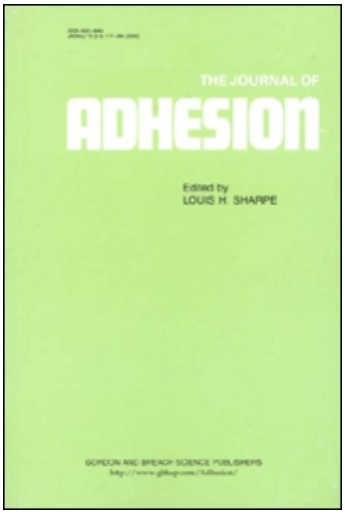

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Conduction Efficiency and Strength of Electronically Conductive Adhesive Joints

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Conduction Efficiency and Strength of Electronically Conductive Adhesive Joints

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Electronically conductive adhesives are being considered as an alternative to solder for interconnection in microelectronics. In order to gain insight regarding electrical and mechanical performance properties of this class of adhesive interconnections, overlap joints were made. Joint resistance and mechanical bond strength were measured before and after environmental stressing.

KEY WORDS: Electrically conductive adhesives; substrate plating; interphase; electric-conduction; joint resistance; joint strength; oxides; surface topography.

INTRODUCTION

The manufacture of electronic devices requires stable connections to be made between literally hundreds of components. The junctions on the often-referred-to "printed circuit boards" are an example. Advances in board manufacturing technology included the replacement of metal solder by electrically conductive, filled polymer adhesives.[1-7] The result is a lighter weight unit which is also environmentally less hazardous when its lead-based solder is replaced. Conductive fillers used in present-day composites are graphite flakes, carbon black, and metals such as aluminum, copper, or silver in the form of micrometer-size particles, with silver being the most commonly used in the electronics industry. When all other parameters are equal, efficient packing of irregular-shaped filler particles facilitate the percolation of electrons through the material. On the other hand, the polymers into which these fillers are placed are usually insulating in character. That is, the electrical conductivity of commercially-available adhesives is due solely to the filler particles which are present in amounts larger than 16% by volume.

Even though they have excellent potential of being a more efficient and less costly alternative to solder joining or brazing in electronic components, electrically conductive adhesives still exhibit a number of problems in the areas of durability and design to

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fit specific needs. It is known that size distribution and aspect ratio for conductive particles affect the formation of the conductive network and the threshold volume necessary for conduction. Particle-to-particle and particle-to-substrate contact resistance, matrix-particle thermal mismatch as affected during cure and in-service heat loads and the ensuing thermal fatigue at the filler and substrate interphases, as well as exposure to environmental stresses may result in interfacial separation and loss of conduction. This problem is usually coupled with chemical reactions including the formation of nonconductive oxide layers at the interphases.

EXPERIMENTS

Samples

A CDA 151 copper substrate was plated with four different metallurgies: tin (Sn), gold (Au), nickel (Ni) and a palladium-nickel (PdNi) alloy. The substrate dimensions were 0.25 mm wide by 0.25 mm thick and 9.5 mm long. A fixture was used to align and bond

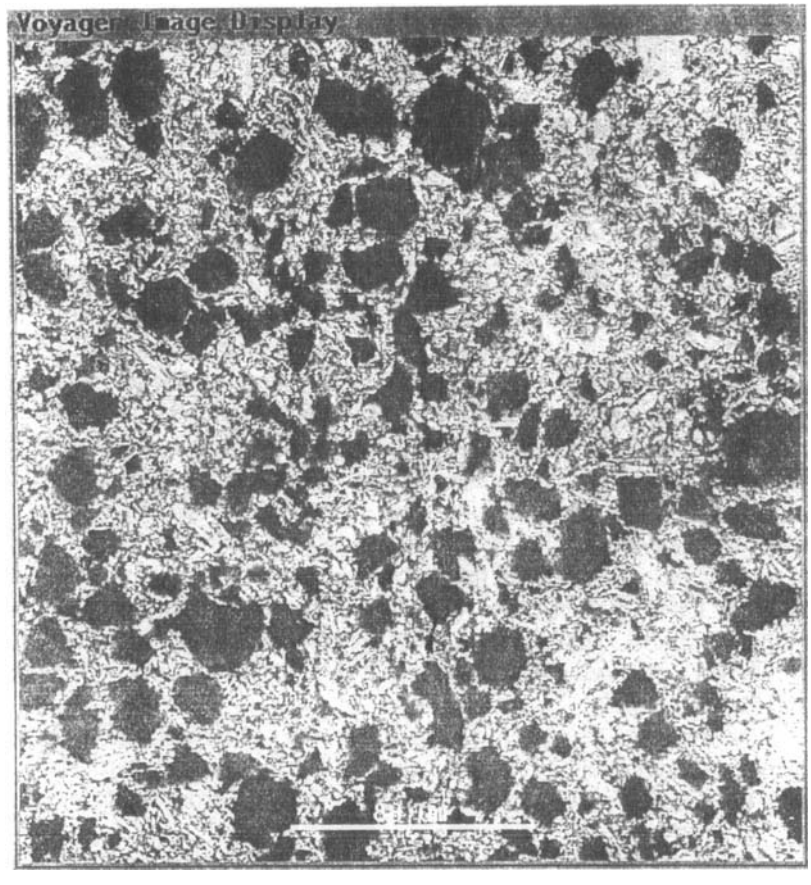


FIGURE 1 SEM photomicrograph (400 X) of the silver particle filled conductive adhesive.

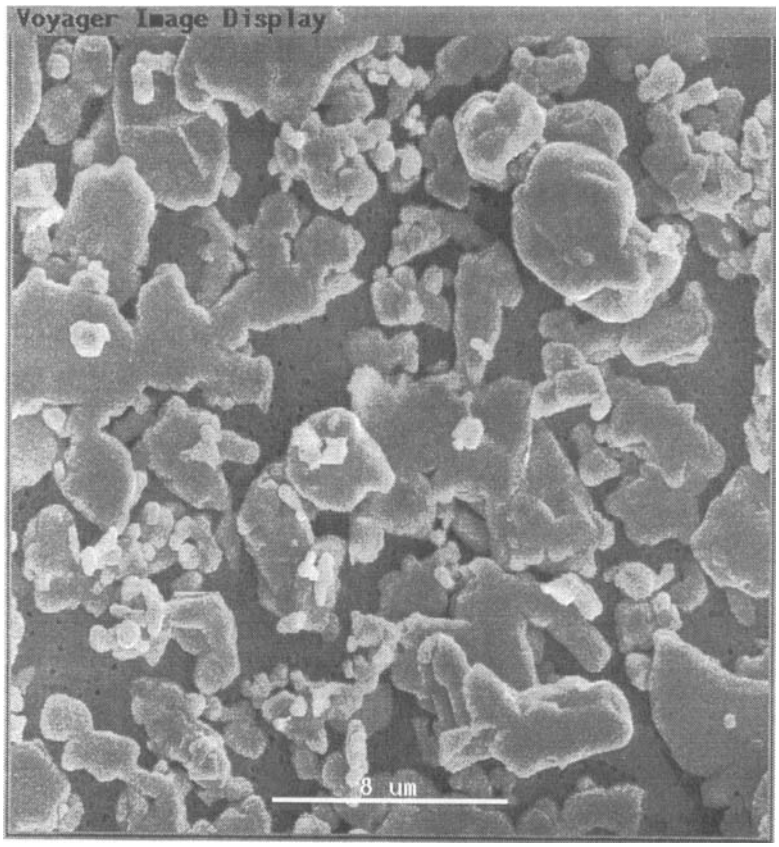


FIGURE 2 SEM photomicrograph (4000 X) of the conductive silver particles.

