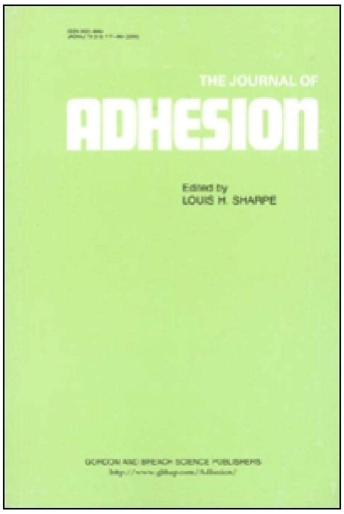


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

New Adhesion Promoters for Copper Leadframes and Epoxy Resin

Rainer Müller; Klaus Heckmann[a]; Manfred Habermann[b]; Thomas Paul[b]; Martin Stratmann[b]
[a] Universität Regensburg, Labor für Grenzflächenchemie, Regensburg, Germany [b] Universität Erlangen-Nürnberg, Lehrstuhl für Korrosion und Oberflächentechnik, Erlangen, Germany

To cite this Article Müller, Rainer , Heckmann, Klaus , Habermann, Manfred , Paul, Thomas and Stratmann, Martin(2000) 'New Adhesion Promoters for Copper Leadframes and Epoxy Resin', The Journal of Adhesion, 72: 1, 65 — 83
To link to this Article: DOI: 10.1080/00218460008029268
URL: http://dx.doi.org/10.1080/00218460008029268

J. Adhesion, 2000, Vol. 72, pp. 65–83
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

New Adhesion Promoters for Copper Leadframes and Epoxy Resin*

RAINER MÜLLER[a,†], KLAUS HECKMANN[a], MANFRED HABERMANN[b], THOMAS PAUL[b] and MARTIN STRATMANN[b]

[a] *Universität Regensburg, Labor für Grenzflächenchemie, Postfach 101042, D-93040 Regensburg, Germany;* [b] *Universität Erlangen-Nürnberg, Lehrstuhl für Korrosion und Oberflächentechnik, Martensstr. 7, D-98058 Erlangen, Germany*

(Received 2 March 1999; In final form 8 July 1999)

New primer molecules have been synthesized to increase the adhesion strength between a copper leadframe and an epoxy molding compound in microelectronical devices. The coupling agents were preliminarily chemisorbed at the surface of copper plates *via* special binding groups like thiol, disulfide, ethylene diamine and phthalocyanine. Binding to the epoxy resin was performed *via* an hydroxyl group. Linear hydrocarbon spacers with various chain lengths connected the copper- and epoxy-binding groups. The self-assembled layers of the organic coupling agents at the metal surface were characterized by X-ray photoelectron spectroscopy. Thermogravimetric analysis was used to study the coating with respect to its corrosion oxidation inhibition. Shear tests clearly indicated that the coupling agents increase adhesion strength and are stable even in extreme humidity and thermal conditions in analogy to IPC-Level-1 pretreatment. Thus, delamination of the microelectronical packages was prevented.

Keywords: Coupling agents; adhesion promoters; self assembly; delamination of microelectronical devices; shear strength; corrosion inhibition; interface

INTRODUCTION

To protect microelectronical devices, especially microchips, from harmful environmental influences, more than 90% of all semiconductors

---

*Presented at the 4th European Conference on Adhesion (EURADH'98) and 1st World Congress on Adhesion and Related Phenomena (WCARP-1), Garmisch-Partenkirchen, Germany, September 6–11, 1998.

[†] Corresponding author. Tel.: +49 941 943 4521, Fax: +49 941 943 4686, e-mail: rainer.mueller@chemie.uni-regensburg.de

are encapsulated with epoxy molding compounds. Almost 50% of them are encapsulated as surface-mount packages. During the soldering process by vapor phase reflow or infra-red reflow, the packages are heated up to 215–260°C. After absorbing moisture from the ambient, the packages develop cracks or swelling in the course of these soldering processes due to the explosive evaporation of absorbed water. This deterioration of the surface-mount, epoxy resin-molded IC packages is called the "popcorn phenomenon", which is a serious problem in the semiconductor industry.

The phenomenon was first described by Fukuzawa *et al.* [1] who further showed that a vent hole through the package prevents the crack. Anjoh *et al.* [2] and Kitano *et al.* [3] analyzed the mechanism of the crack in detail. The four suggested stages of this mechanism are illustrated in Figure 1. This mechanism has been confirmed by Tay *et al.* [4] who compared the delamination caused in adhesion tests with the theoretical results of finite element analysis of IC packages and of computation of stress intensity factors.

Some progress in the prevention of the cracking of the packages was achieved by minimization of water diffusion into the package. Steiner *et al.* [5] have shown that air baking of the IC devices for 6 hours at 150°C before reflow soldering prevents the packages from cracking. Asai *et al.* [6] and Altimari *et al.* [7] have designed new epoxy molding

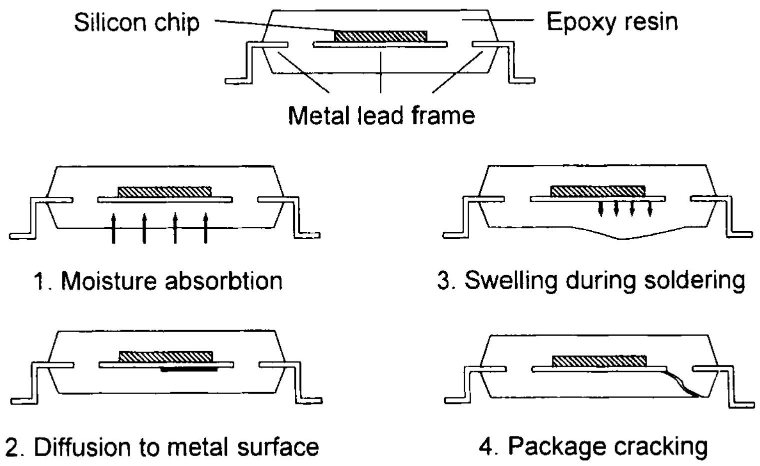


FIGURE 1 Mechanism of the "popcorn phenomenon".

