Kinetics of the Pd/In Thin-film Bilayer Reaction: Implications for Transient-Liquid-Phase Wafer Bonding

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The kinetic behavior of the Pd/In bilayer reaction is analyzed, with emphasis on the effect of nanometer-scale diffusion barriers at the Pd/In interface. It is shown that the Pd/In reaction proceeds rapidly and without a discernable incubation period at temperatures below 200°C if the Pd/In interface is nominally free of either contamination or intentionally-deposited intervening layers. Air exposure of the Pd surface prior to In deposition is sufficient to delay the onset of the reaction to produce the intermetallic phase by $PdIn_3$ for several minutes at 200°C. This incubation period can be further controlled by deposition of a nanometer-scale Ti layer onto the Pd prior to air exposure and In deposition. The implications of these results for the design of transient-liquid-phase wafer-bonding processes based on Pd-In are discussed.

Key words: Intermetallic, palladium, indium, wafer bonding, materials integration, laser lift-off, reaction kinetics

INTRODUCTION

The functionality of integrated microsystems may be enhanced by intimately integrating disparate classes of materials, each of which is chosen for its ability to provide a specific function. For example, potential bioanalytical microsystems might incorporate polymer microfluidics, III-V semiconductor light emitters, silicon-based detectors and control electronics, and electroceramic thin-film actuators. The principal challenge in assembling such a microsystem is the incompatibility of the process steps required to fabricate each materials subsystem.

Integrating disparate materials can be done on a number of levels, with each level offering both advantages and disadvantages over the others. Discrete devices on separate substrates joined to a common printed-circuit board are at the lower end of the integration spectrum, while direct deposition of one material onto a substrate of another is at the higher end (e.g., heteroepitaxy of GaAs on silicon to combine information processing and optical interconnect functions). Although materials integration by heteroepitaxy may be attractive in its potential to reduce assembly costs and increase the performance of a microsystem, the process of heteroepitaxy may be detrimental to materials quality due to lattice mismatch, differences in thermal expansion coefficients, symmetry mismatch with the substrate, and reactions with the substrate at the growth temperature. This trade-off between cost and quality suggests that an intermediate integration approach, one involving the separation and transfer of thin films from their preferred growth substrate to a final receptor substrate, may be optimal for some combinations of materials and functions. Examples of these intermediate integration methods are 1) the epitaxial lift-off (ELO) method for separating III-V heterostructures using selective etching of a sacrificial layer,[1] 2) ion-damage-assisted lift-off,[2,3] and 3) laser lift-off (LLO).[4,5]

For mechanical reasons, the separation and handling of unsupported thin films is undesirable in most cases. Consequently, separation of the growth substrate is usually preceded by bonding the film to a receptor substrate. For microsystems that require a bond with high electrical and thermal conductances, a transient-liquid-phase (TLP) metallization approach may be employed to achieve a robust bond without subjecting the films or substrates to high temperatures.

The TLP and related bonding methods were origi-

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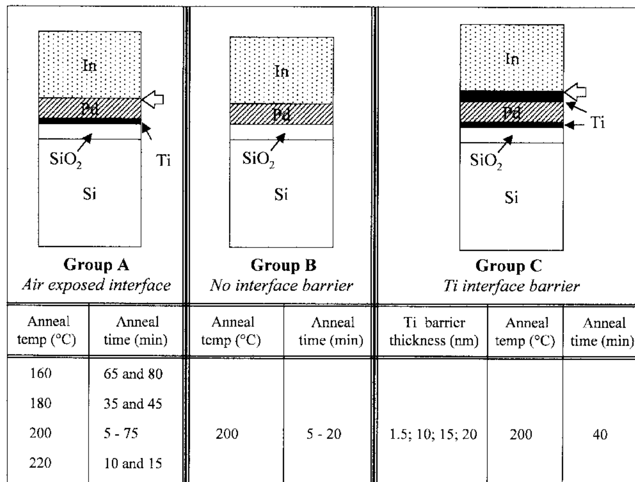

Group A		Group B		Group C		
Anneal temp (°C)	Anneal time (min)	Anneal temp (°C)	Anneal time (min)	Ti barrier thickness (nm)	Anneal temp (°C)	Anneal time (min)
160	65 and 80					
180	35 and 45					
200	5 - 75	200	5 - 20	1.5; 10; 15; 20	200	40
220	10 and 15					

Fig. 1. The three types of samples used in this study. Palladium and indium layers were 300 nm and 1.8 μm thick, respectively, and were deposited on oxidized silicon (100 nm SiO_2) substrates for all three groups. Group A samples were produced by breaking vacuum between the Pd and In deposition, as indicated by the block arrow. Group B samples were produced without breaking vacuum. Group C samples were produced by breaking vacuum between the second Ti film (a diffusion barrier) and the In film.

