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RELIABILITY OF MULTILAYER COPPER/POLYIMIDE

Clarkson University

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13. ABSTRACT (Maximum 200 words)

The reliability of copper/polyimide (PI) multilayer structures was analyzed and found to depend on processing and environmental conditions. Copper films were deposited by thermal evaporation and patterned by contact lithography. Preimidized PI2590-D polyimide films were spin coated over the copper with upper layers deposited as required. While the electrical characteristics of the multilayer structures generally behaved as expected, the softening of the underlying PI films led to observation of film buckling and dielectric breakdown in some samples. Consequently, alternate low temperature plasma and laser techniques for depositing copper on PI films, instead of PI films on copper, were explored to improve the reliability of the resulting Cu/PI multilayer structures. Copper films were deposited on PI substrates by radio frequency (13.56 MHz) plasma-induced reduction and excimer laser-induced ablation of copper formate. While the Cu/PI interface appears clean, the reduction of the formate was not complete with some residual carbon contamination in the copper film. Several methods for improving the purity of the Cu films were investigated. Diamondlike carbon (DLC) films are excellent barriers for the diffusion of Cu in Cu/Si structures. DLC films, due to their excellent compatibility with PI, may play a similar useful role in Cu/PI structures and improve their reliability.

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EVALUATION

Copper metallization is a potential replacement for the electromigration prone aluminum alloys currently used in integrated microelectronic circuits. Copper has lower resistivity and more resistance to electromigration than does aluminum. However, these positive copper properties are offset by the lack of a protective passivating oxide layer and processing difficulties. This project addressed the reliability problems of increased corrosion susceptibility and copper diffusion characteristics through insulators. The authors present observed contamination problems with possible solutions published elsewhere.

The authors conclude that interfacial adhesion will be a major reliability problem which may be solved by diamondlike carbon as a diffusion barrier. The diamondlike carbon films are also compatible with polyimide films adding to their usefulness for integrated circuits.

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RELIABILITY OF MULTILAYER COPPER/POLYIMIDE STRUCTURES

ABSTRACT

The reliability of copper/polyimide (PI) multilayer structures was analyzed and found to depend on processing and environmental conditions. Copper films were deposited by thermal evaporation and patterned by contact lithography. Preimidized PI2590-D polyimide films were spin-coated over the copper with upper layers deposited as required. Underlying polyimide films were observed to soften during deposition of subsequent polyimide films. While the electrical characteristics of the multilayer structures generally behaved as expected, the softening of the underlying PI films led to observation of film buckling and dielectric breakdown in some samples. Consequently, alternate low temperature plasma and laser techniques for depositing copper on PI films, instead of PI films on copper, were explored to improve the reliability of the resulting Cu/PI multilayer structures.

Copper films were deposited on PI substrates by radio frequency (13.56 MHz) plasma-induced reduction and excimer laser-induced ablation of copper formate. While the Cu/PI interface appears clean, the reduction of the formate was not complete with some residual carbon contamination in the copper film. Several methods for improving the purity of the Cu films were investigated. While the results of these investigations have been published in several papers, there was not adequate time to address reliability concerns. However, it was discovered that diamondlike carbon (DLC) films are excellent barriers for the diffusion of Cu in Cu/Si structures. DLC films, due to their excellent compatibility with PI, may play a similar useful role in Cu/PI structures and improve their reliability, as was originally proposed by us.

INTRODUCTION

Polyimide (PI) is well suited to meet many of the strict requirements of both electronic packages and semiconductor devices. Polyimide was first introduced in Japan as an interlevel dielectric for multilayer metal transistors and as a final passivation[1]. More recently, the semiconductor industry is increasingly using PI as an interlevel dielectric/passivation in the manufacture of multilayer VLSI device structures[2,3,4,5], especially in silicon and metal MOS technology. Polyimides may also be used as adhesives and circuit board components[3].

Several characteristics of polyimide make this organic polymer attractive to the modern semiconductor industry. Chemical resistance and high temperature stability[5] allow for a variety of process conditions. Other advantageous properties include the adherence of PI to silicon and various metals[6], planarization[6], patternability[2], and low dielectric constant[4]. However, several problems are associated with the use of PI as an interlevel dielectric. A major concern is the changing electrical characteristics of PI due to the degradation of the polymer by hydrolysis and water absorption[7,8]. Strong interaction of copper with PI at the interface, leading to polymer degradation and subsequent diffusion of Cu into PI, is also a concern[9, 10, 11].

Reliability of polyimide films has been studied on several different levels using many approaches. Ion motion, polarization, water absorption, dielectric properties, and film stresses were studied. Based on these investigations, varying levels of confidence in the ability of PI to perform as an interlevel dielectric were reported[2,3,4,12]. Ion motion in polyimide films was studied by Brown[13] and Neuhaus[14] by measuring the hysteresis in the C-V characteristics at a high temperature in polyimide MOS parallel plate capacitors, from which the mobility and concentration of ions present in PI can be determined. Neuhaus reported no transfer of sodium ions to the oxides at PI cure temperatures[14].

Changes in polarizability and the dielectric constant have also been studied as factors in PI reliability. A useful dielectric will polarize and not break down until an electric field of **200 kV/cm** (20 mV/nm) is applied. It has been reported that the degree of polarizability is dependent upon PI structure[2]. The crosslinks and side chains inherent in rigid structures slow the polarization process. The ability of polyimide to absorb and desorb water is well documented [2,3,4,7,12], with up to a 4.2% by weight of water being absorbed [3,20,21,22]. Over 70% of this weight increase was found to occur in the first several minutes[3]. Jensen reported a linear change in the dielectric constant of PI, from 3.1 to 4.1 with increasing relative humidity. The absorption of too much water can lead to dielectric breakdown.

