QUANTITATIVE EVALUATION AND CONTROL OF SURFACE CHEMISTRY AFFECTING ELECTRONIC DEVICES. ISS AND SIMS SURFACE ANALYSIS.

Gene R. Sparrow
Joe Foley
Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110

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Performance of electronic devices such as low voltage connector, relays and switches, flexible circuits, bonded devices, and high current circuits critically depends on surface chemistry. Understanding and controlling this chemistry through use of corrosion inhibitors and surface chemistry can eliminate failures and optimize processing and design. Examples will cite application of ISS (Ion Scattering Spectroscopy) and SIMS (Secondary Ion Mass Spectroscopy) surface analysis to investigate corrosion, degradation, segregation, and contamination of electronic devices, including correlation of oxide thickness, diffusion, and contamination with performance.

INTRODUCTION

Requirements for decreased voltages and currents in electronic devices, especially contacts and switches, coupled with extreme competition for higher quality and performance have greatly increased the need for complex, well-controlled surface chemistry. The use of copper (Cu) in flexible circuitry, thin film technology, and plating technology places high demands on detailed understanding and control of copper surface chemistry in particular. Conditions under which electronic devices are expected to work have also become more formidable along with greater expectations for device lifetimes. The very outer layer, often substantially less than 50 Angstroms, (about 1/5th of one microinch) is extremely critical to device performance. The two greatest difficulties are 1. controlling surface contamination and 2. controlling corrosion at every stage of processing, storage, shipping and use. Unprotected Cu can readily oxide under normal atmospheric conditions to form oxides and hydroxides which substantially increase contact resistance, degrade bonding performance, and aggravate incorporation of additional contamination. Excess contamination on or in the Cu can greatly aggravate oxidation. These two factors are interrelated. In some components made using Cu,

special cleaners containing VCIs (Vapor phase or Volatile Corrosion Inhibitors) can be used to control oxidation. In other devices, oxidation must be prevented immediately after manufacturing . This can be accomplished using special rinsing or spraying operations or using special VCI emitters. The most common types of VCIs often used in Cu corrosion protection include various benzotriazoles (BTZ), and amine salts. These have been discussed previously (1-4).

The past two decades, many analytical instrumental techniques have been developed to characterize this region and numerous applications of these analytical techniques have been cited (5-9). Nevertheless, the level of detail and sophistication required for some applications has become increasingly difficult to achieve from some of these techniques. In particular, this includes detection of trace contaminants and measuring precise composition of layers only a few Angstroms thick including characterization of the chemical structure of the organic portions. ESCA (Electron Spectroscopy for Chemical Analysis - also termed XPS - Xray Photoelectron Spectroscopy) has been used very effectively for measurements of benzotriazole on Cu (2,10-12). However, due to the inherent escape depths of electron spectroscopies it has been pointed out by Armstrong et.al. that absolute quantitation of the near surface composition is unlikely. The techniques of ISS (Ion Scattering Spectroscopy) and SIMS (Secondary Ion Mass Spectroscopy) are ideally suited to combined use for these types of applications as well as to more general applications in surface analysis. They have been discussed in some detail in application to VCIs used on Cu (2), and in Cu thin films on ployimides (13). More recently, techniques for quantitative analysis and data processing of spectra obtained from ISS and SIMS techniques have greatly improved their capabilities and the simplicity of understanding and presenting results (14). The applications of ISS and SIMS have been extremely helpful in recent years in providing information that is not readily obtainable from any other techniques.

The details of surface chemistry and its effects have been studied in the development and manufacture of flexible films of Cu deposited on polyimide; performance of low voltage, low pressure switches and contacts, corrosion of electronics under very harsh environments, and problems originating from poor bonding. In studying Cu/polyimide metallized films, the interfacial chemistry is extremely important to minimize interfacial delamination. The surface chemistry of the external Cu surface is important to maximize adhesion during laminating or soldering. Contaminants and oxide thickness are critical to performance and stability. Hydroxide Vs oxide levels and degradation of the polyimide were also found to be very important factors but monitoring them is very difficult without careful control of SIMS parameters during analysis and data processing. Details of chemical bonding of the Cu and the polyimide can be determined from careful evaluation of the SIMS spectra when it is performed in the near “Static-SIMS” mode. Also found to be very important, is the extent of inter diffusion and bonding between the Cu and the polyimide.