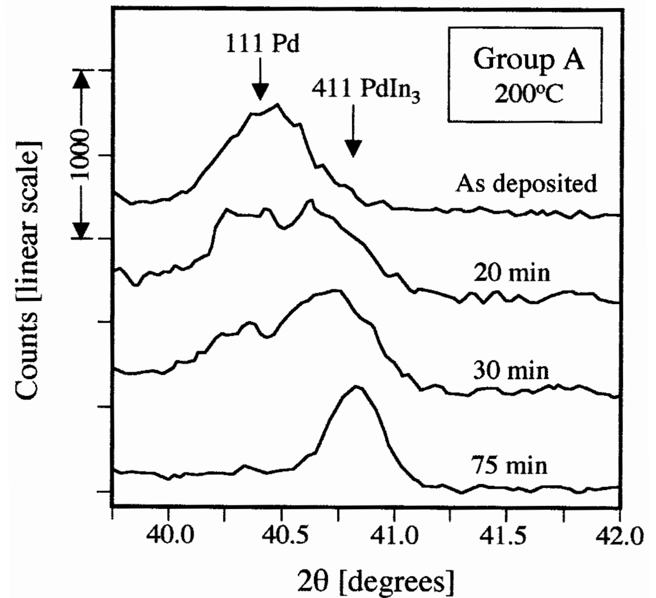

Fig. 2. X-ray diffraction patterns of Group A samples after different annealing times at 200°C. As annealing time increased, the 111 Pd peak decreased in intensity while the 411 $PdIn_3$ peak increased in intensity.

nally developed for joining ceramic parts at temperatures below that typically required for solid-phase sintering. For example, Cu/Pt has been used to join Al_2O_3 at ~1150°C, resulting in a final bond that has a melting point of ~1740°C.[6] The TLP approach has been adapted by the authors and their colleagues for low-temperature (≤200°C) joining of thin films to a variety of dissimilar substrate materials, including polymers.[7]

In low-temperature TLP bonding, a bilayer metallization such as Pd/In is designed to exploit the best features of both conventional solid-phase bonding (e.g., Au cold welding) and conventional liquid-phase bonding (e.g., solder bump bonding). In this process, the low-melting-point component, In, is sandwiched between thin films of the higher-melting-point component, Pd. As in a solder, eutectic, or elemental In bond, the liquid phase of the lower-melting-point component flows to accommodate submicron-scale surface roughness, thus maximizing the bond contact area without high-temperature processing or the need for stringent controls over particulates. The higher-melting-point component, Pd, serves to consume the low-melting-point component at a later stage of the bonding process, thus the "transient" nature of the liquid phase. In the Pd/In TLP metallization, the $PdIn_3$ intermetallic phase is formed at low temperatures (<200°C) yet exhibits a relatively high melting point (664°C). Note that an important TLP design requirement, ensuring a large-contact-area bond, is that the low-melting-point component must not be completely consumed by the intermetallic reaction before reaching its melting point.

In previous reports by the authors and their colleagues, the Pd/In TLP bonding method at 200°C has been utilized for bonding epitaxial GaN- and Pb $(Zr,Ti)O_3$-based heterostructures to silicon, GaAs, and polyimide,[7–9] yielding single-phase $PdIn_3$ bonds of strength sufficient to withstand the thermomechanical shock associated with the LLO process. It has been the experience of the authors, however, that the success of the Pd/In bonding process depends on the methods and conditions utilized for bilayer deposition, and the elapsed time between process steps. Consequently, it was concluded that the reproducibility of the Pd/In TLP bonding metallization needed improvement. For example, initial studies revealed that air exposure between the Pd and In deposition steps was required for a successful bond. These observations, along with the need to design the Pd/In TLP process for a range of bond thickness have motivated the present study of the kinetics of the Pd/In reaction.

