Chemical Composition and Thermal Stability of 2 Butyl, 5 Chloro, Benzimidazole Film

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The stability of a 2 butyl, 5 chloro, benzimidazole film (BCB) before and after a thermal treatment, which simulated the annealing of a typical soldering process, was the main motivation of the present work. The chemical bonds inside the BCB film and between this film and the copper substrate were investigated by x-ray photoelectron spectroscopy (XPS). The thickness of that film was measured by optical ellipsometry. Protection of the film vs oxidation and its physical modification during the thermal treatment were also investigated. The XPS valence data showed that a part of the chlorine was linked to the benzene ring while the other part formed either copper chloride or another chloride linked to the nitrogen of the BCB molecule. The passivation film hardened and became an electric insulator during the thermal treatment, so that any successive electrical test was impaired.

Key words: Benzimidazole, copper surface, inhibitor, x-ray photoelectron spectroscopy (XPS)

INTRODUCTION

Copper oxidation has always been a serious problem in the process of wiring circuit boards by soldering. In the past, strongly reactive fluxes were used to assure copper pickling for a successful soldering. Old reagents were replaced with less active fluxes for ecological reasons.[1] These fluxes however, were less effective for the removal of the oxides. It was then necessary to use special corrosion inhibitors. Organic inhibitors are replacing other protective layers for Cu, notably metallic tin and hot air solder leveled tin/lead alloys (HASL). These, known as organic solderability preservatives (OSP),[2,3] assure a solderable copper surface. In the past, benzotriazole (BTA) was a preferred inhibitor for these applications.[4–10] This benzotriazole solution reacts with the copper surface and gives a thin layer (30–50Å)[11] made of a complex of Cu^{+} and BTA.[12–19] However, the present packed assemblies, due to high densities of electronic circuits, must be able to withstand multiple thermal processing during which well established inhibitors do not adequately protect the copper. More specifically, BTA does not resist to a multiple soldering process. A thick oxide layer forms and the solderability of the printed circuit board decreases, as shown in previous papers.[11–18] New inhibitors were investigated in order to solve this problem. The benzimidazoles (BIM) compounds, which form thicker surface films, provide a better protection against copper oxidation during the thermal treatment of the soldering process. Their complexation mechanism on the copper surface is due to the nitrogen which loses the hydrogen and links with the Cu^{+}. Their corrosion and oxidation behavior was also studied, mainly with electrochemistry techniques.[3–20,21]

One of the most convenient BIM derivates is 2 butyl, 5 chloro benzimidazole (BCB), because of the high yield of the synthetic process used to produce it. Given its complex chemical composition, further investigations of the chemical bonds inside the organic protective film, and with the copper substrate are necessary. The behavior of the chlorine bond during the thermal treatment of the soldering process is of particular interest. The eventual presence of free chlorine will be responsible for corrosion and contamination. The investigation of the chemical bonds in the organic film, and between this film and the copper substrate, was the main motivation for the present work. X-ray photoelectron spectroscopy (XPS) and ellipsometric measurements were performed on BCB films deposited on copper surfaces in order to determine film thicknesses and the chemical state of the elements (Cu, Cl, O, N, C), before and after

(Received September 24, 1996; accepted February 6, 1997)

Table I. Atomic Percentages of Chemical Elements after Sputtering a 10Å Layer with a Low Sputtering Rate

	O	N	C	Cl	Cu
NT	1	10	80	5	4
TA	6	9	72	5	8
TN	1	9	73	5	12

Note: NT refers to samples which were not annealed; TA for samples annealed and successively left in air; TN for samples annealed and left in a nitrogen atmosphere.

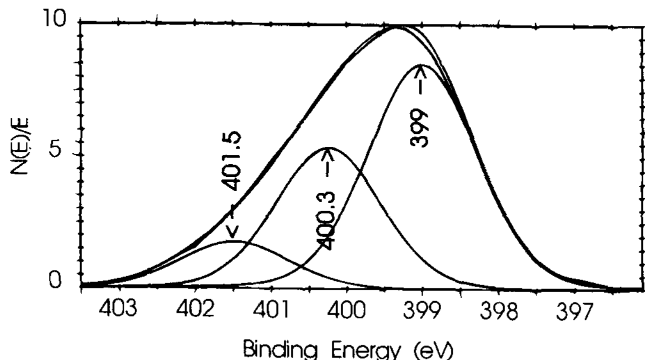

Fig. 1. N 1s curve-fit spectra of unannealed samples after a low-rate sputtering of about ten atomic layers.

thermal treatments, similar to those which take place during the soldering process.