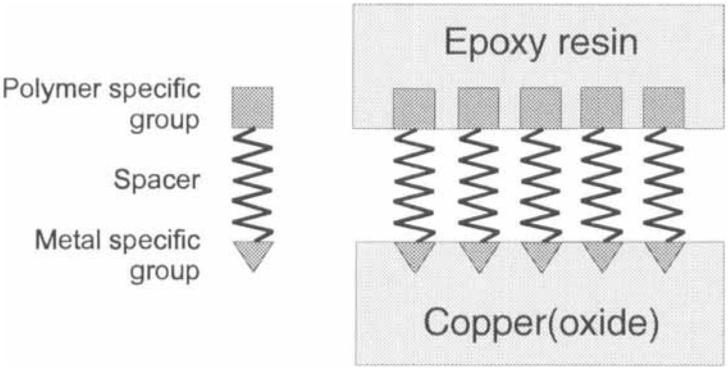


FIGURE 2 Densely-packed monomolecular layer of coupling agents.

compounds with optimized chemical and physical properties, decreasing the diffusion of water.

A more promising approach seems to be an increase of the adhesion strength between the epoxy molding compound and the leadframe. It can be achieved by addition of adhesion promoters to the molding compound. Walker *et al.* [8] introduced organosilanes in combination with epoxide and polyurethane compounds. This approach to increase adhesion as well as addition of other kinds of coupling agents to the epoxy resin are widely used in the modern semiconductor industry.

In this paper new adhesion promoters forming self-assembled monomolecular layers at the surface of a copper leadframe are developed. The densely-packed arrangement of these bifunctional organic molecules in the interface (Fig. 2) is stabilized by van der Waals interactions along the hydrocarbon chains. Such a structure with a highly hydrophobic layer reduces diffusion of water to the copper surface significantly, resulting in a decrease of the delamination during thermal stress.

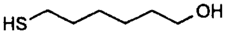
EXPERIMENTAL METHODS

Organic Synthesis

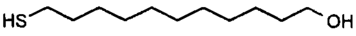
Figure 3 gives an overview of the synthesized organic coupling agents.

The thiols (I, II) and disulfides (V, VI) were synthesized *via* the "Bunte-Salt" according to the methods described by Häussling *et al.* [9]

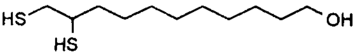
Thiols



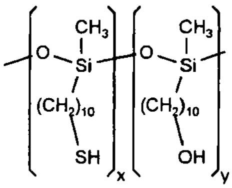
6-Mercaptohexaneol (I)



11-Mercaptoundecaneol (II)

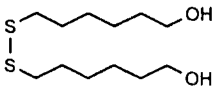


10,11-Dimercaptoundecaneol (III)

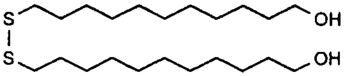


10-Mercaptodecane/methyl-10-hydroxydecane/methyl-siloxanecopolymer (IV)

Disulfides

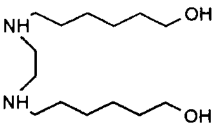


Bis-(6-hydroxyhexane)-disulfide (V)

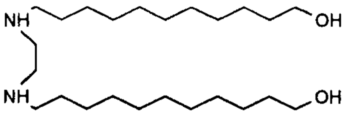


Bis-(11-hydroxyundecane)-disulfide (VI)

Ethylene Diamines

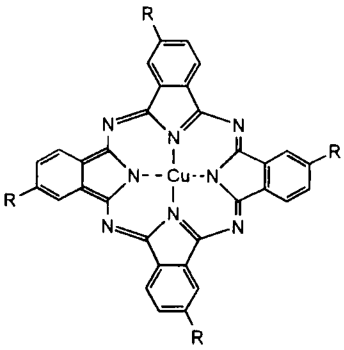


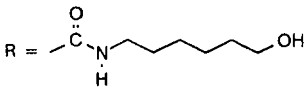
N,N′-Bis(6-hydroxyhexane)-ethylene-diamine (VII)



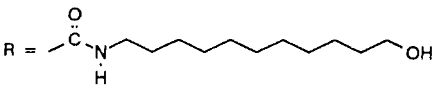
N,N′-Bis(11-hydroxyundecane)-ethylene-diamine (VIII)

Phthalocyanines





Copper-Phthalocyanine-tetracarbonyl-tetra(6-hydroxyhexane)amide (IX)



Copper-Phthalocyanine-tetracarbonyl-tetra(11-hydroxyundecane)amide (X)

FIGURE 3 Chemical structures of the synthesized coupling agents.

and Milligan *et al.* [10]. 6-Hydroxy-1-bromohexane or 11-Hydroxy-1-bromoundecane (both obtained from Aldrich) was heated with an equimolecular amount of sodium thiosulfate (Merck) in a mixture of water and 1,4-dioxane (1:1 v/v) at refluxing temperature for 12 hours. Hydrolyzation of the precipitating salts with dilute hydrochloric acid at 100°C for five hours gave the thiols in the form of white powders in nearly quantitative yields. Reaction of these salts with an equimolecular amount of thiourea (Merck) in combination with dilute hydrochloric acid at 100°C for five hours resulted in the formation of dialkyl disulfides. These compounds were obtained as white powders in nearly quantitative yield.