EXPERIMENTAL

The substrates used for this study were thermally oxidized SiO_2 on (100) Si wafers. The 100 nm SiO_2 layer prevented a reaction between Si and the subsequently deposited Pd. The formation of Pd_2Si is not necessarily deleterious; however, its formation complicates the analysis of reaction kinetics. Three types of Pd/In bilayer films were prepared (see Fig. 1). Samples for Group A were prepared by a two-step deposition process utilizing an electron-beam evaporation step for Ti and Pd, and a thermal evaporation step for In. At a base pressure of $\sim 1 \times 10^{-7}$ torr, a 5 nm Ti layer followed by a 300 nm Pd layer were deposited onto the substrate by electron beam evaporation without breaking vacuum. This first Ti layer was deposited to promote adhesion between Pd and SiO_2. After breaking vacuum and exposing the Pd surface to laboratory air at room temperature for ~15 min, an indium film of 1.8 μm thickness was deposited onto the Pd film by thermal evaporation at a base pressure of 5×10^{-7} torr. The In and Pd layer thicknesses were designed to yield a Pd:In atomic ratio slightly greater

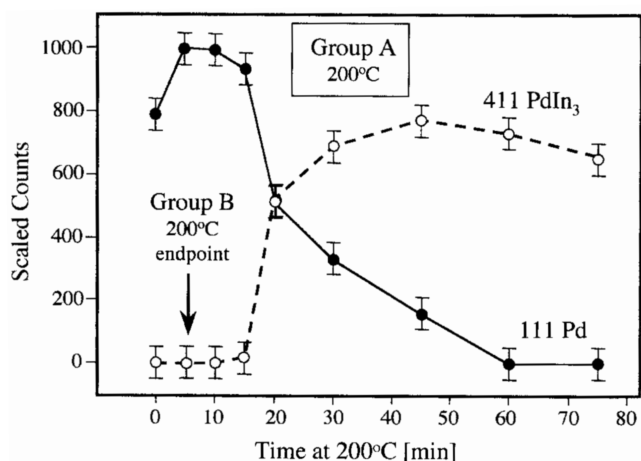

Fig. 3. 111 Pd and 411 $PdIn_3$ peak heights for Group A samples versus annealing time at 200°C. The 15, 45, and 75 min samples were analyzed during a different diffractometer session. The two sets of data were adjusted by equating the 111 Pd peak heights for annealing times of 10 and 15 min. Note the incubation period of approximately 15 minutes.

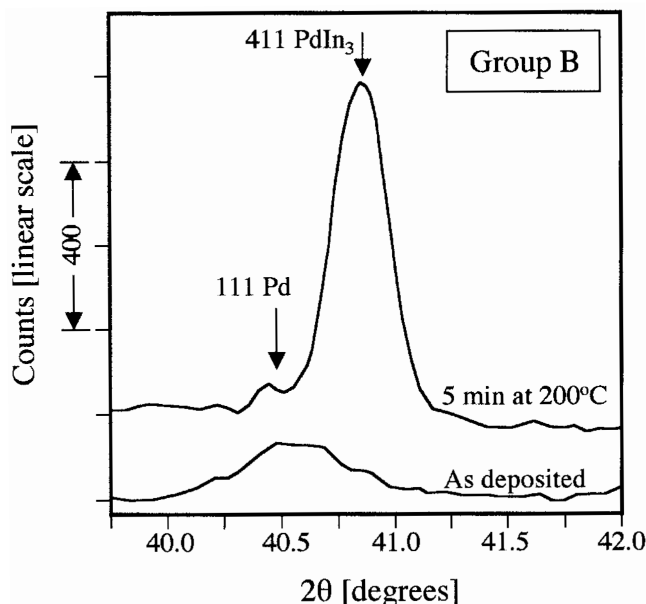

Fig. 4. X-ray diffraction patterns produced from Group B samples. The reaction between Pd and In nearly goes to completion after a 5 min anneal at 200°C.

than 1:3 so as to ensure complete consumption of the low-melting-point In phase. Note that the two-step deposition process was initially chosen to minimize substrate heating during Pd evaporation, and to prevent the splashing of In during electron-beam evaporation. The authors originally believed that the exposure of the Pd surface to laboratory air would not significantly inhibit the reaction due to palladium's resistance to oxidation. To test the effect of the air exposure, a second set of Pd/In samples (Group B) with the same layer thicknesses as the Group A samples, were prepared by thermal evaporation of Pd and In without breaking vacuum. A third set of samples, Group C, were identical to the Group A samples except that a Ti layer of thickness 1.5, 10, 15, or 20 nm was deposited by electron beam evaporation onto the Pd layer before air exposure and deposition of In. The Group C samples were intended to help evaluate the effects of a diffusion barrier on the kinetics of the Pd/In reaction.