Water adsorption can be measured in several ways: change in surface I-V characteristics, gravimetrically, dissipation factor measurements, and standard C-V measurements. Senturia has suggested the use of parallel-plate capacitors with perforated upper electrodes[15]. A reduction in the quantity of moisture absorbed by polyimide films were found when using the Langmuir-Blodgett technique for the fabrication, replacing conventional spin-coating[16].

Mechanical properties and adhesion of PI films were also investigated. Several authors reported favorable results to various stress tests[2,4,12,16]. The fracture strength of PI was reported to be five times greater than the stresses developed by Si due to thermal expansion[4]. Several researchers reported that the relief of the polymer surface defines adhesion[17], while Rantell[18] reported adhesion is due exclusively to the formation of metal-polymer bonds.

The Cu/PI interface was studied using Transmission Electron Microscopy(TEM), Auger Electron Spectroscopy(AES), X-ray Photoemission Spectroscopy(XPS), and Fourier Transform IR(FTIR) Spectroscopy. However, the processes occurring at the molecular level in the interface are still not well understood. Auger spectroscopy was used to determine the interfacial interaction of Cu and PI. Shih et al.[9], used AES depth profiling to investigate the thickness of the Cu/PI interaction zone. The interface conditions were found to be process dependent, with no interaction for a forming gas cured film to a 40 nm interaction zone for a polyimide cured in a high oxygen environment. Nitrogen environment cures produced high levels of Copper oxide in PI. Shih et al., also report that the Cu/PI interaction thickness is dependent on PI thickness, with the thicker films showing no interaction, leading to the conclusion that oxygen diffusion through the PI layer promotes degradation.

AES was used to examine ultrathin PI films spun on Cu substrates. Chambers et al.[23] reported that water played a major role in the oxidation of copper films. Titanium was determined to be an excellent barrier against copper diffusion into PI[11]. XPS spectra were obtained by several researchers[9,11,23-25]. Haight [24] determined that the initial copper interaction is with PMDA, possibly due to the metal d-orbitals reacting with the lowest unoccupied molecular orbitals(LUMO) of the PI. Mack et al. [25] reported initial copper interaction with the planar imide ring followed by copper oxidation, with no Cu-ODA interaction. However, copper was also reported to react predominantly with ODA or the oxygen present in ether[26-28].

The degradation of PI in the presence of copper is well documented [9,29-31]. Shih et al., used XPS to study the degradation of PI films cured in various ambients. It was found that complete PI degradation and subsequent production of volatilized products occurred on the surface of copper. The extent of degradation is heavily dependent on the oxygen content in the curing atmosphere. PI degradation may be caused by cuprous/cupric ions diffusing into the polymer and reacting with hydroperoxides, formed when PI in contact with copper is oxidized, causing their decomposition[29-33]. FTIR has been used to gain a better understanding of the interfacial reaction of Cu with PI [9, 32].

Jellinek et al.,[34] reported that the polyimide oxidation is initiated by the catalytic action of CuO releasing tertiary hydrogens. This produces radicals which reduce copper oxide. The reduction of copper oxide decomposes ROOH groups in the polymer film. The oxidized copper is then reduced to Cu^+ by the decomposition of more ROOH. The radicals produced during the reduction and oxidation of copper then lead to heightened polymer oxidation.

Kelly et al.[32], have used FTIR to study the degradation of PI in contact with copper. They report that oxygen initiated production of nitriles and carboxylate salts by ring cleavage in the polymer. The process yields a fused ring structure based on the produced nitriles. Others, using FTIR, have found that the formation of carboxylate in the bulk phase increased during curing. The formation of carboxylate and nitrile at the interface was also investigated[35, 36], but is not yet fully understood.

Several methods of sample preparation for cross-sectional TEM were reported[9, 10,38]. Shih et al., and Legoues et al., used mechanical sanding to a thickness of 50 microns followed by ion milling to electron transparent thickness, while Kowalczyk et al., used ultramicrotoming. Copper oxide precipitates in PI films were seen by these techniques[9,10,37,38]. However, several authors noted the absence of Cu precipitates if Cu was deposited after PI curing[37, 38], suggesting that CuO reacts with polyamic acid during curing[38]. LeGoues et al., used cross-sectional TEM to document the strong effect of copper deposition temperature and rate on precipitate formation. Low deposition rates caused a greater penetration of copper into the PI, while higher deposition rates tended to produce islands of Cu on the PI surface. Higher temperatures enhanced the diffusion of copper into the polymer.

In this work, Cu/PI thin film interactions were investigated over a variety of environments and process conditions. Copper films were deposited on silicon by thermal evaporation and patterned using contact photolithography. Si/Cu structures were coated with pre-imidized PI (DuPont PI12590-D) using two methods - spin-coating for planar surfaces and slow immersion for patterned structures. Multilayer capacitance structures were characterized using cross-sectional scanning and transmission electron microscopy. The long-term effect of various ambients on the capacitance of these structures and the effect on capacitance of subsequent layers of PI on patterned copper were studied. The Cu/PI interface in Cu/PI/Cu structures was investigated using SEM, TEM, and Auger depth profiling.