The synthesis of a coupling agent containing two thiols as metal binding groups was performed in a two-step reaction. First, an equimolecular amount of bromine was added to a stirred solution of 11-Hydroxy-1-undecene (Aldrich) in chloroform at ambient temperatures. This resulted in the formation of 10,11-Dibromo-1-undecanol in quantitative yield. In the second step, the halides were substituted by heating the intermediate with the double amount of sodium sulfide (Merck) in *n*-butanol at 100°C under permanent inflow of hydrogen sulfide for eight hours [11]. Chloroform extraction of the water-diluted reaction mixture gave the 10,11-Dimercapto-1-undecanol (III) as a colorless liquid in good yield.

For the synthesis of a polymeric coupling agent containing a high amount of thiols and hydroxyl groups a polymethylhydrosiloxane (ICN) was used as flexible backbone. The hydrogen atoms of the siloxane were substituted *via* hydrosylylation with an equimolecular amount of 10-bromo-1-decene catalyzed by some crystals of H_2PtCl_6 in chloroform at ambient temperatures for 10 hours [12]. Parts of the halides were substituted by refluxing the polymer with an equimolecular amount of sodium hydroxide in a mixture of 1,4-dioxane and ethanol (1:1 v/v) for five hours. The remaining halides were substituted with NaSH in *n*-butanol as described before. In this way, a liquid and colorless polymer with thiol and hydroxyl groups (IV) in nearly equimolecular ratio was obtained.

The ethylene diamines (VII, VIII) were prepared by refluxing of two moles of 6-Amino-1-hexanol (Aldrich) or 11-Amino-1-undecanol with one mole of 1,2-dibromoethane in ethanol for 24 hours according to the method described by Mueller-Westerhoff *et al.* [13]. The resulting hydrobromic salts were suspended in methylene chloride and treated with an aqueous alkaline solution to form the *N,N'*-bis-(ϖ-hydroxyalkyl)-ethylene-diamines. The starting material 11-Amino-1-undecanol was prepared by refluxing 11-Bromo-1-undecanol (Aldrich) with an equimolecular amount of potassium phthalimide (Merck) in ethanol for 48 hours according to the method described by Sheehan *et al.* [14]. The resulting *N*-(11-Hydroxyundecane)phthalimide was reduced with sodium borohydride in a mixture of 2-propanol and water (6:1 v/v) at room temperature for 24 hours and then hydrolyzed with acetic acid at 80°C for two hours. After neutralization of the reaction mixture with sodium hydroxide the 11-Amino-1-undecanol was obtained.

The first step in the synthesis of the phthalocyanines (IX, X) was the tetramerisation of trimesic acid with urea, copper-(II)-sulfate and ammonium molybdate (molecular ratio 1:0.6:10:0.01) in nitro benzene at 170°C for three hours resulting in copper-phthalocyanine-tetracarbonyl-tetraamide. This intermediate was then treated with 1. alkaline solution, 2. dilute acid solution, and 3. thionyl chloride to obtain the highly-reactive copper-phthalocyanine-tetracarbonyl-tetrachloride [15]. Heating the reactive intermediate with ϖ-Hydroxy-1-aminoalkanes in DMF at 80°C for 8 hours gave blue-colored crystals of copper-phthalocyanine-tetracarbonyl-tetra-(ϖ-hydroxyalkane)-amides in good yields.

Self-assembly of the Coupling Agents on Pretreated Copper Substrates

Two kinds of copper substrates were used to examine the self-assembly of the organic coupling agents. Copper powder (99%, Aldrich) was de-oxidized by stirring in acidified ethanolic solution at ambient temperatures for 20 minutes. After decanting the acid solution, the powder was washed with pure ethanol twice and then dried in vacuum. Plates of a copper-tin alloy (CuSn 0.15, named K81, Wieland Werke, Ulm, Germany), which is used in semiconductor industry to make power devices, were cleaned in a two-step galvanic process. This procedure included degreasing under cathodic current in alkaline solution (45 g/l NaOH, 65°C, 15 A/dm^2) for 30 seconds and pickling under anodic current in acid solution (400 g/l H_2SO_4, 55°C, 7 A/dm^2) again for 30 seconds. After that, the copper sheets were rinsed with deionized water and dried in a nitrogen stream.

The thiol- and disulfide-based coupling agents were dissolved in acetone (p.a. grade, Merck), the ethylene diamines and the phthalocyanines in ethanol (p.a. grade, Merck) in a concentration of 10^{-4} mol/l. Copper powder was stirred into the organic solution at ambient temperature for 60 seconds. After decanting the solution, the coated powder was washed with pure organic solvent twice and dried in vacuum. The plates were coated by dipping them into the organic solution at ambient temperature for 60 seconds. After that the plates were rinsed with pure organic solvent and then dried in a nitrogen stream.

Surface Analysis by X-ray Photoelectron Spectroscopy (XPS)

Pieces of the copper plates 5 × 5 mm in size were examined by XPS-measurements (Model PHI 5600, Physical Electronics) by application of monochromatic Al-K_α-radiation with an anodic output of 300 mW (14 kV; 21.43 mA) under an analytical angle of 45°. The distribution of the elements at the metal surface was quantified by considering all identified signals of the survey and linear deduction of the background. The values of the binding energies of the occurring elements were corrected relative to the carbon C(1s) standard for C—C and C—H bondings at 285.0 eV.

Thermogravimetric Analysis

Copper powder was heated in a thermogravimetric analyzer (TGA-7-Series, Perkin Elmer) up to 350°C at a heating rate of 10°C/min in synthetic air. The temperature-dependent changes in the relative masses of the probes were interpreted as the effectiveness of the organic coating as a corrosion inhibitor. In another experiment, the powder was rapidly heated up to 200°C and the changes in relative mass were examined as a function of time. To examine the thermal stability of the organic coatings, probes were heated up to 450°C at a heating rate of 10°C/min in nitrogen atmosphere.

