

DIFFUSION AND GETTERING SIMULATIONS OF ION IMPLANTED COPPER IN POLYIMIDE.

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Recently we have observed gettering of ion-implanted copper in polyimide films. In this paper we have modeled the thermal process by incorporating the experimentally obtained dual activation energies into conventional diffusion models. The lower activation energy (small diffusant/substrate interaction) is associated with free atomic diffusion, while the larger activation energy (large diffusant/diffusant interaction) corresponds to diffusants with their movements restricted by clustering within the interaction distance of similar species. Computer simulations of the process validate the observed gettering mechanism via clustering. Experimental high temperature diffusion results are also in agreement with the simulation of the subsequent diffusion of clusters.

INTRODUCTION

In recent years, polymers have found increasing use in integrated circuits and printed circuit board applications due to their thermal stability and usefulness as insulators and protective layers. Metal/polymer structures have become a particularly important area of investigation. There is, however, a lack of proper understanding of interdiffusion mechanisms at metal/polymer interfaces.

Recent studies on metal/polymer interfaces have provided only rather undefined or even elusive diffusion parameters, specially the activation energy, frequency factor, jump length, correlation factor, etc. The results are notably different for the various techniques used to investigate such properties.

One RBS (Rutherford Back Scattering) study of diffusion of Cu films deposited on Dupont Kapton H^o found that diffusion was thermally activated with an activation energy of about 0.5 eV when the films were heated in air. Similar films heated in vacuum exhibited a rather constant diffusion coefficient independent of temperature¹.

Separate TEM (Transmission Electron Microscopic) studies have revealed the formation of small Cu clusters at the Cu/polyimide interface and Fickian type diffusion in the polymer².

A recent direct measurement of Cu diffusion into polyimide by means of low energy ion sputtering in combination with a radiotracer technique reported a two part penetration profile into the polymer: an initial non-Fickian steep drop in the diffusion activity and a Fickian tail into the polymer. The former was attributed to cluster formation via surface diffusion of the Cu tracer during deposition³.

In all of the above, the Cu was deposited as a surface film. With ion implanted Gaussian profiles of Cu in polyimide we have observed a three-part activity of the implanted Cu ions, namely: (1) a low temperature (below 460 K) diffusion with an activation energy of 0.41 eV, (2) a high temperature (above 525 K) activation energy of 1.9 eV, attributed to cluster motion, and (3) an intermediate range of temperatures over which self-gettering was observed, in which the half width of the profile decreased and the peak concentration increased⁽⁴⁻⁶⁾.

A summary of these results is shown in Figure 1. By comparison it can be concluded that our low temperature results are in fair agreement with other results obtained by various techniques, while there are large discrepancies in the high temperature results. It is believed that the cluster diffusion is only observable at the low concentrations resulting from the ion implantation technique.

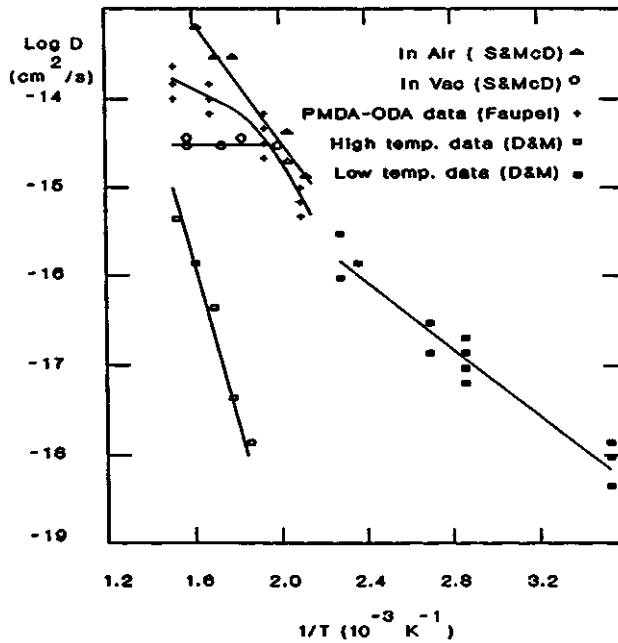


Figure 1. Arrhenius plots of the Cu diffusion constant in polyimide. Data replotted from Shanker and MacDonald¹, Faupel et al³ and Das and Morris⁶. The D&M high temperature data are attributed to clusters.

