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Universal solders for direct and powerful bonding on semiconductors, diamond, and optical materials

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The surfaces of electronic and optical materials such as nitrides, carbides, oxides, sulfides, fluorides, selenides, diamond, silicon, and GaAs are known to be very difficult to bond with low melting point solders (<300 °C). We have achieved a direct and powerful bonding on these surfaces by using low temperature solders doped with rare-earth elements. The rare earth is stored in micron-scale, finely-dispersed intermetallic islands (Sn_3Lu or Au_4Lu), and when released, causes chemical reactions at the interface producing strong bonds. These solders directly bond to semiconductor surfaces and provide ohmic contacts. They can be useful for providing direct electrical contacts and interconnects in a variety of electronic assemblies, dimensionally stable and reliable bonding in optical fiber, laser, or thermal management assemblies.
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Electronic devices generally contain base semiconductor materials, diffusion barriers, dielectrics, electrical conductors as well as heat sink materials. A variety of electrical paths, lead wire contact bonds, and mechanical bondings are made at different packaging levels. 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 in order to ensure and maximize optical signal transmission.

Electronic solders such as Pb–Sn, Sn–Ag, Bi–Sn, Au–Sn are widely used for bonding of components and circuits in electronic and optoelectronic devices.[1,2] We have selected two lead-free solders, Au-20 wt % Sn eutectic solder (melting point$=\sim$278 °C) and Sn-3.5 wt % Ag eutectic solder (melting point$=\sim$221 °C), and doped these base solders with 2–2.5 wt % of rare earth (RE) element such as lutetium (Lu), erbium (Er), or cerium (Ce). The synthesis of the rare-earth-containing solder was not easy. The problem arises primarily because of the tendency of rare earth pieces to get oxidized rapidly during the heating process even in a relatively high vacuum of $\sim 10^{-5}$–10^{-6} Torr, forming a skin of very stable and high-melting-point (~2300 °C) rare earth oxide, which prevents the needed melting and alloying reaction at the interface between the liquid solder and the solid rare earth. We overcame this difficulty by employing magnetic remote maneuvering to plunge cold rare earth into molten base solder under $\sim 10^{-5}$ Torr vacuum.

For solder bonding experiments, various substrates were heated on an electric hot plate to a temperature typically about 50–80 °C above the solder melting points, e.g., ~270–300 °C for the case of Sn–Ag–Lu, Sn–Ag–Er, and Sn–Ag–Ce solders, and ~340–380 °C for the case of Au–Sn–Lu solder. The tip of a thin and flexible wire thermocouple (alumel–chromel) was placed on the substrate surface to monitor the temperature. A hand soldering operation was carried out by tacking a small piece of solder ($\sim 1\,\mathrm{mm}^3$ in volume) with the tip of the soldering gun, and applying it onto the substrate surface in air for 1–5 s. 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 shear pull test to determine the bond interface strength. The shear test was conducted by attaching the wire to either a known weight, calibrated spring scale, or the tensile test grip of an Instron machine. All three test methods gave essentially comparable breaking stress levels for the solder-substrate interface. The melting temperatures of the solder alloys, Sn–3.5%Ag–2.5%Lu and Au–19.5%Sn–2%Lu, have been determined by differential scanning calorimetry analysis to be ~224 and ~283 °C, respectively, which are about the same (~3 °C higher) as those for the corresponding binary eutectic alloys without the rare earth alloying.

We have evaluated direct solder bonding (without using any substrate metallization) of our universal solders on various types of important electronic and optical materials. The rare earth containing solders produce powerful bonding to various surfaces, as indicated in Table I. The shear stress for fracture was determined by dividing the fracture load with the solder bond interface area. As indicated in Table I, the universal solders provide high shear fracture stress typically in excess of ~1000 psi (6.9 MPa). We have also utilized other rare earth elements such as erbium (Er) and cerium (Ce) instead of lutetium (Lu) in some of our universal solders. These solders also produced bond strengths comparable to those obtained by the Lu-containing solders. When the solder bond is subjected to a stress level beyond the breaking stress, the fracture often occurs either in the substrate material or at some point along the length of the bonded metal wire being pulled instead of at the solder bond interface.