Low voltage, low current electrical contacts and connectors are extremely susceptible to changes in surface contamination and oxidation whether they are

composed of Ag, Au, or Cu. Contaminants can be traced to processing of the original metals, and associated with surface segregation during operation. Adverse effects are even more pronounced when the devices must operate for extended periods in harsh environments. New methods and expressions for surface contamination or surface purity are presented and correlated with performance. The "thickness" of the oxide layer coupled with exactly where in this oxide layer certain contaminants are found is shown to have a major effect on device performance. In some cases, the variation of the thickness of such layers was found to be less than 10 Angstroms yet dramatically different performance as measured by contact resistance or current flow. One of the most disastrous contaminants often encountered in electronics, is silicone. Because these materials are very common, often moderately volatile, and damaging at extremely low levels, their detection is one of the most routine and common applications of ISS and SIMS. Surface layers of silicones of even less than 1% of a single molecular layer are readily detectable and can be unequivocally identified as silicones even when they are undetected by techniques such as ESCA.

The chemical bonding of plated Cu varies considerably depending on plating conditions. Most of these variations relate to minor or trace impurities and chemical structure which is extremely difficult to detect by means other than SIMS. It is shown to relate to the incorporation of small amounts of small organic groups, such as C2H groups, and other impurities, especially CN, O, OH, and alkali ions. This is remarkably different than sputtered Cu films and changes considerably when exposed to various environmental conditions such as heating, or humidity exposure.

Many different methods of surface treatment have been investigated to control surface chemistry of electronic devices, especially for bonding and adhesion. One surface treatment which is very effective is use of VCI (Vapor phase or Volatile Corrosion Inhibitors) chemical treatments to dramatically reduce surface corrosion of Cu under a variety of harsh conditions including high atmospheric concentrations of Chloride ion, H2S, SO2, and microbes. Yet only extremely small amounts of these volatile chemicals are required to provide very effective corrosion control for periods extending past 2 years. It is common practice to utilize thin antistat bags of polyethylene which provide both the corrosion controlling VCIs and anti static control. Mechanisms of bonding of the Cu to these materials has been investigated. Results from ISS, SIMS and including some analysis by ESCA, strongly indicates that the bonding to Cu is most likely through strong pi-bonding to aromatic / heterocyclic ring structures.

In most processing, optimum performance can only be obtained through proper cleaning of the surfaces involved. This may involve solutions during and after processing or dry techniques involving vacuum ion milling, plasma, or corona treatment. In all cases, it is essential to understand surface chemistry before cleaning as well as after. The results after cleaning are often found to be considerably different than those expected. Use of VCI corrosion inhibitors in cleaners and other factors which influence cleaning of surfaces will be discussed along with typical applications indicative of unusual results.

EXPERIMENTAL

The following studies involved detailed surface analysis of Cu under three common conditions:

Raw Cu coils and standard test panels before and after subjecting to a series of

different cleaners, including some containing VCIs.

Cu and Au devices used in relays and switches where low contact resistance and

good solderability are needed.

Thin vacuum deposited Cu films on polyimides.

Initial testing was done by treating standard 202-110 Copper CDA-110 metal test specimens obtained from METASPEC, San Antonio, TX. These were thoroughly cleaned by physical polishing and by using a commercial water based cleaner followed by short cleaning in deionized water. The coupons were then subjected to several different treatments as listed.

#1. Control - dried immediately
#2. Reference - panel not cleaned
#3. 316 - panel immediately rinsed in commercial water based copper cleaner containing VCI.
#4. 416 - panel immediately rinsed in commercial general water based cleaner containing VCI
#5. 238 - panel immediately sprayed with commercial solvent based cleaner with VCI containing spray.

Some of these treatments contained several different volatile corrosion inhibitors including tolybenzotriazole, and amines. Standard ASTM corrosion of panels with these treatments has been done previously and illustrated the corrosion inhibition provided by treatments #3, #4, and #5. Abbott (15) has illustrated the usefulness of the "Mixed Flowing Gas Testing Concept" for VCIs and testing by Contech Research, Inc. clearly illustrated that VCI emitters provided sufficient corrosion protection for most indoor electronic components under polluted environmental conditions (16).

Additional analyses were conducted on samples obtained from coils of Cu electroplated on Zn. Some of these samples were subjected to treatment with VCI containing cleaners followed by extensive rinsing in deionized water.

All samples were subjected to detailed surface analysis by ISS and SIMS using instrumental conditions and procedures which have been routine and standard for over 10 years at Advanced R & D, the independent laboratory which supported this work. These analysis were performed on a modified KRATOS 3/M combined ISS, SIMS system equipped with an Advanced R & D computer system. Additional inspection and analysis of the samples was performed using an ISI Scanning Electron Microscope (SEM)

equipped with a Princton-Gamma Technology (PGT) Energy Dispersive Xray (EDS) spectroscopy analysis system.

