Investigation of Copper and Tantalum atoms Diffusion in Polymers by *ab initio* Molecular Dynamics

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Abstract:

Ab initio MD simulations were carried out to characterize the diffusion of Cu and Ta atoms/clusters inside a SiLK-like amorphous polymer. The diffusion coefficients of Cu and Ta atoms and their atomic clusters in linear amorphous and crosslinked polymers were calculated. The speed of a single Cu atom within the polymer suggests that Cu atoms diffuse in amorphous polymers by jumping or hopping between cavities inside polymers. The diffusion speed of Ta is much lower than that of Cu. This is not only due to its larger mass but also due to the chemical interactions between Ta and polymers. It was found that the degree of polymer crosslinking doesn't have strong effects on metal diffusion. Studies on the diffusion of metal clusters showed smaller diffusion coefficients with larger cluster size. This is the first effort to calculate the diffusion coefficients of metal atoms/clusters inside polymers using *ab initio* MD simulations; it provides a framework for metal-polymer diffusion investigations.

Keywords: Diffusion, Diffusion coefficient, *Ab initio* molecular dynamics, Copper, Tantalum.

Introduction

The continuous miniaturization of electronic products has raised new issues in interconnections between transistors. As transistors become smaller and consequently faster, delays in interconnects start to account for a considerable proportion of processing time [1]. One promising solution is to replace the conventional Al/SiO_2 interconnects with Cu/silk-like polymer (SiLK) interconnects [2]. In order to curb the diffusion of copper into SiLK, a pre-coating of metal tantalum is required before Cu deposition. [3]. However, the diffusion of the metals into the polymer has not been eliminated completely. The understanding of metal-polymer diffusion mechanisms at the atomic level and a way to quantify such diffusion provides a basis for the selection of materials for actual applications.

There is neither theoretical research work on the modeling of metal-polymer diffusion nor an established measure to quantify metal-polymer diffusion. Pervious theoretical works on diffusion coefficient calculation were mainly focused on small molecules in the gaseous state, such as hydrogen, oxygen or methane, into polymers using classical molecular dynamics (CMD). Li *et al.* [4] calculated diffusion coefficients of some small molecules into amorphous polymer by CMD and found that calculation results were in good agreement with experimental values only for systems of hydrophobic molecules diffusing through hydrophobic polymers. For other material systems, predictions of diffusion coefficients from the calculation could range from 0.04 to 2400 times the experimental results. A more accurate simulation was carried out by Gray-Weale *et al.* [5] who proposed a method for simulating diffusion behaviors of gases or organic solvents through glassy polymers by CMD. It was found that these penetrants occasionally jumped between cavities inside polymers. That approach was also able to predict diffusion coefficients observed in actual experiments. Charati and Stern [6] calculated the diffusion coefficients of He, O_2, N_2, CO_2 and CH_4 at 300K in four silicon polymers by CMD shortly after Gray-Weale's work. Their simulation showed that gases exhibit two types of motions - jumping between cavities, which also known as hopping, and oscillations within cavities. More recently, Bharadwaj and Boyd [7] studied temperature effects on the diffusion of methane in three highly impermeable aromatic polyesters. It was pointed out that hopping between cavities occurs for temperatures up to 600K.

Methodology

While CMD has been successful in the study of the diffusion of gases in polymers and details of molecular motion may be revealed through such simulation, it cannot be used for the investigation of metal-polymer diffusion because there is no force potential describing metal-polymer interaction. The assumptions made in studying gas-polymer diffusion may also not be valid for metal-polymer. For one, the interaction between gas molecules is very weak because only van der Waals interaction dominates, whereas, the

interaction between metal atoms is relatively strong and metal-metal bonds may form easily during the diffusion processes. Metals may diffuse into polymers as a single atom or as atomic clusters of different sizes. Therefore, *ab initio* calculation based on first-principles is the only theoretical approach to study metal-polymer diffusion. In the current work, we used quantum molecular dynamics (QMD) to investigate Cu and Ta diffusion into SiLK. The diffusion coefficients under various conditions were obtained and the diffusion mechanisms at the atomic level are described.