Clustering at the film surfaces has been attributed to the relatively weak chemical interaction between Cu and polyimide, in contrast to the significantly higher Cu/Cu interaction energy. In the case described below, with a lack of abundance of Cu atoms (dilute dose), clustering was rather unexpected.

Although the mechanism responsible for the gettering is still not completely understood, there is a second order relaxation process over the gettering temperature range. The polyimide phase transition which would account for such a phenomenon could also initiate clustering by a change in bulk and/or interfacial energies⁶.

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The gettering process has also been investigated through computer simulations of diffusion where we have included the Cu/Cu interaction in the diffusion model, thus allowing copper atoms to be trapped by other atoms/clusters within the interaction or capture distance. Simulation results validate the gettering process under the above assumptions and reveal several interesting dependences of the process itself upon the initial implant profiles and doses.

High temperature diffusion was simulated by allowing individual atoms to migrate freely (smaller activation energy) while clusters were treated as units. The migration of such units was allowed at a reduced frequency (higher activation energy) in a conventional diffusion model. Simulation results are in good agreement with the experiments.

THEORY

Diffusion

An atom in the lattice, with its normal thermal vibration frequency $\nu \sim 10^{13}$ Hz about the equilibrium site, strikes the potential barrier E_m , ν times per second. However, an atom needs an adjacent vacancy for a successful jump. The frequency of jumping f_m to a neighboring lattice site with Z nearest neighbors is given by

$$f_m = Z \cdot \nu \cdot \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

where $E_a = E_m + E_v$ is the activation energy of diffusion and E_v is the formation energy of a vacancy⁷.

From macroscopic diffusion, we have a net flow of atoms across a plane per second dN/dt , provided there exists a concentration gradient dC/dx in the region around that plane. dN/dt can be expressed as

$$\frac{1}{L^2} \frac{dN}{dt} = -D \frac{dC}{dx} \quad (2)$$

With a cross-sectional area L^2 and d as the nearest neighbor distance, a three dimensional diffusion coefficient D is defined as

$$D = \frac{f_m d^2}{6} \quad (3)$$

Equation (2) is known as Fick's Law of Diffusion. Several features about these expressions are of particular interest as they provide a means of measurement of the diffusion of atoms in the direction favored by the concentration gradient and hence of the activation energy of diffusion.

The Distribution Profile

The implant profile of copper can be approximated as Gaussian with a peak concentration $N_p(t)$ at range R_p and a half-width $W(t)$. The solution to the diffusion equation is particularly simple provided the diffusion constant D is concentration independent⁸. The concentration $N(x, t)$ at a depth x after a diffusion time t is expressed as

$$N(x, t) = N_p(t) \cdot \exp\left(-\frac{(R_p - x)^2}{2 \cdot W(t)^2}\right) \quad (4)$$

Also $N_p(t)$ and $W(t)$ are related by

$$N_p(t) = \frac{0.399Q}{W(t)} \quad (5)$$

where Q is the total concentration per unit area.

The Rutherford Backscattering Spectroscopy (RBS) profile 1 of Figure 2 shows an as-implanted distribution of 220 keV ion implanted Cu in polyimide. Profile 2 of Figure 2 shows the gettering effect with an increase in $N_p(t)$ and a decrease in $W(t)$ with time. The profile has the appearance of a distorted Gaussian. Profile 3 of Figure 2 shows a typical distribution at 623 K, with a higher $W(t)$ and a lower peak than profile 2, showing a subsequent high temperature diffusion.

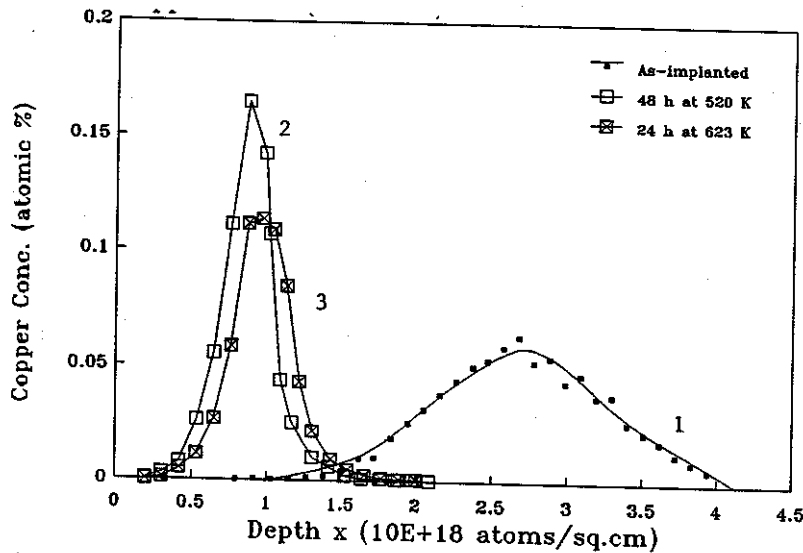


Figure 2. Concentration of Cu in VN-type Kapton as a function of depth and thermal treatment [experimental].