EXPERIMENTAL PROCEDURE

Copper samples were cleaned with a 10% HCl solution, and successively with a 90 gr/l $Na_2S_2O_8$ solution. They were rinsed with 18 Mohm deionized water after each step. Films of BCB were deposited by immersing the copper in an aqueous BCB solution with a pH = 2.8 at 45°C. The films were investigated by XPS and ellipsometric techniques before and after annealing in air and nitrogen atmospheres at 220°C for 2 min. This thermal treatment was chosen in order to simulate the temperatures and times typical of a soldering process. In addition, some of the annealed samples were left in air for 24 h and others for 72 h before the execution of the XPS and ellipsometry measurements. The reason was to establish whether the exposure to air induced any chemical alteration in the film and in its bonding to the copper substrate.

XPS measurements were carried out with a PHI 5600ci ESCA spectrometer equipped with a Mg anode (MgKα = 1.254 KeV). This x-ray source, which was not monochromated, was chosen to compensate the charge effect on the nonconductive surface. It is known that the positive charge of an insulator surface, which is due to the emission of photoelectrons, is compensated by the low-energy electrons emitted by the window of the x-ray tube. The x-ray tube was operated at 14 kV and a power of 300 W. The spherical capacitor analyzer (SCA) had an input aperture set for an analysis area of 0.125 mm^2. The pass energy was 117.4 eV for survey spectra and 11.75 eV for high resolution spectra with an energy resolution of 0.9 eV for the Ag3d5/2. The spectrometer was routinely calibrated with the XPS signal of Au, Ag, and Cu. Before the collection of the data at full power, the x-ray tube was operated at low power to check the presence of Cu^{2+} which is sensitive to x-ray radiation damage.[26] In this way, any eventual alteration of the data due to radiation damage was avoided. However, as specified in the following paragraph, bivalent Cu was never found.

Ellipsometric measurements were done on the inhibited, unannealed samples to determine the film thickness. It is well known that ellipsometry is a precise, versatile, and nondestructive technique for measuring thin film thicknesses, as shown in recent publications.[18–24] A Gaertner ellipsometer L116B, equipped with a HeNe laser source (λ = 6328Å) and a rotating analyzer was used for the optical measurements. The light spot was about 30 μm and the incidence angle of the light beam on the film surface was 70°. The method and program used to elaborate the data were given in a previous publication.[18] They are based on a trial and error procedure in which the refractive index n, the absorption coefficient k, and the film thickness are variables. As specified in the following paragraph, attempts to fit the experimental data obtained by assuming that only one film was present were not successful. It was necessary to adopt a two-film model. It was not possible to perform any ellipsometric measurement on the annealed samples. Apparently, the reflectivity or the absorption (or both) of the surface films increased during the annealing so that no light reflected by the copper substrate could be detected by the analyzer.

A knowledge of the film thicknesses permits the calibration of the sputtering rate for the depth profiles.

EXPERIMENTAL RESULTS

Unannealed Samples

The BCB examined by XPS in samples that were not annealed was not stoichiometric. There was an excess of carbon due to the surface contamination and to the organic products which were added to the BCB solution for improving wettability and reactivity (see Table I).

The nitrogen peak is illustrated in Fig. 1. The deconvolution of the peak shows the presence of three binding energies: the lowest one (399 eV) corresponds to the N complexing the Cu^+, the second (400.3 eV) is characteristic of the pure BCB, and the third (401.5 eV) corresponds to the ammonium chloride compound $R_4N^+Cl^-$.[23] About 60% of the BCB is complexing the copper, as given by the best fitting procedure. This estimate is confirmed by the atomic percentage data of Table I and by the Cu LMM Auger spectrum (Fig. 2). This spectrum shows that the greatest amount of copper is complexed into organic compounds and a small amount only is detectable as metallic copper.[23] It is mentioned below that a small percentage of Cu may be bonded to Cl. Bivalent Cu was never found, as

shown in Fig. 3, where the shake-up peaks are completely absent.

The XPS Cl spectrum is illustrated in Fig. 4. A best fit was tried by assuming three binding energies: 200.66 eV typical of the chlorine bond to the benzene ring, 199.73 eV corresponding to the Cu-Cl bond, and 198.65 eV attributed to the ammonium chloride $R_4N^+Cl^-$.[23] It follows that 44% of the chlorine is bonded to the benzene ring, 33% to Cu and the rest to the $R_4N^+Cl^-$ compound. The presence of the three above-mentioned binding energies is supported by the results of the chemical analysis of the BCB solution. There are 88.7 mg of free Cl per liter of solution which correspond to about 0.01 g of free Cl per gram of the deposited BCB film. The free chlorine is not due to the hydrochloric acid pickling which was performed before the passivation treatment. In fact, the free Cl atomic percentage is the same for the Cu samples pickled with hydrochloric acid and for those pickled with sodium persulphate.

