

Lead-Free Universal Solders for Optical and Electronic Devices

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Widely used electronic components and optical materials are made up of a variety of inorganic materials, such as nitrides, carbides, oxides, sulfides, fluorides, selenides, diamond, silicon, and GaAs. The surfaces of these materials are known to be very difficult to bond with low-melting-point solders. A direct and powerful bonding on these surfaces has been obtained in air, without using any flux, by using low-temperature solders containing rare earth (RE) alloying elements. The nature of the bonding is based on chemical reactions at the interface, and hence, strong bonds are obtained. The Sn-3.5%Ag-2.5%Lu (by weight) solder and the Au-19.5%Sn-2%Lu solder, for example, exhibit interfacial-bond strengths in excess of 6.9–13.8 MPa. They can be useful for providing direct, ohmic-electrical contacts and interconnects in a variety of electronic assemblies and for producing dimensionally stable and reliable bonding in optical fiber, laser devices, or thermal-management assemblies.

Key words: Solder, lead-free, bonding, optical, electronic devices

INTRODUCTION

For construction of modern electronic and optical devices, such as computers and telecommunication systems, a reliable bonding of dissimilar materials is often one of the essential fabrication steps. Electronic devices generally contain base-semiconductor materials (such as Si, GaAs, SiC, and doped diamond), diffusion barriers (such as TiN and TaN), dielectrics (such as SiO₂, Ta₂O₅, and Si₃N₄), electrical conductors (such as Al, W, Cu, and CoSi₂), as well as heat-sink materials (such as Al, AlN, and diamond). A variety of electrical paths, lead-wire contact bonds, and mechanical bondings are made at different packaging levels.¹ Telecommunication optical fibers need to be bonded on an assembly substrate with submicron accuracy and stability in alignment with respect to lasers and other optoelectronic components to ensure and maximize optical-signal transmission.²

For convenience and simplicity of device assembly as well as for reliability and a broadened design capability, it is desirable to find a way of achieving a direct and strong bonding onto these electronic, optical, thermal, and other inorganic materials. The sur-

faces of nitrides, carbides, oxides, sulfides, fluorides, selenides, diamonds, silicon, and GaAs are known to be very difficult to bond with solders. A direct and powerful bonding on these surfaces has been achieved by using low-temperature solders containing rare earth (RE) alloying elements. The new solders are universal in that they bond to essentially all inorganic surfaces.³ In this paper, the characteristics of the universal solders and their potential applications in bonding of various optical and electronic devices will be described.

EXPERIMENTAL PROCEDURES

Two lead-free solders, Au-20wt.%Sn eutectic solder (melting point: $T_m = \sim 278^\circ\text{C}$) and Sn-3.5wt.%Ag eutectic solder ($T_m = \sim 221^\circ\text{C}$) have been selected and doped with 2–2.5 wt.% of a RE element, such as lutetium (Lu), erbium (Er), or cerium (Ce). The synthesis of the RE-containing solder was carried out by melting the component metals inside a quartz tube in a vacuum at $\sim 10^{-5}$ torr.

The melting temperatures of the RE-containing ternary alloys were determined to be close to those of the binary alloys without RE by differential scanning calorimetry (DSC). For solder bonding, various substrates were heated on a hot plate to a tempera-

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ture typically about 50–80°C above the solder melting points. A hand-soldering operation was carried out by tacking a small $\sim 1\text{-mm}^3$ piece of solder with the tip of the soldering gun and applying it onto the substrate surface in air for 1–5 sec. The use of an inert-gas atmosphere was not a necessary condition for strong bonding. A 0.5-mm-diameter nickel or copper wire was also bonded onto the same solder joint in parallel with the substrate surface for the purpose of a shear pull test to determine the bond-interface strength.

