Hyperthermal vapor deposition of copper: athermal and biased diffusion effects

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Abstract

The kinetic energy of an adatom during its impact with a growth surface significantly affects the morphology and microstructure of vapor-deposited films and coatings. Atomic-scale reconstruction processes including 'athermal' and 'biased' diffusion are in part responsible. A three-dimensional molecular dynamics method has been used to characterize the extent of these diffusional processes following hyperthermal adatom impacts. Athermal diffusion was shown to result from a significant transient increase in effective temperature near the impact site due to the partitioning of the latent heat of condensation and the adatom's incident kinetic energy amongst the vibrational modes of the lattice. The diffusion induced by this mechanism was found to be more or less independent of the substrate temperature. Simulations of oblique hyperthermal deposition indicated that adatoms can overcome surface potential-energy barriers without thermal activation and sometimes skip large distances over the substrate surface. This results in significant forward-directed biased diffusion. The dependence of the transient heating (responsible for athermal diffusion) and the biased diffusion distance upon the adatom's incident energy and angle have been determined for the {100}, {110} and {111} surfaces of copper and fitted to simple relations that are convenient for use in atomistic deposition models.

Keywords: Adatoms; Atom–solid interactions; Copper; Growth; Metallic films; Models of surface kinetics; Molecular dynamics; Surface diffusion

1. Introduction

Many physical vapor deposition (PVD) techniques including molecular-beam epitaxy (MBE), thermal evaporation and ion-beam/ion-beam-assisted deposition, as well as diode and magnetron sputtering [1], are widely used for the growth of thin metal and metal compound films for a host of applications in microelectronic devices [2,3], giant magnetoresistance (GMR) sensors [4–6], ferroelectric memories [7], high Tc superconductors [8] and thermal barrier coatings [9]. This multiplicity of deposition approaches enables the growth of thin films and coatings under a wide range of process conditions, resulting in films with widely varying surface morphology and microstructure. However, selecting the best technique and optimizing it for a new material can take considerable time and involve significant expense. The design of a vapor deposition technology for the manufacture of the metal interconnects used in microelectronic components is one of the examples. The performance and durability of ultra-
large-scale integrated circuits are strongly influenced by the resistivity and electromigration resistance of the metal films used for interconnecting individual devices. In the past, these interconnects were fabricated by sputter depositing aluminum alloys on to the surface of wafers with diameters up to 200 mm. Today, interest is growing in the use of a dual damascene method for also depositing copper (because of its higher electrical conductivity and electromigration resistance) into narrow, high-aspect-ratio trenches etched into the surface of larger-diameter wafers [10,11]. It has been difficult to use existing processes to uniformly deposit low-defect-density copper or aluminum on to the interior surface of such trenches and to completely fill them across the entire wafer surface. The major problem is that the deposit often accumulates at the lip of the trench opening. This caps the trench before filling is complete, resulting in the trapping of large internal voids in the metal conducting lines and premature failure of the interconnects.

Three modifications to the vapor deposition approach are being explored to enhance the filling of trenches [2]: (1) collimated deposition in which only the adatoms that make near-normal impact with the wafer surface are used for deposition so that they can ballistically move to the trench bottom [12,13]; (2) the use of high substrate temperatures to permit atoms to migrate to trench bottoms by surface thermal diffusion [14–16]; and (3) increase of the adatom (or assisting ion) incident energy to sputter away overhangs [2]. Experimental studies have shown that optimizing the incident energy is crucial for all three approaches. Techniques that enable convenient control of incident energies such as bias sputtering have been developed by Hamaguchi and co-workers [27,28]. While these computationally efficient approaches provided significant insight into the effect of adatom-energy-dependent resputtering upon surface morphology, they did not consider other effects such as the local surface-heating-induced diffusion, biased diffusion or the usual thermal diffusion. As a result, these approaches did not fully incorporate impact energy effects and could not address the role of substrate temperature upon surface morphology and microstructure of vapor-deposited films.

