Angle-resolved x-ray photoelectron spectroscopy comparison of copper/Teflon AF1600 and aluminum/Kapton metal diffusion

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We use angle-resolved x-ray photoelectron spectroscopy to study metal diffusion in the cases of evaporated Cu on Teflon AF1600 and evaporated Al on Kapton polyimide. Although minimal diffusion is essential for long term stability and reliability of microelectronic devices, neither the presently used Al/polyimide nor any new candidates, such as Cu/fluoropolymer, has been sufficiently characterized and compared. Diffusion constants for infinite dilution in both cases were evaluated supposing Fickian diffusion as a first approximation. For the Al/polyimide interface, we found little, if any, diffusion after annealing for 30 min at 150 °C. In the case of the Cu/Teflon AF1600 interface, the same annealing induces significantly more copper diffusion. These results are discussed with respect to the diffusion equation, and it is shown that the experimental results indicate a concentration-dependent diffusion coefficient; experimental values, measured at infinite dilution of metal in polymer, are also reported. © *1998 American Institute of Physics.*
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I. INTRODUCTION

The drive for higher circuit speeds has led to the examination of new materials for the replacement of the presently used Al/polyimide technology, which provides signal delay times too long to be used in ultralarge scale integrated (ULSI) and giga scale integrated (GSI) applications.[1] New materials, having lower resistivities and lower permittivities, are required for decreased delay times, $\tau = R \times C^1$, where R is the resistance along the line the signal travels and C is the capacitance of the surrounding dielectric. Additionally, these new materials and their associated metallization techniques must meet several conditions for long-term stability and reliability.[2] Interfacial adhesion, diffusion, and electromigration are among the more important physical characteristics, which can seriously affect the choice of a particular material or technological process.

Metal diffusion into an insulator during manufacture or use life strongly affects the stability of electronic circuits. When the deposited metal diffuses into the insulator substrate, (1) the metallic layer thickness decreases, which leads to an increased resistivity, (2) the effective insulator thickness and permittivity are modified, changing the circuit impedance, and (3) the probability of a fatal short-circuit increases, affecting the overall reliability of the device.

Higher conductivity metals such as Cu and lower permittivity insulators, such as fluoropolymers, are an excellent combination for future high speed chips.[3] Additionally, Cu has better electromigration characteristics than the presently used Al, while the Teflon AF series of fluoropolymers have the advantage of being soluble in perfluorinated solvents, allowing spin-on deposition. However, the relatively high diffusion of Cu into polymers such as polyimide[4] raises the question of whether its diffusion into fluoropolymers such as Teflon AF1600 is tolerable compared with the generally accepted minimal diffusion of Al into polyimide. While the extent of such diffusion has never been quantitatively measured, the lack of any large changes in the dielectric properties of Al/polyimide microelectronic devices over their use life indicates it to be acceptable.

Angle-resolved x-ray photoelectron spectroscopy (XPS) is a nondestructive technique based on an electron emission signal intensity which has a sufficiently strong and defined angular dependence on the analyzed depth.[5] Since the instrumental developments and new discoveries at Uppsala by Siegbahn *et al.* in the 1960's,[6] this method is frequently used in surface-sensitive depth profiling studies.[5] The in-depth distribution of the chemical composition of a sample can be obtained by analyzing the intensity of photodetected electrons recorded at different take-off angles.

The aim of this paper is to compare metallic diffusion in Cu/Teflon and Al/polyimide systems using XPS. First, we will demonstrate our approach, which uses an algorithm based on Laplace transforms to treat angle-resolved data[5] in order to obtain depth profiles and diffusion coefficients. A secondary aim is to show that this method is capable of following *changes* in depth profiles due to metal diffusion. Here we have found that Cu diffuses noticeably into Teflon AF1600 even after 30 min at 150 °C. All the profiles found were similar in form to those found previously for several metals on polymers of various chemical structures.[7–10] The diffusion constants evaluated in this paper and those estimated by other methods[7] give gratifyingly similar values. The single annealing condition used in this preliminary study (150 °C/30 min) was meant to show the feasibility of our approach. A more detailed study is in progress.

II. EXPERIMENT

A. Materials

Teflon AF1600 was purchased from DuPont as a solution containing 12% solids. After 75% further dilution in

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Sigma Fluorinert FC-77, the solution was filtered and spun onto a clean Si wafer at 3000 rpm. The samples were subsequently heated in stages to 330 °C for 20 min, as recommended by the manufacturer,[11] in order to remove solvent and improve layer uniformity. A sample thicknesses of 1–2 μm was obtained.

The polyimide was a previously untouched 50 μm sheet of DuPont Kapton H, which was cleaned, exposed to a nitrogen jet to remove dust, and introduced into the preparation chamber. Special care was taken during sample manipulation to prevent further chemical contamination, such as by fingerprints.