Deposition of copper films on PI substrates by rf plasma-induced reduction and excimer laser induced ablation of copper formate was investigated as an alternative technique for the preparation of more reliable copper/PI structures. The copper films were characterized by Auger analysis and x-ray diffractometry. The results from these investigations appear promising even though there is some residual carbon contamination from the formate in the copper films. The technique has been applied to deposition on polystyrene and PTFE as well as to silicon and glass substrates. The results have been published in several papers [39-42].

EXPERIMENTAL STUDY

A modified Mikkros thermal evaporation system was used for the deposition of copper films. Films were deposited on 1.5 inch square silicon substrates using 99.99% pure 10 μm Cu powder (Alfa Products, Inc.). Deposition pressure was less than 10^{-4} Torr. The copper A 0.75 μm thick film was deposited in about 7 to 8 min. The films were annealed for 2 hours at 250°C in vacuum.

Film thickness was determined using a Dektak profilometer A Keithley Instruments Model 220 current source and Model 617 electrometer were used for electrical measurements.

A Solid State Equipment Corporation spin-coater was used for the spin-coating of PI films (DuPont preimidized PI2590-D). The PI was dissolved in N-methyl pyrolidone (Aldrich) in a 70:30 ratio by weight and film thickness was calibrated with spin speed and confirmed by profilometry. The spin-coater was mounted in a steel cage and isolated with styrofoam to minimize vibration. Two methods were employed to coat the Si/Cu structures with PI films. In the first method, a film was formed by spinning about 2 mL of PI on the Si/Cu structure at 3500 rpm for 60 seconds, followed by curing in vacuum at 150 °C for 45 minutes and a final bake at 250 °C for 1.25 hours. These Si/Cu/PI structures were used for long term capacitance measurements. An alternate method was used to coat the nonplanar patterned copper structures to ensure that the PI films are free of pinholes. Pinholes are caused by trapped air bubbles at the PI/Cu interface which rise and expand during curing. Very slow immersion of the Si/Cu structure into a 100ml PI solution allowed time for the advancing solution/solid contact line to penetrate the uneven topography and prevent bubble entrapment. The back of the substrate was cleaned with toluene/NMP mixture(Aldrich) and the spin-coating procedure was followed. The resulting structures were used for measuring the change in capacitance over a number of curing cycles.

On some of these structures a second layer of copper, with somewhat smaller dimensions, was deposited through a metal mask. This size differential was necessary to make electrical contacts for subsequent capacitance measurements. The Cu/PI structure was placed on the metal mask centered with respect to the lower layer. The lower copper layers were 2.4 cm x 3.5 cm, with the upper layer being a 1.6 cm square. The 0.75 μm thick copper films were patterned using contact lithography [Kasper Instruments, Inc. Model #OMA-500] and Microposit S1400 series (Shipley) positive photoresist, using a mask provided by IBM. The patterned films were imaged using a PME optical microscope (Olympus) using polarized light.

Characterization using Electron Microscopy

Transmission Electron Microscopy

To prepare TEM samples, a small oval section of a finished Cu/PI/Cu structures was covered with epoxy, which was allowed to harden at 60°C for 3 days. The hardened epoxy sections were peeled off the silicon substrate to obtain an epoxy/Cu/PI/Cu structure. A second coat of the epoxy was applied to the back side and cured, thus obtaining the Cu/PI/Cu section sandwiched between two layers of hardened epoxy. Transverse and parallel samples were cut with a Sorvall ultramicrotome. A Philips EM-201 TEM was used to analyze the sections. Micrographs were produced at 15,000 to 100,000X.

Scanning Electron Microscopy

The Cu/PI structures were halved by scoring the back side of the silicon with a diamond scribe and embedded in Castolite Resin(Buehler) or surface mounted on SEM studs. The resin embedded samples were allowed to harden for two days at room temperature. The sectioned chip and hard resin were sanded to a smooth fine surface, going from 200 grit paper to 0.05 micron Alumina powder on a polishing wheel. The polished top surface was gold coated and SEM micrographs were taken at 750 to 2500X. The surface mounted samples permitted topographic analysis while the sectioned and polished samples were studied by EDAX for the location of copper.

PI Film Capacitance Measurements

For these measurements, the polyimide was partly etched in an O_2 plasma. The upper copper layer was masked using a glass slide, exposing a thin outer section, allowing an etch back of PI to the lower layer of Cu. Capacitance of these structures was measured using a Philips PM2525 Multimeter. After the initial measurements, the structures were placed in three different environments for 1000 hours. The three environments were air at room temperature, a silica gel desiccator at room temperature, and a constant temperature (85°C) and controlled humidity (85% RH) chamber (Tenney). The chamber temperature was monitored with an internal thermocouple.

Electrical measurements were made immediately following the O_2 plasma etching for the multilayer structures. The samples were placed in a vacuum oven at 120°C for 1.5 hours to remove solvent and water absorbed during the wet etching processes. Two upper layers of PI were applied separately using 5 mL of PI in NMP. The layers were spun at 3500 rpm for 60 seconds and cured using the procedure previously described. Capacitance was measured initially and after the application of each PI layer.

Auger Analysis

Si/Cu/PI/Cu and Si/Cu/PI/Cu/PI structures were characterized by Auger electron spectroscopy at Rome Laboratory, under the guidance of Dr. Lois Walsh. The top 2 - 3 micrometers of polyimide in samples with upper PI layers were etched with a CF_4/O_2 plasma at 50 W rf power and 100 mTorr for 40 min in a Plasmod (Teagal Corporation) reactor. The structures were cut into 1 in^2 pieces using a diamond scribe and cleaned with compressed nitrogen before Auger analysis. Base pressure in the Auger sample chamber was 1.8 x 10[illegible] Torr and during depth profiling the pressure was 2×10^{-8} Torr.