The ISS analyses were performed by obtaining detailed depth profiles of the concentration gradients from the outer atomic layer to a depth of about 100 Angstroms using $^3He^+$ ion beam at 2000 eV across a sample area of about 10 mm^2. This included a series of about 20 spectra, each at a slightly greater depth into the surface. Each spectrum was subjected to an interactive computer quantitative analysis which included automatic computer peak deconvolution and elemental sensitivities to calculate atomic concentrations. This included indirect detection and quantitation of Hydrogen. Figure 1 is a typical ISS depth profile obtained from one of the samples, in this case, an electroplated Cu on a Zn coil which had been exposed to a commercial cleaner (termed VCI-316) containing VCIs. This sample exhibited excellent corrosion resistance as well excellent lubricity during subsequent operations. All of the individual raw spectra are shown plotted sequentially in the bottom half of the figure. They are all normalized to reflect the same relative sensitivities with the spectrum on the very extreme left representing the atomic composition of the very outer atomic layer and each successive spectrum representing the composition at successively greater depths into the surface. The X axis reflects the sputtering time for each spectrum in seconds with the sputtering rate estimated at about 3 to 5 Angstroms per minute. Two spectra indicated by the * are shown expanded in the upper left quadrant and the atomic concentrations of the elements are shown plotted in the upper right corner. Figure 2 illustrates the raw spectral data obtained from a similar sample of Cu plated Zn but one which showed very poor lubricity. This is plotted as a “Z-Plot” illustrating the depth as the Z axis.

SIMS results were obtained using Ar at 500eV at near Static conditions but with sufficient sputtering to obtain a series of spectra corresponding to a depth similar to that of the ISS. Most of these spectra were obtained by scanning the mass range from 1 to 150 but each series of spectra included one spectrum covering the mass range from 150 to 300. This spectral range provides some useful information regarding the bonding characteristics of each sample. Spectra obtained from the plated Cu sample of Figure 1 are shown plotted in Figure 3 where the first spectrum obtained is shown in the upper left quadrant. In most SIMS Figures, the spectra are plotted on two sensitivity scales, the upper trace illustrating an expansion factor of either 8 or 16. The spectrum in the upper right quadrant is from mass 100 to 250 and in some cases from 150 to 300.

A series of Cu / Ag alloy contacts used in very low pressure, low voltage, low current electronic switches were subjected to ISS and SIMS analysis to determine the effects of surface contamination on contact resistance. These samples were not exposed to any known VCIs or corrosion protection.

The most complex studies involved detailed analysis of the Cu / polyimide interfaces of several samples. We have reported on studies involving the nature of the chemical bonding of this system earlier (3,13) and there are numerous references to this interface reported in (9,12). The primary purpose of these studies was to determine the

chemical changes which occurred at the interface due to exposure to prolonged temperatures and due to continuous exposure to high relative humidity. Test samples of vapor deposited Cu on a commercial grade of polyimide were prepared and subjected high humidity for approximately 10 days or to high temperature of approximately 200° C for several hours. Physical testing of relative adhesion was performed on 1” strips using a sample mount designed to pull the specimen at 90°. Both ISS and SIMS analysis were performed on both sides of freshly exposed interfaces; the freshly exposed polyimide side and the freshly exposed Cu strip which was peeled off. The delamination of the test strips were all obtained using a 90° peel angle.

RESULTS & DISCUSSION

Cu Coils and Test Coupons. Figures 1 and 2 illustrate the large difference in surface chemistry between the well behaved Cu plated coil sample and the sample with poor performance as well as the effect of the VCI containing solutions. One of these Figures is a 3-dimensional "Z-Plot". Figure 3 illustrates a typical SIMS spectrum from one of these samples. The VCI treated samples appear to have higher levels of contamination compared to reference Cu which was merely cleaned but not exposed to VCIs. This is misleading since the function of the VCIs is to coat the surface with a thin molecular layer of organic material to prevent corrosion and also to provide a slight amount of lubricity. Unfortunately, an acceptable method for cleaning the standard Cu test coupons for surface chemical experiments was not found. This was due to the difficulty in removing the protective film coating on these panels as they were received. Cleaning methods included use of many commercial paint removers, water based and solvent based cleaners, strong mineral acids including HNO_3 and finally polishing with various fine grade sanding medium. In all cases, the resulting surface was found by ISS and SIMS to contain substantial organic and inorganic material to a depth of about 60 Angstroms. Clean Cu was not observed on these samples. However the SIMS results from these samples and the plated Cu coils provided indications that the structure of the materials on the original uncleaned Cu is different than the structure of the VCIs. These results definitely indicated that the VCIs; do indeed attach very strongly to the surface and are readily detected. The ISS indicates the inhibitor layer is approximately 40 to 60 Angstroms which is consistent with the work we reported previously using ESCA (Electron Spectroscopy for Chemical Analysis also termed XPS) (3) and (12) which indicated that the inhibitor layer thickness was dependent on the pH of the solution. However, the extreme surface element as well as its location or distribution in depth in this layered surface area. SIMS provided excellent detection of the trace contamination and very strong evidence for various bonding characteristics.