After dicing, samples were annealed in a flowing N_2 ambient, thus mimicking the thermal process used for Pd/In bonding.[7] The thermocouple was calibrated using a bead of In and observing its melting temperature. All temperatures were maintained to within ±5°C during the anneal. Samples prepared by two-step deposition without the Ti-diffusion barrier (Group A) were annealed at 160°C for 65 and 80 min; at 180°C for 35 and 45 min; at 200°C for 5, 10, 15, 20, 30, 45, 60, and 75 min; and at 220°C for 10 and 15 min. Group B samples were annealed at 200°C for 5, 10, 15, and 20 min. Samples in Group C, including a control sample without the Ti layer between the Pd and In, were annealed at 200°C for 40 min.

The primary aim of this study was to quantitatively determine the kinetics of the Pd/In reaction and the factors that affect the kinetics. Hence, it was necessary to measure the extent of the reaction by evaluating the amount of the product phase $PdIn_3$, and/or the amount of the elemental metals consumed. Several methods were considered, including cross-sectional transmission electron microscopy (XTEM), cross-sectional scanning electron microscopy (SEM), Auger electron spectroscopy/depth profiling (AES), Rutherford backscattering spectrometry (RBS), and quantitative x-ray diffraction (XRD).

Selection of the characterization method was based on the ease of sample preparation and the ability to accurately measure the extent of the Pd-In reaction. The XTEM technique suffers from time-consuming sample preparation difficulties and sampling limitations. Quantitative AES depth profiling generally requires standards, and the elemental depth profiles may be "smeared" due to knock-on and orientation-dependent ion milling effects. The SEM image contrast between the elements and the product phase in fracture cross-section samples was found to be insufficient for reliable kinetic studies. The small atomic mass difference between Pd and In prevented accurate deconvolution of the elemental contributions to the RBS spectra. Finally, the XRD method was chosen for the ease of sample preparation and the ability to ascertain the relative progress of the Pd-In reaction in a systematic fashion.

Although the XRD method requires complete mapping of reflection intensity in reciprocal space in order to achieve a rigorously quantitative analysis, a simplified comparison between the relative peak heights of 111 Pd (nominally at $2\theta = 40.4°$) and 411 $PdIn_3$ (nominally at $2\theta = 40.7°$) in a θ-2θ symmetric scan was found to provide a reproducible indicator of the extent of reaction. These two reflections were chosen due to their proximity and lack of interference with substrate and indium peaks. Samples were analyzed in a Siemens D-5000 diffractometer without the monochrometer, using Cu Kα x-rays and slits of 0.2 and 2 mm before and after the Ni filter, respectively.

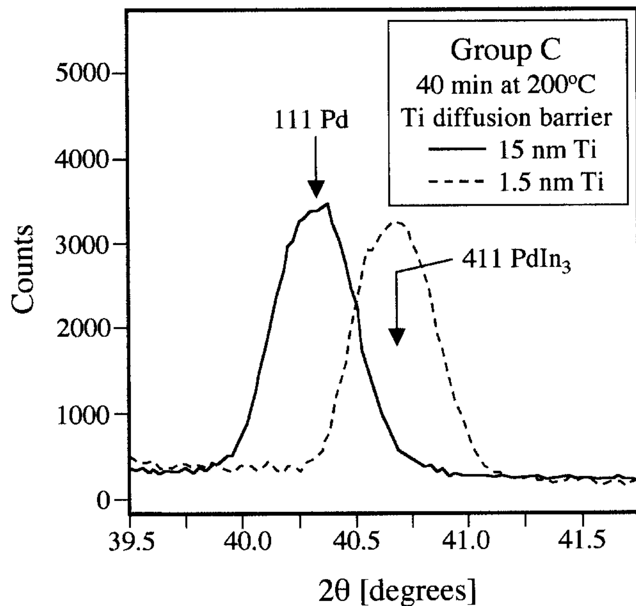

Fig. 5. X-ray diffraction patterns from Group C samples. The 15 nm Ti diffusion layer completely suppresses the reaction at 200°C for 40 min. Under the same annealing conditions but with a 1.5 nm Ti diffusion barrier, the reaction proceeds to completion. The thin Ti diffusion barrier ensures that the In layer melts prior to its consumption by the reaction to form $PdIn_3$.