RESULTS AND DISCUSSION

As indicated in Tables I and II, the RE-containing solders produce powerful bonding to various electronic materials and optical materials. The shear stress for fracture was typically in excess of 6.9 MPa (~ 1000 psi). We have also used other RE elements, such as Er and Ce, instead of Lu in some of our universal solders. These solders also produced bond strengths comparable to those obtained by the Lu-containing solders. The universal solders directly bonded to semiconductors provide desirable ohmic contacts with relatively low contact resistance, as illustrated in Fig. 1. Four-point and three-point measurement configurations⁴ were used to evaluate the contact-resistance properties. Further optimization of solder materials and bonding procedures may lead to further improved contact-resistance behavior.

To understand the behavior of the universal solder and the underlying mechanism of the observed strong bond onto the typically solder-nonwetable surfaces, cross-sectional microstructure and compo-

sitional analyses by energy dispersive x-ray analysis (EDXA) were carried out. Figure 2a–d show the microstructures of the Sn-3.5%Ag-2%Lu and Au-19.5%Sn-2%Lu solder bonds on GaN, Si, GaAs, and SiO₂, respectively. It is seen that the interface between the solder and the substrate is smooth and flat. Extensive EDXA indicates that within the resolution of the EDXA, the RE Lu is essentially nondetectable in the Sn-Ag eutectic-solder matrix but is present primarily in the rectangular-shaped intermetallic islands⁵ of Sn₃Lu (marked A in Fig. 2a, c, and d), or Au₄Lu (marked B in Fig. 2b) with an average size of $\sim 3\ \mu\text{m}$. The fact that the RE atoms are desirably trapped in the solder as fine, micron-sized islands ensures a safe storage of the reactive RE elements within the solder matrix before use. A small size of the islands is desirable as the required diffusion distance for the movement of the RE element from the dissolving intermetallic islands toward the interface (and, hence, the needed soldering time) for chemical-bonding reaction is reduced. Transmission electron microscopy (TEM) and TEM EDXA (Fig. 3) indicate the presence of a layer of Lu oxide as thick as a few nanometers at the interface between the universal solder and the quartz substrate and the concentration of the RE element at the interface. Therefore, the bonding mechanism for the universal solder, for example, on SiO₂, is believed to be the diffusion of RE in the molten solder toward the interface and the chemical interaction of RE reducing the SiO₂. The formation of chemically more stable compounds of RE-carbide, -nitride, -oxide, -fluoride, -sulfide, and so on is thermodynamically favorable,^{6,7} as the heat of formation ($-\Delta H_f$) of RE compounds

Table I. Bond Strengths* (in MPa) of Universal Solders on Electronic Materials

Solders	Sn-Ag	Sn-Ag-Lu	Au-Sn	Au-Sn-Lu
Substrates				
Semiconductors				
Si	0	>11.04	0	—
GaAs	0	>8.11	0	—
GaN	0	>14.08	0	—
Diamond	0	>14.5	0	1.4
SiC	0	>7.80	0	>7.04
Diffusion barriers				
TiN	0	21.11	0	3.73
TaN	0	2.21	0	>10.56
Dielectrics				
Si ₃ N ₄	0	>12.21	—	—
Ta ₂ O ₅	0	5.59	—	—
Al ₂ O ₃	0	>11.52	0	>13.11
SiO ₂	0	>7.04	0	>17.94
Metallizations				
Al	0	>21.15	—	>14.50
CoSi ₂	0	>13.39	—	—
Heat sinks				
Diamond	0	>14.5	—	—
AlN	0	9.66	—	—
SiC	0	>7.80	0	>7.04

*Bond strengths in shear stress parallel to the interface.