For a Gaussian distribution of free atoms, half-widths $W(t_1)$ and $W(t_2)$ provide a measure of the diffusion constant, given by

$$D = \frac{W(t_2)^2 - W(t_1)^2}{2(t_2 - t_1)} \quad (6)$$

which implies that the half-width increases with time due to diffusion of the atoms. Consequently the peak concentration decreases in order to conserve the total number of atoms in the Gaussian as shown by Equation (5), and can similarly provide the means to determine D.

Application of Equation (6) to profiles 2 and 3 of Figure 2 gives rise to a negative value of D. The simple diffusion represented by Equations (5) and (6) is not an adequate representation of the migration processes.

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Initial Distribution

Due to the randomness of the distribution process, a certain number of the as-implanted atoms are expected to be implanted within interaction distances even for dilute dosage. Therefore, the initial distribution is expected to contain both free atoms and atoms in clusters. Since the number of available sites in a lattice is fixed, one can expect the number of atoms in clusters to increase with $N_p(0)$. Figure 3 shows normalized as-implanted profiles of the remaining free atoms $N_{free}(x,0)$ in the simulated lattice. As the peak concentration C_0 (given by $N_p(0)/N_Y$, where N_Y is the total number of lattice points in the Y direction of the lattice) is increased the profiles begin to distort as clustering begins to take effect (as is visibly evident from the dips in the profiles.) We have observed an exponential $N_{free}(R_p,0)$ decrease with increasing C_0 .

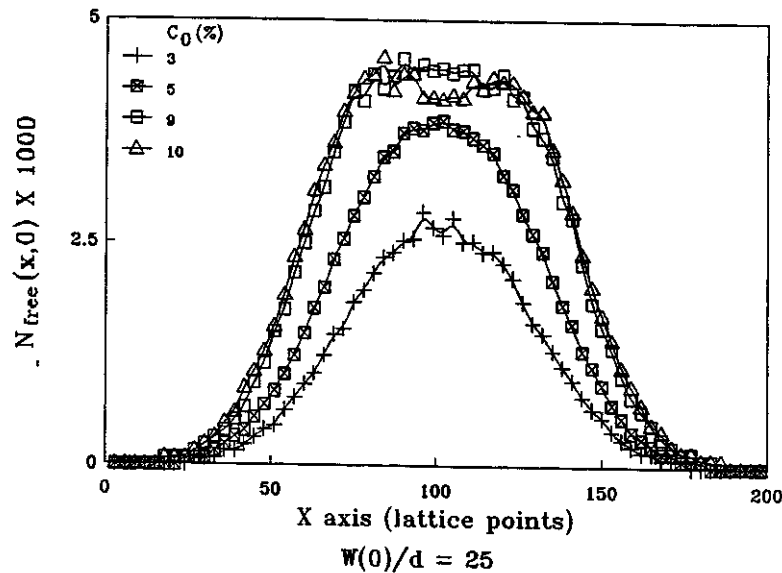


Figure 3. Initial distribution of free atoms in the lattice for constant normalized profile half-width $W(0)/d=25$ [Simulation]. The central dip is due to atoms in clusters which are not included in N_{free} .

Simulation Model

We have simulated the experimental situation in the model in the following fashion: If a diffusant has no other diffusant within its interaction distance, it is regarded as rather loosely bound to the lattice and requires less energy for a jump. This state corresponds to the relatively small 0.41 eV activation energy of diffusion. On the other hand, an atom within interaction distance of another atom/cluster is considered to be "stuck" due to the large interaction energy, and further migration of atoms in this state requires the migration of the cluster as a whole with a much larger activation energy. This state corresponds to the 1.9 eV value observed for clusters. Note that by formally considering the higher activation energy to be associated with the individual atoms within the cluster, one retains the possibility of the individual atom subsequently escaping from the cluster.

To investigate the gettering process, it has been simulated up to 90 nearest neighbour jumps of free atoms with the clusters fixed, assuming a negligible cluster migration during such a small period of simulation and a moderate thermal activation in the temperature range of gettering.