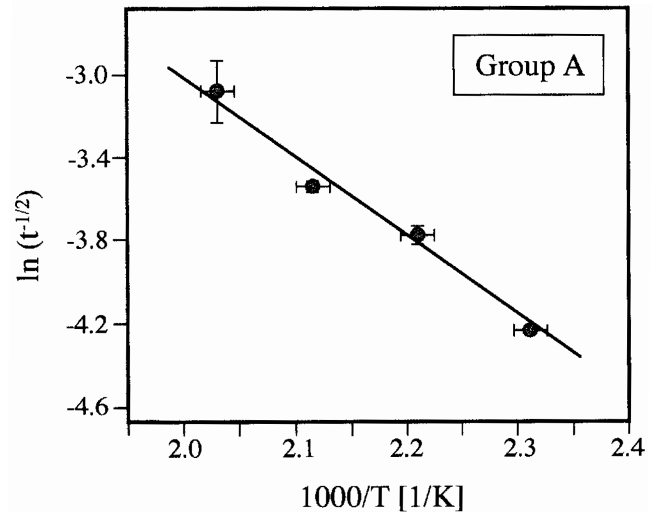

Fig. 6. Arrhenius plot produced with Group A samples. The annealing time required to generate x-ray patterns with 111Pd and 411 $PdIn_3$ peaks of equal height was used to mark an intermediate point in the reaction. The vertical axis is the natural log of the square root of the number of seconds required to achieve this intermediate point in the reaction. The data yield an effective activation energy of 0.63 ± 0.05 eV.

The heights of the peaks as deconvolved by curve fitting were extracted for analysis. Peak heights from samples of the same area, from the same wafer, and acquired during the same diffractometer session were compared directly. Where data from two sessions were analyzed together, peak heights were scaled by the 111 Pd peak height attained in samples annealed at 200°C for annealing times approximately equal to the incubation period for the $PdIn_3$ reaction. For determination of an effective activation barrier for the reaction, the annealing times required to achieve equal 111 Pd and 411 $PdIn_3$ peak heights were evaluated.

As both the Pd film and the $PdIn_3$ reaction product were found to be crystallographically textured, it was necessary to monitor the mosaicity and its variation with annealing. Rocking curves (Ω) revealed a typical full-width at half maximum (FWHM) of 3° for the 111 Pd reflection and 5° for the 411 $PdIn_3$ reflection. Neither FWHM varied appreciably with annealing. The 111 Pd peaks from as-deposited samples were found to increase in intensity and decrease in Ω width after the first annealing treatment above the In melting point. Reflections from indium were found to be irreproducible in intensity, width, and 2θ position due to melting and solidification of In during each annealing treatment (e.g., see Fig. 4 of Ref. 7).

RESULTS AND DISCUSSION

The θ-2θ XRD spectra in Fig. 2 illustrate the systematic evolution of the 111 Pd and 411 $PdIn_3$ reflections for a sample from Group A as a function of annealing time at 200°C. Note that the Pd peak decreases in intensity as the $PdIn_3$ peak grows, until the Pd is consumed. Figure 3 shows the evolution of normalized Pd and $PdIn_3$ peak heights for a set of samples from the same Group A wafer as a function of annealing time at 200°C. The significant feature in these data is the incubation period of approximately 15 min. The incubation period was found to be consistent for a given Group A wafer and annealing temperature, but varied from wafer to wafer. For example, a second Group A wafer, processed under nominally identical conditions as that analyzed in Fig. 3, was found to exhibit a 20-minute incubation period at 200°C. Although this incubation period ensures that the In melts before being consumed by the Pd/In reaction, the variability in the incubation period is believed to be a major yield issue in wafer bonding using the Group A two-step deposition process. The origin of the incubation period may be an adsorbed hydrocarbon layer resulting from air exposure of the Pd surface prior to In deposition. The thickness and chemical character of such a layer would be difficult to control, perhaps explaining the variation in incubation period from wafer to wafer.