two overlapped substrates. A commercially-available, one-part, bisphenol epoxy resin filled with silver flakes was used for bonding. An SEM photomicrograph (400 X) of the adhesive in cured and polished form is shown in Figure 1. Figure 2 shows a 4000 X photomicrograph of the conductive silver flakes typically used in conductive adhesives.

Initial preparation of the specimens was accomplished as follows: A 0.25 mm thick copper stock was the substrate. Through a photolithographic process, fingers 0.25 mm wide and 9.5 mm long were defined on a pitch of 0.64 mm. Both surfaces of the substrate were etched simultaneously to remove unwanted copper.

Eight comb patterns comprised one lead frame strip and were electroplated with the following plating combinations:

1. 1.5 micrometers of tin;
2. 1.5 micrometers of nickel underplate followed by 1.1 micrometers of hard gold;
3. 1.5 micrometers of nickel;
4. 1.5 micrometers of nickel underplate followed by 1.5 micrometers of palladium-nickel alloy.

In preparation for bonding, an individual comb pattern was located in a fixture that aligned the fingers. Next, adhesive was dispensed on the tips of the fingers with

TABLE I
Electrical Resistance Values for Adhesively Bonded Joints

	Joint Resistance $10^{-3}\Omega$			
Sample No	Group 1 Sn	Group 2 Au	Group 3 Ni	Group 4 Pd + Ni
39			418.2	
38		4.7	218.9	
37			271.4	5.35
36		5.0	456.6	4.6
35		5.2		5.35
34		5.1		5.25
33			700.8	
32		4.7	270.1	4.9
31		5.85		5.65
30			588	4.8
29			655.7	5.85
28		4.6	107.4	4.7
27		5.95		5.85
26		4.3	1192.5	5.0
25		6.1	775.2	6.1
24		5.05	411.5	5.05
23		5.95	801.6	5.9
22				5.4
21				5.85
20		4.7	502.1	5.1
19				5.65
18	59.2	4.75	839	
17	76.25			5.3
16	44.5	4.55		
15		5.1		
14	12.1			
13				5.65
12	28.85			
11				
10	28.3			
9	17.25			
8	12.75			
7	24			
6	10.65			
5				
4	13.2			
3	16.0			
2	10.6			
1	28.2			
Average	27.2 ± 19.9	5.1 ± 0.5	547.2 ± 287.1	5.3 ± 0.4

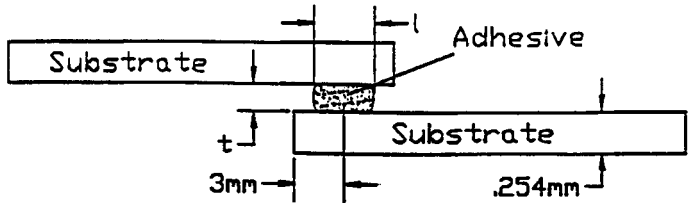


FIGURE 3 Single lap joint bonded with silver filled conductive adhesive.

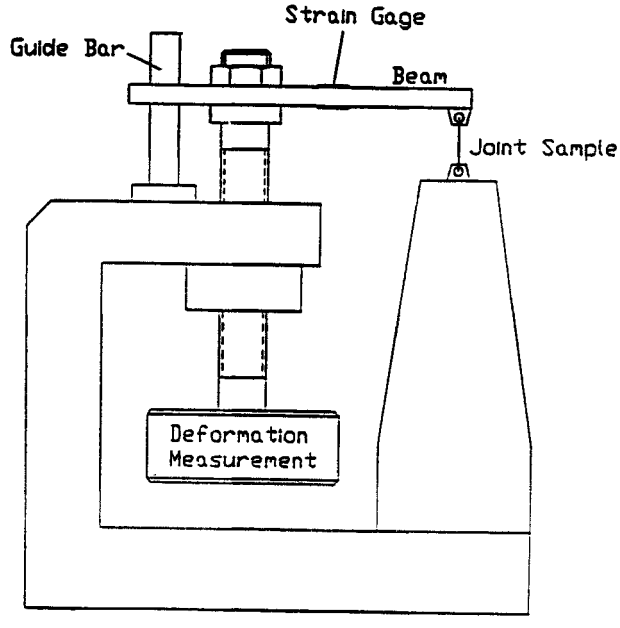


FIGURE 4 Miniature tensile testing machine used for testing electronically conductive joints.

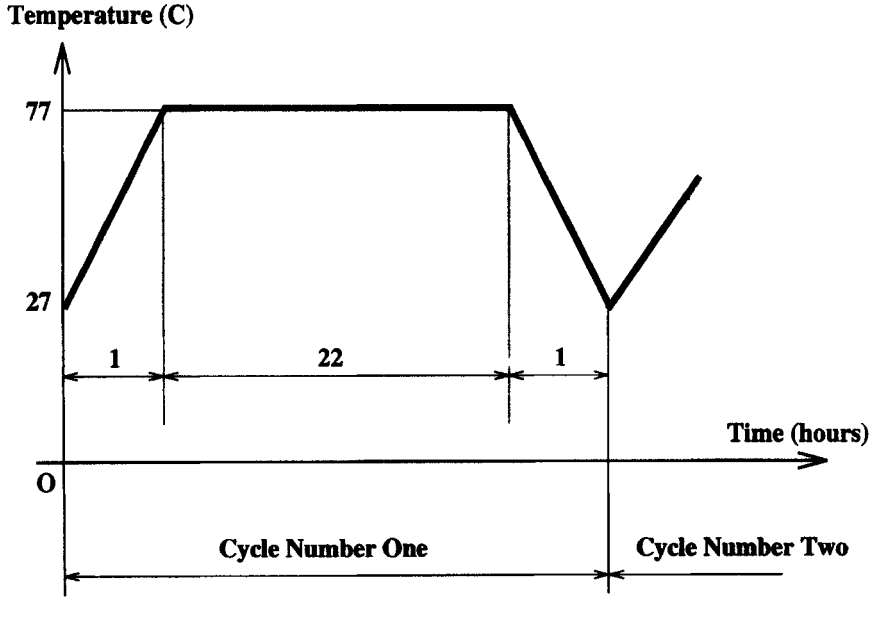


FIGURE 5 Thermal cycle ramp and duration for the thermal cycle used to test bonded joints.

