 2.3, Cu – 16.6, only Ni can be used as a damping layer, in which the CLTE is 12.54, while in silver – 19.

Another important property, which should have a layer when welding with such a fragile material as silicon – is to facilitate the establishment of physical contact and activation throughout the welded surface through the use of a layer of plastic metals and here the priority of silver, which has a relative elongation of 48 %, while nickel – 35–40 %.

However, practice is the criterion of truth, so only experimental studies can give an answer to the question, which of the metals will provide the required set of properties of the diffusion welded joint of monocrystalline silicon with copper.

References
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