In an alternative approach, a two-dimensional (2D) SIMulation of BAllistic Deposition algorithm named SIMBAD [14,15,29–35] has been quite widely used to incorporate the effects of substrate temperature [14,15], resputtering [15,30], incident flux angle [31,32], trench geometry [33], biased diffusion (in the impact direction), (3) resputtering of previously deposited atoms, and (4) reflection of impact atoms. The relative contributions of these four mechanisms to the atomic assembly of a thin film or coating are likely to depend on the adatom’s incident energy and angle, as well as the morphology and type of the surface. The final surface morphology, microstructure and defect populations of deposited films or coatings are then controlled by these energy-dependent atomic processes together with the usual temperature- and deposition-rate-dependent thermal diffusion. The relative importance of the different mechanisms depends upon many process variables. Experimental ‘trial-and-error’ searches for an optimal process are therefore difficult, and are frequently time-consuming. Interest has grown in the development of predictive models for relating the surface morphology, microstructure and defect populations of deposited materials to the growth conditions. Since a key growth-controlling variable is the energy of the atoms in the depositing flux, several studies have sought to integrate one or more of the energy-dependent atomic assembly mechanisms into a growth-modeling scheme. Bader and Lardon [3] used elementary resputtering (and redeposition) data in a string algorithm to simulate the surface profile across a trench during the biased sputter deposition of aluminum. A similar approach has also been developed by Hamaguchi and co-workers [27,28].
Diffusion [34] and sticking coefficient (i.e., one minus the atomic reflection probability) [35] into numerical simulations of vapor deposition into trenches. SIMBAD predicts the surface morphology and structure of films using a disk accretion technique that approximates the ballistic movement of collections of vapor atoms. While this method is computationally efficient, it is based on a 2D approximation and an oversimplified treatment of surface diffusion. As a result, SIMBAD can only simulate the trends between temperature or deposition rate and surface morphology or microstructure; its quantitative predictions are problematic. In addition, data that set the relative contributions of energy-dependent effects such as local heating-induced diffusion, biased diffusion, resputtering yield, energy and angular distribution functions of the resputtered atoms, etc. have to be supplied as inputs in a SIMBAD model. For many materials systems of interest, these data are not available.

The central problem with both of the approaches mentioned above is that they do not explicitly include the atomic assembly processes induced by an energetic adatom impact in a way that is consistent with those involved in subsequent thermal diffusion. The contribution of thermal diffusion is determined by the substrate temperature and the available diffusion time, which in turn depends on the deposition rate. Transition-state techniques such as the kinetic Monte Carlo (k-MC) method do enable the rates of different atomic jumps to be calculated as a function of substrate temperature. These methods use the Arrhenius equation and therefore require the knowledge of activation energies and pre-exponential factors for various atomic jump paths. Although there are many different types of atomic jump on a typical growing surface due to many possible local atomic configurations, the most important activation energies and pre-exponential factors can be obtained through molecular dynamics/statics simulations [36–42] using well-calibrated interatomic potentials such as those based on the embedded atom method [36–39] or the corrected effective medium method [42]. For many simple metals, the activation energies and pre-exponential factors determined from these calculations are consistent with experimental results from field-ion microscopy (FIM) [43–45]. Using look-up tables for the different types of atomic jump, computationally efficient multipath kinetic Monte Carlo approaches have recently been developed for simulating thermally driven diffusion assembly processes at realistic deposition rates [39]. This methodology is beginning to be applied to model low (thermal) energy (e.g., MBE or electron-beam evaporation) processes, and to investigate the thin film morphology and structure as a function of substrate temperature, deposition rate, and incident angle [39]. It is helping resolve many of the experimental observations [46].

Current models based on the Monte Carlo approach neither incorporate the effect of hyperthermal impact nor the effect of the latent heat release (associated with the condensation of vapor atoms) [39]. For thermal evaporation processes, the incident kinetic energy is low (∼0.1 eV) and the kinetic energy deficiency is relatively insignificant. However, failure to account for the latent heat (which is 2–4 eV per adatom) can result in discrepancies between experiments and predictions. For low-pressure sputtering deposition processes, the energy of the incident atoms can peak in the 3–6 eV region with an energy distribution tail extending to 20 eV or more [47]. In this case, the energy of the impacting atom is comparable to, or larger than, the surface diffusional barriers, and impact-energy-induced effects during atomic assembly can be very significant.

Here we use molecular dynamics (MD) and an embedded atom method (EAM) potential to simulate hyperthermal adatom impacts and to analyze athermal and biased diffusion. Since the trajectories of all the atoms during and after impact are determined based upon Newton’s equations of motion, the MD approach is reliable provided a well-validated interatomic potential is used. The study has investigated the dependence of local heating (which controls the degree of athermal diffusion) and biased adatom diffusion on the adatom’s incident energy and angle. The contribution of the latent heat of condensation to atomic hopping has been explicitly identified. An analysis of adatom reflection and impact-atom-induced resputtering and a Monte Carlo method incorpo-
rating these energy-dependent results will be presented in companion papers [48,49]. Copper has been chosen for the study because of interest in its use for integrated circuit interconnects [10], its growing role as the conducting spacer layer in GMR devices [5,6], and the availability of a well-validated EAM interatomic potential for copper [50].