Cu/Ag Low Voltage Relay Contacts. The atomic concentrations of all elements detected were tabulated for each spectrum in the depth profiles. Although the surface chemistry was complex and composed of many different contaminants which gave rise to several different distinct layers in the outer 100 Angstroms of the surface, a rough correlation of contact resistance was evident. Figure 4 illustrates the atomic concentrations of Cu and Ag combined at a depth of about 10 to 15 Angstroms. Figures 5 and 6 indicate the typical ISS and SIMS compositions of the entire surface for one of these samples. Each sample represents a different processing treatment. The purity, as indicated by the total concentration of the Ag+Cu, showed a very high correlation with the contact resistance of these devices. These results were instrumental in locating where excess contamination originated and in the development of cleaning techniques and methods to minimize contamination as well as corrosion. Note that these concentrations represent the composition at only one depth of the surface. Plotting the Ag+Cu concentration vs depth or plotting the total of all contaminants vs depth provides a unique, very useful plot of Purity and Total contamination vs depth. Both ISS and SIMS give clear indications that each surface is multilayered. Comparison to our previous

ESCA data was possible by integrating or adding together the results of several spectra from the surface to any particular depth desired.

Cu on Polyimide. There are three factors of the composition of the interface which appear to contribute to the degradation of the normal bonding at this interface.

1. the level and location of oxidation.
2. the type and amount of contamination.
3. the bonding chemistry of the Cu, especially bonding with O, OH, and N.

ISS indicated that excessive oxidation occurred during heat treatment of some samples, yet not to others exposed to similar conditions. This lead to extremely poor interfacial bond strength and very homogeneous delamination along an oxidized copper boundary and the polyimide. When the oxidation at the interface was less severe, the delamination was more heterogeneous and occurred somewhat between the oxide layer and the polyimide but a significant amount of diffusion of Cu into the polyimide was observed. The resulting delamination showed substantial amounts of Cu within the polyimide boundary layer but without evidence for severe oxidation. However, the **location** of the oxide layer was as important as the amount of oxidation. In cases of severe delamination, the oxygen appeared to be well into the polyimide itself but it was accompanied by high levels of Cu. This strongly suggest that migration of Cu into the polyimide probably occurs first and is followed by oxidation. Unfortunately, the close binding energies of Carbon to oxygen and Carbon bonded to Nitrogen in ESCA make it difficult to distinguish or quantitative the relative amounts of each using ESCA. However, there was weak evidence from SIMS suggesting that some of the oxygen detected in this Cu / O rich layer within the near boundary of the polyimide Cu may be associated with oxidized polyimide. This would certainly contribute to a substantial weakening of the bonding in this area and preferential interfacial delamination in this area as we have observed. i.e., The amount of Cu and Oxygen detected on the backside of the freshly delaminated polyimide side of the interface was much higher than for non oxidized samples. In addition, the Cu and O were not at the immediate interfacial surface but extended a considerable distance into the polyimide, about 50 Angstroms, and they were accompanied by H, C, and N throughout the depth profile. The Cu opposite side of the interface also showed moderate amounts of H, C, and N further indicating that the interfacial failure was not at the original Cu / polyimide boundary.

SIMS results obtained at higher mass provided substantial detail into the bonding of Cu along this boundary through a comparison of ion clusters. Figure 7 illustrates some of these characteristics. These characteristics are generally indicated by ion clusters. Although a large number of such ion clusters was monitored, the figure shows the ion clusters which were considered most representative of structural details. All of the peak intensities were normalized on the basis of Cu_2 as 1000 units. We have already discussed the strong evidence for Cu bonding with Nitrogen in our previous work (3). It is again indicated in this figure by the relative intensities of the Cu_nC, Cu_nO, and Cu_nCN ion clusters. In addition, this figure offers significant insight into the mechanisms which

occur during heat treatment and humidity exposure. For example, note that the heat treatment causes a significant decrease in Cu_n C_m intensities but an increase in the Cu-Oxide peaks. This is accompanied by dramatically reduced Cu_3 which indicates some of the Cu metal is undergoing oxidation. The changes for the sample exposed to high relative humidity for 2 days showed fewer changes in the Cu metal but significant increases in most other peaks indicating there is most likely a penetration of some moisture throughout the interface. The extended heat treatment caused dramatic increases in the oxide peaks but also significant increases in the Cu_nCN peaks. This suggests, that unless excessive oxidation is involved, there may be an increase in Cu bonding with polyimide during the period of its migration and diffusion into the polyimide. Under these dry heat conditions the oxidation may not occur which suggests that the actual oxidation may involve water or moisture. It is proposed that when this diffusion zone becomes sufficiently thick, probably 10 to 20 atomic layers, it may become sufficient unstable and stressed to permit the beginning of oxidation.