The high temperature diffusion was investigated by increasing the probability of such cluster diffusion to correspond to the 1.9 eV activation energy. The process was simulated for 500 nearest neighbour jumps of the free atoms.

THE SIMULATION

Recently, there has been increasing interest in the physical mechanisms governing the geometrical structure in diffusion limited aggregation (DLA)⁹⁻¹⁰. Several growth mechanisms have been proposed¹¹⁻¹³.

The model presented here is a variant of the Eden one¹⁴. In this model all particles were distributed throughout the lattice at the beginning of the process to simulate an implant profile given by Equation (4) with varying N_p and $W(0)$. These particles walk randomly until they visit a site adjacent to another particle and get "trapped". Edges of such clusters tend to grow more rapidly than other perimeter sites because perimeter sites near the center are "shadowed"¹³.

The 15×10^6 lattice was chosen to be a 3D simple cubic structure, with the number of lattice sites varying to accommodate the dose and half width requirements.

Figure 4a shows a cross-section of such a simulated initial distribution with $C_0=8\%$ and $W(0)/d=35$ showing mostly free atoms with a few initial clusters, whereas in Figures 4b and 4c the same lattice is seen after time $40t_{nn}$ and $120t_{nn}$ respectively, where t_{nn} is the required time per nearest neighbor jump. Clustering is evident and the number of free atoms clearly decreases with time as atoms which are not trapped diffuse away.

SIMULATION RESULTS

Gettering process

Growth mechanism. In order to explain the simulated gettering process, a time dependent gettering rate, $G(t)$, is defined as a measure of the growth in the distribution peak, compared to its initial value $N_p(0)$, as

$$G(t) = \frac{N_{max}(t)}{N_p(0)} \quad (7)$$

where the total number of atoms at the peak at time t , $N_{max}(t)$, analogous to $N_p(t)$, which can be expected at or near R_p , can be expressed as

$$N_{max}(t) = N_{mfree}(t) + N_{mclust}(t) \quad (8)$$

where $N_{mfree}(t)$ and $N_{mclust}(t)$ are the number of free atoms and numbers of atoms in clusters at the peak.

Since the cluster movements are restricted by a much larger energy requirement, for the purposes of the simulations, which were limited between 50 and 90 nearest neighbor jumps of free atoms, clusters were considered to be fixed in the lattice.

During each random jump a fraction of $N_{mfree}(t)$, denoted by $N_{tc}(t)$, is lost to clustering. Hence $N_{mclust}(t)$ of Equation (8) is expected to increase with time as the sizes and the numbers of such clusters increase in this region. Another fraction of these atoms will continue to migrate

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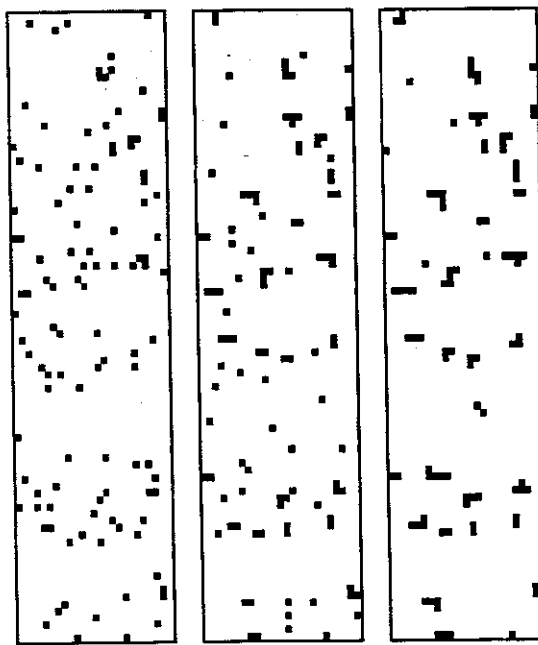
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Figure 4. A cross section of the lattice xy plane showing progressive clustering.

as free atoms according to concentration gradients of their distributions. Hence, $N_{nfree}(t)$ at an incremental time $t+1$ can be expressed as

$$N_{nfree}(t+1) = N_{nfree}(t) - N_{fc}(t) + [N_{din} - N_{dout}(t)] \quad (9)$$

Where $N_{din}(t)$ and $N_{dout}(t)$ are the atoms diffusing in the and out of the peak region, respectively.