Attempts to fit the ellipsometric data by assuming the presence of only one film were not successful. It was necessary to adopt a two-film model. The best fitting of the experimental data gave a bottom film, close to the Cu substrate, with n = 1.6, k = 0 and a thickness equal to 1700Å; a top film with n = 3.89, k = 0.106, and a thickness of 80Å. The validity of this two-film model is supported by XPS which shows the presence of a Cu valence typical of Cu_2O in the first few layers. This should correspond to the top film detected with ellipsometry. As stated above, the XPS data show also the valences typical of the expected organic film.

Annealed Samples

The amount of carbon found in the samples annealed in air was closer to the stoichiometric composition of BCB. A possible explanation is that some thermal etching removed the C due to sample contamination. A greater amount of Cu in metallic form was also found (Fig. 5). An appreciable amount of Cu diffusion toward the film surface may have taken place (see Table I). The total amount of Cl did not change but the fraction of Cl bonded to the benzene ring decreased, while the fraction forming chloride increased, as shown by the XPS spectra (Fig. 6). Oxygen was present in the first few layers. Only a small fraction was bonded to Cu and the greatest amount was absorbed, since the binding energy was 533 eV[11] (Fig. 7). N had three valences as previously discussed in the case of the samples which were not annealed.

There were only small differences between the samples annealed in a nitrogen atmosphere and those annealed in air, excepting obviously the increase of oxygen in the air treated samples.

No appreciable differences were found in the samples which were left in air after the thermal treatment, for periods of either 24 or 72 h. The XPS data were the same as those found in the samples examined right after the annealing.

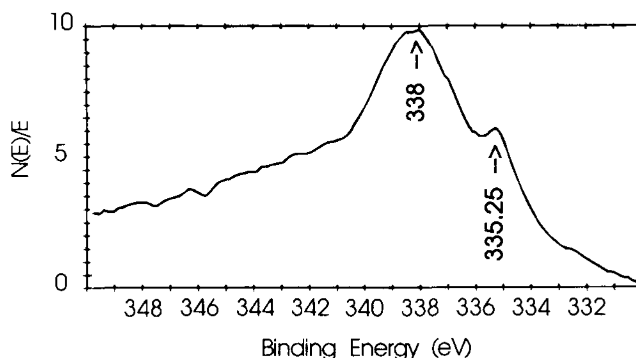

Fig. 2. Cu LMM Auger line spectrum of unannealed samples after a low-rate sputtering of about ten atomic layers.

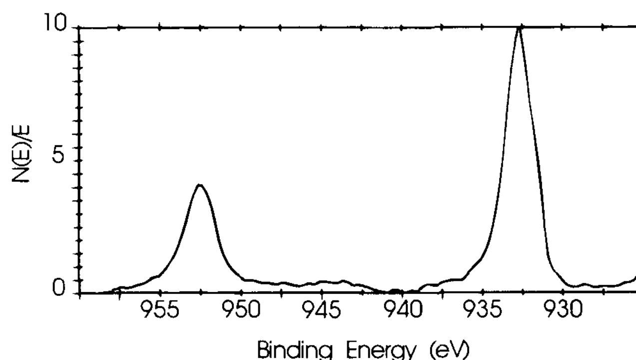

Fig. 3. Cu 2p photoelectron spectrum of unannealed samples after a low-rate sputtering of about ten atomic layers.

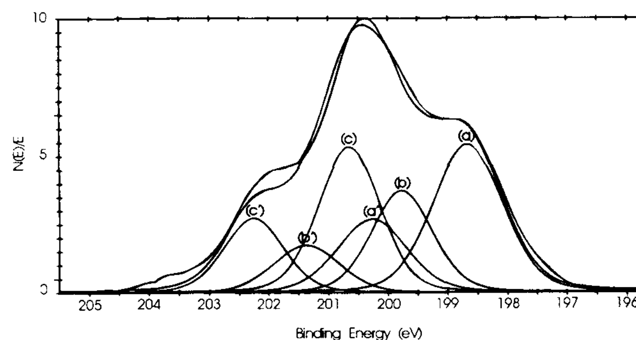

Fig. 4. Best fitting of the Cl 2p spectrum of unannealed samples after a low-rate sputtering of about ten atomic layers. The peaks 2p3/2 of the Cl are indicated by (a), (b), and (c), and the peaks 2p1/2 by (a′), (b′), and (c′).

