# Reaction rates for ionized physical vapor deposition modeling from molecular-dynamics calculations: Effect of surface roughness

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We carefully analyze the surface adsorption, reflection, and etching reactions taking place during ionized physical vapor deposition using molecular-dynamics techniques and calculate their relative probabilities. We discuss in detail the angular and energetic distributions of hyperthermal Al atoms impinging on flat and stepped Al surfaces and investigate the influence of surface roughness on the rates obtained within our approach. On flat surfaces, we predict a preferred direction of emission for the sputtered particles, that depends on crystal structure and surface orientation. In addition, we compare for Al and Ti the total sputter yield and find a lower threshold energy for Ti in agreement with experimental observations. [S0163-1829(99)09143-2]

The filling of contacts and vias is a well established technique for the advanced multilevel metalization especially for the sub $\mu$m technology.[1] As semiconductor linewidth dimensions have shrunk and the aspect ratios of vias and trenches have increased (aspect ratio = depth / width of feature), it has become evident that conventional magnetron sputtering cannot meet future technology needs.[2] Currently aspect ratios for vias of 2:1 are common and ratios of 4:1 and 5:1 are expected in the near future.[3] Conventional sputtering is generally characterized by a spatial emission profile for the sputtered atoms, which is roughly described as a cosine distribution. This yields to a very broad angular distribution in the arrival of sputtered atoms at the sample surface and provides good step coverage on low-aspect features, but filling of deep features is poor due to the buildup of overhanging sidewalls.[2] The presence of a physical filter or collimator between cathode and sample limits the angular spread of the deposition, but severely reduces the deposition rate.[4] Rossnagel *et al.*[2] developed a new deposition technique that combines conventional magnetron sputter deposition with a radio frequency inductively coupled plasma. Using this technique a large fraction, up to 80%,[5] of the metal atoms sputtered from the magnetron cathode are ionized in the plasma. By placing a bias voltage on the sample, the metal ions are accelerated across the sample sheath and deposited at near normal incidence. Hence, ionized magnetron sputtering improves the filling characteristics of the features by reducing the buildup of overhanging metal deposit at the mouth of the structure and allows the control of the energy range of the metal atoms by adjusting the bias voltage. Due to the increasing technological demands for the sputter process an understanding of the underlying atomistic processes is required.[6] Hence there has been increased effort[7–10] to model highly nonthermal deposition techniques using the molecular-dynamics approach.[11,12] But previous studies were restricted to ideal and perfectly flat surfaces and did not take into account any effects due to surface roughness. The strengths of the molecular-dynamics technique is that one can study atomic trajectories and thus pursue the atomistics of the deposition. Since predictions resulting from this atomic level understanding offer a microscopic physical view, that cannot be obtained from experiment they are proving increasingly accurate and useful.[13]

In this article, we present numerical results for the angular and energetic distribution of Al atoms impinging on flat and stepped Al surfaces in order to investigate the impact of surface roughness on the rates obtained from molecular-dynamics calculations. In addition, we compare the total etch rates for aluminum and titanium atoms and discuss the dependence of the preferred emission direction on different material properties. Knowledge of the effects of surface roughness and the angular dependence of reemitted atoms are a further key element for a predictive and reliable modeling of metal thin-film growth.

Our theoretical approach is based on classical molecular-dynamics using empirical interatomic potentials for the Al-Al and Ti-Ti interaction. For Al we use the extensively tested model of Refs. 10 and 14. For Ti, we employ a modified version of the model developed in Ref. 15. Both models were augmented by an exponential repulsive pair potential[16] to account for the short-range interaction of atoms exceeding 10 eV; this is a key requirement as the kinetic energies of deposited atoms can exceed 150 eV during ionized physical vapor deposition.

We determined, as a function of the energy and off-normal angle of incident Al/Ti atoms, the probability of three processes: adsorption, reflection, and etching (in the latter case, the incoming atom's impact on the surface causes the kickout of one or more substrate atoms). We also analyzed the angular and energetic distribution of atoms reflected from the surface or etched from the surface upon impact. Supercells containing more then 1000 atoms arranged in typically 10 atomic layers are employed; cell dimensions are chosen so as to avoid artifacts of the in-plane periodicity. The starting configuration is chosen to be a flat (111) surface for the case of Al and a flat (100) surface for Ti (corresponding to

 

the thermodynamically most stable surfaces with the lowest formation energy). For the studies of surface roughness we used the highly stepped Al(211) surface, which consists of terraces two atomic rows wide with (111) orientation. All atomic coordinates are allowed to evolve dynamically, except those of the two bottom layers of the supercell. The surface temperature is set 20% larger than the bulk Debye temperature.