Table II. Bond Strengths* (in MPa) of Universal Solders on Optical and Other Materials

Solders	Sn-Ag	Sn-Ag-Lu	Au-Sn	Au-Sn-Lu
Substrates				
Optical materials				
Optical fiber	0	>16.60	0	17.25
LiNbO ₃ (z cut)	0	>11.87	—	—
ZnS (110)	0	>11.66	—	—
ZnSe (001)	0	>11.18	—	—
MgF ₂	0	>18.36	—	—
CaF ₂ (100)	0	>7.45	—	—
YAG (001)	0	>13.35	—	—
Other materials				
YSZ (100)	0	>14.08	—	—
SrTiO ₃ (100)	0	>9.45	—	—
Stainless steel	0	15.02	—	>18.90
Ti	0	2.49	—	>7.59
NiTi (shape memory)	0	4.45	—	—
TiC	0	4.83	0	4.45

*Bond strengths in shear stress parallel to the interface.

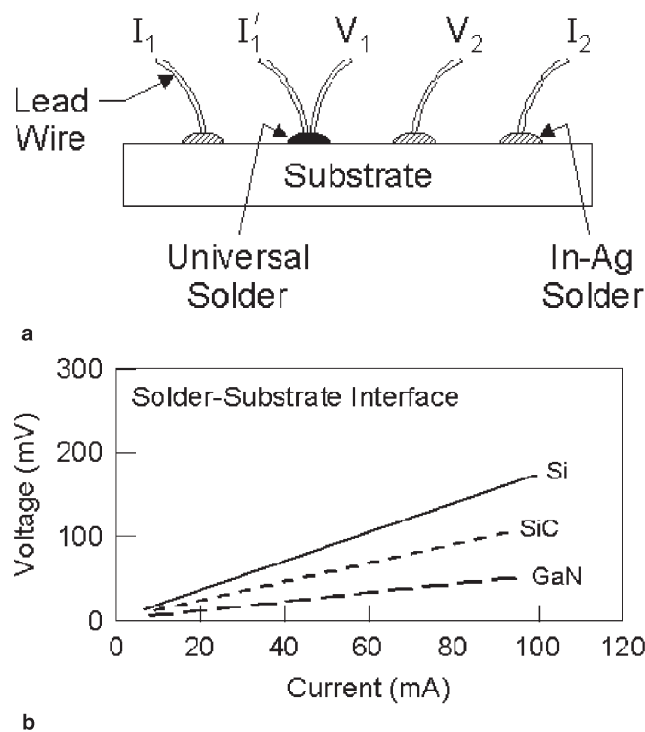


Fig. 1. The contact-resistance measurement for the universal solder/substrate interface: (a) solder bond and measurement configuration and (b) I-V curves through the interface.

tends to be greater (more negative) than those for most of the non-RE metal carbides, nitrides, oxides, fluorides, and sulfides.

In addition to the excellent bonding on semiconductors, the universal solders also bond well on the surfaces of various other electronic materials including diffusion barriers (TiN and TaN), dielectric layers (Si₃N₄, Ta₂O₅, SiO₂, and Al₂O₃), metallizations (Al and CoSi₂), and heat-sink materials (diamond, AlN, SiC, and Al), as shown in Table I. Diamond is one of the most stable materials because of

the strong atomic bonding involved. Diamond has the highest thermal conductivity of all known materials,^{8,9} about five times better than the best metallic conductors, such as copper. Low-cost, large-area chemical-vapor-deposition diamonds offer great promise for fast heat removal, especially with the recent trend of higher and higher density of electronic circuits in modern electronic devices where more heat needs to be dissipated. To the best of our knowledge, a direct, low-temperature bonding of diamond in the ~250–350°C regime, such as presented here, has never been reported previously. Mechanically and thermally reliable bonding of a heat-sink material, such as diamond, is an issue. The bond between diamond and adjacent materials is crucially important for the flow of heat across the boundary. Because solders generally do not wet and bond to the diamond surface, multilayer metallizations, such as Ti/Pt/Au are often added to make the diamond surface solderable.¹⁰ Relatively easy attachment of heat-sink components, such as diamond wafer, AlN, or SiC, using a low-temperature, mechanically ductile universal solder, such as Sn-Ag-Lu, can be useful in a variety of assembly processes for electronic packages. Using this approach, a powerful bonding is produced at temperature ranges safe for semiconductor devices and without incorporating metallization layers or high-temperature braze materials.