Shear Test

Copper plates of raw material K81, which had been cleaned and coated with coupling agents as described previously, were used for molding with epoxy resin. The dimensions of the sheets were 10 cm in length, 2 cm in width and 0.5 mm in thickness. After coating, the sheets were immediately transferred into a molding machine (Model Brilliant 100, Fico) and heated up to 180°C for one minute. Then, a commonly-used molding compound (CG 2180-7, Ciba-Geigy) was pressed onto the surface of the sheets under a molding pressure of 100 bar, obtaining molded bodies 2 × 2 mm in size and 1 mm in thickness. Then the probes were transferred into a hot-air oven and cured for two hours at 180°C. All these procedures were performed in strict analogy to the procedures used in chip production.

One-third of the specimens were sheared off right after the cooling to determine the adhesion strength in the dry state. Another third of the specimens were pressure-cooked (121°C, 100% RH, 2 atm., 168 h), whereby the effect of extreme humidity became visible. With the last third of the specimens a simulation of the soldering process under wet conditions was performed. The molded copper sheets were first stored for 168 hours in humid ambient (85°C, 85% RH) and finally three times abruptly heated to 260°C without previous drying.

RESULTS AND DISCUSSION

XPS-measurements

First the distribution of the elements at the surface of copper plates in the as-received state and after galvanic cleaning was examined. The XPS-spectrum for the as-received material (Fig. 4) showed peaks of high intensity for carbon C(1s) with a maximum at 285 eV and oxygen O(1s) with a maximum at 532 eV. These signals refer to an oxidation of the copper surface and a contamination with organic molecules, which may be adsorbed from the ambient or may consist of residue oils from the milling process. In addition to the peaks for copper Cu(2p) at 933 eV and 952.5 eV, so called "satellite-shake-ups" at binding energies of 944 eV and 964 eV were found. The presence of these signals is characteristic of the $3d^9$-state of copper corresponding to copper-(II)-ions primarily as CuO or $Cu(OH)_2$. Therefore, the pretreatment of the copper surface before assembling the organic molecules was inevitable in order to remove the organic contamination and to reduce the oxide layer.

A highly-effective and practicable cleaning procedure was found in the two-step galvanic process described in the experimental part of this

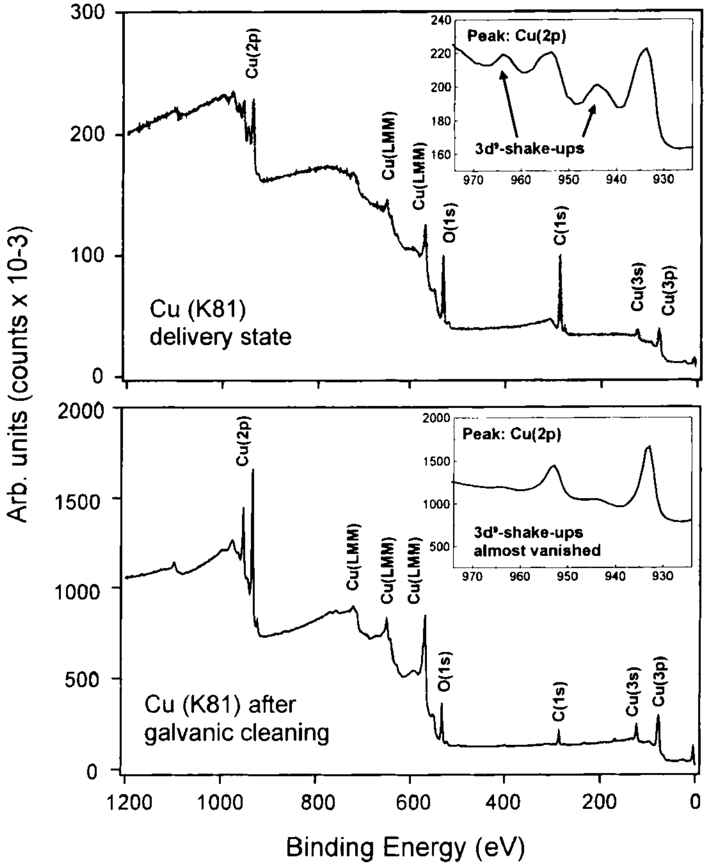


FIGURE 4 XPS-spectra of copper surface (K81) as-received and after galvanic cleaning.

paper. This process can easily be accomplished in the semiconductor industry, where the galvanic cleaning of leadframes in the form of ribbons is a well-established technique. The efficacy of the cleaning procedure has been confirmed by the XPS-spectra (Fig. 4): After galvanic cleaning, the peaks for carbon and oxygen displayed only low intensity while the 3d^9-shake-ups have almost vanished. In this way, copper surfaces with reproducible compositions were obtained.

In order to determine whether the coupling agents are bound to the copper surface by the proper functional groups, XPS-spectra of the pure organic molecules are compared with spectra of the same molecules adsorbed on the interface. The shift of the binding energy of a functional group indicates changes in its binding state. In Table I the binding energies of the sulfur-containing molecules with a chain length of eleven carbon atoms are shown. The molecules with six carbon atoms in chain length and the dithiol could not be studied by XPS because of their exceeding by high vapor pressures under UHV conditions.