Periodic modules were employed in metal-polymer simulations (Fig-1). Based on the original chain structure of SiLK given by Martin *et al.* [2], the amorphous polymer was created by Monte Carlo method [8]. The periodic cell of amorphous polymer has a lattice of 10.5 Å ($a = b = c$) and contains about a hundred atoms to give the measured density of 1.14g/cm^3. CMD was implemented at the initial stage to relax the overall amorphous structure followed by the QMD calculations. To investigate single metal atom diffusion in linear amorphous polymer (LAP), a single Cu or Ta atom was placed randomly in the amorphous polymer cell at reasonable distances from neighboring atoms in the polymer to avoid high strains and unreasonable bonds.
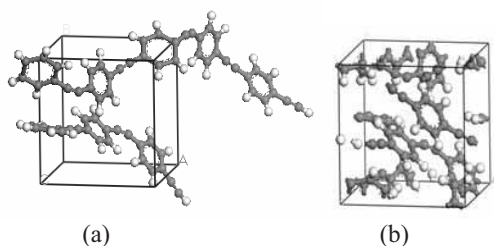

(a)   (b)

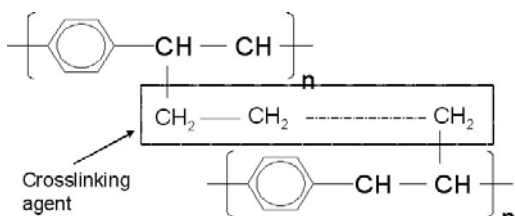Fig-1: Periodic model of amorphous polymer. (a) original view; (b) in-cell view.

Fig-2: Aromatic chains are crosslinked by series of –CH$_2$– groups.

In most cases, polymers are crosslinked. Crosslinking is expected to affect metal diffusion. Here, we selected a series of methylene (–CH$_2$-) groups to link the backbone chains. As shown in Fig-2, the carbon-carbon double bonds were saturated by the crosslinking agent and H atoms. The crosslinking resulted in slightly tighter packing of the amorphous polymer and introduced some strain into the system. A structure relaxation was therefore first carried out using CMD followed by QMD. After relaxation, the density of crosslinked polymer was 1.15 g/ cm^3, which is almost the

same as that of LAP. Single metal atoms, Cu or Ta, were put into the cell at random locations.

Ab initio molecular dynamic (MD) simulations were carried out with Car-Parrinello MD (CPMD) [9] on an IBM690 supercomputer platform. The Kohn-Sham formula of energy based on the density function theory was used for the calculation [10]. Plane waves are used as the basis set for the valence electron wave functions and pseudopotentials are applied to describe the interactions between the valence electrons and the central cores. Prior to the diffusion simulation, a wave function optimization was implemented to quench the electrons to the ground-state followed by *ab initio* MD simulations at a temperature of 300K. By recording the trajectory of the metal atom, the diffusion coefficient, D, can be calculated from [4]

$$D = \frac{1}{2FN} \lim_{t \to \infty} \frac{d}{dt} \left\langle \sum_{i=1}^{N} \left[r_i(t) - r_i(0) \right]^2 \right\rangle \qquad (1)$$

Here, F represents the number of dimensions of freedom; N is the number of penetrants (metal atoms); $r_i(t)$ is the position of penetrant i at time t. Terms in angular brackets denote the mean square displacement of the penetrants. The diffusion coefficient is a factor of proportionality representing the amount of penetrants diffusing across a unit area through a unit concentration gradient per unit time.

Result and Discussion

The CPMD process was continued until a stable value of the diffusion coefficient was obtained. To characterize the motion of the metal atom, the total diffusion time was divided into a series of equal intervals and the average speed of the penetrant within each interval was calculated. The chart of diffusion speed against time for Cu and Ta atoms in the LAP is given in Fig-3.
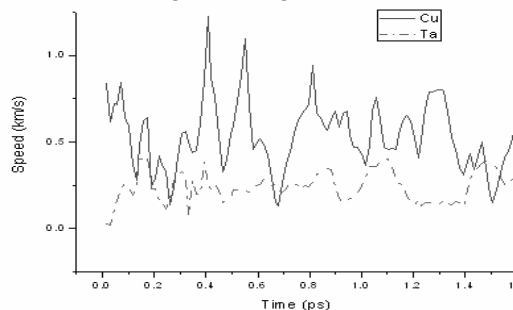

Fig-3: Diffusion speed of Cu and Ta atoms in LAP.