All profiling was done using ion gun sputtering. Beam voltage and current were varied to minimize charging, with the maximum usable voltage and current utilized for each individual sample. The probe voltage was varied from 3 - 5 kV with a current of 25 - 75 nA. The ion gun sputtering voltage was varied from 3 - 5 kV. Oxygen was used as the feed to the ion gun. Atomic concentration profiles of copper, silicon and carbon were obtained as a function of sputtering time. Carbon was used to symbolize the PI, which is 58% C, and silicon was used to detect the presence of SiO_2.

The internal scanning electron microscope of the SAM was used for documenting visible faults responsible for device failure. These micrographs were taken at magnifications of 100 - 300X. A copper map of a fault was produced, utilizing another internal feature of the PHI600. The map is a computer generated photograph which is dependent on the signal strength of a specific element.

RESULTS AND DISCUSSION

Resistivity Measurements

The resistivity of the annealed copper films was found to average twice that of bulk copper, perhaps due to the presence of impurities and small grain structure. The unannealed films had a resistivity that was higher than that reported from in situ measurements of CVD deposited Cu films[45]. The higher resistivity may be due to oxidation of the copper films. The polycrystalline structure in the thermally evaporated films may also result in grain boundaries perpendicular to the current flow, contributing to the higher film resistivity.

Long-Term Capacitance Measurements

A: Desiccator Ambient

Five Cu/PI/Cu samples were left in a silica gel desiccator at room temperature, each for an average of 1000 hours. Four samples showed the expected initial value for the dielectric constant of polyimide[4]. All four had an initial decrease of 5% in the dielectric constant, followed by a constant but slightly fluctuating value. The initial small decrease in the dielectric constant is probably the result of dehydration of the PI film in the desiccator. The remaining sample had a larger than expected capacitance which increased with time. The final value was 50% greater than the original. Perhaps delamination occurred.

B: Air

Five Cu/PI/Cu structures were left at room temperature in air for approximately 1000 hours. They had initial dielectric constant values consistent with published results[4], and these values fluctuated about 3 - 5% from the initial values over time. Since the humidity in the room was not controlled, small changes in the total mass of water absorbed by the polyimide films may have occurred leading to these fluctuations.

C: Humidity Chamber

Five more Cu/PI/Cu samples were placed in a Tenney humidity chamber for an average of 925 hours. The chamber was operated at 85°C/85 % r.h. All the samples showed initial dielectric constant values consistent with previous measurements. Initially, the dielectric constant decreased sharply. After this initial drop, the dielectric constant fluctuated slightly. The sharp drop in dielectric constant coincided with noticeable oxidation of the upper copper film, reducing the capacitor area by as much as 75 - 85%. The value of the dielectric constant obtained using the reduced area is consistent with other measurements.

Change in Capacitance Over Several Curings

A set of sixteen Cu/PI/Cu samples were vacuum dehydrated and coated with two serial overlayers of polyimide to form Cu/PI/Cu/PI/PI structures. The dielectric constant of the first layer in the Cu/PI/Cu structure was remeasured following deposition and cure of each subsequent PI overlayer. Three distinct types of behavior were observed: a) a large increase in the dielectric constant, ranging from 78 - 3200%, b) a decrease in the dielectric constant of approximately 80%, and c) dielectric breakdown.

Mobility of the patterned upper copper layer relative to the lower copper film explains all three observations. The large increase in the dielectric constant was due to film buckling (wrinkling) which generally increased the PI layer thickness and reduced the area of the electrodes. The large decrease in the apparent dielectric constant corresponded to separation of parts of the upper electrode with loss of electrode area and/or conductivity and a decrease in observed capacitance. Dielectric breakdown resulted from shorting between the layers and appearance of other faults.

Fault Documentation

All the samples that failed after the application of upper layers of polyimide structures contained faults visible under high magnification. The effect of the defects on the dielectric constant was enhanced by the application of additional layers of polyimide, causing a previously benign defect to induce dielectric breakdown. The spin-coating of polyimide solution over the upper copper layer leads to potential migration of copper (as part of the wrinkled film) and enhancement of dielectric breakdown. Figure 1 is a photomicrograph at 100X of a blanket Cu/PI/Cu/PI structure which was not spun out and baked immediately but spun and

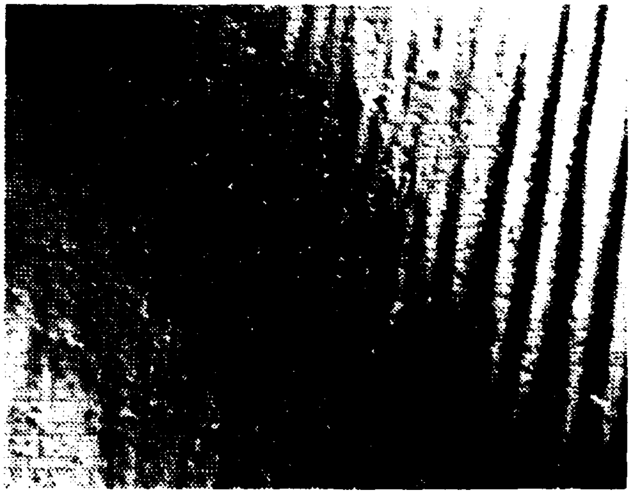

Figure 1

allowed to age 1 hour at room temperature. Note the wrinkled and pocked upper copper film