TABLE II
Strength, Deformation and, Resistance Measurement on Virgin Samples

	No.	Joint Strength (Mpa)	Joint Deformation (mm)	Joint Resistance ($10^{-3}\Omega$)
	15	31.3	0.127	5.1
	18	28.8	0.195	4.75
Au	26	29.8	0.142	4.3
	35	31.7	0.116	5.2
	Average	**30.4 ± 1.3**	**0.145 ± 0.03**	**4.8 ± 0.4**
	32	40.4	0.107	270.1
	36	41.2	0.091	456.6
Ni	39	40.2	0.116	418.2
	Average	**40.6 ± 0.5**	**0.105 ± 0.01**	**381.6 ± 98.5**
	1	33.4	0.085	28.2
	4	36.4	0.109	13.2
Sn	10	38.1	0.143	28.3
	14	33.6	0.124	12.1
	Average	**35.4 ± 2.3**	**0.115 ± 0.02**	**20.5 ± 9**
	13	33.8	0.096	5.65
	17	33.5	0.129	5.3
	20	32.6	0.089	5.1
Pd +	24	31.0	0.138	5.05
Ni	28	29.6	0.107	4.7
	30	28.6	0.164	4.8
	32	29.2	0.091	4.9
	36	29.5	0.121	4.6
	Average	**31.0 ± 2**	**0.117 ± 0.03**	**5.0 ± 0.3**

automated syringe dispensing equipment, using a needle with a 0.25 mm diameter orifice. The fixture allowed a second comb pattern to be aligned with the first in a lap fashion. A clamping bar applied a mating force to the lap joints that controlled typical bond thickness to 0.08 mm and held the bonds in place during the temperature-driven bonding process. After the clamp was secured, but prior to cure, the commoning bar of the second comb pattern was broken off.

The geometry of the joints is shown in Figure 3. The range of adhesive overlap length was 0.54–1.1 mm and the adhesive thickness range was 0.06–0.11 mm. Cure was accomplished at 150°C for 30 minutes.

Joint Resistance Measurement

A micro-ohmmeter was used to make a four-wire resistance measurement of every joint. Two replicate measurements were averaged and are summarized in Table I. The initial readings reveal that Au and PdNi plated surfaces provide lower joint resistance than either Sn or Ni. Also the scatter band for Au and PdNi is narrower.

Joint Strength and Deformation

Single lap shear tests were performed using a miniature tensile test system (Fig. 4) to measure the joint strength and deformation. This instrument was built in-house at

Clarkson University and possesses 3.8×10^{-4} mm accuracy in deformation measurement. The results are summarized in Table II. Sn and Ni have higher strengths than Au and PdNi. It is interesting that Ni has the highest strength but makes the least conductive joint.

Joint Resistance and Strength after Thermal Cycling

A mild thermal cycling test from ambient temperature to 75°C was used to stress the joints. Figure 5 shows the cycle ramp and duration. Twenty-one of these 24-hour long cycles were completed. Joint resistance, strength and deformation were measured on these stressed samples. The conductivity of the joints did not change with cycling. The results for joint strength and deformation are shown in Table III. After the twenty-one 24-hour cycles, the joint strengths measured for Au and Ni samples are 67% and 76%, respectively, of the strength measured before stressing. These results show that the interphase between the conductive adhesive and Au or Ni is sensitive to mild thermal cycling. As shown in Table III, strength and deformation values for Sn and PdNi were stable.

Joint Resistance and Strength after Water Immersion

The samples were immersed in deionized water at 70°C for 24 hours. The joint resistance was stable with no change. However, mechanical strength degraded with all four platings as shown in Table IV. The worst degradation was observed on Au, which

TABLE III
Results of Thermal Aging Tests on Adhesively Bonded Joints

	Time	24 hours			504 hours	
	No.	Joint Strength (MPa)	Deformation (mm)	No.	Joint Strength (Mpa)	Deformation (mm)
	38	26.5	0.128	28	24.4	0.144
Au	36	Nil	–	27	17.3	0.138
	34.	25.0	0.119	25	18.4	0.152
	32	24.1	0.136	20	21.2	0.139
	Av.	**18.9 ± 12.6**	–	Av.	**20.3 ± 3.1**	**0.14 ± 0.01**
	38	35.6	0.122	28	27.4	0.121
Ni	37	39.2	0.134	26	30.8	0.112
	30	35.8	0.109	25	34.0	0.132
	29	35.0	0.117	23	31.2	0.130
	Av.	**36.4 ± 1.9**	**0.12 ± 0.01**	Av.	**30.8 ± 2.7**	**0.12 ± 0.01**
	2	35.3	0.125	7	36.1	0.132
Sn	3	35.9	0.118	12	37.3	0.122
	6	38.7	0.133	16	33.6	0.098
	Av.	**36.6 ± 1.8**	**0.13 ± 0.01**	Av.	**35.6 ± 1.8**	**0.12 ± 0.01**
	34	Nil	–	26	32.1	0.091
Pd	31	30.2	0.127	23	32.7	0.142
+	29	34.4	0.144	22	27.2	0.122
Ni	27	31.3	0.089	21	33.8	0.136
	Av.	**23.9 ± 16.0**	–	Av.	**31.4 ± 2.9**	**0.12 ± 0.02**

TABLE IV
Results of Water Attack Test Under High Temperature

	No.	Joint Strength (Mpa)	Joint Deformation (mm)
	16	16.8	0.133
	23	Nil	–
Au	24	Nil	–
	31	19.5	0.146
	Mean	**9.0 ± 10.5**	–
	18	28.9	0.142
	20	22.8	0.124
Ni	24	27.4	0.136
	33	23.1	0.137
	Mean	**25.6 ± 3.1**	**0.13 ± 0.01**
	8	25.7	0.116
	17	31.2	0.141
Sn	18	26.3	0.130
	9	24.6	0.121
	Mean	**27 ± 2.9**	**0.13 ± 0.01**
	37	24.6	0.132
	35	Nil	–
Pd	25	19.3	0.129
+ Ni	19	25.7	0.122
	Mean	**17.4 ± 11.9**	–

* All samples in this experiment were immersed in 70°C dionized water for 24 hours.