It can be seen that the diffusion speed of Cu fluctuates greatly compared to that of Ta. This suggests that copper atoms diffuse in the polymer through some jumping motion, which is similar to gas diffusions predicted previously by CMD [4]. Jumping motions dominate in the diffusion process, while oscillations, which always exist even at 0 K, may just be a necessary mechanism for energy accumulation. When the energy of the metal atom is large enough to move it from one cavity to another,

jumping/hopping occurs. Oscillations, which are also accounted for in equation (1), result in a slight over-estimation in the calculated values, although it contributes little to overall motions.

The average diffusion speed of the Cu atom in the LAP is 0.54 km/s. This is about 1/3 to 1/4 that of common gases such as oxygen and nitrogen. The computed value for Ta is only about 0.25 km/s, less than half that of Cu. The Ta atom also displays less fluctuation in speed. This suggests that Ta diffuses less readily into the polymer compared to Cu; a strong indication why Ta is effective as a barrier layer between copper and silk. The diffusion coefficient of Ta, calculated from equation (1), is much smaller than that of copper as shown in Fig-4.
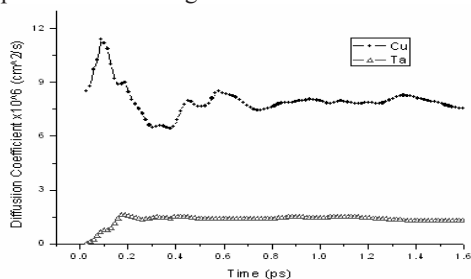

Fig-4: Diffusion coefficients of Cu and Ta in SiLK-like LAP.

Fig-4 shows that the diffusion coefficient calculation for Ta starts to converge much earlier than that for Cu. This is because the jumping motion of Cu results in larger fluctuations in the calculations. Our calculation gives a diffusion coefficient of 8.0×10^{-6} cm^2/s for single Cu atoms in the LAP and 1.4×10^{-6} cm^2/s for single Ta atoms. It is noted that the diffusion coefficient of Cu is about 4 times that of Ta even though the mass of metal Ta is only twice that of Cu. Hence, although the mass of penetrants is likely to affect diffusion, it may not be the most influencing parameter. The following calculations show that the diffusion coefficient of Ta is much smaller than that of Cu dimers, and even smaller than that of Cu triple clusters. This means the chemistry between metals and polymers may play a more important role than the mass of penetrant during the diffusion.

Crosslinkings within polymers were expected to affect the diffusion of metal atoms into them. The same CPMD procedure was carried out to study the motion of single Cu and Ta atoms in crosslinked polymers. The simulation results in Fig-5 suggest that crosslinkings do not hamper diffusion significantly. This implies that the polymer matrix may not have transformed significantly during the diffusion processes; i.e. polymer structures only need undergo a slight re-orientation when metal atoms penetrate it. This was confirmed by comparing the position of each atom of the polymer before and after diffusion. We believe that the parameters having greatest effects on diffusion are chemical structure (i.e., the elements and functional groups), and the polymer density. In our LAP and crosslinked polymer models, the functional groups are similar because both

comprise essentially benzene rings. The density is also only slightly greater for the crosslinked polymer. These marginal differences are negligible compared to difference in the interaction energies of the benzene ring of the polymers to Ta (~1.91 eV) and to Cu (< 0.02 eV). These interaction energies suggest that the chemistry strongly affects the diffusion mechanisms.
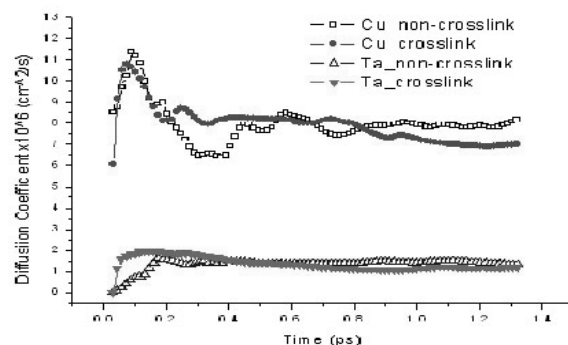

Fig-5: Diffusion coefficient for non-crosslinked (LAP) and crosslinked polymers.