In each case, the signals of the sulfur atoms shift towards lower binding energies which is good evidence for correct attachment of the coupling agents onto the copper surface. The binding energies of the oxygen atoms remain constant in all measurements which indicates the presence of free hydroxyl groups. The spectrum of the surface-bound polymeric thiol (IV) shows an additional S(2p) peak at 163.5 eV which implies that not all thiol groups are fixed at the surface. These groups may react with the epoxy resin in analogy to the hydroxyl groups. The appearance of sulfonic acid groups (binding energy 169.0 eV) after assembling of the disulfide (VI) on the copper surface means that parts of the molecules became oxidized. However, there are no data in the literature that sulfonic acid is able to bond to a copper surface or to react with the epoxy resin. In Table II the binding energies of the nitrogen-containing coupling agents are listed.

The signal of the nitrogen atoms of the ethylene diamine (VIII) shifts by 1 eV towards higher binding energies, whereas the binding energy of the oxygen does not change. This may indicate that the

TABLE I Binding energies of functional groups of pure thiol and disulfide molecules compared with those adsorbed onto copper

Coupling agent	*Sulfur S(2p) [eV]*		*Oxygen O(1s) [eV]*	
	Pure mole.	*Adsorbed mole.*	*Pure mole.*	*Adsorbed mole.*
Thiol (II)	164.0	162.5	532.5	532.5
Polym. Thiol (IV)	164.0	162.0/163.5	532.5	532.5
Disulfide (VI)	164.0	162.5/169.0	532.5	532.5

TABLE II Binding energies of functional groups of pure ethylene diamine and phthalocyanine molecules compared with those adsorbed onto copper

Coupling agent	*Nitrogen N(1s) [eV]*		*Oxygen O(1s) [eV]*	
	Pure mole.	*Adsorbed mole.*	*Pure mole.*	*Adsorbed mole.*
Diamine (VIII)	399.5	400.5	532.5	532.5
Phthalocyanine (X)	399.5	400.0	532.5	532.0

ethylene diamine group binds to the copper surface. No data on binding energies of surface-attached nitrogen atoms has been found in the literature. Therefore, it is rather difficult to evaluate the results of the phthalocyanine molecules (X), where no significant shift in the binding energies is observed.

XPS data of the copper leadframes coated with the different adhesion promoters did not show any changes of the copper oxidation state in comparison with the non-coated reference sample. Only the Cu(2p) signals at 933 eV and 952.5 eV corresponding to Cu(I) and Cu(0) have been found. Moreover, the content of oxygen on the surface also has not changed significantly due to adsorption of the organic molecules. No evidence on the formation of an oxide layer with differences in thickness and structure which may influence the final adhesion strength has been found.

Thermogravimetric Analysis

A densely-packed layer of coupling agents acts as a diffusion barrier for small molecules like water or oxygen and, therefore, protect the metal surface from corrosion. A simple method was developed to measure a relative inhibition of copper oxidation. Heating of copper powder in synthetic air leads to copper corrosion which corresponds to oxygen uptake. This is indicated by a rapid increase of the relative mass during thermogravimetric measurement. The temperature shift can be used to compare different corrosion inhibitors. The following compounds were compared by this method: the thiol, disulfide, ethylene diamine and phthalocyanine with eleven carbon atoms per chain, the dithiol and the polymeric thiol. Figure 5 shows the results of heating copper powder at a heating rate of 10°C/min. In order to encapsulate the microelectronic device with epoxy resin the leadframe is heated to 180°C for approximately 3 minutes in air. Therefore, the organic coatings should be stable during this procedure. This is studied by comparison of the oxygen uptake as a function of time when heating the probes to 200°C (Fig. 6).

Both experiments indicated that non-coated copper powder starts oxidation at temperatures of about 200°C. The strongest inhibition was observed with a coating from the polymeric thiol protecting the copper surface up to temperatures above 300°C and for at least 20 minutes on

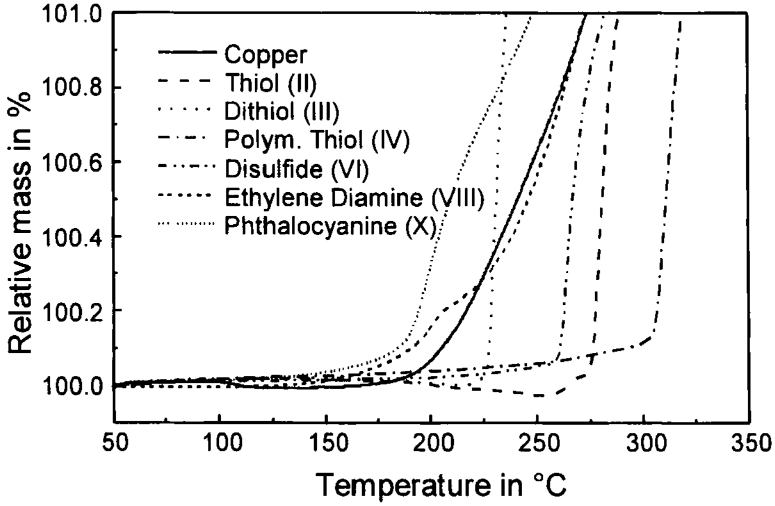


FIGURE 5 Copper oxidation as a function of assembled coupling agents (TGA-Diagram, heating rate 10°C/min).