2. Molecular dynamics computational method

The MD algorithm used for the computer simulations of vapor deposition has been described previously [51]. The EAM originally developed by Daw and Baskes [52] has been employed to calculate the interatomic forces in fcc copper. The EAM potential was derived for fcc materials from ab initio methods but is now widely applied in a generalized empirical form. Compared with the universal pair potential [53] that is fitted to the experimental data for high-energy (keV and above) bombardment, the free parameters of the EAM potential are calibrated with measured material properties such as the equilibrium lattice constant, the sublimation energy, the surface energy, the elastic constants, the vacancy formation energy and the heat of solutions for dilute alloys [54]. Because the sublimation energy is exactly reproduced [50], EAM correctly accounts for the energy transfer during vapor atom collision on a surface. On the other hand, high-energy impacts cause atoms to approach each other closely and short-range interaction dominates. If the impact energy is not too high (say, less than 100 eV), the EAM potential should reasonably capture the impact phenomenon and accurately reveal the subsequent atomic relaxation processes because its environment-dependent potential form realistically describes the energetics of local non-equilibrium atomic configurations. The EAM function of copper determined by Foiles et al. [50] was used for the present calculations.

Atomic impacts on the low-index (100), (110) and (111) surfaces of a copper crystal have been studied. Three computational substrate crystals corresponding to the three surfaces were created by assigning copper atoms to their bulk equilib-
Fig. 1. Geometries of crystals with different surfaces: (a) {100} surface; (b) {110} surface; (c) {111} surface.
for the entire impact process (usually this lasted for about 2–5 ps of real time) and the positions and kinetic energies of atoms were recorded as a function of time. Because of periodic oscillation of the kinetic energy (due to lattice vibrations), the recorded kinetic energy was time-averaged for 0.1 ps. To reduce statistical variations, all the results presented are the average of five separate MD simulations using a different random number seed for each.

3. Energetics of adatom–surface interactions

Since the dynamics of an adatom impact are determined by the interaction energy between the adatom and a surface, a set of molecular statics (MS) calculations was first carried out to determine the binding (\(E_b\)) and the migration (\(E_m\)) energies for an adatom on the \{100\}, \{110\} and \{111\} surfaces, together with the corresponding surface energies (\(\gamma\)). The MS method calculates the potential energy and atomic positions of equilibrium crystals at a temperature of absolute zero by using a conjugate gradient energy-minimization procedure [56].

The equilibrium surface configurations and the corresponding potential energies of the crystals with and without an adatom were determined by running the MS calculation with periodic boundary conditions in both the \(x\)- and \(z\)-directions (the periodic lengths were fixed in this case), a free boundary condition for the top \(y\)-surface, and a fixed boundary condition within \(d_0\) of the bottom \(y\)-surface. Since the potential energy of a vapor atom far from the substrate is defined as zero, the binding energies of the adatom on different surfaces were calculated as the energy difference between the corresponding crystals with and without the adatom. The potential energy of an equilibrium bulk crystal was obtained from the MS calculation using periodic boundary conditions in the three coordinate directions. The potential energy of a crystal with two surfaces was determined from the MS calculation using periodic boundary conditions in the \(x\)- and \(z\)-directions and a free boundary condition in the \(y\)-direction. The surface energy was then calculated from the energy difference between a crystal with surfaces and a bulk crystal with an equal number of atoms, and the total \((x-z)\) surface area. The results of the adatom binding energies and the surface energies are shown in Table 1, together with the relative surface packing density, the interplanar spacing, and the number of neighbors nearest to the adatom (i.e., its coordination number).

It can be seen that the binding energies of an adatom on the three surfaces decrease with the interplanar spacing, but increase with the surface energy. Table 1 also shows that the binding energy of an atom increases with the number of its nearest neighbors. Because atoms on a surface always have fewer nearest-neighbor atoms than those in the bulk, all the surface atom binding energies are significantly lower than the 3.54 eV cohesive energy of a bulk copper atom [57].

Standard procedures were used to calculate adatom migration energies on the different surfaces [58]. To compare with the threshold energies for kinetic-energy-assisted jumps, the energy barriers (i.e., the migration energies) by the direct hopping mechanism were considered. There are two different direct hop paths available on the \{110\} and \{111\} surfaces. The two on the \{110\} surface correspond to jumping in the \(\langle 110\rangle\) and \(\langle 100\rangle\) directions, and the two on the \{111\} surface correspond to \(fcc\rightarrow hcp\) and \(hcp\rightarrow fcc\) surface stacking transitions. The calculated migration energy results for these jump paths are listed in Table 2. For comparison, the migration energy of an atom in the crystal lattice (i.e., the vacancy migration energy) is also included [59]. It is noted that the migration energy of copper adatoms on a copper