B. Metallization

Metal depositions were performed in the preparation chamber of our spectrometer, using a modified Waldrop & Grant electronic beam evaporator.[12,13] Electrons, thermally emitted from a tungsten filament, were accelerated in the electric field between the filament and the evaporation source. Their kinetic energy, converted into heat, was used to evaporate the metal. The thickness of the deposited metal was measured by a SYCON quartz crystal monitor. At a preparation chamber pressure of 2×10^{-7} Torr, an electron beam power of 5 kV×1.2 mA gave a deposition rate of 0.2 Å/s. After rate stabilization and a preconditioning time of 2 min, depositions of 30 Å were carried out for both Cu and Al. Some samples were subsequently annealed for 30 min in the preparation chamber of our spectrometer, at a temperature of 150 °C. Both annealed and nonannealed samples were directly transferred to the analysis chamber without atmospheric exposure.

C. XPS analysis

Angle-resolved XPS was performed using a VG ESCALAB 3 Mark II with a nonmonochromatic Mg K_α source. Our preliminary studies showed that the experimental error in the peak area measurements was $\pm1.4\%$ when the sample was not removed from its positioner. The error in angle positioning was estimated as $\pm1°$, while the perpendicular take-off angle (90°), used as reference, was established with an absolute error of $\pm3°$.

In order to avoid polymer degradation during analysis, XPS spectra were accumulated at a low x-ray source power (10 mA and 10 kV).[14] The vacuum in the analysis chamber was maintained at 10^{-9} Torr. The take-off angle for each sample was varied from 30° to 90° from the sample plane, at increments of 10°.

High resolution spectra were analyzed after a Shirley background subtraction. The total areas of the Cu $2p_{3/2}$, Al $2p$, and C $1s$ envelopes were measured and used as initial experimental data for the angle-resolved study. These experimental intensities are related to the take-off angle by the equation[5]

$$I_{\exp}(\theta)=(I_0/\lambda_{\text{eff}})\int_0^\infty c(z)\exp(-z/\lambda_{\text{eff}})dz, \quad (1)$$

where $c(z)$ = atomic concentration distribution, I_0 = constant, chosen so that $I_{\exp}=I_0$ for $c(z)=1$, λ_{eff}

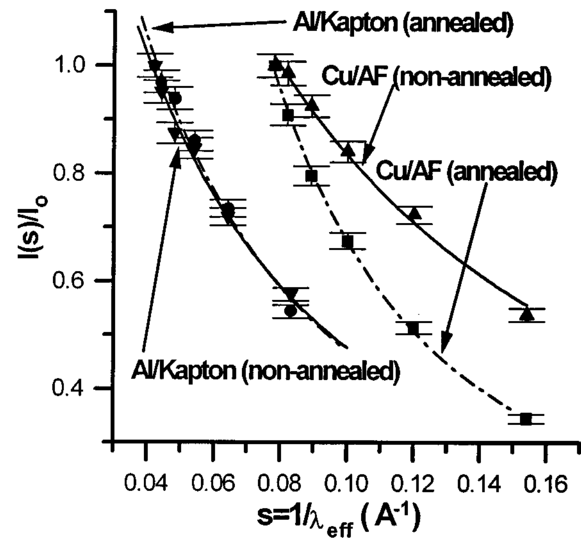

FIG. 1. XPS intensities, $I(s)$, $s=1/\lambda_0\sin\theta$, for copper and aluminum.

$=\lambda_0\sin\theta$=effective escape depth, and λ_0=inelastic mean free path (IMFP) for electrons of a defined energy, calculated from Powell's empirical formula,[15] being 13 Å and 24.2 Å for copper and aluminum, respectively.

Referring to Eq. (1), $I(1/\lambda_{\text{eff}})=\lambda_{\text{eff}}I_{\exp}(1/\lambda_{\text{eff}})$ is proportional to the Laplace transform of the atomic concentration distribution $c(z)$. The solution leads to the normalized atomic concentration $C(z)=c(z)/c_{\max}$, given by

$$C(z)=\mathscr{L}^{-1}I(1/\lambda_{\text{eff}}), \quad (2)$$

where $\mathscr{L}^{-1}$ is the inverse Laplace transform. Because the correct forms of the fitting functions are not known, *a priori*, one must *heuristically* assume a physically meaningful distribution for $c(z)$ with a minimum of parameters and use this profile to calculate the form of the most reasonable fitting function.