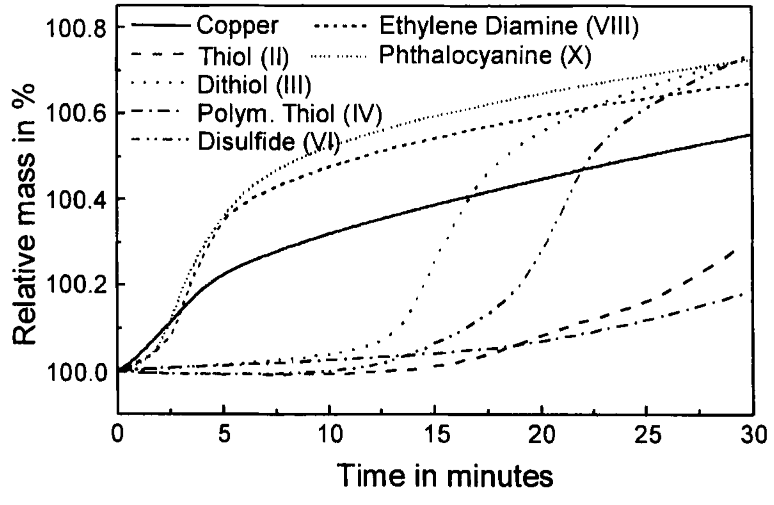


FIGURE 6 Copper corrosion as a function of assembled coupling agents (TGA-Diagram, constant 200°C).

heating at 200°C. This result indicates the formation of a palisade-like structure where the hydrocarbon chains of the polymer are densely packed and slow down the diffusion of oxygen towards the metal surface. Coatings of the monomolecular thiol, which should form similar structures at the interface, showed inhibition up to 275°C and for about 15 minutes on heating at 200°C. The higher inhibition efficacy of the polymeric thiol can be explained by the formation of multiple bondings to the surface, which increases thermal stability. This effect was not observed with coatings of dithiol whose inhibition efficacy stopped at 225°C and after 10 minutes of heating at 200°C. The inhibition of copper oxidation performed by coatings of disulfides was less efficient than with the thiol coatings. It is obvious that the two hydrocarbon-chain-containing disulfide molecules are subject to steric hindrance while assembling on the metal surface. This may cause cavities in the assembled layer and, therefore, an easier diffusion of oxygen towards the copper surface is enabled. The coatings with ethylene diamine and phthalocyanine molecules showed no inhibition of oxidation at all. On the contrary, it seemed that layers of these compounds accelerate oxidation of the copper powder because the beginning of the weight increase shifts towards temperatures of about 150°C. Also, the increase in weight while heating at 200°C occurs much more rapidly compared with the non-coated copper powder. We conclude that the ethylene diamine and the phthalocyanine layers contain a high density of defects which may act as nucleation sites for the formation of copper oxide. In this way the oxidation of the copper surface is accelerated.

In the next experiment with the thermogravimetric analyzer coated copper powder was heated in nitrogen atmosphere (Fig. 7). A comparison of the weight decrease of the probes allows the determination of the desorption rates of the organic molecules from the metal surface. In this way, the thermal stability of the thiol and phthalocyanine coatings was studied. For the thiol a maximum desorption rate was observed at temperatures of about 225°C, which corresponds to data published by Nuzzo *et al.* [16]. For phthalocyanine the maximum desorption rate was found at 340°C, thus indicating an enormous thermal stability for the binding of this molecule on the copper surface.

Shear Test

Figures 8–10 show the results of different kinds of shear tests which are described in the experimental section of this paper. Each of the

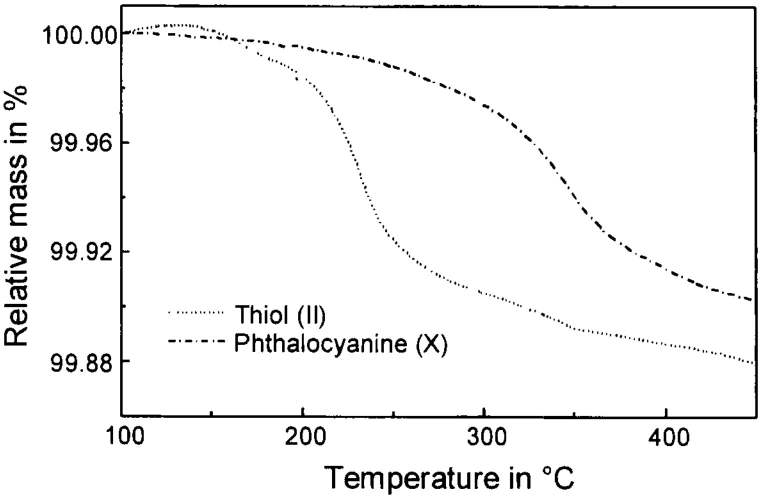


FIGURE 7 Desorption of thiol (II) and phthalocyanine (X) compounds from copper surface at rising temperatures (TGA Diagram, heating rate 10°C/min).

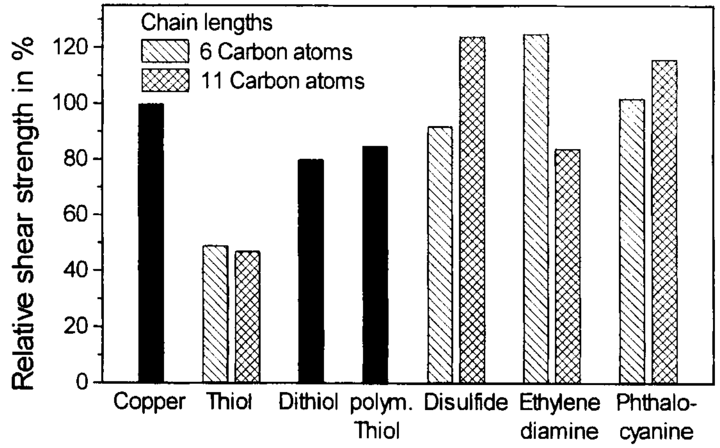


FIGURE 8 Shear strength immediately after the molding procedure.

results shown represents an average of 16 individual measurements. For better comparison, all values were normalized to the value of the non-coated probe measured directly after molding. The values of the standard deviation do not exceed 20% and are not indicated.