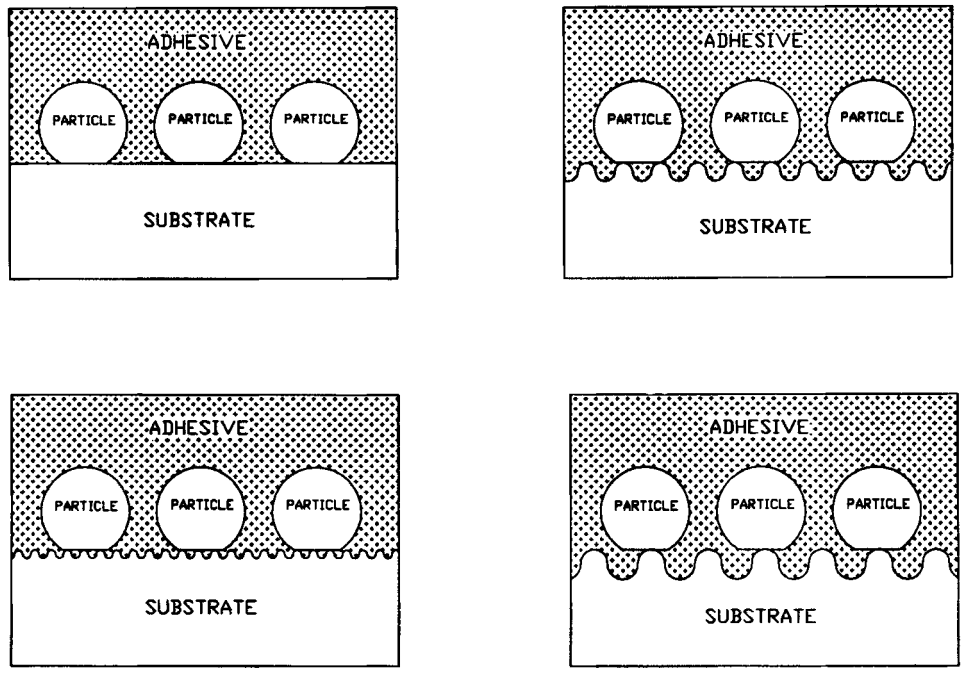


FIGURE 6 Pictorial representation of the different contact behaviors which may occur between the conductive particles and the substrates.

had 30% of the strength measured before stressing. The PdNi plated joints dropped 44% in joint strength while the joint strength loss for Ni-plated samples and Sn-plated samples were 37% and 24%, respectively.

Plated Substrate Surface Characterization

i) The surfaces of the plated substrates were examined using a JEOL JSM-6300 scanning electron microscope (JEOL, Japan). The sample surfaces were sputter coated with gold and viewed under an excitation voltage of 15 KV. The resolution of this SEM is four nm.

ii) Elemental composition of the plated surfaces was determined by using an ESCA/AUGER electron spectrophotometer (phi Model 548, Physical Electronics Industrial, Inc.). The voltage of the electron gun was two KV. The resolution of this instrument is two ev.

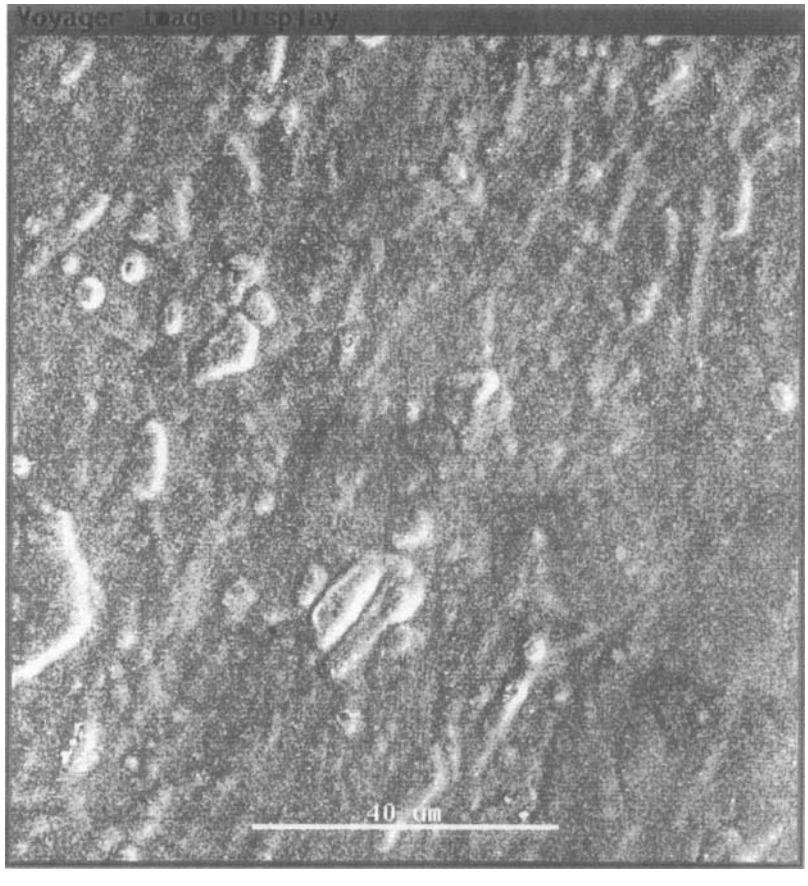


FIGURE 7 SEM photomicrograph of Ni-plated surface. The magnification is 1,000X.

DISCUSSION

Failure Type and Locus

In all shear tests, the loci of failure were visually observed to be mostly in the vicinity of the interphase between the adhesive and the plated substrates. Interfacial failure is an expected mode of failure for joints bonded with conductive adhesives due to the presence of metal particle inclusions at the adhesive/substrate interphase. In fact, these metal fillers (silver) are the main path to carry the electrons between the substrates. Experimental results revealed that the bulk conductivities of all four groups of plated substrates were approximately the same. When bonded with the same conductive adhesive, however, the joint resistances are quite different from each other. This indicates that the contact resistances at the interfaces between the adhesive and the substrate surface of the four platings are different. The interfacial contact area, which