<table>
<thead>
<tr>
<th>Surface type</th>
<th>{100}</th>
<th>{110}</th>
<th>{111|</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative density, (\rho)</td>
<td>2</td>
<td>(\sqrt{2})</td>
<td>(4/\sqrt{3})</td>
</tr>
<tr>
<td>Interplanar spacing, (d) ((\text{Å}))</td>
<td>1.81</td>
<td>1.28</td>
<td>2.09</td>
</tr>
<tr>
<td>Coordination number, (Z)</td>
<td>4</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Binding energy, (E_b) (eV)</td>
<td>2.880</td>
<td>3.251</td>
<td>2.513</td>
</tr>
<tr>
<td>Surface energy, (\gamma) (eV (\text{Å}^{-2}))</td>
<td>0.080</td>
<td>0.088</td>
<td>0.074</td>
</tr>
</tbody>
</table>
Table 2
Migration energies, $E_m$, for adatoms on different surfaces

<table>
<thead>
<tr>
<th>Surface type</th>
<th>([100])</th>
<th>([110])</th>
<th>([111])</th>
<th>Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jump path</td>
<td>(100)</td>
<td>(110)</td>
<td>(111)</td>
<td>(100)</td>
</tr>
<tr>
<td>Migration energy, $E_m$ (eV)</td>
<td>0.410</td>
<td>0.244</td>
<td>1.145</td>
<td>0.036</td>
</tr>
</tbody>
</table>

The \([100]\) surface has been determined experimentally to be about 0.4 eV by both Breeman and Boerma [60] and DeMiguel et al. [61]. This value is in good agreement with the one shown in Table 2.

### 4. Local heating

Experimental results for DC sputter-deposited thick films (~25 μm) of various metals have indicated that increasing the incident energy (by decreasing the background argon pressure) results in a flatter surface morphology and a less porous microstructure [46]. Detailed observation of the thermal evaporation deposition at a temperature of 20 K revealed the formation of an empty zone near atom clusters when adatoms have near-zero incident energies [62]. During impact with a substrate, an adatom’s kinetic energy can be transferred to substrate atoms near the impact site. In addition, the potential energy before the vapor-phase atom impact is also transferred to nearby surface atoms during the vapor atom’s condensation (i.e., release of the latent heat of condensation). Both effects result in a local increase in lattice translational energy which allows additional local atomic diffusion (and structure reconstruction) over that expected from usual (thermally assisted) processes. This can lead to a smoother surface morphology and fewer vacancies.

#### 4.1. Defect removal

An example of a 10 eV normal incident adatom impact near a subsurface vacancy in a lattice at 300 K is shown in Figs. 2a and b. In Figure 2, part of the crystal has been removed to reveal the region near a subsurface vacancy. After the adatom had transferred energy to the surface atoms, the surface atoms’ vibrational amplitudes were found to increase. This increased vibrational energy was rapidly transferred to the atoms adjacent to the vacancy. One of these atoms subsequently acquired sufficient energy and momentum to overcome the bulk (vacancy) diffusional energy barrier, and jumped into the vacant site. Once this vacant site was filled, the neighboring atoms rapidly relaxed to new equilibrium locations, resulting in a defect-free region of crystal, Fig. 2b. This all occurred within 0.4 ps of initialization of

![Fig. 2. Atomic configurations near a vacancy beneath a \([100]\) surface as a function of time during a 10.0 eV copper atom impact. The bulk vacancy was annihilated within 0.4 ps of the initiation of the impact: (a) before impact; (b) 0.4 ps after impact.](image-url)
the impact. Using a lattice vibration frequency of $5 \times 10^{12}$ s$^{-1}$ and an activation energy of 0.7 eV (Table 1), we note that a normal thermally activated mechanism would have taken about $10^{11}$ ps at 300 K to remove the vacancy.

4.2 Transient local heating

The defect elimination shown in Fig. 2 has been related to enhanced atom ‘athermal’ diffusion due to the impact-induced higher energy of surface atoms. During an impact, the energy of the adatom is transferred to vibrations of the crystal atoms at the impact site. This vibrational energy is then spread (and the extra jump probability dissipated) by thermal conduction via the lattice. The calculations indicated that this energy decay is extremely rapid. For practical deposition processes, the lattice can return to its quiescent temperature and remain there for extended periods between adatom arrivals. Defect reconstruction by impact-atom-induced atomic jumping therefore occurs in addition to that resulting from the usual thermal diffusion mechanism whose rate is dependent upon the substrate temperature. For comparison with usual thermally activated processes, the average kinetic energy of surface atoms, $\langle E \rangle$, can be related to an ‘effective’ temperature, $T$, through $T = (2\langle E \rangle/k) [63]$, where $k$ is Boltzmann’s constant. Both $\langle E \rangle$ and the local effective temperature $T$ following the impact are a function of time ($t$) after the impact and distance ($S$) from the adatom’s impact site. $T(t, S)$ values were determined at discrete values of $S$ corresponding to lattice points.