CONCLUSIONS.

The above results clearly support previous references pertaining to surface analysis of Cu exposed to VCIs and to the bonding of Cu on polyimide. Through use of ISS and SIMS, we have offered new information which provides more detail pertaining to the bonding characteristics, the detailed multilayered structure of the Cu surface and the polyimide interface and the effects of heat treatment on this surface. We have offered a more detailed hypothesis of the progressive mechanisms which may affect degradation and oxidation of this interface through heat treatment and a possible role of moisture in the reactions. A very strong correlation of surface purity and contact resistance was also shown for devices where use of techniques other than ISS and SIMS were not sufficiently sensitive to provide enough accuracy for the correlation. In addition, these data were sufficiently precise to offer quantitative treatment by multiple regression analysis to enable prediction of performance by measurement of surface chemistry. Extensive testing with Cu and Ag protected with VCIs clearly indicates that use of these materials in the contact assemblies and manufacturing process would dramatically reduce the build up of the oxide on the relay contacts to help eliminate erratic relay performance. Unfortunately, this work also provides very strong indication that standard Cu test coupons contain an organic coating which is extremely difficult to remove to perform acceptable surface analysis experiments.

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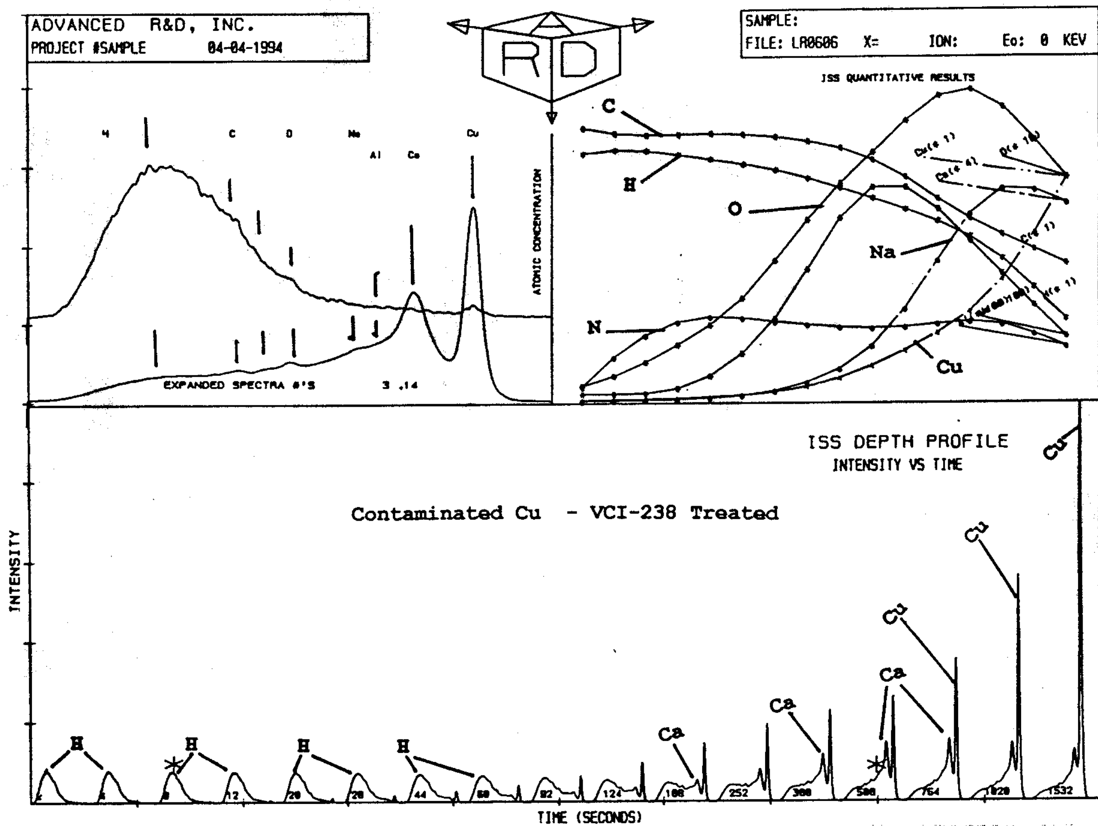
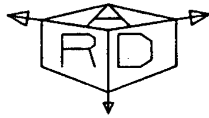


Figure 1. Typical ISS depth profile of VCI-316 treated Cu plated sample showing Good performance. Raw spectra plotted sequentially from left to righ on botton half from surface to about 100 Angstroms. Expanded individual spectra appear iin upper left and atomic concentrations of the elements are plotted in the upper right corner.