The discovery of the incubation period motivated the study of Group B samples, which were prepared entirely by thermal evaporation in a single vacuum pump-down. As is shown in Fig. 4, the 411 $PdIn_3$ peak may be present in the as-deposited sample. After a 5-min anneal, the $PdIn_3$ peak dominates over the Pd peak suggesting that the incubation period is effectively eliminated by the lack of contamination at the Pd/In interface. Such behavior is clearly undesirable for bonding, as the intermetallic reaction is likely to have proceeded significantly before the In melts. Furthermore, it was observed that the reaction advanced measurably over periods of several weeks at room temperature.

To confirm the effect of interfacial contamination on the incubation period of the reaction and to pro-

duce a reliable kinetic barrier, Group C samples were prepared, with 0, 1.5, 10, 15, and 20 nm of Ti at the Pd/In interface. Note that the Ti was exposed to air prior to In deposition; thus it is likely that the Ti was at least partially oxidized. These samples were annealed at 200°C for 40 min and the results for the 1.5 and 15 nm Ti barrier layers are shown in Fig. 5. As expected, the Ti barrier layers of thicknesses ≥15 nm completely suppressed the reaction. The 10 nm Ti barrier layer greatly slowed the reaction, but did not completely prevent the formation of $PdIn_3$ for this annealing condition. The reaction went to completion for both the 0 and 1.5 nm barrier layer samples. In practice, an air-exposed 1.5 nm Ti diffusion barrier has been found to result in satisfactory yield and day-to-day reproducibility of the Pd/In wafer bonding process.

Despite the complications introduced by the presumed hydrocarbon adsorption during air exposure of Pd, the extraction of reaction kinetics from Group A samples was attempted. Such information could prove valuable in designing bonding layers for a variety of applications that require different total bonding layer thicknesses (e.g., from 0.1–10 microns). Samples from a single wafer were annealed for various times at 160, 180, 200, and 220°C. The annealing time at a given temperature that yielded a θ-2θ diffraction pattern with 111 Pd and 411 $PdIn_3$ diffraction peaks of equal height was used as a benchmark. An Arrhenius plot of these data (Fig. 6) yielded an effective activation energy, E_A, of 0.63 ± 0.05 eV, as determined from the slope, which was taken to be $E_A/2k$ where k is Boltzmann's constant. This analysis would be appropriate for a diffusion-controlled reaction without an incubation period, in which case the growth of the $PdIn_3$ reaction layer would be expected to be given by $x = (Dt)^{1/2}$, where x is the thickness of the $PdIn_3$ product, t is the annealing time, and D is the effective diffusivity, which is given by

$$D = D_o \exp[-E_A/kT]$$

The prefactor, D_o, is a constant. Although the x-ray diffraction data are consistent with a Pd/In reaction that is diffusion limited after the incubation period, it is likely that the failure of the contamination barrier is controlled by a distinct Arrhenius process with a different activation barrier. With this caveat aside, the prefactor, D_o, was estimated from the calculated $PdIn_3$ layer thickness at the completion of the reaction, and the estimated time at which the elemental Pd peak disappeared (~60 min at 200°C for the sample used in the kinetic study). This prefactor was estimated to be 1.3×10^{-6} cm²/s, yielding an effective reaction diffusivity at room temperature of 3.5×10^{-17} cm²/s. This result is in good agreement with a study by Marinkovic and Simic[10] who reported the effective reaction diffusivity at room temperature as 1.9×10^{-17} cm²/s.

CONCLUSION

The Pd-In reaction in Pd/In bilayers without interfacial diffusion barriers (Group B in this study) proceeds too rapidly for the application of this bilayer as a transient-liquid-phase wafer-bonding metallization. By simply exposing the Pd surface to air prior to In deposition, the Pd-In reaction at 200°C is impeded sufficiently to ensure melting of the In layer prior to its consumption by the reaction to form the intermetallic phase, $PdIn_3$. This behavior is attributed to an adsorbed hydrocarbon layer, presumed to be of nanometer-scale thickness. Once the reaction has initiated, the kinetics are described by an Arrhenius process with an effective activation barrier of 0.63 ± 0.05 eV. Greater control over the incubation period can be attained by deposition of a Ti diffusion barrier prior to air exposure and In deposition. The results of this study suggest that Ti diffusion barriers with thicknesses in the 1–5 nm range will provide the range of control needed for the design of Pd-In TLP bonding processes for specific applications. Future work will focus on Pd/Ti/In TLP metallizations deposited in a single vacuum cycle.

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