Following impact, the ‘temperature’ of nearby surface atoms reaches a peak at a time that depends on the adatom’s initial velocity. To compare peak values and their decay rates, we defined $t=0$ as the time when the nearest-neighbor atoms to the adatom achieve their highest temperature. Examples of the temporal decay of the effective temperature for nearest-neighbor surface atoms following impact are shown in Fig. 3 for incident atom energies of 0.0, 2.0, 10.0 and 20.0 eV. The spatial distributions of the temperature (from the impact point) at $t=0$ are shown in Fig. 4 for the same incident energies. In Figs. 3 and 4, the three
different symbols correspond to MD simulations of impacts with the three low-index crystal surfaces. The lines are best-fit curves, and the shaded regions indicate the contribution of the latent heat release (i.e., the heating deduced from a zero-incident-energy impact calculation).

The results shown in Figs. 3 and 4 reveal that the heating associated with a hyperthermal impact can be very large, but it is highly localized in both time and space. For instance, Fig. 3b shows that following a 2.0 eV impact, the temperature of the nearest-neighbor atoms reaches about 2000 K and then drops by about 1300 K in only 0.1 ps. It can be seen that this local heating decays completely within 2.0 ps, even after the most energetic (20.0 eV) impacts. We note that atoms arrive at each surface lattice site on a substrate surface about every 10 ms during high-rate deposition of 20 m s\(^{-1}\). Hence, the local heating effects associated with individual atom impacts are likely to be independent. Fig. 4b indicates that during the 2.0 eV impact, the local maximum temperature is about 2000 K for the atoms adjacent to the adatom. This is well above the melting point of copper (1356 K). However, because this high temperature affects only a small number of atoms within one or two atomic spacings of the impact site, and is not sustained, surface melting does not occur. Nevertheless, the effective temperature near an impact site is sufficient to result in a high probability for surface atomic hopping and therefore atomic-scale reconstruction during film growth. It is also noted that the type of crystallographic surface has relatively little effect upon the local temperature. To a good approximation, the temperature data for all three surfaces can be described by a single function.

4.2.1. Latent heat release

The temporal and spatial thermal profiles shown in Figs. 3 and 4 are a consequence of the combined contributions of latent heat of condensation and kinetic energy dissipation. The latent heat contribution to the thermal transient is shown in Figs. 3a and 4a. The latent heat release causes the nearest-neighbor atoms to experience a rapid increase of effective temperature from 300 to about 1000 K. Despite the different values of the latent heat (i.e.,

binding energies), the local temperature profiles are seen to be similar for different crystallographic surfaces. At first sight, it is surprising that the significantly higher binding energies of the {110} surface does not result in a higher kinetic energy per atom (or effective temperature) near the impact site. However, recall that the binding energy is related to the number of nearest surface-atom neighbors. Since the potential energy of the adatom is more or less evenly partitioned among these atoms, the typical vibrational energy per atom is then similar for all surfaces.

Fig. 3a indicates that the temperature rise associated with a latent heat release usually persists for less than 0.5 ps following the impact. Nevertheless, it can still play a role in atomic assembly and affect surface atomic configurations. For instance, the site residence time for an atom to jump over a low surface-energy barrier of 0.06 eV is about 0.5 ps at 1000 K.

Incorporation of the effects of local heating in the modeling of thin film surface morphology and microstructure requires expressions for the temporal and spatial thermal distributions. To quantify the contribution of the latent heat release to the local temperature as a function of time and distance from the impact point, a functional form derived from the heat flow equation for a point source was fitted to the simulation data obtained for zero incident adatom energy. The fitted result is listed as Eq. (1) in Table 3. The curves determined by Eq. (1) are shown in Figs. 3a and 4a and were used to define the boundaries of the shaded regions in Figs. 3a–d and 4a–d.

4.2.2. Incident kinetic energy

The far-field incident kinetic energy of an adatom prior to its deposition is also partitioned amongst the surface atoms upon impact. This results in additional local heating and a further increase in the probability of elimination of surface or near-surface vacancies (Fig. 2) as well as surface-diffusion-enhanced flattening of the growth surface [64]. To enable the incident energy contribution to the local heating to be characterized, Eq. (1) was extended to fit the MD data obtained at various incident energies, and the result is listed as Eq. (2) in Table 3. Figs. 3b–d and 4b–d show the temporal and spatial dependence of the local temperature on the three surfaces during an adatom’s impact at energies of 2.0, 10.0 and 20.0 eV. The temperature rise resulting from the impact energy is not sensitive to the type of crystallographic surface. As the incident energy is increased, more energy is transported to the atoms beyond the nearest-neighbor atoms to the adatom. Hence, the energy rise depends more on the bulk crystal structure than on the crystallographic surface. The curves of Eq. (2) are also shown in Figs. 3 and 4.

They match well with the MD data obtained.