Activity at the peak: $N_{max}(t)$. Figure 5a shows the time variation of activity $G(t)$ (Equation 7) for implants with various implant dosages.

Several interesting features can be observed from these results: There exists a primary growth process with a higher rate of growth in $G(t)$, which is followed by a secondary growth process with a much lower growth rate. Considerable fluctuation of the $G(t)$ magnitude is seen at dilute dosages which is seen to be decreasing with the increasing C_0 . The magnitude of both primary and secondary growth decreases with increasing C_0 .

When the quantity $[N_{din}(t) - N_{dout}(t)]$ in Equation (9) is positive, there is a growth in the peak, due to diffusion of the free atoms surrounding the gettering region.

Activity at the peak: $N_{nfree}(t)$. Figure 5b shows the variation of $N_{nfree}(t)/N_p(0)$ with time for various initial atomic distributions. According to Equation (9) the number of these atoms decreases with time due to ongoing clustering and diffusion of the free atoms. The loss rate is seen to increase with C_0 which is expected; $N_p(0)$ affects the peak concentration and hence the clustering at the peak, while the $W(0)$ variation has negligible effect on the rate of loss there.

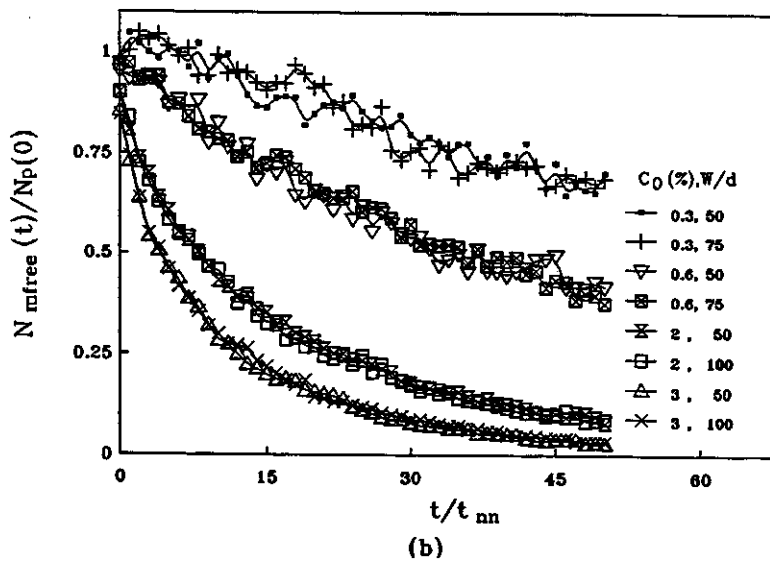
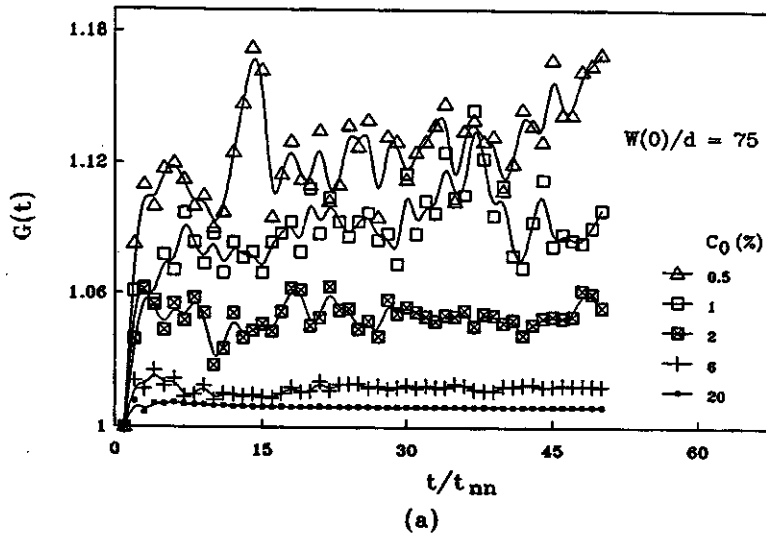


Figure 5. Time variation of (a) $G(t)$ and (b) $N_{mfree}(t)/N_p(0)$ showing the effects of cluster growth. The reduction in $N_{mfree}(t)$ reflects the diffusion and clustering of the free atoms.