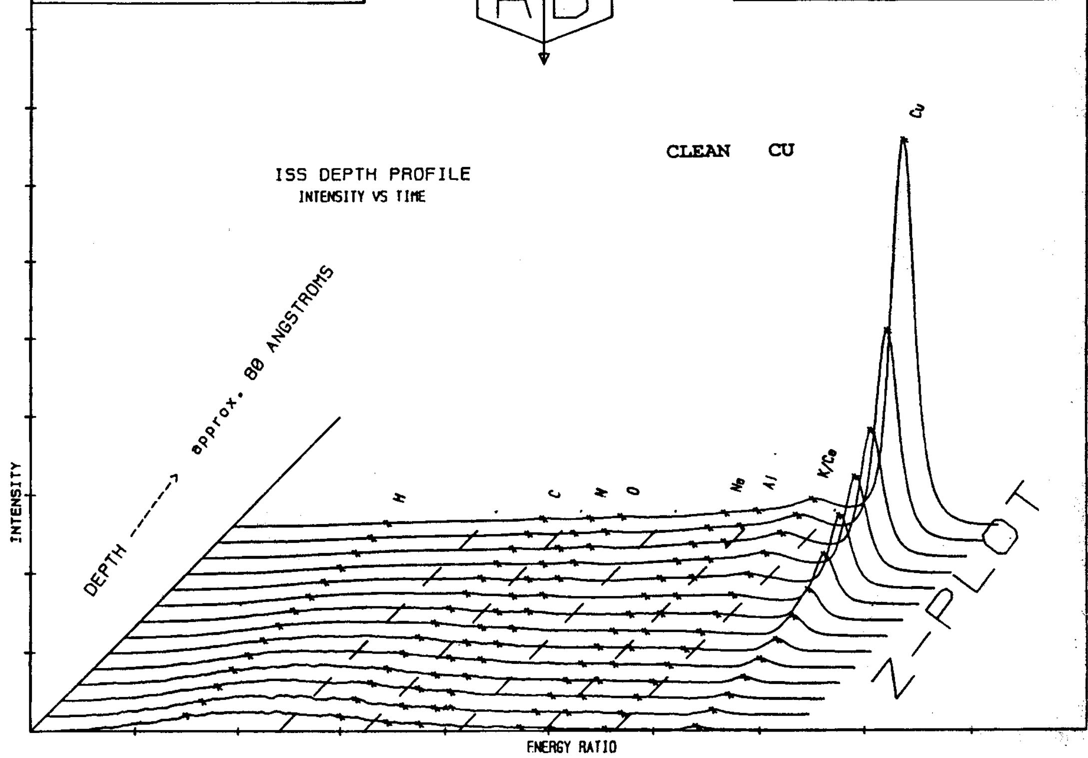


Figure 2. ISS Depth profile of raw spectra obtained from VCI-316 treated Cu Plating showing poor lubricity. Three dimensional aspect shown by "Z-Plot".