5. Kinetic-energy-assisted adatom jumping

Unlike the atomic jumping due to the vibrational movement of a collection of heated atoms, an impacting adatom usually possesses a much higher energy than the surroundings. It is then possible for the adatom to achieve an energy level higher than a threshold value, $E_c$, to directly jump over an energy barrier. Because continuous energy dissipation to the surrounding atoms occurs during a jump event, the threshold energy $E_c$ for this type of kinetic-energy-assisted jump must be larger than the energy barrier, $E_m$. To investigate this scenario and obtain estimates for $E_c$, an atom was placed at a lattice site on the surface. After thermal equilibration, different initial kinetic energies were assigned to the atom and the threshold energy ($E_c$) for it to jump across an energy barrier of known height was determined by MD simulation. The energy barriers on the {100} and {110} surfaces are sufficiently large for the thermally activated jumps to be separated from the kinetic-energy-assisted jumps, and hence various jump paths on the {100} and {110} surfaces could be investigated. It was found that when the initial direction of the hopping atom is close to the minimum-energy transition path, such as the [110] direction on a flat (110) surface, Fig. 1b, $E_c$ ranges between 1.3 and 1.7 $E_m$.

To relate this observation to a hyperthermal impact, we note that, during impact, an adatom achieves a maximum kinetic energy, $E_p$. $E_p$ is
Table 3
Best-fit expressions for local effective temperature, $T$, adatom kinetic energy peak, $E_p$, and adatom biased diffusion, $d_s$

<table>
<thead>
<tr>
<th>Equation</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Local effective temperature due to latent heat release: $T(t, S) = T_{sub} + 29.76(e^{0.05t} - 0.05) - 3.21e^{-2.00S^2}/(t+0.05)$</td>
<td>$t =$ time, $S =$ distance from adatom, $T_{sub} =$ substrate temperature</td>
</tr>
<tr>
<td>(2) Local effective temperature due to latent heat release and incident kinetic energy: $T(t, S) = T_{sub} + 51.0 + 3.0E_i - 21.24e^{-3.21E_i}/(t+0.05) - 3.21e^{-2.00S^2}/(t+0.05)$</td>
<td>$E_i =$ incident energy</td>
</tr>
<tr>
<td>(3) Adatom kinetic energy peak: $E_p(E_i) = 1.95 + 1.0E_i$</td>
<td></td>
</tr>
<tr>
<td>(4) Adatom biased diffusion: $d_s(h, E_i) = zE_l^n[1 - 1/2(h/h_m)^n]$</td>
<td>Parameters: $z = 1.03 \times 10^{-17}$, $4.03 \times 10^{-12}$ and $4.11 \times 10^{-7}$, $l = 1.2$, $1.37$ and $1.09$, and $n = 5.54$, $6.08$ and $3.77$ for the {100}, {110} and {111} surfaces, respectively. $h_m = 81.0 - 30.0 e^{-0.18E_i}$</td>
</tr>
</tbody>
</table>

always higher than the initial incident energy, $E_i$, since the latent heat of condensation causes adatom acceleration near the surface. However, the difference between $E_p$ and $E_i$ is always less than the latent heat release per atom because a part of the energy of condensation immediately begins to be partitioned amongst the surface atoms. Clearly, it is the kinetic energy peak $E_p$ that determines the likelihood of a kinetic-energy-induced adatom relocation. Values of $E_p$ as a function of $E_i$ were calculated and the results (the average of five MD simulations for each case) are shown in Fig. 5.

Fig. 5 indicates that, to a good approximation, $E_p$ is essentially the sum of $E_i$ and about 2 eV of the binding energy. Thus, about 60–70% of the binding energy between a single adatom and a flat surface (see Table 1) is converted into the adatom kinetic energy, while the remainder is partitioned amongst the surface atoms. An interesting finding in Fig. 5 is that the different surfaces have only a minor effect on $E_p$. This is again consistent with the notion that a surface with a high adatom binding energy has a high number of nearest-neighbor atoms which absorb a high fraction of the latent heat during the adatom's condensation. An empirical equation for $E_p$ as a function of $E_i$ was fitted and is listed in Table 3 as Eq. (3) for all three surfaces. Based on the data in Table 2, it can be seen that kinetic-energy-assisted jumps are highly likely to occur when adatoms have a kinetic energy exceeding 1 or 2 eV. However, Fig. 5 shows that even an adatom with zero incident energy can achieve an energy peak ($E_p$) of about 1.5 eV or more and therefore has a significant probability of making a kinetic-energy-assisted jump to another lattice site.
6. Biased diffusion

Reflection high-energy electron diffraction (RHEED) experiments have indicated that during deposition of copper at 77 K, the deposited copper atoms often skip across the surface before coming to rest at island edges, resulting in quasi layer-by-layer growth [21]. FIM experiments have also shown that copper atoms deposited on to a cold (200−400 K) tungsten tip can migrate over anomalously long distances (even reaching the back side of the tip) in the time available during deposition [22]. It has been argued that since thermally activated diffusion is negligible in these temperature ranges, the observed phenomena are indicative of biased diffusion induced by the high momentum of the incoming atoms [21,22]. SIMBAD simulations have indicated that this mechanism of diffusion could have a profound effect upon trench filling [34]. However, no complete experimental characterization or atomistic simulation of the dependence of this type of biased diffusion on incident energy and angle has been reported to date.