Primary growth. The primary contributor to the growth is attributed mostly to the localized depletion of free atoms created by as-implanted atoms in clusters. Due to these depleted regions the concentration gradient of free atoms around them favors diffusion in the inward direction resulting in further growth of the existing clusters and the formation of new clusters since all atoms are essentially "trap" sites. Such diffusion causes a rapid increase in $G(t)$. As the localized

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concentration gradient vanishes, the rate of migration decreases, resulting in a slowdown in the overall growth process. The magnitude of such growth is also seen to decrease with increasing dosage, since increased dose represents an increased number of atoms in the initial clusters leaving fewer free atoms in the peak region. In addition the increased number of atoms in the lattice due to the higher dose also reduces the lifetime of the available free atoms, since all atoms are essentially "trap" sites.

Secondary growth. The secondary growth mechanism can be attributed to the atoms in the entire distribution. Due to the longer time duration of the process, atoms far away from the initial peak region have the opportunity to diffuse toward the peak region and contribute to the gettering process.

In the case of $C_0=20\%$ in Figure 5a, the gettering is seen to be negligible due to a much reduced concentration of free atoms in the initial distribution and an abundance of "trap" sites. The activity under the peak region ceases within a short time, showing a complete clustering of atoms at the peak.

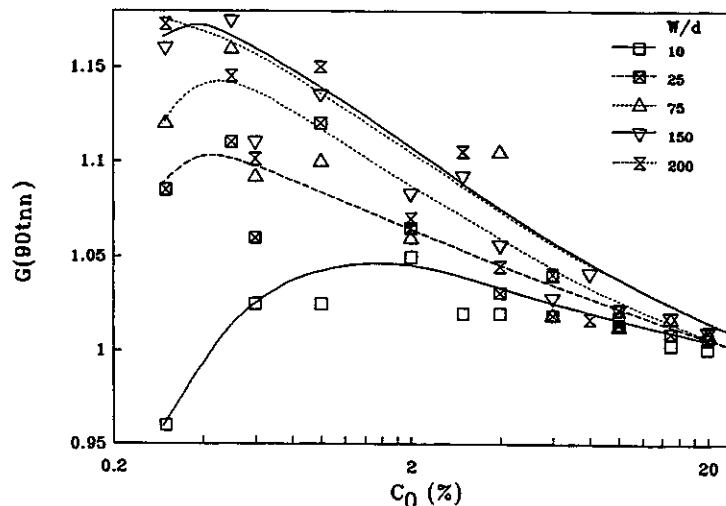


Figure 6. The variation of gettering with C_0 , showing competing trends.

For a given C_0 , a smaller $W(0)/d$ also represents an increased concentration gradient at the edge of the distribution. At lower C_0 , a

$G(t)$ versus implant-profiles. In order for an increase in the $G(t)$ magnitude to occur, an abundant supply of free atoms near the gettering region is required to provide a large $N_{\text{pin}}(t)$ for gettering. Longer lifetimes of the free atoms surrounding the gettering region are also essential in order to increase the gettering, which requires fewer clusters surrounding the gettering region. Hence there is an optimum distribution profile suitable for a maximum gettering effect.

$W(0)$ variation. Figure 6 shows the variation of $G(90t_{\text{nn}})$ (as defined by Equation 7) with C_0 for various $W(0)/d$. At lower C_0 (below 1%), a sharp drop in $G(t)$ can be seen with decreasing $W(0)/d$. According to Equation (5), at these low concentrations; and for small $W(0)/d$ cases, there are relatively fewer atoms in the lattice.

lack of "trap" sites (atoms) and the large concentration gradient favors conventional diffusion of free atoms and the overall gettering effect is diminished. In one case, with $C_0=0.3\%$, $G(t)$ falls below 1, again showing dominant conventional diffusion of free atoms.

At higher C_0 (above 1%), with increasing $W(0)/d$, the distribution spreads out and the contribution of the atoms at and near the edge of the distribution becomes less significant and the effect of $W(0)/d$ variation on $G(t)$ is seen to be diminishing.

N_p variation. Figure 6 also shows the effect of the variation of $G(t)$ with C_0 and hence N_p . N_p influences both the concentration gradient at the edges and the concentrations at the peak of the distribution. At larger $W(0)/d$ and dilute dosages, initial clustering is small providing an abundance of free atoms with a longer lifetime, favoring large activity at the peak region, resulting in an increased $G(t)$ in these moderate dosages. A further increase in C_0 still implies more "trap" sites but the density of initial clusterings begins to dominate the process, resulting in a reduction of the number of free atoms and a reduced lifetime of such free atoms. Consequently, a decrease in $G(t)$ is seen with further increases in C_0 .