III. RESULTS

A. In-depth distribution

Diffusion processes are generally described by a second order differential equation known as Fick's second law, $\partial c(z,t)/\partial t=D\partial^2c(z,t)/\partial z^2$, where $c(z,t)$ is the concentration of the diffusing material, D is the diffusion coefficient, assumed to be independent of the spatial coordinate z, and t is time. Assuming that the diffusion is Fickian, as a first approximation and the initial distribution is a metallic layer, buried at a depth z_0 under the surface, we found that $c(z,t)\propto[\exp(-(z-z_0)^2/4Dt)+\exp(-(z+z_0)^2/4Dt)]/\sqrt{Dt}$. Differentiation shows that this is, indeed, a solution of Fick's second law; the boundary conditions are also satisfied, since $\partial c(z,t)/\partial z=0$ for $z=0$ (there is no mass flux through the interface) and $c(z,t)\rightarrow0$ as $z\rightarrow\infty$. Because there is no analytical form for the Laplace transform of this solution, it cannot be used as a fitting function for the intensities $I(1/\lambda_{\text{eff}})$ of the Cu $2p_{3/2}$ (copper/Teflon AF1600) and Al $2p_{2/3}$ (aluminum/Kapton) XPS spectra which, for both nonannealed and annealed samples, are shown in Fig. 1. A

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TABLE I. Fitting parameters for copper, aluminum, and carbon XPS intensities.

Thermal treatment	Interface	Fitting parameter $P1$	Fitting parameter $P2$	D (cm^2/s)
Nonannealed	Cu/Teflon	15.629 65	0.093 08	3.86×10^{-18}
	Al/Kapton	26.329 55	0.049 09	1.16×10^{-17}
Annealed	Cu/Teflon	32.609 07	0.083 84	2.8×10^{-17}
	Al/Kapton	27.722 97	0.050 43	1.4×10^{-17}
C 1s	Cu/Teflon	0.93	2.8×10^{-3}	
	Al/Kapton	0.99	-1.5×10^{-3}	

more tractable formula, such as $C(z)\propto\exp[-(z/P_1)^2]\times\exp(P_2 z)$, closely approximates the *real* solution. Its Laplace transform $\mathscr{L}C(z)=I(s)$ is given by[16]

$$(\sqrt{\pi}/2)\exp[P_1(s-P_2)/2]^2\operatorname{erfc}[P_1(s-P_2)/2], \tag{3}$$

where s is the argument of $I(1/\lambda_{\text{eff}})$, $s=1/\lambda_{\text{eff}}$.

Equation (3) was used to fit the experimental data presented in Fig. 1. The values of the fitting parameters P_1 and P_2 are presented in Table I. Figure 2 shows the normalized atomic concentration in-depth distributions, which are the inverse Laplacian transforms of the functions (3). Similar distributions were previously found.[10–13]

For the C 1s spectral intensities, the same procedure was used in an effort to determine the carbon distribution in the probe depth. Unlike the copper case, the exponential distribution $C_c(z)\propto\exp-(P_2z/P_1)$ was found to be the simplest function fitting the data, $\mathscr{L}C_c=1/(P_1+P_2s)$.[16] The small values of the $|P_2/P_1|$ ratio, presented in Table I, indicate that the carbon distribution is essentially uniform, within experimental error, as expected for this small amount of evaporated metal.

B. Diffusion coefficients

The small amount of deposited copper, initially buried, broadens during annealing. The general approach to estimate

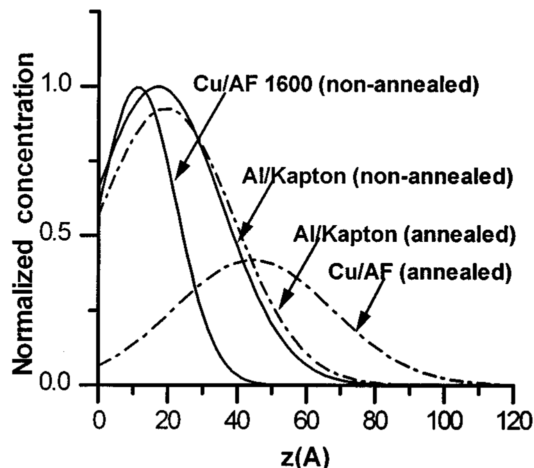

FIG. 2. Normalized atomic concentration distributions, $C(z)$, showing metal diffusion into Teflon AF1600 and Kapton polyimide.

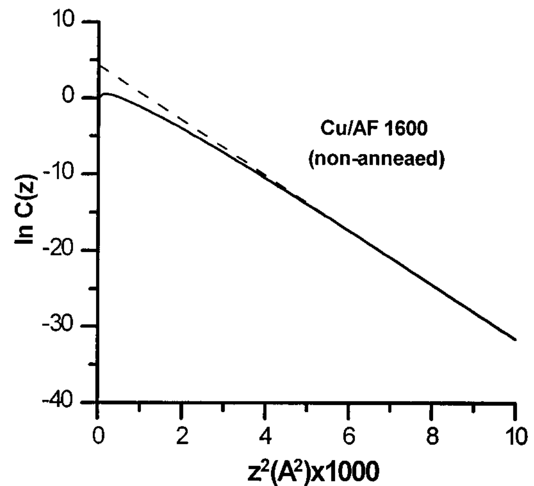

FIG. 3. Ln $C(z)$ vs z^2 for Cu/AF1600 (nonannealed) interface; the slope, $-1/4Dt$, was used to evaluate the diffusion coefficients.

the diffusion coefficients[7,17] is to neglect the initial parts of these profiles and apply the simple solution of Fick's law only for the tails of the curves

$$c(z,t)\propto\frac{1}{\sqrt{\pi Dt}}\exp\left(-\frac{z^2}{4Dt}\right), \tag{4}$$

where D is the diffusion coefficient and t is the annealing time.