MD simulations over a wide range of incident energy (1.0−20.0 eV) and various incident angles (0−85°) were conducted to explore the biased diffusion and its dependence on incident energy and incident angle. To illustrate biased diffusion, a time lapse picture is used to show the positions of the adatom at 0.1 ps time intervals and the positions of substrate atoms at the start of the impact. Fig 6 shows an example of a 20.0 eV oblique (incident angle of 80°) adatom impact with a flat {100} surface, where adatoms and substrate atoms are marked with dark and light balls, respectively. It can be seen that the adatom skipped over the surface a considerable distance (in excess of 100 Å) before coming to rest about 2.5 ps after the impact. By purely thermally activated diffusion, an atom would normally take about 10⁷ ps to diffuse this distance. To quantify the biased diffusion effect, a skipping distance, \( d_s \), is defined (see Fig. 6) as the distance between the adatom’s rest location and the point where a straight projection of the adatom free flight path intersects the surface. While the skipping distance is larger than zero when significant biased diffusion occurs, it should be noted that in some cases it can be negative because the adatom is attracted by the surface and its path can then be bent towards the surface. The skipping distance was calculated for a range of incident energies and incident angles. The results are summarized in Figs. 7 and 8, where the three different symbols again distinguish data for three different types of surface plane.

Figs. 7a, b and c plot the skipping (biased diffusion) distance as a function of incident angle for incident atom energies of 2.0, 10.0 and 20.0 eV. Fig 8 shows the skipping distance as a function of incident energy for a constant incident angle of 60°. From Fig 7a it can be seen that at low incident energies (e.g., 2.0 eV), the skipping distance is close to zero for most angles, but becomes slightly negative at large (grazing) angles of incidence. This negative biased diffusion is a manifestation of adatom path curvature resulting from the attraction of the surface. At low incident energies, the adatom has insufficient energy to overcome the energy barrier for surface skipping and it is arrested near the first site of impact. This
The skipping distance as a function of incident angle for different substrate surfaces at a constant temperature of 300 K and various incident energies: (a) 2.0 eV, (b) 10.0 eV, and (c) 20.0 eV.

Fig. 8. Skipping distance as a function of incident energy for different substrate surfaces at a constant temperature of 300 K and a constant incident angle of 80°.

leads to a negative skipping distance being recorded. As the adatom energy is increased, the adatom begins to have sufficient energy and momentum to overcome the energy barrier for skipping. As a result, a positive skipping distance is recorded. Figs. 7b and c show that, at high incident energies above 10.0 eV, the skipping distance increases with incident angle θ when θ is less than ~80°, reaches a maximum at a θ value of about 80°, and then decreases. At low θ, the adatom has a high-velocity component normal to the surface which does not contribute to skipping but does result in energy transfer from the adatom to the surface. Increasing θ increases the atom’s velocity component parallel to the surface and thus increases the skipping distance. For θ > 80°, skipping is decreased due to surface attractions which bend the adatom path and result in a large discrepancy between the actual impact point and the one predicted for an undeflected path. Since the kinetic energy helps atoms overcome the energy barriers during skipping, the skipping distance increases with incident energy. Fig. 8 shows that at an incident angle of 60°, the skipping distance has an almost linear dependence upon the incident energy.

Both Figs. 7 and 8 reveal the biased diffusion to be highly sensitive to the type of crystallographic surface: the longest skipping distance occurs on the most densely packed {111} surface, and the shortest skipping distance occurs on the least densely packed {110} surface. As seen in Tables 1 and 2, both the binding and the adatom migration energy are the lowest on the {111} surface and highest on the {110} surface. In a sense, the binding energy is a measure of the attraction between the adatom and the surface, while the migration energy is indicative of the barrier (resistance) that impedes adatom skipping. Lowest binding and migration energies therefore lead to the longest skipping distance.