Scanning Electron Microscopy

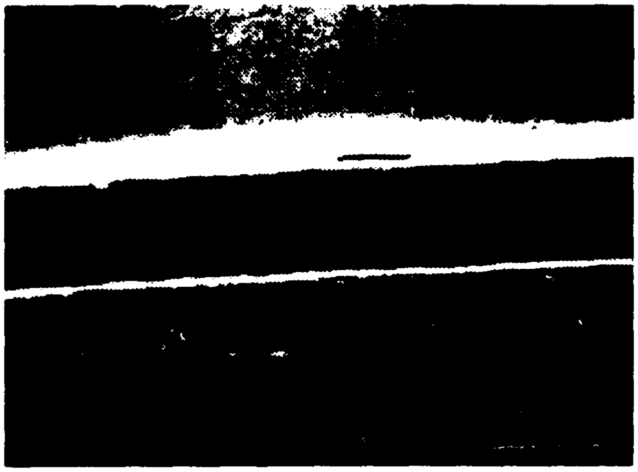

Figure 2

Cross-sectional scanning electron microscopy was used to determine the quality of the copper/polyimide interface. The micrographs were taken at magnifications of 750X - 2100X, and an example is shown in Figure 2. A clean, well defined interface can be seen. Copper films appear bright, with the polyimide present in the dark central region between the two copper layers. The intermediate shade is the epoxy used for mounting the structure. The Cu/PI/Cu film was separated from the silicon substrate in several places along the length of the cross section. This separation may be a function of sample preparation techniques or poor adhesion at the metal/polymer interface.

Transmission Electron Microscopy

Cross-sectional transmission electron microscopy was used to determine the abruptness of the Cu/PI interface in the Cu/PI/Cu structures. The copper films bordering the polyimide layer were unpatterned. Figures 3 is an electron micrograph taken at a magnification of 100,000 and electron beam voltages of 80 kV. The micrograph shows one dark area representing copper. The lighter areas bordering the copper consist of polyimide and the epoxy employed in sample preparation.

Figure 3

The ability of copper to diffuse into polyimide and form islands or clusters is well documented[3,23,24]. There is a 15-20 nm region at the Cu/PI interface where small amounts of copper appear. The presence of copper in the polyimide and the thinning of the film suggest enhanced polymer degradation due to contact with copper.

There is little doubt that some of the copper present in the polyimide film is due to atomic diffusion. However, copper diffusion is noticeable on one side of the film only, leading to the belief that this diffusion occurred during spin-coating and curing of the polyimide film. The absence of copper at the upper polyimide interface is reasonable since the copper was deposited on the cured polymer and did not come in contact with the resin/solvent system. It has been reported that copper has a significantly lower diffusion coefficient when deposited on cured polyimide than when deposited on uncured PI. With a diffusion coefficient of 10^{-15} cm^2/s[43] in cured PI, copper should not be present at the depth of 20 nm in the upper PI/Cu interface.

Auger Analysis

Two structures were depth profiled using Auger spectroscopy. The samples profiled were a Cu/PI/Cu/PI structure that failed upon application of the upper PI layer, and a Cu/PI/Cu structure. Figure 4 shows the lower copper layer in a Cu/PI/Cu structure. The copper/polyimide interface is not sharp. The lower copper layer shows an area of copper penetrated by the polyimide, as seen in the gradually falling copper peak. This would correspond to deposition of polyimide onto a rough copper surface or the diffusion and precipitation of copper oxide in the immediate layer of polyimide. The profiles from other samples show no noticeable difference in copper penetration between the Cu/PI/Cu/PI and Cu/PI/Cu structures, with some copper in each polyimide layer. Details are available in ref. 44.

LASER AND PLASMA DEPOSITION OF COPPER FILMS

To improve the reliability of the copper/PI structures, two new low temperature techniques for the deposition of copper films on PI substrates were investigated [39-42]. One was the excimer laser-induced deposition from copper formate targets and the second was the 13.56 MHz radio frequency (rf) plasma-induced reduction of spin-coated copper formate films. While the results appear promising, the reliability of the resulting Cu/PI structures could not be explored further due to limited time and the absence of continued funding.

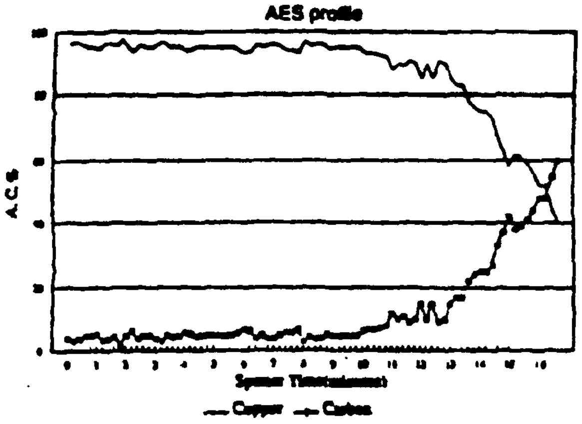

Figure 4

Deposition of Copper Films by Plasma-Induced Reduction of Copper Formate [39,40]

The deposition technique consists of the preparation of a thin film of copper formate precursor by spin-coating, followed by reduction of the precursor to metallic copper in a hydrogen rf plasma. Since the reduction process is carried out at a low substrate temperature (20°C to 30°C), temperature sensitive polymeric materials can be used as substrate materials. Several polymeric substrates including polystyrene, Kapton®, polytetrafluoroethylene (PTFE), as well as silicon and glass were used as substrates. The efficiency of the process and the product quality are dependent on the nature of the precursor and the spin-coating process. This technique is especially suitable for large area deposition of very thin Cu films.