Using Eq. (4), D can be determined from the slope $-1/4Dt$ of the ln C vs z^2 plot, seen in Fig. 3. The diffusion coefficients, evaluated in this fashion, are presented in Table I.

IV. DISCUSSION

The experimental results for Al/polyimide show, within experimental error, little or no diffusion. Buried layerlike distributions ($\sim$10–20 Å deep) have already been found for metals deposited on several polymers.[7–10] This study confirms that our method is simple and gives results which compare well with those of other workers.[7–10] The results suggest that the heat of metal condensation is sufficiently intense to create a buried layer under the polymer surfaces for the limited amount of metal used here. We found that, while aluminum diffuses little in Kapton on annealing, the diffusion of copper in Teflon AF1600 is substantially larger for the same annealing conditions.

The estimated diffusion coefficients for Cu/AF1600, shown in Table I, have values similar to those previously found for metals in other polymers.[7] To investigate the validity of the diffusion coefficients values, D were calculated as a function of depth. The $D(z)$ curves, presented in Fig. 4, show that the diffusion is larger near the surface. It is the asymptotic value, at infinite dilution of metal in polymer, which is obtained from plots such as those in Fig. 3, and reported in the literature as being of practical interest.

A computer-assisted one-dimensional simulation, based on the algorithm described by Crank,[18] was performed to determine the profiles $c(z,t)$ for various $D(z)$, correspond-

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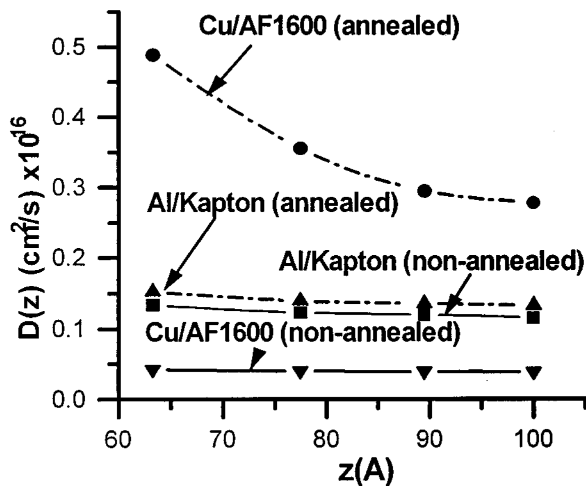

FIG. 4. Variation of experimental diffusion coefficients as a function of depth, $D(z)$.

ing to different annealing temperatures. These numerical calculations show that the peak *shift* on annealing, observed in Fig. 2, can be qualitatively explained only assuming a position-dependent diffusion coefficient, $D=D(z)$ increasing gradually towards the surface. This supports our findings of a position-dependent diffusion coefficient, as shown in Fig. 4.

The uncertainty at the sample surface was limited by the surface roughness. The average roughness, determined by atomic force microscopy at several 100×100 nm regions was estimated at 10–15 Å for both polymers, which is the same range as the initial buried depth of Cu/Teflon AF1600, in Fig. 2. We are, therefore, uncertain as to whether this particular initial profile is that of a buried layer or simply due to surface roughness. However, as with previous determinations,[7–10] there is no doubt that all other profiles are those of buried layers.

V. CONCLUSION

Depth profiles were obtained from angle-resolved XPS data, using an algorithm based on the Laplace transform. Diffusion coefficients were determined for Cu in Teflon AF1600 and Al in Kapton polyimide. The buried layerlike diffusion profiles found are similar to those found by other methods[7] and supports the validity of our approach. A more detailed approach showed that, in fact, the diffusion constants decrease with depth. This variation depends on annealing temperature and may explain the profile shift, which has not been considered in previous papers. The reported diffusion coefficients are shown to represent only asymptotic values at infinite dilution. A comparison of the relative concentration curves (Fig. 2) reveals that, while Al undergoes little diffusion into Kapton polyimide on annealing, Cu diffuses noticeably into Teflon AF1600. Although further study is necessary, these preliminary findings suggests that a diffusion barrier may eventually be necessary in the case of the Cu/Teflon AF1600 interface.

ACKNOWLEDGMENTS

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