To characterize the dependence of adatom biased diffusion on incident energy $E_i$ and incident
angle $\theta$, the MD data were fitted to a function and the result is listed in Table 3 as Eq. (4). The curves determined by Eq. (4) are also shown in Figs. 7 and 8. It is important to note that, during real deposition processes, adatoms are likely to be deposited on atomically roughened surfaces. Atomic-scale roughness can affect the skipping distance. To illustrate, simulations were conducted on surfaces containing ledges and terraces. Fig. 9 shows the biased diffusion of an adatom moving either towards a ledge or on a terrace. In each case, the adatom had an incident energy of 15.0 eV and made an oblique angle impact (incident angle of 80°). The simulation shows that the adatom moving towards a ledge preferentially comes to rest at the ledge, Fig. 9a, in agreement with experimental observations [21]. Fig. 9 also indicates that both the atomic-scale ledges and terraces reduce the biased diffusion distance. The behavior captured in Eq. (4) is therefore likely to be a higher bound that will increasingly overestimate biased diffusion distances as the surface becomes progressively rougher (e.g., as the deposition rate increases or the deposition temperature decreases).

7. Discussion

Athermal and biased diffusion has been shown to occur during hyperthermal deposition. Athermal diffusion originates from the local heating of the substrate surface as a result of the latent heat release and partitioning of the incident atom’s kinetic energy amongst the vibrational modes of the atoms close to the impact site. Because of thermal conduction, the temperature rise is very brief: for impact energies below 20.0 eV, the lattice returns to its equilibrium within about 1 ps. Nonetheless, the significant vibrational energy present during the transient is sufficient to cause a high atomic hopping probability both on the surface and within the bulk near the impact site. Biased diffusion occurs during oblique hyperthermal deposition where adatoms are able to propagate large fractions of a $\mu$m by a skipping mechanism. The functional dependence of both these diffusion processes upon the incident energy and incident angle has been estimated, enabling an assessment of their significance for processes where the incident energy and angular distributions of the deposition flux are known.

In many applications, a low substrate temperature must be used to prevent thermal damage to substrates or interdiffusion with previously deposited materials. In other applications, a very high deposition rate is desired to increase process speed. Because the degree of thermal diffusion can be small in both cases, the deposited films are frequently porous and have very rough surfaces [39,46]. The results reported here indicate that increasing the incident energy by using low sputtering pressure and/or bias techniques can induce large, but highly localized temperature spikes during deposition. These allow surface atoms to make extra jumps to nearby, more stable, lattice sites without significantly elevating the substrate temperature. It is likely to result in a significant flattening of a surface, a denser film, and a reduction in the defects without incurring excessive

![Fig. 9. Examples of adatom skipping on rough surfaces. Substrate temperature 300 K, incident angle 80°, incident energy 15.0 eV and {100} surface: (a) rest at the edge of a ledge; and (b) skip down from a terrace.](image-url)
thermal di\textit{V}usion reaction with previously deposited layers.

During deposition on patterned surfaces (e.g., to deposit interconnects), the incoming flux is often collimated in a direction near normal to the wafer surface to promote the ballistic transportation of adatoms to the trench bottom. However, adatoms close to the sidewalls of the trench can still be deflected towards the sidewalls due to the surface attraction. The accumulation of these atoms on the sidewalls then leads to the formation of overhangs near the upper end of the trench. These overhangs eventually pinch-off the trench openings before the trench is completely filled, resulting in the trapping of large voids inside the trench. Since the collimated flux makes oblique incidence with the sidewalls, the results reported here suggest that significant adatom biased di\textit{V}usion along the sidewalls can occur under hyperthermal deposition conditions (e.g., low sputtering pressure). This will tend to shift the deposition profile towards the bottom of the trench and is likely to improve filling.

The relative contributions of local heating and biased di\textit{V}usion have been characterized with simple relations suitable for incorporation in simulations of vapor deposition processes. These promise an opportunity to systematically investigate the effects of impact energy and angle on thin film morphology and microstructure and a better understanding of the atomic-scale mechanisms responsible [49].

8. Conclusions

Molecular dynamics analyses of adatom impact during the deposition of hyperthermal copper atoms have revealed that significant athermal and biased di\textit{V}usion occurs. Detailed relationships between the extent of these effects and the (process-dependent) incident energy and angle of the atoms have been established. It has been found that:

1. The latent heat release during a thermal adatom’s condensation leads to a brief (<1 ps) local temperature increase of about 700 K. This is sufficient to promote atomic hopping and therefore athermal di\textit{V}usion on a growth surface.

2. Hyperthermal atoms with high incident energies (up to 20.0 eV) can cause an additional local temperature increase to between 2000 and 4000 K. The local region of heating is only a few atomic spacings wide and deep, and decays quickly with time. However, extensive athermal di\textit{V}usion does occur, and this is likely to promote flatter, less defective films.

3. When the incident energy and angle are high (oblique, hyperthermal deposition), adatoms can skip over the growth surface, resulting in biased di\textit{V}usion in the direction of incidence. Increasing the incident energy generally increases the distance of the biased di\textit{V}usion to 0.01 µm or more. The biased di\textit{V}usion distance exhibits a maximum at an oblique angle of incidence (θ about 80°). Biased di\textit{V}usion may promote better trench filling during the manufacture of microelectronic interconnects.

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