The universal solders may also be useful for securing reliable and convenient, low-temperature hermetic sealing using the bare surfaces of semiconductors, oxides, nitrides, or metals, thus avoiding or minimizing the fabrication and reliability complications associated with additional metallization layers, which are normally required on solder nonwetting surfaces in hermetic packaging. Hermetic sealing is very important for the reliable packaging of high-performance electronic devices or some of the emergent microelectromechanical-systems (MEMS)

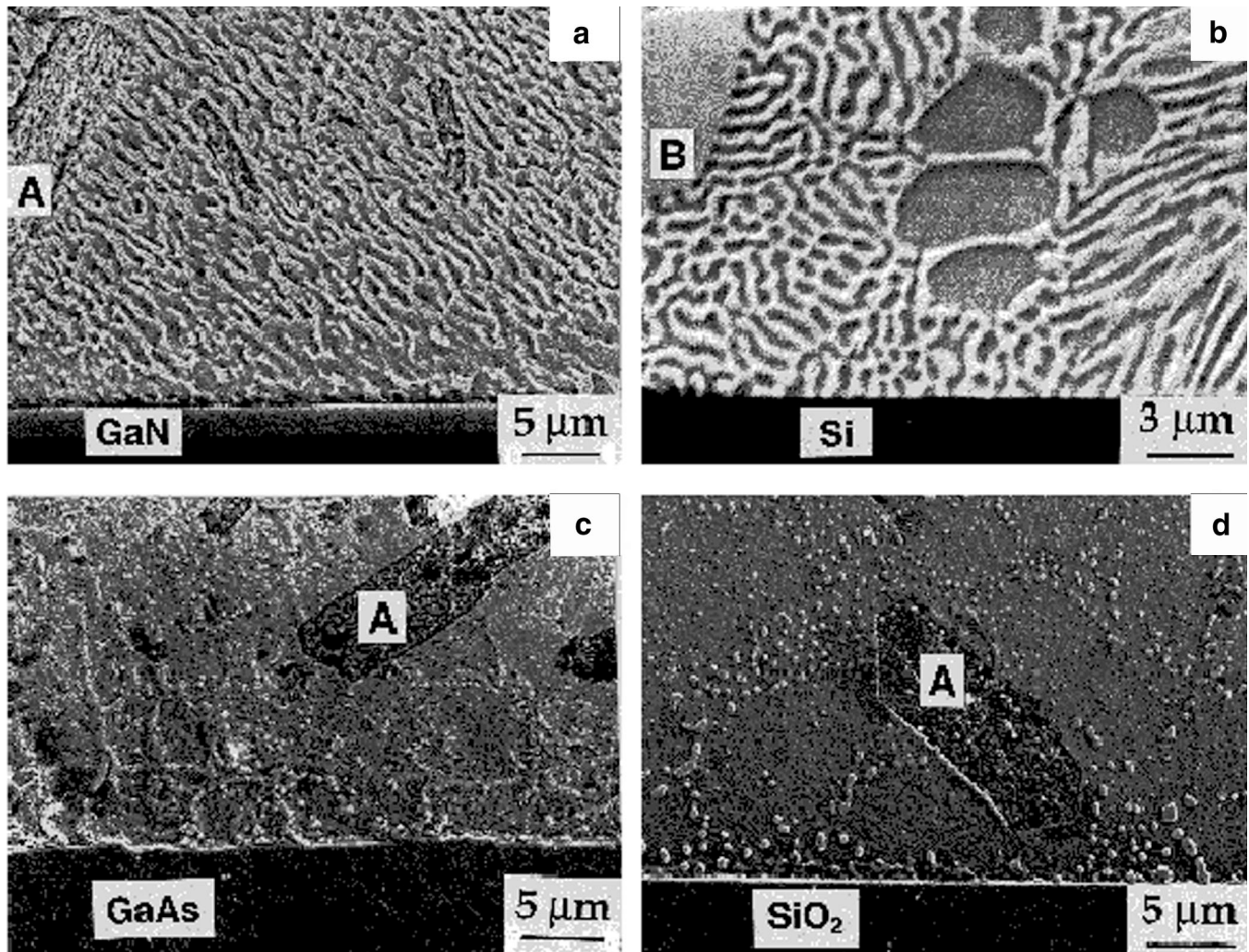


Fig. 2. The cross-sectional microstructure of (a) Sn-Ag-Lu on GaN, (b) Au-Sn-Lu on Si, (c) Sn-Ag-Lu on GaAs, and (d) Sn-Ag-Lu on SiO₂.

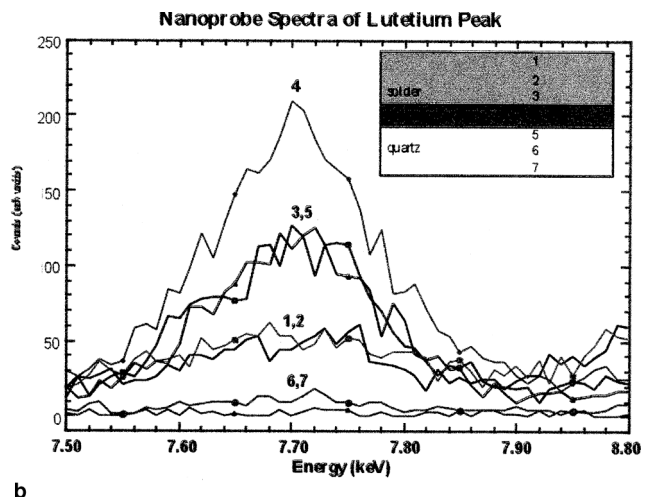
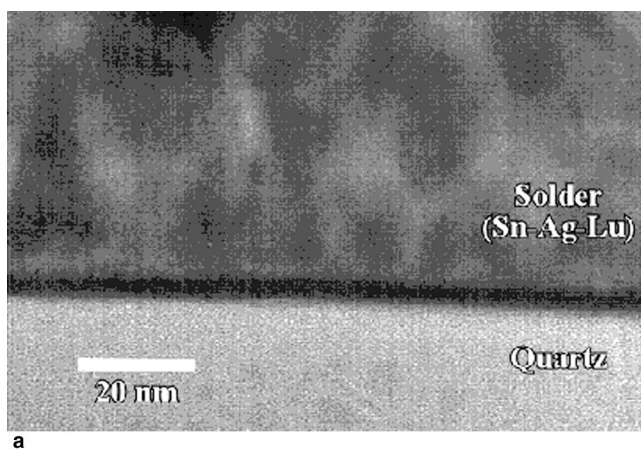


Fig. 3. (a) A high-resolution TEM micrograph showing the nanometer-scale bonding layer at the solder-quartz interface. (b) An EDX nanoprobe spectra of the Lu peak as the 1–2-nm-sized probe moves across the interface from solder (position 1) to quartz (position 7).

devices. The universal solder may also be useful for assembly of MEMS devices, for example, for flip-chip bonding of a moving part layer (such as a lithographically fabricated, an SOI silicon wafer contain-

ing movable, optically-reflecting MEMS membrane mirrors) to an actuation layer (such as a silicon wafer containing electrostatically actuating circuits for mirror movement). For the flip-chip bonding of

silicon and silicon oxide, as shown in Fig. 4a, universal solder can make the deposition of under-bump metallization layers unnecessary. In Fig. 4b, an example of hermetically sealing a MEMS device, using the universal solder, is schematically illustrated. The ability of the universal solder to directly bond to both Si and SiO₂ is useful as the electrical lead wires for MEMS actuation have to be accessible from outside through the hermetic wall. An hermetic seal for vacuum operation of MEMS devices often enables the MEMS moving membranes to perform at a much higher speed or at a higher frequency (such as in MEMS relays, switches, tiltable mirrors, and so on) because of much reduced damping by air.