A PlasmaTherm reactor(model 730/740) and a multi-port reaction chamber were used in the deposition studies. A 600 W generator supplied the rf power at 13.56 MHz through an automatic matching network. The electrodes were cooled by an ethylene glycol-water mixture. The deposition chamber was pumped by a Roots blower backed by a mechanical pump to a base pressure of about 1 mTorr. The pressure, regulated by an exhaust valve controller, was monitored by a capacitance manometer. The flow rate of hydrogen was controlled by a mass flow controller (MKS 5850E).

An additional, smaller plasma reactor, fabricated from a six-way stainless steel cross was also used in the deposition studies. This reactor used the control panel and the pumping units of the PlasmaTherm system. The rf power was coupled into the discharge volume through a U-shaped stainless steel tube (o.d. 1/8"), through which the cooling liquid was circulated. A much higher power density compared to the PlasmaTherm reactor could be maintained in the chamber due to the reduced discharge volume.

The polymeric substrates were pretreated in an appropriate (O_2, H_2, Ar) plasma prior to the spin-coating process. The plasma treatment improved the wettability and the copper formate solution could be applied easily. Thin uniform films of copper formate were prepared on the plasma pre-treated substrates by placing a few drops of saturated aqueous copper formate solution on it and turning the substrate at a slow speed to spread the solution. An infrared heating lamp was used for evaporating the water from the spreading solution. The spinning speed was increased once most of the water evaporated. The entire coating process took about a minute.

The copper formate coated substrates were placed on the powered electrode and reduced to copper in a low pressure hydrogen plasma discharge at room temperature. Typical process conditions were 0.2 to 2 Torr pressure, 100 sccm H_2 flow rate and 200-600 W of rf power. The substrates were left in the plasma discharge for about 15 minutes.

An optical microscope was used for observing the deposit morphology. Crystallinity of the films was measured by an X-ray diffractometer (Siemens model D500). Elemental analysis and depth profiling of the deposition product were performed by Auger electron spectroscopy (Perkin-Elmer PHI 600 equipped with a 04-303 differentially pumped ion gun) The electron gun was operated at a voltage of 3 kV and 100nA to obtain the Auger survey and the ion gun was operated at 2 kV and 3 μA for sputtering. The copper films sputtered at a rate of about 9 nm/min under these conditions.

The copper films deposited by this technique have morphological features similar to those of the starting spin-coated films. Therefore, the spin-coating process is critical and the presence of impurities or particulates effects the final morphology of the films. While the films obtained from aqueous copper formate solution were smooth, copper chloride films contained needle like structures, similar in shape to $CuCl_2.2H_2O$ crystals. However, the morphology of the copper chloride films was greatly improved when ethanol was used as the solvent instead of water, but it was still not as good as that of copper formate films. Thus the choice of the solvent is critical in determining the final film morphology.

Films obtained by plasma reduction of copper formate as well as copper chloride showed low resistivity(~10-15 μΩcm), with films prepared in the smaller plasma reactor having the highest conductivity. Even though the film morphology was comparatively poor, films obtained with copper chloride precursor showed comparable resistivity. The copper films obtained by the reduction of copper formate on all the polymeric substrates passed the "Scotch tape test", but those obtained on silicon substrates and with copper chloride showed comparatively poor adhesion. The characteristic peaks of copper formate are absent in the X-Ray diffractogram of copper films, indicating that the reduction was complete.

The Auger depth profiles of copper films on Kapton* substrates showed that while the surface layers are rich in copper(~92-95%), there was some carbon contamination at greater depths. The films contained negligible amount of oxygen throughout the depth of the film. The Auger profile of a Cu film on a Si substrate was found to be essentially similar to that obtained with Kapton* as the substrate, indicating that polyimide is not the source of carbon in the film. It appears that the removal of carbon by hydrogen was not as efficient as the removal of oxygen.

In a hydrogen plasma, dissociation of copper formate may proceed by reaction with hydrogen, as shown below:

$$Cu(HCOO)_2 + H_2, H \rightarrow Cu + C + H_2O + CO_2 \qquad (1)$$

$$m\,C + n\,H \rightarrow C_mH_n \qquad (2)$$

The presence of carbon at greater depths in the films indicates that the second reaction does not completely volatilize the carbon. Under the conditions used, the occurrence of this reaction appears to be limited to a depth of 20 - 25 nm from the surface due to either slow hydrogen diffusion into the film or slow product hydrocarbon diffusion out of the film. Thus, it may be possible to reduce the carbon content in the bulk of the films further either by longer reaction times or by using a higher substrate temperature. The increased temperature should facilitate hydrogen diffusion into the film as well as removal of product hydrocarbon from the bulk of the film. Alternately, the cycling of process gas between oxygen and hydrogen plasma may also lead to enhanced removal of carbon from the bulk. These two methods for the improvement of the film composition were investigated further and the results are presented in ref. 40. Also, a microwave discharge containing a higher concentration of reactive hydrogen radicals should enhance diffusion fluxes to the substrate and improve film composition.