High Temperature Diffusion

In contrast to ideal cases of gettering (clusters immobilized) of figure 5a, figures 7a and 7b show the time variation of the peak of the distribution for various cluster diffusion probabilities with $C_0=1$ and $W(0)/d=25$ and 50, respectively.

In all cases the primary growth process is evident, which can be attributed to the fast and brief nature of the primary growth mechanism. Subsequent variation can be attributed to the combined effects of the secondary growth process and the cluster diffusion away from the peak region. The cluster diffusion is seen to reduce $G(t)$ and the rate of reduction is seen to increase with increasing probability of cluster movement. A comparative study of figures 7a and 7b reveals that diffusion is enhanced in all cases with the reduced half width providing larger concentration gradients at the edges of the distribution.

At smaller migration probability, N_{max} is seen to increase in a similar fashion to that of the ideal cases of figure 4a. Simulation results are in general agreement with the experimental gettering results at moderate temperature.

Figure 8 shows the as-implanted distribution profile and the distribution profile after a simulated cluster diffusion with a 0.01 cluster diffusion probability. The process was simulated for 500 nearest neighbor jumps of free atoms. In this early stage of gettering the peak of the profile is seen to increase together with a decrease in its half-width.

DISCUSSION

Due to the randomness of the implant process some atoms are found to be in clusters even at a dilute implant dose, creating a void in the free atom distribution profile. Such a distribution is favorable for further clustering through diffusion.

The lack of movement of the clusters and their further growth in numbers and sizes results in an accumulation of total atoms in excess of the initial distribution at or near its peak resulting in the further gettering of free atoms.

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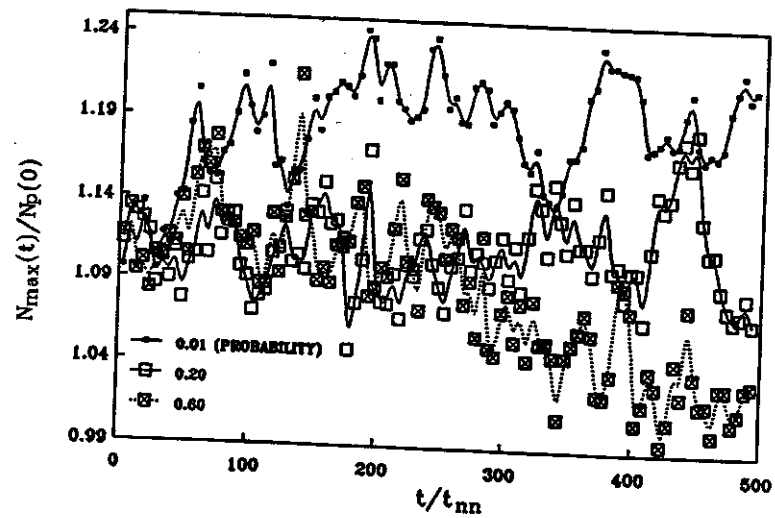
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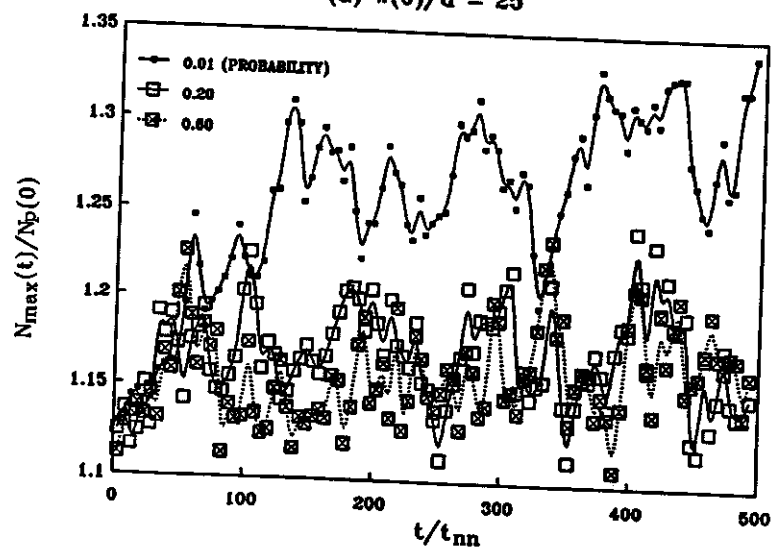
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(b) $W(0)/d = 50$

Figure 7. Time variation of $G(t) = N_{max}(t)/N_p(0)$ showing the effects of cluster diffusion. Out-diffusion of clusters dominates the inward diffusion of free atoms for narrow implants and/or high temperatures (high diffusion probability.)