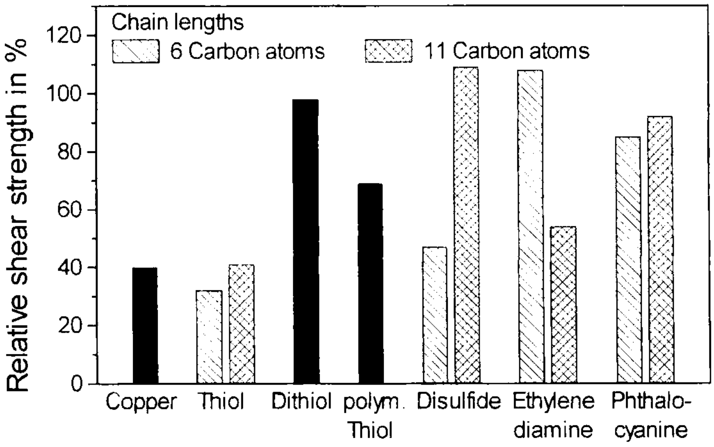


FIGURE 9 Shear strength after the pressure-cooker test (168 hrs at 121°C, 100% RH).

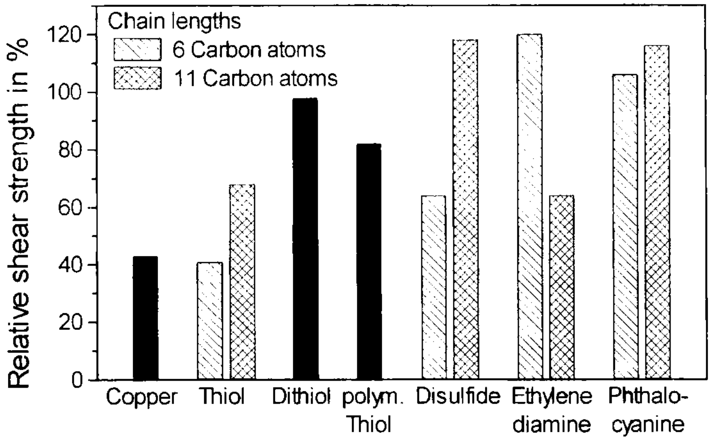


FIGURE 10 Shear strength after the simulation of the soldering process (168 hrs at 85°C, 85% RH, 3 times heated to 260°C).

The adhesion of the epoxy resin on the non-coated copper plates decreased down to 40% after pressure-cooker exposure and to 45% after the simulation of the soldering process. These results impressively indicate the destroying effects of humidity and of thermal stress on the copper-epoxy-system. Probes coated with thiols show a very low adhesion strength of about 50% compared with the reference which decreases to 30–40% after the stress tests. Only the thiol molecule with eleven carbons in the chain showed a better adhesion than the reference with about 70% after the soldering simulation. These results are surprising, because the thiol molecules are supposed to produce the most densely-packed coatings on the copper surface. Adding a second thiol group to the primer molecule increases the shear strength, especially after humidity and temperature stress, to values of almost 100%. The polymeric thiol only partly corresponds to the initial idea that multiple bondings to the copper surface and to the epoxy resin would result in an increase of the adhesion strength. The initial strength in adhesion reached only 80% compared with the reference and did not change significantly after the stress tests. However, the polymeric thiol showed the best results of this group of coupling agents but it does not fulfill our expectation to enhance the stability of the copper-epoxy-system significantly.

The efficacy of the disulfide compounds strongly depended on the length of the hydrocarbon chain. With a coating of Bis-(6-hydroxyhexane)-disulfide an initial adhesion strength of about 90% and with a coating of Bis-(11-hydroxyundecane)-disulfide an initial adhesion strength of about 120% was obtained. The extension of the hydrocarbon chain from six to eleven carbon atoms resulted in doubling of the adhesion strength after the stress tests. The stability of the composite after humidity and temperature stress was three times higher than that of the reference. The dependence of the adhesion strength on the length of the hydrocarbon chains may be explained by the presence of densely-packed monomolecular layers in the interface. In this case, an increase in chain length would lead to more intensive van der Waals interactions. This also results in a stronger suppression of oxygen and water diffusion. Surprisingly, the presence of oxidized disulfide molecules found in the XPS measurements did not decrease their function as adhesion promoters.

The different results in the adhesion strength of coatings with thiols and disulfides need to be discussed in detail. Bain *et al.* [17] and Biebuyck *et al.* [18] showed that the assemblies of thiols and disulfides on gold from the same species on the metal surface. This specie has been described as a gold alkanethiolate RS^-Au^+. Both molecules adsorb as highly-oriented and densely-packed monomolecular layers on gold surfaces. On copper, however, only the assembly of thiols has been described. Laibinis *et al.* [19] showed that thiols form copper alkanethiolates (RS^-Cu^+) similar to those on gold. However, self-assembled monolayers were only obtained on the surfaces of copper films which had been freshly prepared by evaporation onto silicon wafers. Keller *et al.* [20] suggested that the occurrence of copper-(II)-ions on the metal surface leads to the formation of thiol multilayers. This occurs by dissolving of copper ions from the metal surface by the thiol molecules which is followed by a precipitating of copper-thiolate-complexes. It is likely that this effect is responsible for the low efficacy of the thiols for adhesion promotion in our system. The formation of a multilayer in the interface between the leadframe and the epoxy resin certainly produces weak adhesion conditions due to the low stability between the layers of the organic molecules. On the other hand, the assembly of disulfides seems to result in the formation of a monomolecular layer. This might be explained by the occurrence of oxidized species as sulfonic acid in the disulfide coating. An oxidation of a disulfide molecule can only take place with a simultaneous reduction of the copper surface. In this way, oxygen atoms are removed and the copper atoms at the surface change to a low oxidation state. Presuming similar binding mechanisms of the disulfides and the thiols in this way, excellent conditions for a monomolecular assembly are present.