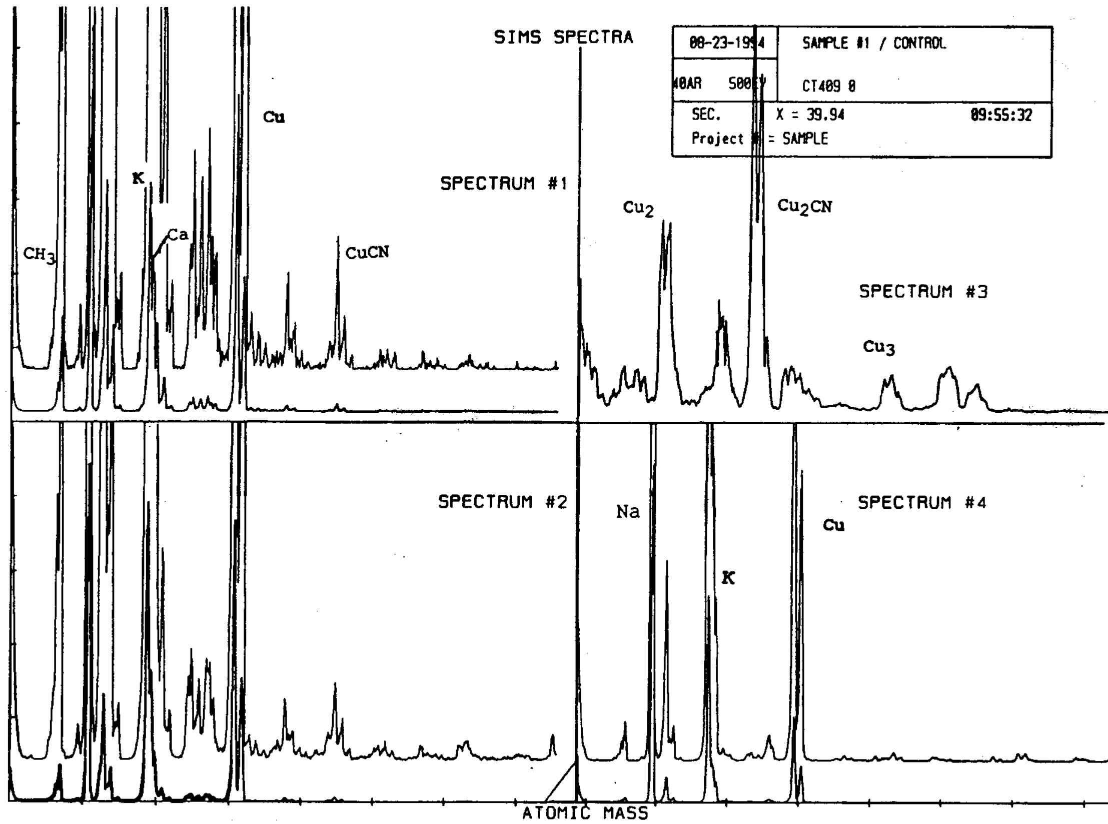


Figure 3. Typical SIMS spectra obtained for a VCI-316 treated Cu plated sample showing Good performance. Each spectrum represents a greater depth into the surface. Spectrum 3 shows the mass range from 100 to 250.

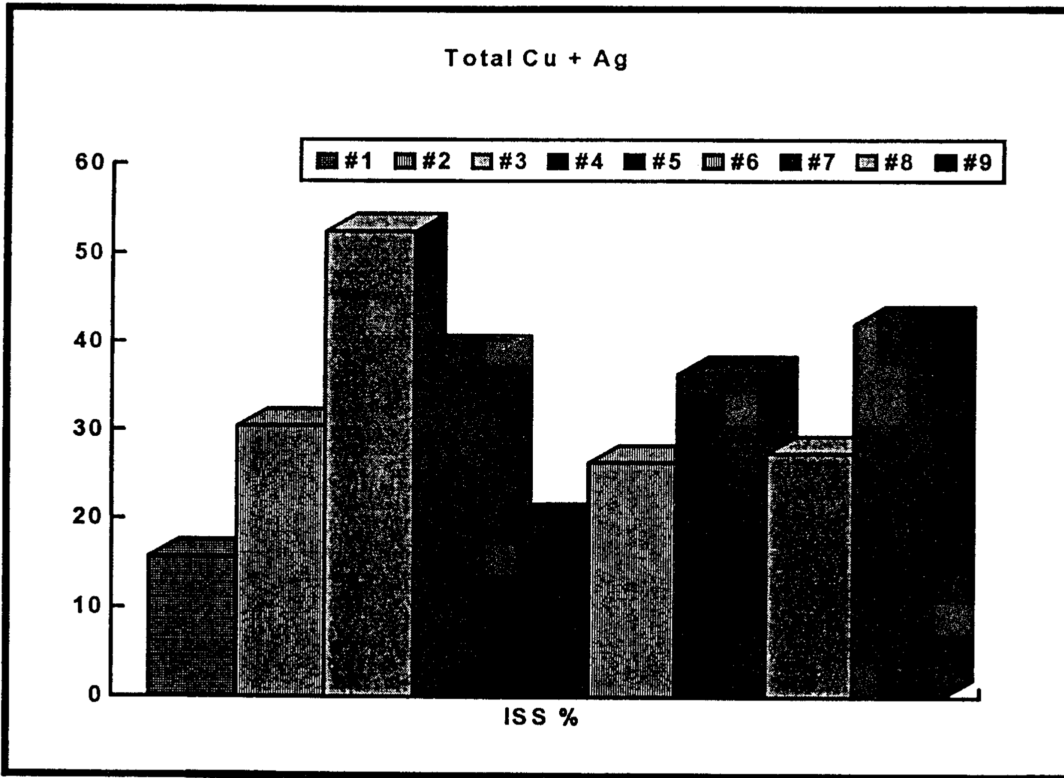


Figure 4. The total atomic contentrations of Cu + Ag within the first 10 Angstroms of several low voltage electrical contacts.