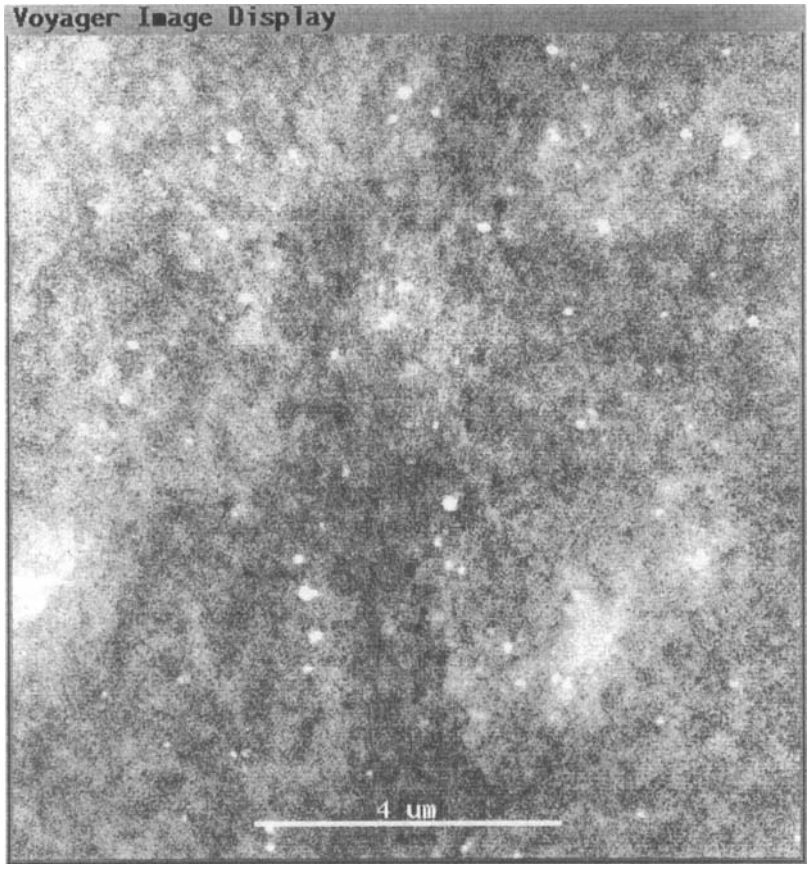


FIGURE 8 SEM photomicrograph of Ni-plated surface. The magnification is 10,000X.

can be defined as the area occupied by the fillers that contact the substrate directly (or through a conductive interphase), is one possible explanation for the observed difference in joint conduction and strength and, as we will illustrate later, this is affected by surface topography. This contact area is made up of contact paths between the substrates for conduction. Consequently, the more paths formed the more contact area, and the less contact resistance to the current. At the same time, however, more metal-to-metal contact means relatively less adhesion.

It is known that Au and PdNi present surfaces that resist oxidation. On the contrary, it is known that Sn and Ni develop a native oxide film. This expected absence and presence of an oxide film also correlates with the joint conductances measured. As shown in Table II, the Au and PdNi plated samples have higher conductivity, but lower strength, and the Sn-and Ni-plated samples have lower conductivity, but higher strength. Therefore, we expect that the higher interface strength will correspond to lower joint conductivity in the newly-bonded joints that we studied.

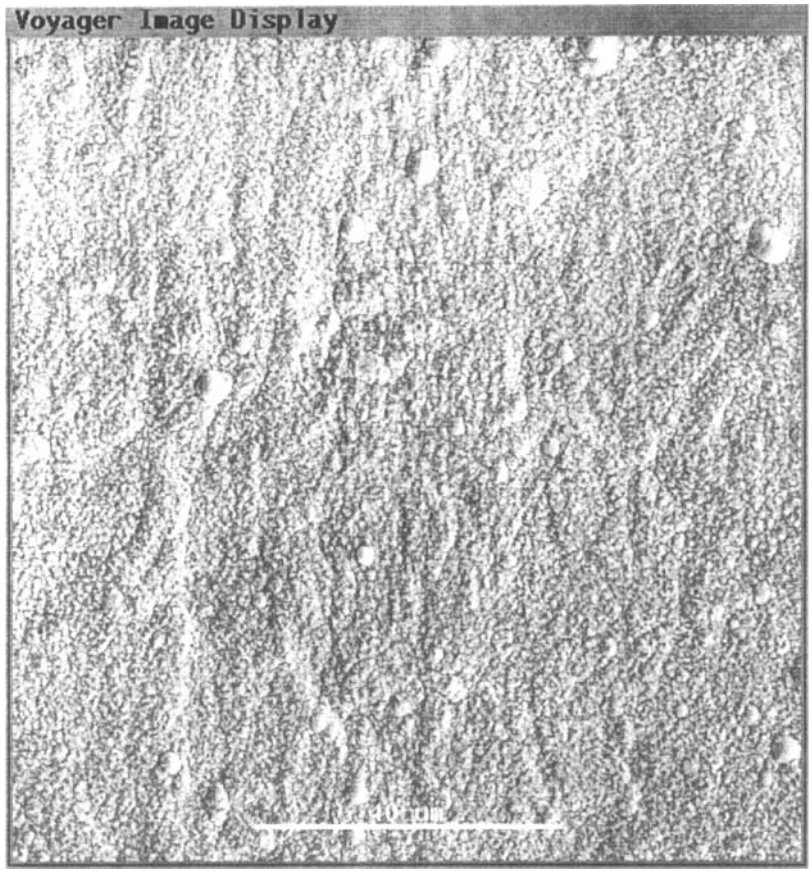


FIGURE 9 SEM photomicrograph of PdNi-plated surface. The magnification is 1,000X.

The Characteristics of the Substrate Surface

As discussed, the electrical and mechanical properties of the joint are very much dependent on the characteristics of the substrate surface. Consequently, the analysis of the surface characteristics such as asperity distribution and chemical composition on the plated substrate can provide insight into understanding the joint behavior. Different contact behaviors which may occur between the conductive particles and the plated substrates are expected to depend on the relative sizes of the particles and the surface asperities of the substrates, as pictorially illustrated in Figure 6 in caricature format. It is expected that the surface microstructure which allows maximum contact with interphase fillers will provide the highest conductivity, provided that insulating layers such as oxide layers are not present as part of the interphase. Our assumption is that the conductivity of the adhesive joint increases with increasing number of conducting contact junctures between the particles and the substrates.

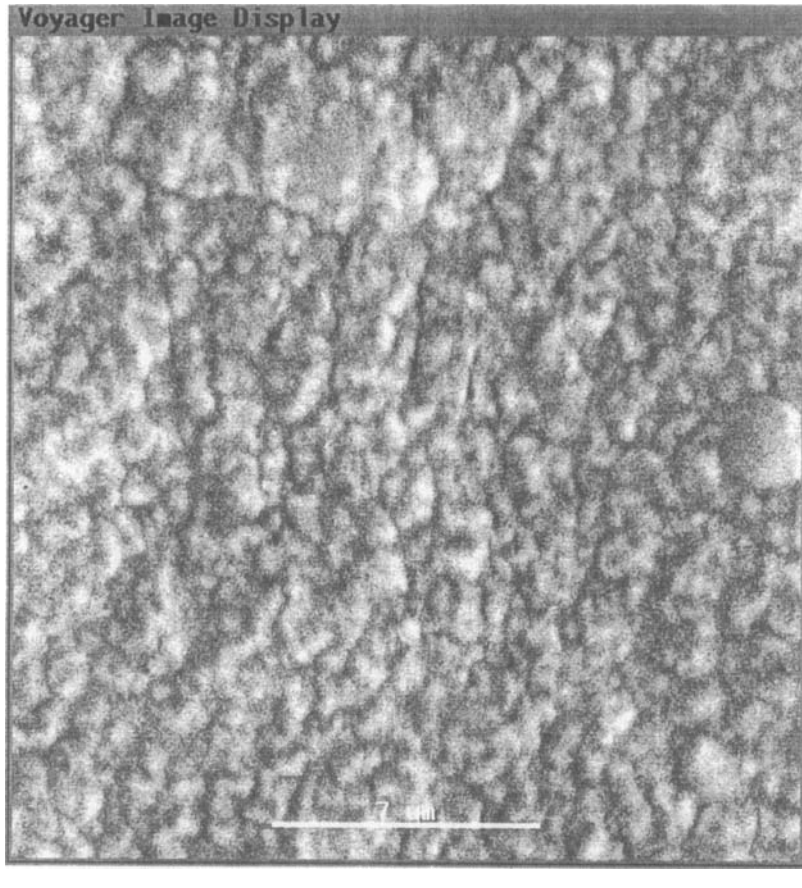


FIGURE 10 SEM photomicrograph of PdNi-plated surface. The magnification is 5,000X.