Conventional lithographic techniques may be used to obtain patterned copper films by this process. However, since copper formate is soluble in water, a photoresist that can be developed in a non-aqueous solvent has to be used. Thus a negative photoresist like Riston may be used for wide lines. For finer line patterns, dry processing of the exposed photoresist may be necessary.

Deposition of Copper Films by Laser Ablation of Copper Formate [41,42]

Copper was also deposited by reactive ablation of copper formate using a partially focused excimer (KrF, λ = 248 nm) laser beam in a flowing hydrogen gas or a hydrogen plasma ambient. Copper was deposited on a substrate located in close proximity to the target copper formate. A key feature of this laser deposition process is the laser-induced decomposition of target material, followed by evaporation/sputtering of the products and reaction in the gas phase. In contrast to the conventional laser evaporation techniques[45] using organometallic compounds, a much smaller fluence was adequate (the laser focus spot on the target was about 20 mm^2). This technique is somewhat similar to the activated reactive evaporation[46] method.

An excimer laser (Lambda Physik Model EMG 101) operating at 248 nm (KrF) was used in the deposition studies. The laser was operated at a repetition rate of 10 Hz with an average pulse energy of 300 mJ, measured with a Gentec joulemeter. The beam was focused to a 20 mm^2 area on the copper formate target using a fused silica bi-convex lens (f=150 mm). The laser beam entered a parallel plate plasma reactor (PlasmaTherm Model 730) through a fused silica window. Rf power was supplied to the chamber through the upper electrode(0.28 m dia) which was cooled by a water/ethylene glycol coolant mixture circulated from a heat exchanger. Heating of substrates placed on the lower, grounded electrode was achieved by a resistance heater and controller.

The copper formate target was placed at an angle of 45^0 to the incident beam, while the substrate to be coated with copper film was placed making a smaller angle (20^0-40^0) with the target. The reducing atmosphere of a hydrogen plasma or a hydrogen gas was maintained during the deposition. The discharge was sustained by 600 W of rf power and a hydrogen flow rate in the range 35-500 sccm at 2 Torr. The average pulse energy of the laser beam during the deposition process was held constant at about 300mJ, corresponding to a fluence of 1.5 J/cm^2 on the target. The deposition area on the substrate surface under these conditions was about 3 cm^2. Subsequent to deposition, the films were exposed to a hydrogen plasma at 200^{0}C for 30 minutes. The plasma was maintained with 200 sccm of hydrogen at a pressure of 3 Torr and 600 W of rf power. All the samples were stored in a vacuum desiccator prior to analysis.

The copper films displayed excellent morphology. The deposit thickness was in the range of 0.2 to 0.5 μm. The resistivity of the films, measured by a four-point probe, improved from 18μΩcm for the as-deposited films to 5μΩcm after plasma treatment. This value is comparable to that reported for copper films deposited by other techniques but higher than the 1.9μΩcm reported by Kaloyeros et al[47] with higher substrate temperatures in the range of 300 - 450^{0}C.

The X-Ray diffractogram of the copper films contains only the peaks of copper and the peak intensities increased after plasma treatment. AES depth profiles of as-deposited and plasma treated copper films show that while the as-deposited films contained small amounts of carbon and oxygen as impurities, the hydrogen plasma eliminated most of the oxygen from the bulk of the film. However, the reduction in the carbon content was not as appreciable.

Copper formate absorbs the 248 nm UV radiation of the excimer laser strongly, which leads to dissociation. In the absence of a hydrogen atmosphere, it is possible to envision several reaction pathways for the dissociation of the formate [41]:

$$2\,Cu(HCOO)_2 + hv \rightarrow Cu_2O + 2\,CO_2 + 2\,CO + H_2O + H_2 \quad (3)$$

$$Cu(HCOO)_2 + hv \rightarrow Cu + 2\,CO_2 + H_2 \quad (4)$$

$$Cu(HCOO)_2 + hv \rightarrow Cu + CO + CO_2 + H_2O \quad (5)$$

$$Cu(HCOO)_2 + hv \rightarrow CuO + C + CO_2 + + H_2O \quad (6)$$

The dissociation of the hydrogen molecules themselves is perhaps catalyzed by the metallic copper or its oxides in the laser heated zone. The hydrogen atoms for this reduction are also available from the ambient when a hydrogen discharge is maintained. Thus, complete reduction of copper formate might be a two step process. Alternatively, hydrogen may take part in the reduction of the copper formate on the surface of the target under the influence of the excimer laser pulse according to the following reactions:

$$Cu(HCOO)_2 + H_2, 2\,H + hv \rightarrow Cu' + C + CO_2 + H_2O \quad (7)$$

$$2\,Cu(HCOO)_2 + H_2, 2\,H + hv \rightarrow 2\,Cu + C + 2\,CO_2 + CO + 3\,H_2O \quad (8)$$

It is not known what intermediate reaction steps, if any, may be involved in each of the above reactions. Also it has not been determined if one or more of these reactions dominate.

The deposition rates of the various vapor phase species generated by the laser pulse depend on their rates of nucleation, which in turn depend on supersaturation among other things. Since the vapor pressure of carbon is much lower than that of copper and oxides of copper, evaporation of carbon is the least probable [41]. However, volatilization of carbon can occur by the formation of high vapor pressure oxides of carbon. Hydrocarbon species having high vapor pressures may also form if sufficient reactive hydrogen is available. The plume generated by a laser beam targeted on copper formate will, therefore, comprise of mostly Cu, CuO, Cu_2O, H_2O, CO_2, CO, C_mH_n and H species. Of these, oxides of carbon, hydrocarbons, and water have relatively high vapor pressure and less supersaturation. Consequently, a cold substrate placed in the laser plume will be coated preferentially with copper and oxides of copper due to their higher supersaturation. Hence, films deposited by laser decomposition in the presence of hydrogen should consist of mostly Cu and O. The very small amount of carbon in the films confirms that a significant amount of carbon is being transformed into high vapor pressure oxides or hydrocarbons.