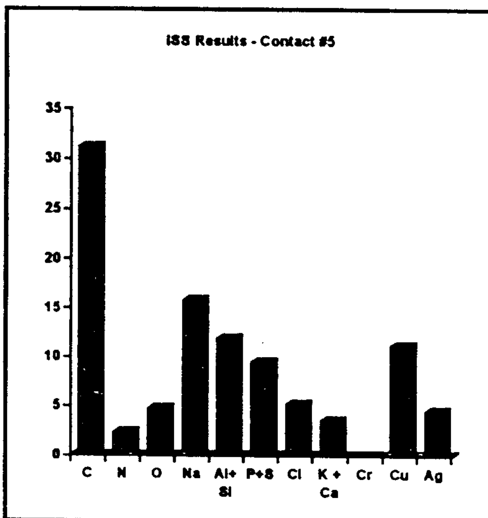


Figure 5. Typical atomic concentrations of Cu Ag contact #5 as obtained from ISS at a depth of about 10 Angstroms.

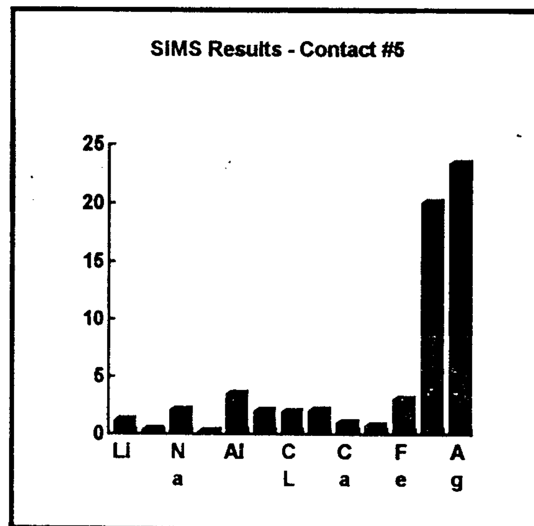


Figure 6. Typical atomic composition of Cu/Ag contact #5 as obtained from SIMS at a depth of about 10 Angstroms. H,C,N and O are excluded.

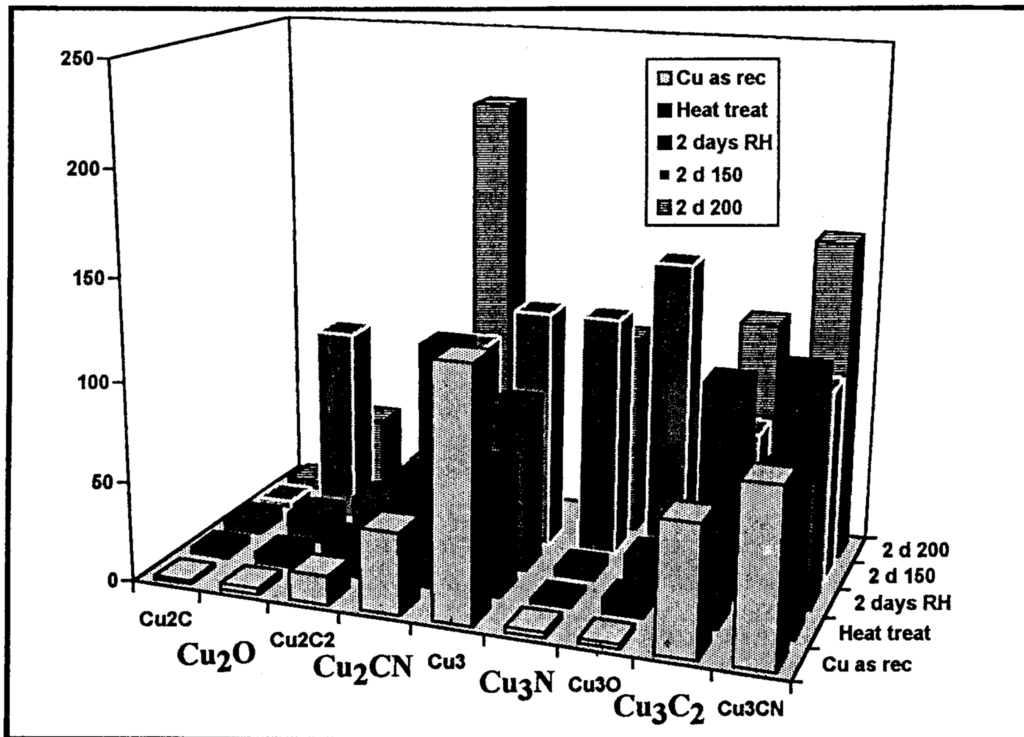


Figure 7. BAR graph of relative peak intensities of ion clusters from SIMS analysis of treated Cu coated polyimide. All peaks are normalized to the intensity of Cu_2 as 1000. Ar at 500 eV across 30 mm^2.