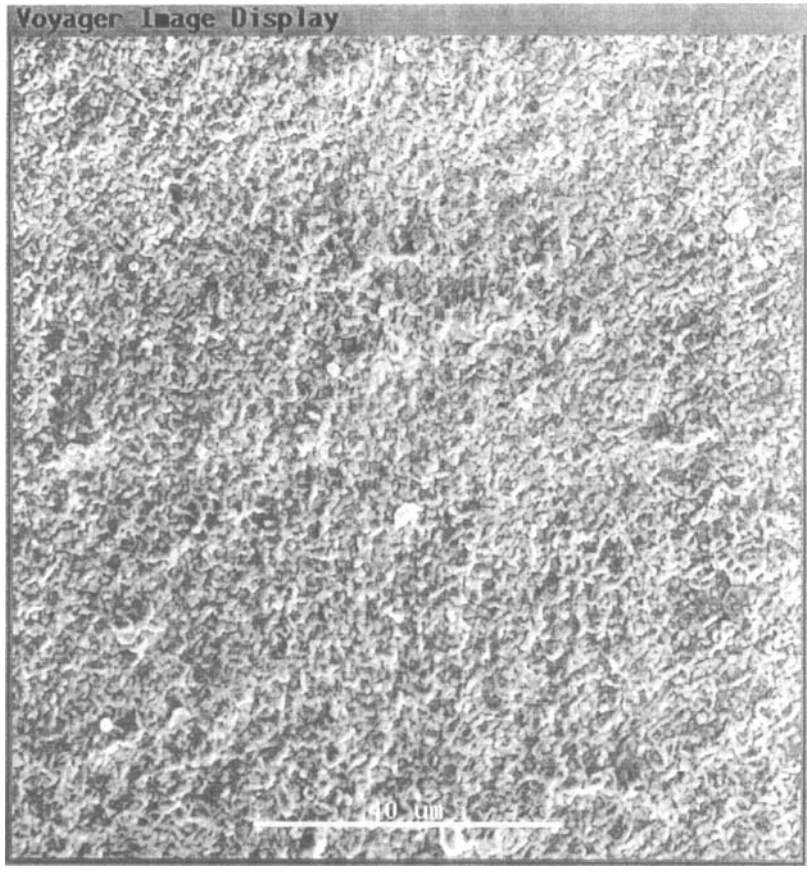


FIGURE 11 SEM photomicrograph of Sn-plated surface. The magnification is 1,000X.

SEM studies revealed that the microstructures of the four groups of samples with different metal platings are quite different. The Ni surface (Figs. 7 and 8) appears to have more pronounced peaks and valleys in frequency roughly equal to or larger than the particle size (Fig. 2). Perhaps adhesive accumulates preferentially in the valleys providing increased adhesion. Substrate-particle juncture contact in this case, however, is not expected to be as high as that on PdNi surfaces shown in Figures 9 and 10 or on Sn surfaces shown in Figures 11 and 12. Note that even though the electrical resistivity of Sn is higher than that of Ni (Table V)[8] its joint resistivity is much lower than that with Ni plated substrates (Table I) because tin oxide is conductive. Furthermore, much of the juncture contact on Ni surfaces may be through an oxide layer which is insulating. The presence of this oxide layer on Ni surfaces has been verified using Auger Electron Spectroscopy.

For the Ni plating, in addition to oxygen, the element carbon is also observed on the surface prior to sputtering, as shown in Figure 13. We must note that the

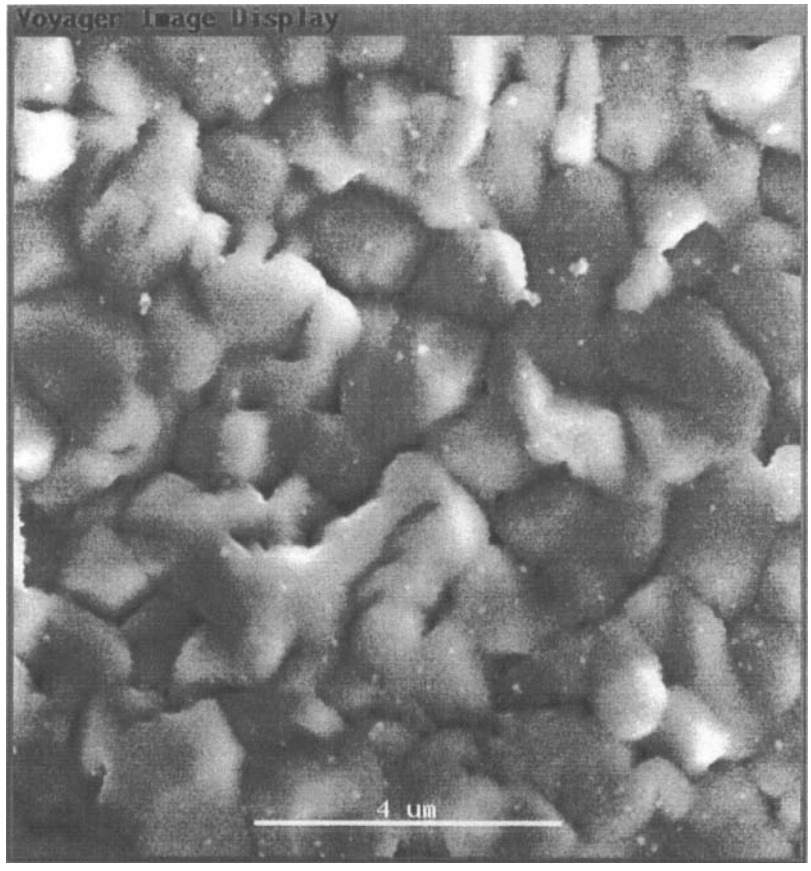


FIGURE 12 SEM photomicrograph of Sn-plated surface. The magnification is 10,000X.