The random diffusion process was simulated by scanning each XY plane of the lattice back and forth sequentially. The XY planes were scanned in an odd/even fashion producing a "combing effect" on the lattice to enhance randomness of the process.

A comparative study of distribution profiles of Figure 3 for $C_0=10\%$ and 9% , respectively, reveals that for relatively larger dosages (C_0 greater than 5%) there exists a certain distribution profile for which the initial clustering will be most favorable for the secondary growth

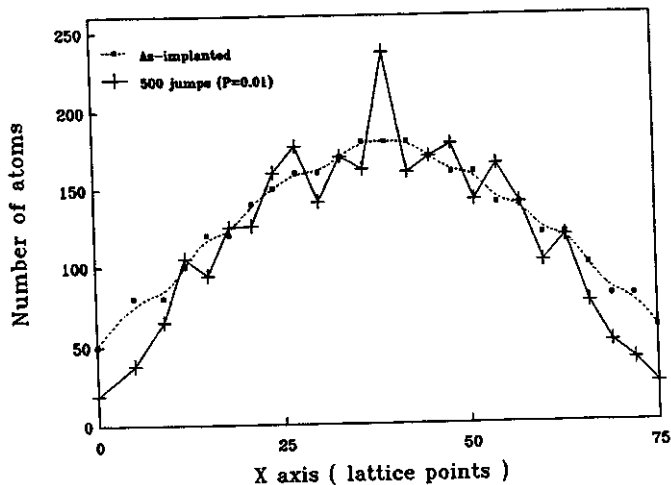


Figure 8. Simulation of thermal diffusion of atoms with a Gaussian distribution, showing the overall tendency to sharpen the profile.

process, and one can in fact expect a secondary $G(t)$ peak at that distribution. Such a $G(t)$ peak can be expected to be much smaller than the primary peak shown in Figure 6 located around $C_0=1\%$. The magnitude of this peak is expected to be reduced by the reduced lifetimes of the free atoms at such high concentrations. The $G(90t_{an})$ plot failed to record such a peak due to (1) the longer time requirements of secondary gettering, and (2) the expectation of the magnitude of such a gain to be below the accuracy of our simulation methods.

There exists a minimum requirement on Q below which gettering cannot be observed.

The secondary growth rate was found to be dependent upon the concentration gradients at the edges of the distribution and also upon the cluster distributions in the initial distribution, while the primary growth mechanism was dominated by localized depletion of free atoms produced by initial clusters.

Though the process was simulated for the ion-implanted case, the simulation is a gross approximation of the process: (1) Boundary errors were large for extreme cases, e.g. small doses and also large $W(0)/d$ points. (2) The choice of lattice, though apparently large, is a gross approximation to an infinite lattice. (3) The randomness of the process was simulated in a sequential fashion. (4) Due to limitation of the lattice size, the best lattice for the simulations was only 80 planes thick compared to about 20×10^3 planes of 1 mm^2 window of the RBS profiles.

In Figures 5 and 7 large fluctuations in $G(t)$ can be noted, particularly at very dilute dosages. Such fluctuations are also attributed to the limitations of the simulation where an infinite lattice was represented by a finite lattice.

CONCLUSIONS

The diffusion and clustering of ion-implanted metal ions in a polymer have been simulated by computer for comparisons with experiments on copper in polyimide.

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Overall simulation results are satisfactory and consistent with the experimental observation of gettering and high temperature diffusion. The simulations adequately describe the gettering process via clustering of adjacent atoms due to strong inter-atomic interactions, and a much smaller cluster migration rate than that of free atoms due to large activation energy of cluster motion.

The simulation results predict a fast primary growth in peak height which is attributed to localized depletion of free atoms due to initial clustering of the implanted atoms at and near the peak region. The rate and magnitude of such a growth is strongly dependent upon the initial dosages and profiles of the implants. The primary growth is subsequently followed by a much smaller secondary growth rate which is attributed to the free atoms in the entire distribution contributing to gettering.

The high temperature diffusion of clusters formed by large interactions, requiring a higher activation energy for subsequent migration, is also in agreement with high temperature diffusion results. The simulation shows a gettering peak which is attributed to the primary growth mechanism prior to the subsequent diffusion of clusters at these higher temperatures.

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