In the single metal atom diffusion models, the metal atom only interacts with the polymer; there is no metal-metal atom interaction. The situation is similar to gas diffusion in polymers. However, in actual processes, Cu and Ta are deposited onto the substrates through a sputtering process. Under such conditions, the metal is likely to deposit as clusters of atoms rather than insolated single atoms. Subsequently, these metal clusters will diffuse into the polymer as blocked species, because the metal-metal bond is strong compared to the interaction between metals and polymers, especially for polymers without oxygen or nitrogen elements. Three models were built to study the diffusion of metal atom clusters - a dimer, a planar triple structure; and a pyramidal quadruple structure, which is the basic configuration of copper fcc crystal structure (Fig-6). The distance between Cu atoms is set at the Cu-Cu bond length of 2.56 Å. These three structures were also used for Ta clusters with the bond length set at 2.86 Å. However, it should be noted that the actual crystal structure of Ta is bcc. These metal clusters were inserted into the amorphous polymer individually in the same way as for single metal atoms.
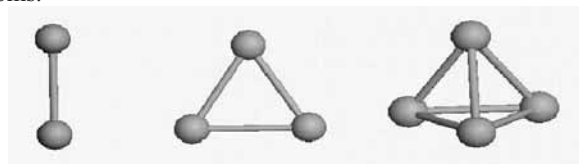

Fig-6: Metal cluster models for Cu and Ta.

For the metal cluster diffusion, equation 1 was still employed to calculate the diffusion coefficient. During the diffusion processes, metal clusters may not maintain their original geometry exactly, but if the metal bonds are not broken, it can still be treated as a molecule and the mass center of the cluster can be used as the reference point to track cluster motion. In gas diffusion calculations, for

example, for the diffusion of CH_4 into polymer, the mass centre was also used as the reference point in equation 1 [4]. However, if metal bonds of the clusters are broken during the diffusion, equation 1 is not used because the original metal cluster has changed to other species. The diffusion coefficient of each species must then be calculated individually, which means these two metals can diffuse into the polymer either as single atoms or atomic clusters. It was found that for both Cu and Ta clusters, there was no bond breakage when they penetrated through the crosslinked polymer at room temperature. Diffusion coefficients of these clusters of Cu are given in Fig-7.
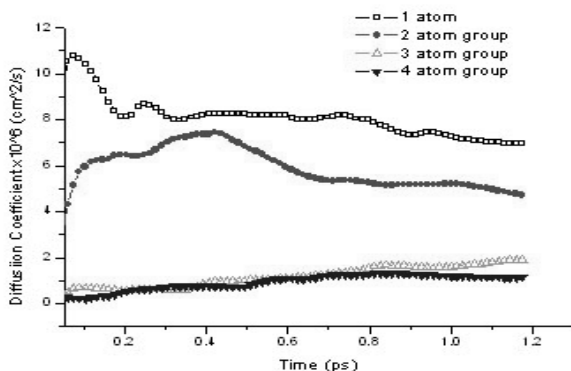

Fig-7: Diffusion coefficient curves for Cu Clusters in SiLK.

It is obvious that diffusion coefficients decrease with increase in cluster size but the change is not linear.

In the actual processes, single metal atoms co-exist with atom clusters. The smaller the cluster, the faster it moves. These motions are random and it is likely that single metal atoms or small clusters may combine together to form a bigger cluster during diffusion. At high enough temperatures, metal clusters may even split into two or several small clusters or even single atoms. Thus, diffusion will then become complex motions of metal clusters and atoms, along with the coalescence and splitting of clusters. Single metal atoms and small clusters are likely to form bigger clusters or even metal blocks during the diffusion process due to strong metal-metal interactions. In the diffusion processes, metal blocks are often detected by TEM [11]. This is characteristic of metal diffusion into polymer.

Conclusion

The diffusion of Cu and Ta atom/clusters in the amorphous polymers has been studied via *ab initio* MD simulations. It was found that the Cu receives impulse interactions from ambient elements while Ta is quite lazy with vibrating motions. The crosslinking of the polymer has limited effects on the metal diffusing motions. Metal clusters have much lower diffusion coefficients than single atoms and the metallic bondings are strong that the clusters keep the original shape throughout the diffusion motions.

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