TABLE V
Electrical Resistivity of Metallic Plating Elements

Element	Electrical Resistivity Micro ohm-cm
Au	2.19
Ni	6.84
Pd	10.8
Sn	11.5

presence of carbon was common to all plating metallurgies examined using Auger Electron Spectroscopy. In order to look at the element profile in the depth direction, an ion gun was used to sputter the surface using different sputtering times. With increasing sputtering time, more of the element oxygen is observed

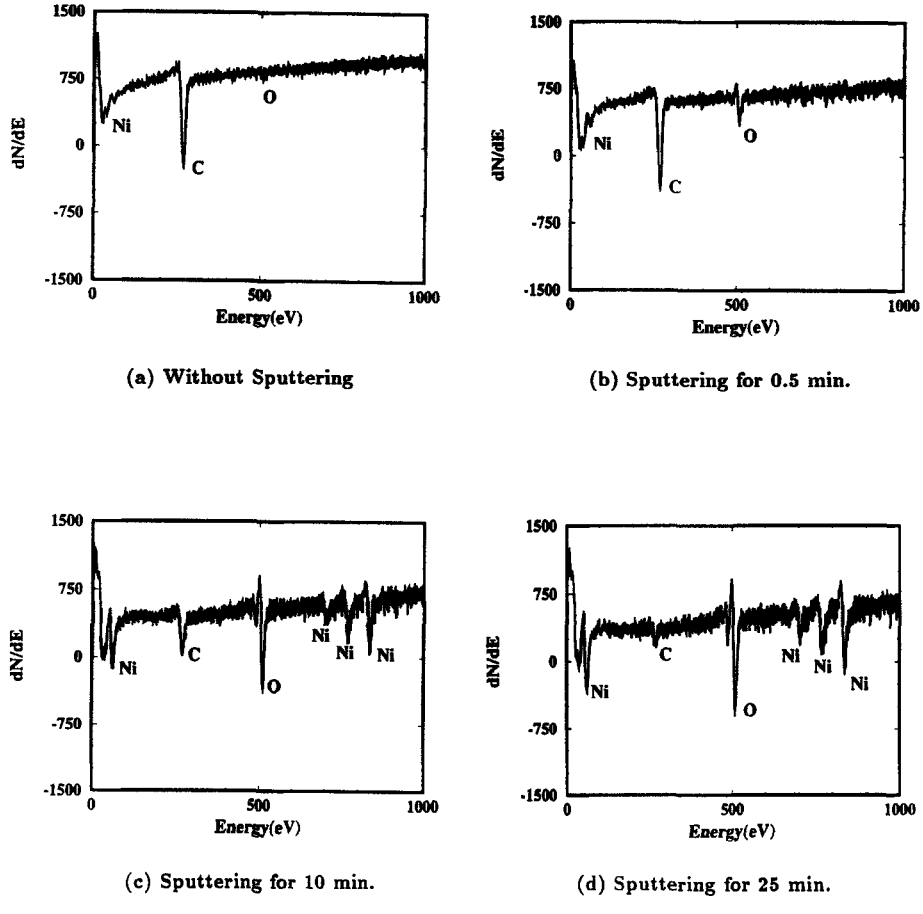


FIGURE 13 Auger spectra for different durations of sputtering on Ni plating.

on the Ni-plated surface (Fig. 13). This result confirms that the presence of oxygen is very significant on the Ni-plated surface. This oxidation is presumably the reason why the joints with Ni-plated substrates have much higher resistance than the other groups.

For the PdNi coating, the Auger analysis does not reveal significant levels of oxygen (Fig. 14). Note that the joints with PdNi plated substrates manifest low joint resistance electrically (Table I) and this should be at least partially attributed to the absence of an oxide layer on their surfaces. This was also the case for joints with Au-plated substrates. The Auger spectra for Au plated surfaces are shown in Figure 15. We note that the joint resistances with Au plating and PdNi plating were within 4% of each other (Table I).

For the Sn plating, however, the element oxygen is observed on the surface before and after sputtering (Fig. 16). We note that oxygen is present even after sputtering the

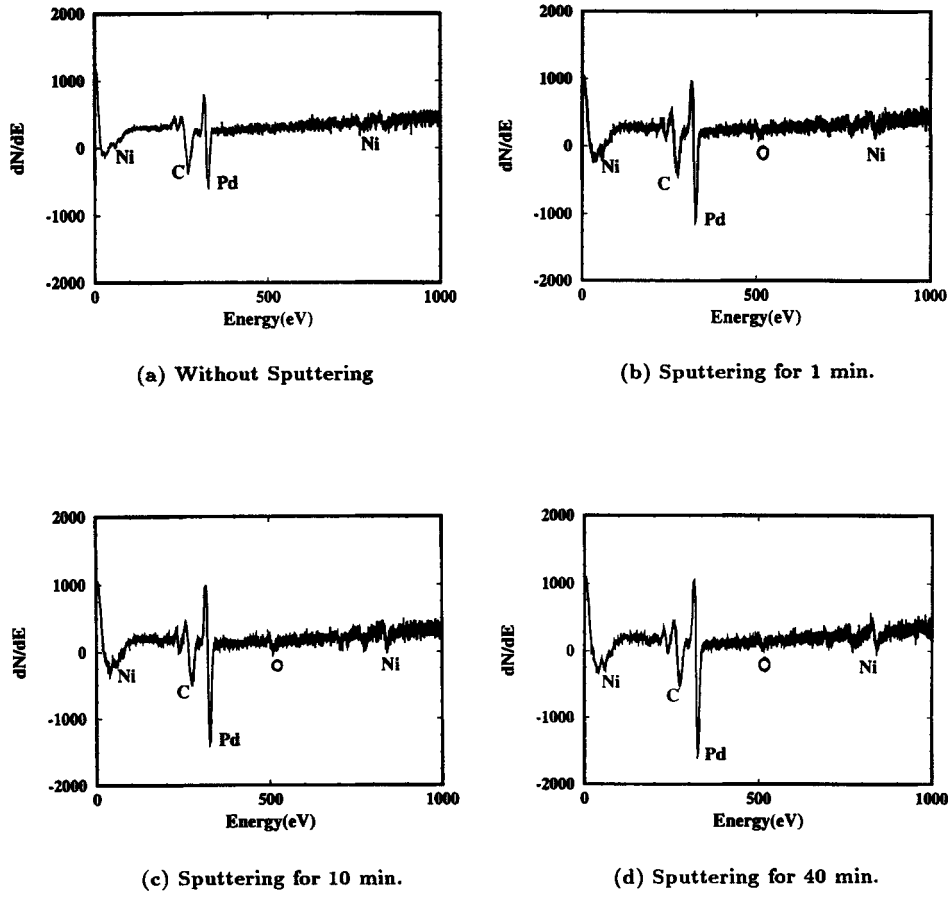


FIGURE 14 Auger spectra for different durations of sputtering on PdNi plating.

surface for 26.5 minutes (Fig. 16). This is a commonality between the Sn and Ni platings, both of which provided higher joint strengths in comparison with those for Au- and PdNi-plated substrates (Table II) both of which lacked any substantial amount of oxygen.