In order to study the role of the ambient during the deposition, films were deposited in the absence of the glow discharge. Since the plasma environment is richer in highly reactive species, the films deposited in plasma ambient were expected to display better quality. However, the films deposited with and without the plasma ambient displayed almost identical compositions, indicating very little influence of the plasma environment on the deposition process. Several plausible conclusions may be drawn based on this observation[41]:

- The residence time of the evaporated species in the laser plume (estimated as 10^{-5} s based on the measured velocities of species ejected from polymer surfaces by excimer laser ablation) is not sufficient for gas phase reactions to occur prior to the condensation on the substrate.
- The nature of the processes occurring during the laser pulse and afterwards must be such that atomic hydrogen or excited hydrogen molecules are not essential for them.
- The reactivity of the carbon containing species and the oxides of copper, generated during the laser pulse, with molecular hydrogen is high enough to facilitate their conversion into high vapor pressure species.
- Freshly formed oxides of copper are sufficiently energetic to be reduced by molecular hydrogen to atomic copper, accounting for the low oxygen content in the films deposited in the absence of plasma.
- The minimal impact of the plasma discharge on the carbon concentration in the deposited films suggests that the formation of oxides of carbon, and not hydrocarbon formation, is the primary process for the consumption of carbon.

To further understand the role of hydrogen during the deposition process, copper films were deposited in a pure argon atmosphere under conditions that were otherwise identical to those with hydrogen. The AES depth profile of such a film[41] shows that it contains similar amount of carbon but a higher concentration of oxygen. The similar amounts of carbon in the films deposited with or without hydrogen ambient supports the argument that volatilization of carbon occurs primarily due to the formation of oxides of carbon. Hydrocarbon formation, if any, should be minimal. The crystallographic orientation of the formate molecules in the target film must be such that the hydrogen and oxygen necessary for the volatilization of carbon are supplied by the dissociating formate molecules themselves. The films deposited in the absence of hydrogen have a higher concentration of oxygen, since, in the presence of argon, the decomposition of formate resulting in CuO or Cu_2O is not succeeded or accompanied by reduction to metallic copper.

The laser deposition technique described here, when combined with laser patterning or other forms of patterning, should be an efficient way of creating sub-micron copper patterns over large areas. Ability to process uneven topography as well as temperature sensitive substrates is one of the advantages of this technique. Furthermore, this deposition method should be more efficient than direct laser-writing of the pattern, especially for complex sub-micron patterns. The minimum feature size for copper metallization obtained so far by direct laser-writing is only about 5 microns.

DLC Films as Barrier Layers for the Diffusion of Cu [42]

In an interesting extension of these studies, it was observed using Rutherford backscattering studies (RBS) that copper silicide is formed at the Cu/Si interface even when the deposition temperature is, nominally, only 40°C. However, the same RBS study also confirmed that the presence of 140nm thick diamondlike carbon (DLC) film at the Cu/Si interface completely prevented the formation of the copper silicide even after heating to 300°C for one hour. Since DLC films are much more compatible with polymers, this result suggests very strongly that similar diffusion resistance, and presumably improved reliability, can be achieved for Cu/PI multilayer structures by the "appropriate" inclusion of DLC layers.

SUMMARY AND RECOMMENDATIONS

Initially, Cu/PI multilayer structures were fabricated using thermal evaporation and spin-coating techniques. The Cu/PI interfaces in these structures were characterized using transmission and scanning electron microscopy. The lower magnification scanning electron micrographs showed a smooth interface with no **bulk** copper diffusion. However, cross-sectional TEM demonstrated the inconsistency of the polyimide film near the interface. This, in conjunction with diffusion, accounts for the presence of copper in a 15-20 nm region of PI near the interface.

Auger depth profiling showed that for Cu/PI/Cu structures, undistorted films are evident. However, when overlayers of PI were spun onto the Cu/PI/Cu structures, the lower PI layer was affected by solvent permeation and flow with concomitant wrinkling of the copper films. This led to the appearance of carbon in the copper films. The presence of copper in the polyimide, verifying the TEM results, was also observed. The continuation of this study is recommended. The cause of the structural changes found through the thickness of the polyimide film should be investigated, along with the role of this change on copper diffusion.

It was felt that reliability may be improved by depositing Cu films on PI substrates, instead of PI films on copper. Low temperature rf plasma reduction and laser ablative deposition methods were investigated. In these studies, copper formate was used as the source of copper. While the films were rich in copper (~95%), they were contaminated with carbon and oxygen. Several variations of the deposition methods were utilized to improve purity[39-42]. Finally, it was discovered that DLC films offer excellent resistance for the diffusion of copper and prevented the formation of copper silicide even after heating to 300°C for one hour[42]. It is expected, since DLC films are much more compatible with polyimide, that a similar benefit and improved reliability can be achieved by the inclusion of DLC films in multilayer structures of Cu and PI.

Based on these results, investigation of the reliability of such Cu/DLC/PI structures, prevented here by lack of time, is strongly recommended.

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