For circuit connections, ohmic contact with low contact resistivity on semiconductor surfaces is desirable. The development and evaluation of ohmic contact materials, especially for the wide band gap semiconductors such as GaN, is a

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TABLE I. Bond Strengths[a] (in psi) of universal solders on electronic, optical, and other materials.

SOLDERS:	Sn–Ag–Lu	Au–Sn–Lu	SOLDERS:	Sn–Ag–Lu	Au–Sn–Lu
SUBSTRATES:			SUBSTRATES:		
Semiconductors			Optical materials		
Si, GaAs	>1200		Optical fiber	>2400	2500
SiC, GaN	>1130	>1020	$LiNbO_3$(z cut)	>1720	
Diffusion barriers			ZnS (110)	>1690	
TiN	3060	540	ZnSe (001)	>1620	
TaN	320	>1530	MgF_2	>2660	
Dielectrics			CaF_2 (100)	>1080	
Si_3N_4	>1770		YAG (001)	>1935	
Ta_2O_5	810		Other materials		
SiO_2,Al_2O_3	>1020	>1900	YSZ (100)	>2040	
Metallizations			$SrTiO_3$ (100)	>1370	
Al, $CoSi_2$	>1940	>2100	Stainless steel	2177	>2740
Heat sinks			Ti	361	>1100
Diamond	>2100		NiTi (shape memory)	645	
AlN, SiC	>1130	>1020			

[a] Bond strengths in shear stress parallel to the interface. 1 psi=6.9 $\times 10^{-3}$ MPa.

[b] Sn–Ag and Au–Sn binary eutectics do not bond at all to most of the substrates above.

subject of intense current effort.[3] The use of multilayer metallizations and high temperature annealing treatment (e.g., at ~900 °C) is often required in order to achieve low contact resistance. The contact resistance behavior of the interface between the universal solder and the directly bonded semiconductor was evaluated after the low temperature soldering. We used four-point and three-point measurement configurations[4] as illustrated in the schematic cross-sectional diagram of Fig. 1(a). Four stripe-shaped solder bonds were made on rectangular semiconductor substrates (~3 mm × 12 mm) of Si, GaN, SiC, and GaAs. One of the four bonds is the Sn–3.5%Ag–2.5%Lu universal solder joint while the other three are In–10%Ag solder joints (m.p. ~ 150 °C) added later by lower temperature soldering operation. Thin silver wires (0.125 mm in diam) were attached to each bond as lead wires. A dc current of up to ~100 mA was applied through the I_1 (or I_1') and I_2 leads while the voltage developed was measured with the V_1 and V_2 leads. The four-point voltage data (using the current leads I_1 and I_2) were subtracted from the three-point voltage data (using current leads I_1' and I_2) to obtain the voltage drop across the interface between the universal solder and the semiconductor.

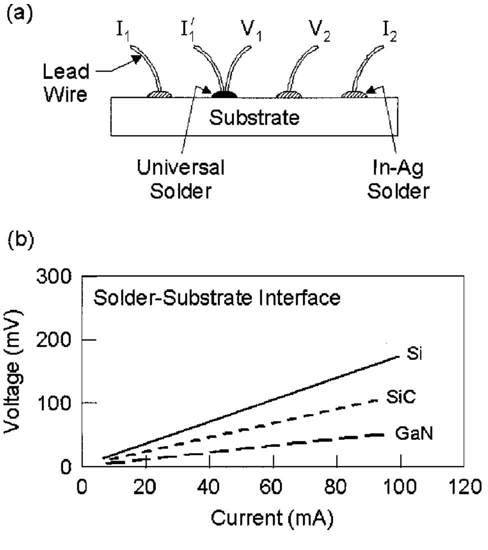

FIG. 1. Contact resistance measurement for universal solder-substrate interface. (a) Solder bond and measurement configuration, (b) *I*–*V* curves through the interface.