It should be emphasized that the BCB organic film hardened during the annealing in air or nitrogen. This film becomes an insulator layer that impairs the electrical contact between the tester probe and the sample. It was not possible to remove this film by immersing the annealed sample in a butanol solution. The BCB film was, instead, almost completely removed from the surface of samples which had not been annealed, after immersion in the same solution: only an organic film about 100Å thick remained.

CONCLUSIONS

Free chlorine which is present in the aqueous BCB solution forms CuCl and the quaternary salt of ammonium chloride of 2 butyl, 5 chloro, benzimidazole and only 44% of the chlorine atoms are bonded to the

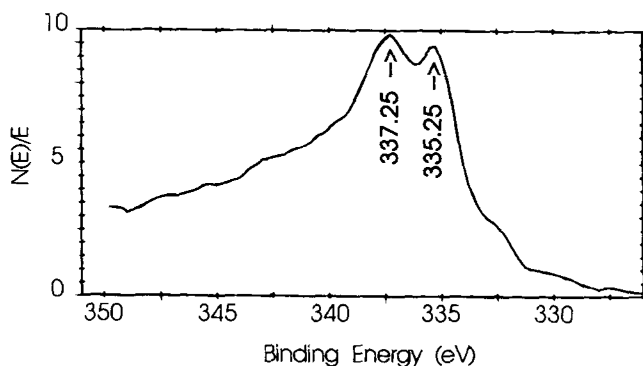

Fig. 5. Cu LMM Auger line spectrum of the sample annealed in air after a low-rate sputtering of about ten atomic layers.

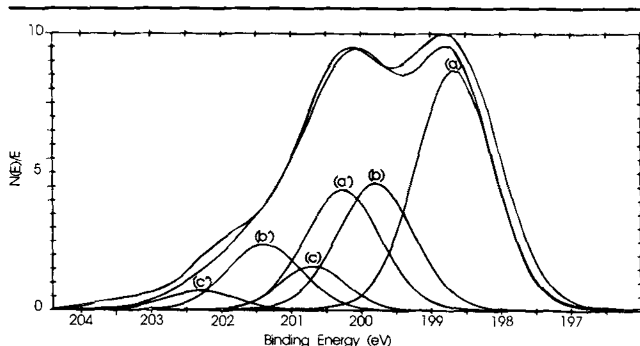

Fig. 6. Best fitting of the Cl 2p spectrum of the sample annealed in air after a low-rate sputtering of about ten atomic layers. The peaks 2p3/2 of the Cl are indicated by (a), (b), and (c), and the peaks 2p1/2 by (a′), (b′), and (c′).

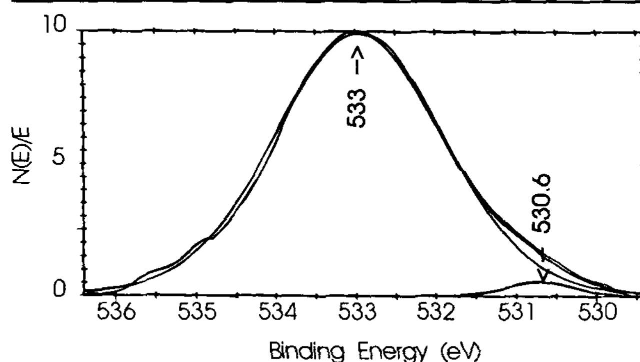

Fig. 7. Curve fitting of the O 1s spectrum of samples annealed in air after a low-rate sputtering of about ten atomic layers.

benzene ring in the passivated samples.

After heating at 220°C for 2 min, the atoms of Cl bonded to the benzene ring decrease and the amount of CuCl and hydrochloride increase.

Most of the Cu is complexed by the nitrogen in the BCB molecule and the remainder forms compounds with chlorine. The amount of metallic Cu in the top film increases. This is probably due to Cu diffusion through the BCB film to the sample surface during annealing. There is no evidence of bivalent Cu. Most of the oxygen is absorbed in the first few layers (about 100Å), and only a small fraction forms copper monoxide during the thermal treatment in air.

The present results show that the benzimidazole, whose molecule contains the Cl atom, is not recommended as an inhibitor because of the effects due to the free chlorine ions present in the solution. Moreover, molecules similar to 2 butyl, 5 chloro, benzimidazole give cross linking with a consequent hardening of the organic BCB film during heating at 220°C.

There are two main disadvantages associated with the free Cl ions and with the hardening of the BCB film during the soldering of the passivated samples. The free Cl ions are responsible for corrosive phenomena at the copper surface, and the hardened BCB film becomes an insulator layer which hinders the electrical tests. One advantage of the BCB film is the inhibition of further oxide growth in the annealed samples left in air.

ACKNOWLEDGMENT

The authors are grateful to Doctor A. Manara and Doctor A. Merlini for their constructive suggestions and for valuable discussions.

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