The results with ethylene diamines were rather contrary to those obtained with the disulfides. The molecule with six carbon atoms per chain displayed an initial adhesion strength of about 120% compared with the reference. This value did not decrease significantly even after the stress tests. So, adhesion strengths three times higher than that of the reference were obtained. This strong binding is certainly indicated by a strong affinity of the ethylene diamine to the copper. However, the molecule with eleven carbon atoms per chain showed only a poor efficacy as an adhesion promoter. The initial value was about 90%, which drastically decreased after pressure cooking to 50% and after soldering simulation to 60%. This converse dependence on the chain length and the results of the thermogravimetric measurements imply that the ethylene diamines did not form densely-packed layers on the metal surfaces. Nevertheless, the molecule with six carbon atoms per chain promotes adhesion strength and withstands humidity and temperature stress.

The initial adhesion strengths of phthalocyanine-coated probes resulting in 100% with six carbon atoms per chain and 110% with eleven carbons per chain are comparable with those of the reference. No significant dependence on the chain length was displayed which can be explained by the formation of defects in the monomolecular layers. Nevertheless, both molecules showed essential increasing of adhesion strength in comparison with the non-coated copper after the stress tests. This was also observed by Hettiarachchi *et al.* [21] who explained the effects by a high affinity of the macrocyclic head group to metal surfaces.

To reduce the effects of the popcorn phenomenon, it does not seem to be necessary to have strongly-ordered and densely-packed monomolecular assemblies in the interface. Diffusion of water and formation of water clusters at the metal surface can be diminished even by the presence of a defective organic layer. The organic coupling agents only have to be resistant against exchange with water molecules, thus preventing the water from clustering. "Small" water clusters present in the interface between the leadframe and the epoxy resin are not able to build up high-pressure steam when evaporating at elevated temperatures. So the stability of such microelectronic devices, which have absorbed moisture from the ambient during soldering processes, is increased.

CONCLUSION

Monomolecular layers of organic coupling agents assembled at the surface of copper *via* disulfide, ethylene diamine and phthalocyanine groups promote adhesion strength to molded epoxy resin. They withstand thermal stress and minimize the formation of water clusters at the metal surface when exposed to high humidity. Assembled in the interface between a leadframe made of copper and the epoxy molding compound of microelectronic packages, they minimize the effects of the destroying popcorn phenomenon and increase the reliability of these composite structures.

Acknowledgments

This work was carried out as part of the INNOMONT project which has been supported by the German Federal Ministry of Education and

Research (BMBF). The authors wish to thank Mr. E. Schmidhuber, Mrs. A. Atzesdorfer and Mr. A. Neu from SIEMENS AG Regensburg, Semiconductors Packaging Technology, for the excellent cooperation during this project.

References

[1] Fukuzawa, I., Ishiguro, S. and Nanbu, S., *Proc. of IEEE Int. Reliability Phys. Symp.* p. 192 (1985).
[2] Anjoh, I., *Brazing and Soldering* **14**, 48 (1988).
[3] Kitano, M., Nishimura, A. and Kawai, S., *Proc. of IEEE Int. Reliability Phys. Symp.* p. 90. (1988).
[4] Tay, A. A. O., Tan, G. L. and Lim, T. B., *IEEE Trans. on Components, Packaging and Manufacturing Tech.-Part B*: Advanced Packaging, **17**(2), 201 (1994).
[5] Steiner, T. O. and Suhl, D., *IEEE Transactions on Components, Hybrids and Manufacturing Technology* **10**(2), 209 (1987).
[6] Asai, S., Saruta, U. and Tobita, M., *J. Appl. Polym. Sci.* **51**, 1945 (1994).
[7] Altimari, S., Golwalkar, P., Boysan, P. and Foehringer, R., *Proc. of IEEE Int. Reliability Phys. Symp.* p. 945 (1992).
[8] Walker, P., *J. Oil Color Chem.* **65**(11), 415 (1982); **65**(12), 436 (1982); **66**(7), 188 (1983).
[9] Häussling, L. *et al.*, *Angew. Chem.* **103**, 568 (1991); *Makromol. Chem. Makromol. Symp.* **46**, 145 (1991).
[10] Milligan, B. and Swan, J. M., *J. Chem. Soc.* **62**, 2172 (1962).
[11] Beanblossom, J. E. and Kimball, R. H., *Chem. Abs.* **40**, 6496 (1946).
[12] Chalk, A. J. and Harrod, J. F., *J. Am. Chem. Soc.* **87**, 16 (1965).
[13] Mueller-Westerhoff, U. T. and Zhou, M., *J. Org. Chem.* **59**, 4988 (1994).
[14] Sheehan, J. C. and Bolhofer, W. A., *J. Am. Chem. Soc.* **72**, 2786 (1950).
[15] Shirai, H., Mayurama, A. and Kobayashi, K., *Makromol. Chem.* **181**, 575 (1980).
[16] Nuzzo, R. G., Dubois, L. H. and Allara, D. L., *J. Am. Chem. Soc.* **112**, 558 (1990).
[17] Bain, C. D., Biebuyck, H. A. and Whitesides, G. M., *Langmuir* **5**, 723 (1989).
[18] Biebuyck, H. A., Bain, C. D. and Whitesides, G. M., *Langmuir* **10**, 1825 (1994).
[19] Laibinis, P. E. *et al.*, *J. Am. Chem. Soc.* **113**, 7152 (1991); *J. Am. Chem. Soc.* **114**, 1990 (1992); *J. Am. Chem. Soc.* **114**, 9022 (1992).
[20] Keller, H., Simak, P. and Schrepp, W., *Thin Solid Films* **244**, 799 (1994).
[21] Hettiarachchi, S. *et al.*, *Proc. Electrochem. Soc.* **89**, 320 (1989); *Corrosion* **45**, 30 (1989).