Both the four-point *I*–*V* and the three-point *I*–*V* curves were linear. Shown in Fig. 1(b) are the differential (four-point minus three-point voltages) *I*–*V* characteristics of the solder-semiconductor interface for (100) Si (*n*-doped with phosphorous, $\sim 10^{18}$ /cm^3 carrier density), SiC semiconductor [4H SiC, (1120), *n*-type doped with $\sim 5 \times 10^{17}$/cm^3 of N, procured from Stirling Semiconductors, Inc.], and (0001) GaN which is *n*-type doped with Si ($\sim 1.5 \times 10^{18}$/cm^3 carrier concentration), with a thickness of 2.5 μm and grown on 0.04 μm AlN on (0001) sapphire (procured from Epitronics). It is seen that the interface *I*–*V* characteristics are Ohmic for both semiconductors. The contact resistance appears to scale with the bond area when the bond area was made smaller. The contact resistivity, which is the contact resistance value multiplied with the bond interface area, is estimated to be about 0.01 – 0.02 Ω cm^2. Qualitatively similar results were obtained for the case of solder bonding on GaAs.

Shown in Figs. 2(a)–2(d) are the microstructures of the Sn–3.5%Ag–2%Lu and Au–19.5%Sn–2%Lu solder bonds on GaN, Si, GaAs, and SiO_2, respectively. In Fig. 2(a), it is

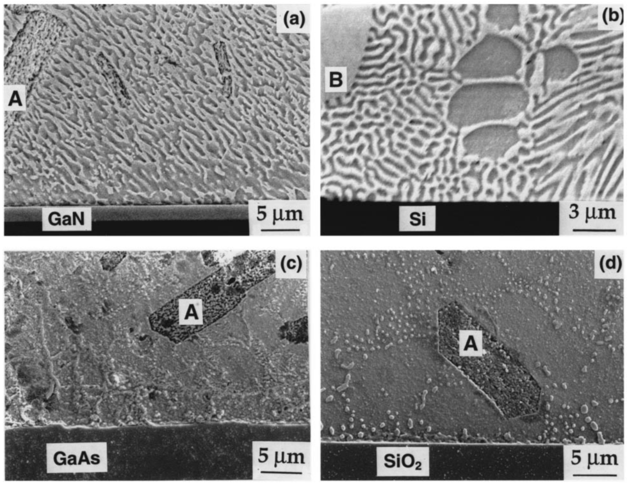

FIG. 2. Cross-sectional microstructure of (a) Sn–Ag–Lu on GaN, (b) Au–Sn–Lu on Si, (c) Sn–Ag–Lu on GaAs, (d) Sn–Ag–Lu on SiO_2.

seen that the interface between the Sn–Ag–Lu solder and the GaN semiconductor is flat and smooth. The bond strength is strong, with the shear fracture stress in excess of 2000 psi or 13.8 MPa. The eutectic lamella structure of the Sn–Ag matrix is also evident, with the light phase being the Ag-rich Ag_3Sn intermetallic phase and the dark phase being the Sn-rich phase. Extensive EDXA analyses indicate that within the resolution of the EDXA, the rare earth Lu is essentially non-detectable in the Sn–Ag eutectic solder matrix but is present primarily in the rectangular-shaped islands [marked A in Fig. 2(a)] with an average size of ~3 μm. These islands have been identified as the intermetallic compound with a composition close to Sn_3Lu.[5] The fact that the rare earth atoms are desirably trapped in the solder as fine, micron-sized islands ensures a safe storage of the reactive rare earth elements within the solder matrix before use. Upon soldering, the rare earth, on account of the fine precipitate size, rapidly dissolves in the molten solder and makes itself available for interfacial reaction to produce strong chemical bonding. When the solder solidifies, the remaining rare earth atoms again go back to and stored in the intermetallic islands. A small size of the islands is desirable as the required diffusion distance for the movement of rare earth element in the dissolving intermetallic islands toward the interface (and hence, the needed soldering time) for chemical bonding reaction is reduced. This, in turn, minimizes the degree of undesirable oxidation of rare earth element on the surface of molten and solidifying solder, which occurs rather rapidly.