The universal solders also provide strong bonding onto various optical materials (Table II). The optical materials tested here for bonding includes SiO₂, which is widely used as optical fibers (important for high-speed, high-volume telecommunications of voice, data, and internet information); LiNbO₃ crystals widely used for optical-signal modulators; ZnS and ZnSe used for display phosphors, electroluminescent devices, and photoconductors; MgF₂ and CaF₂ used for optical windows and lenses; and yttrium-aluminum-garnet (YAG) used for lasers and other optical applications. The universal solders with bond strengths typically exceeding 6.9–13.8 MPa (Table II) can be useful in a variety of optical or optoelectronic device assembly and packaging.

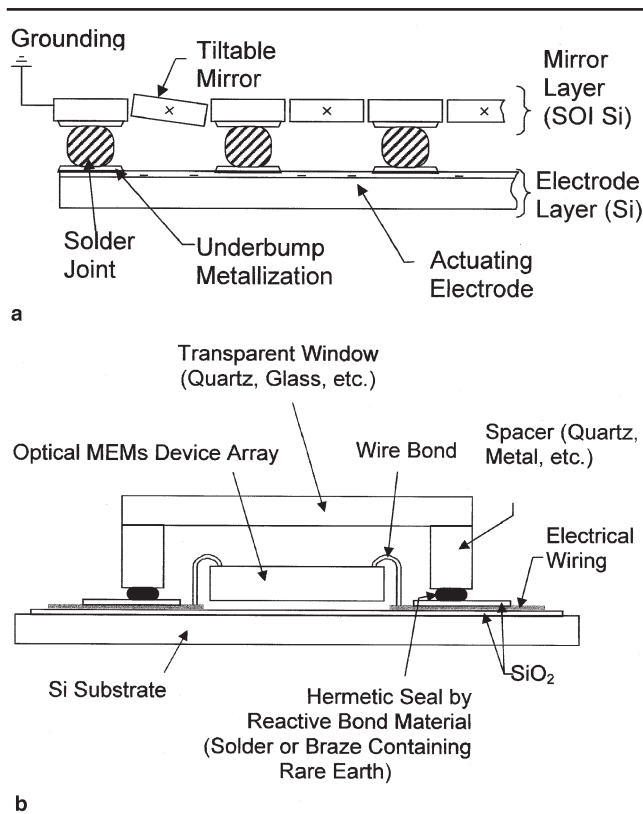


Fig. 4. (a) The flip-chip solder bonding of Si-based MEMS components. (b) A schematic illustration of hermetic sealing of the MEMS device using the universal solder.

An optical-fiber-based telecommunications network is essential for modern Internet and voice communications. Our RE-containing solders directly solderable to optical fibers are technically useful for a variety of applications in optical-fiber devices, as illustrated in Fig. 5. Strong creep resistance of bonds or joints is of tremendous importance in optoelectronic packaging because of the need for maintaining positional accuracy of the components over extended periods of time.² Time-dependent, gradual misalignment results in a reduced transmission intensity, or in some cases, even a complete loss of light-wave communication signals. Creep-resistant solders, such as those based on Sn-Ag or Au-Sn eutectic including directly bondable solders, are essential for securing and maintaining the optical alignment between the laser and the single-mode optical fiber (Fig. 5a), where a tight, micrometer-level tolerance in dimensional stability is required. Optical-fiber gratings are SiO₂-based optical fibers with internal, periodic, refractive-index perturbations along