The surface topographies of Au-plated substrates (not shown) were similar to those plated with Ni. For both of these platings the frequency of surface oscillations is roughly equal to or larger than the typical silver filler particle size (Fig. 2). It is interesting to note that joints with these two platings (Au and Ni) had high degradation in joint strength (70% with Au and 37% with Ni) as a result of hydration (water attack) tests as well as the highest strength loss (33% loss with Au and 24% loss with Ni) as a result of 21 cycles of thermal aging.

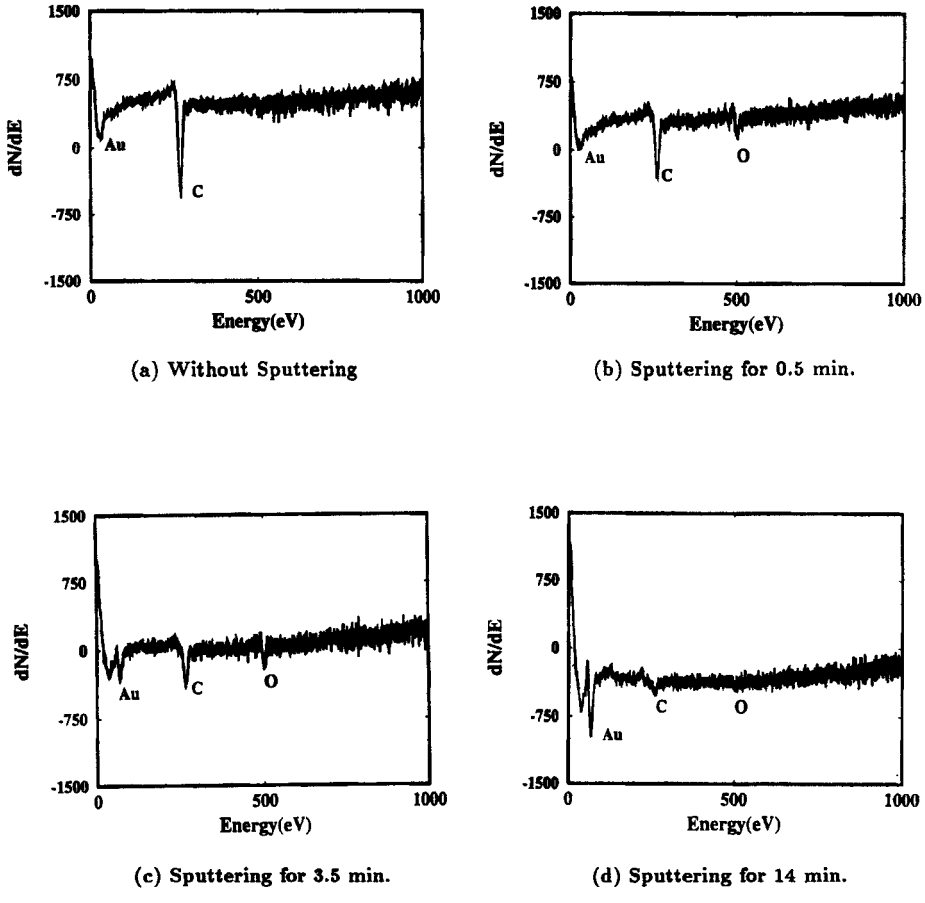
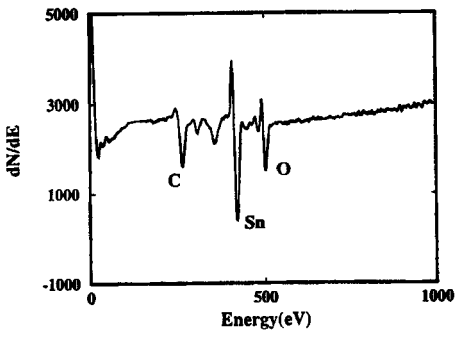


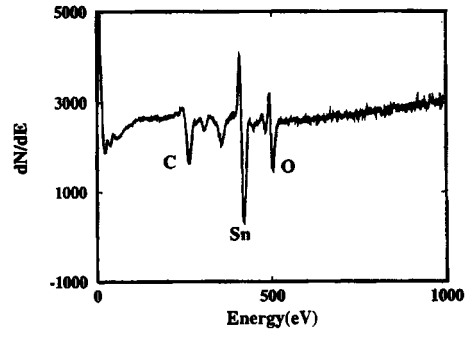
FIGURE 15 Auger spectra for different durations for sputtering on Au plating.

CONCLUSIONS

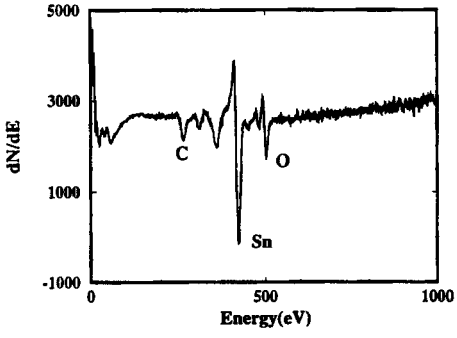
The experimental results with silver filled adhesive revealed that the adhesive/substrate interphase has a strong influence on the conduction and strength behavior of the bonded joints. In general, conductivity and joint strength seem to be inversely related in newly-bonded joints. Hydration tests did not result in significant changes in joint resistivities even though the joint strength deteriorated significantly after 24 hours of water attack. Obviously, if the joints are bonded efficiently to result in the desired conductivity initially, subsequent reductions in the joint strength do not necessarily result in a similar reduction in electrical conduction. This reveals the importance of metal-to-metal contact in the conduction process. The oxidation of nickel coating on the substrate surfaces seems to increase the joint resistance significantly in comparison with Au; PdNi- and Sn-coated substrates.



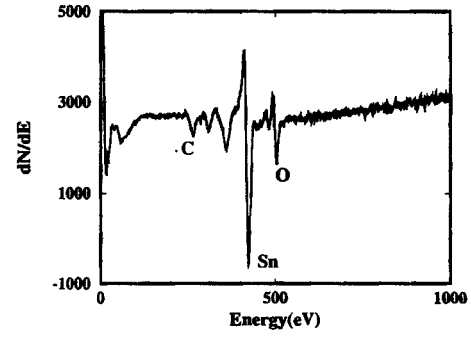
(a) Without Sputtering



(b) Sputtering for 0.5 min.



(c) Sputtering for 16.5 min.



(d) Sputtering for 26.5 min.

FIGURE 16 Auger spectra for different durations of sputtering on Sn plating.

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