Shown in Fig. 2(b) is the scanning electron microscopy cross-sectional micrograph of the Au–19.5%Sn–2%Lu solder bonded on the *n*-type Si substrate. The lamellae type eutectic structure consisting of the (~90%Au–10%Sn) phase and the (~62%Au–38%Sn) phase is clearly seen. The solder-semiconductor interface is smooth and flat. The rare earth Lu in this case is trapped and stored in the islands of Au_4Lu intermetallic compound marked B in the figure. Lu was essentially absent in the Au–Sn solder matrix. Since the storage environment for Lu (i.e., the Au_4Lu islands) is rich in oxidation-resistant Au in this case, Lu is kept even safer than in the case of the Sn-based Sn–Ag–Lu solder.

Figure 2(c) represents the microstructure near the bond interface between the Sn–Ag–Lu solder and (100) GaAs semiconductor surface . The general trend of Lu trapping in micron sized intermetallic islands appears to be the same in this case as well. Figure 2(d) shows the microstructure for the Sn–Ag–Lu solder bond on quartz substrate (SiO_2). SiO_2 is an important and indispensable dielectric for Si-based semiconductor technology, as well as for optical fibers widely used for internet and other telecommunications networking. The universal solder produces direct and powerful bonding to quartz as shown in Table I. The shear strength to break the bond is in excess of 1000 psi (6.9 MPa). The microstructural features near the bond interface show the same general trend as in the case of other substrates.

In all cases of Figs. 2(a)–2(d) samples for which the soldering time was kept to about or less than a few seconds, the solder-substrate interface region showed no detectable Lu peaks by EDXA. However, if we increase the soldering time to more than several seconds, a faint Lu peak begins to appear, indicating a time-dependent, diffusional reaction of the rare-earth element migrating in the molten solder toward the interface to react with the substrate materials. For an exaggerated soldering operation of 2 min, high-resolution transmission electron microscopy (TEM) microscopy indicates the presence of a layer of Lu oxide as thick as 5 nm at the interface of the universal solder and the quartz substrate. Therefore, for the typical soldering time of a few seconds used for most of the bond experiments in this work, the RE-containing bond layer is estimated to be on the order of a few atomic layers thick or less, and may or may not be a continuous layer. Further TEM analysis is required to understand the exact nature of bond layer and mechanisms involved. Such a formation of chemically more stable compounds of RE-carbide, -nitride, -oxide, -fluoride, -sulfide, etc. is thermodynamically favorable[6,7] as the heat of formation ($-\Delta H_f$) of rare earth compounds tends to be greater (more negative) than those for most of the non-RE metal carbides, nitrides, oxides, fluorides, and sulfides.

A direct, low-temperature bonding at ~250–350 °C regime of diamond, one of the most stable, high thermal conductivity[8] materials, such as presented here (Table I) has never been reported previously. The universal solders also provide strong bonding onto various optical materials (see Table I) including SiO_2 used for communication optical fibers, $LiNbO_3$ crystals for optical signal modulators, ZnS and ZnSe for display phosphors and photoconductors, MgF_2 and CaF_2 for optical windows, and yttrium– aluminum–garnet for lasers and other optical applications. Strong and reliable solder bonding to optical fiber can also be useful to other fiber-related devices, such as those based on fiber Bragg gratings for wavelength selection and filtering.[9,10]As our rare-earth doped solders bond strongly to essentially all inorganic materials, they can be viewed, in essence, as *universal* solders.

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