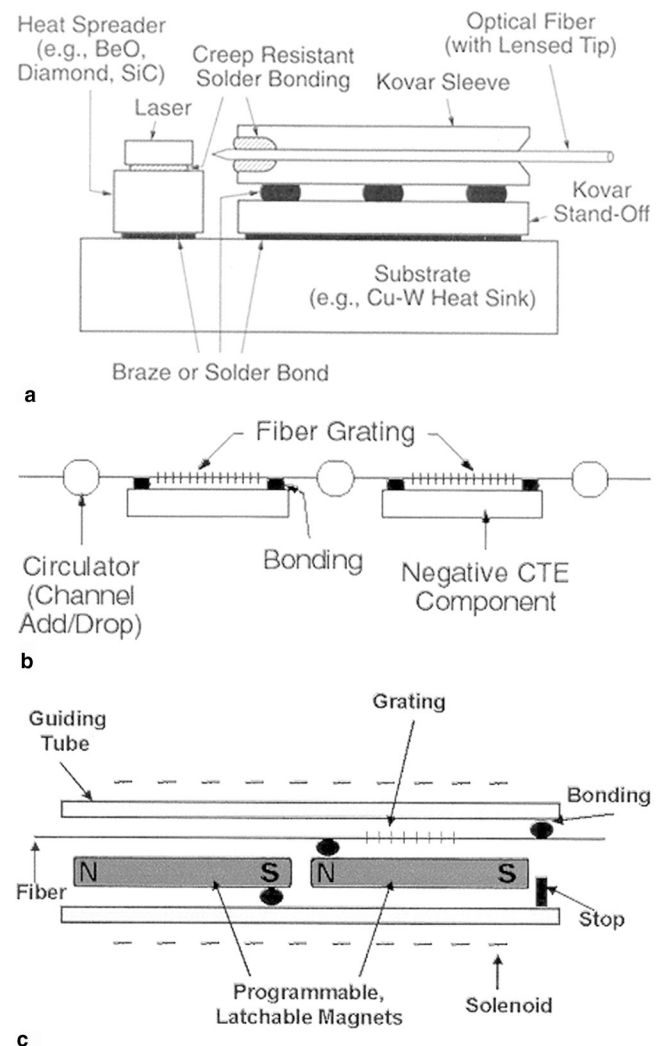


Fig. 5. The universal solder bonding for various devices: (a) fiber positioning in alignment with laser beam, (b) temperature-compensated frequency filter using fiber gratings, and (c) wavelength-tunable fiber, Bragg grating filter device.

the fiber length, corresponding to specific Bragg reflections for a certain wavelength of optical signals. They are frequently used for filtering specific, designated wavelength channels in wavelength-division-multiplexed optical communication systems. They need to be temperature-compensated¹¹ to eliminate the fluctuation of the refractive index of the grating with ambient temperature. One way of accomplishing this is to attach a negative coefficient of thermal expansion (CTE) material,^{12,13} such as Ni-Ti or Zr-tungstate, on the elastically prestrained fiber grating such that when the ambient temperature rises, the strain in the grating is reduced by the attached negative-CTE material. This is schematically illustrated in Fig. 5b. The RE-containing solders are useful for convenient assembly of wavelength-tunable fiber gratings,¹⁴ as illustrated in Fig. 5c. The straining of the fiber grating alters the characteristic Bragg-reflection wavelength so as to allow the fiber Bragg grating to filter other wavelength channels in a wavelength-division-multiplexed optical telecommunication network.

SUMMARY

Using RE-doped solders, we have achieved a direct and powerful bonding on a variety of inorganic materials, such as nitrides, carbides, oxides, sulfides, fluorides, selenides, diamond, silicon, and GaAs. The surfaces of these materials are known to be very difficult to bond with low melting-point solders. The nature of the bonding is based on chemical reactions at the interface, and hence, strong bonds are obtained. The Sn-3.5%Ag-2.5%Lu (by weight) solder and Au-19.5%Sn-2%Lu solder, for example, exhibit interfacial-bond strengths in excess of 6.9–13.8

MPa. They can be useful for providing direct, ohmic-electrical contacts and interconnects in a variety of electronic assemblies and for producing hermetic seal joints on silicon or silicon-oxide surfaces and dimensionally stable and reliable bonding in optical-fiber devices, laser devices, or thermal-management assemblies.

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