We start our simulations with the incident Al atom placed outside the interaction range of the surface. Its initial kinetic energy is set in the range of 25 to 125 eV, and its starting angle off the surface normal in the range 0° to 80°, which corresponds to typical ionized physical vapor deposition conditions. Due to the assumption of validity of the Born-Oppenheimer approximation implicit in classical molecular-dynamics simulations, intra-atomic electronic excitation effects are not accounted for in our calculations. This is justified since typical relaxation times for electronic excitations are much shorter than the timescale of interest in our study, and also because the energies involved are much smaller. The trajectories of the incident atom, and of any other atom that may be etched away from the surface upon impact, are then monitored until either a certain time span has elapsed, or the outcoming atoms (in the case of reflection or etching) have traveled a distance of 10 Å away from the surface. Analyzing 200–1000 trajectories per incident energy and angle, we collected a statistically significant sample of well-defined adsorption, reflection, and etching events. The relative probability of the corresponding process is calculated as the ratio of the number of events of each kind to the total number. The typical statistical error in the reaction probabilities thus determined is below 5%.

*Effect of surface roughness.* To the best of our knowledge there is neither any experimental nor theoretical prediction about the surface morphology during ionized physical vapor deposition conditions. Due to the very high-experimental growth rate [not well controlled, but in the order of 0.5 $\mu$m/min, or roughly 40 monolayer/sec (Refs. 17 and 18)] the surface will neither be perfectly flat nor be amorphous. The impact of surface roughness is analyzed by looking at the angular and energetic distribution of Al atoms leaving the flat Al(111) and the highly stepped Al(211) surface. An impinging particle experiences an average surface morphology that will be something in between the latter two extreme cases.

Panel (a) of Fig. 1 depicts results from the impact of Al atoms with an initial kinetic energy of 100 eV (typical for ionized physical vapor deposition conditions) on the flat Al(111) surface. It shows the relative probability of atoms (etched away or reflected from the surface) having a certain angle after the interaction with the surface. The total probability for atoms having a certain angle after the impact is shown as a black bar, the contribution of etch processes as striped bars and the contribution of the specular reflection events are marked as light gray bars. The sequence of the figures corresponds to three different impact angles towards the surface normal. For near normal incidence, i.e., 10° towards the surface normal, the reflected and sputtered atoms have a broad cosine-shaped angular distribution centered around 45° and no specular reflections occur in this case. Increasing the angle of incidence to 60° yields a shift in the

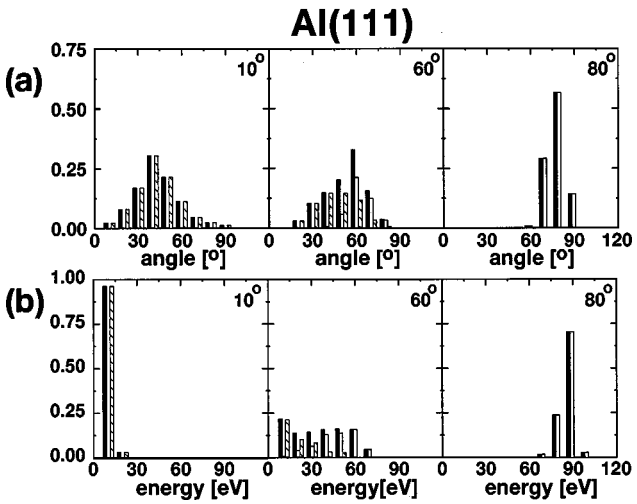


FIG. 1. Panel (a) angular distribution of Al atoms leaving the Al(111) surface after the impact of an Al atom with an initial kinetic energy of 100 eV for three different off-normal incident angles, namely 10°, 60°, and 80°. Panel (b) energetic distribution for the case of incidence as in panel (a). The black columns depict the total probabilities, the striped column the contribution due to etch events and, the light grey columns the contribution due to specular reflection events.

angular distribution and we now also get a significant contribution due to specular reflections. Finally, for incident angles in the regime of 80° all atoms undergo specular reflections with a sharply peaked angular distribution around 80°. Thus, there is a clear transition from diffuse to specular depending on the angle of incidence. For the deposition process not only the angular but also the energetic distribution plays an important role. The energetic distribution determines if an atom can undergo multiple reflection/etching events or will be adsorbed during its next surface interaction. Hence, it is also inevitable to analyze the energies of the atoms after impact. Panel (b) in Fig. 1 shows the latter quantity for an initial kinetic energy of 100 eV and impact angles of 10°, 60°, and 80°. For normal incidence specular reflections are completely absent and basically all the atoms have energies in the range of 10 eV. When they again encounter a surface they will be most likely adsorbed. For an impact angle of 60° there is a broad distribution of sputtered and also specular reflected atoms. Most of the atoms with high energies stem from specular reflection events. Finally, for near grazing incidence there is a distinct maximum in the energy distribution for 90 eV as all the atoms undergo specular reflections. These atoms are still highly energized after their interaction with the surface and can subsequently take part in multiple other surface reactions.[17]

On the flat Al(111) surface we thus observe a transition from a diffuse angular distribution for small impact angles to a sharply peaked distribution for nearly grazing incidence. This transition is accompanied by a change in the energetic distribution, which displays a distinct peak at low energies for small impact angles and a sharp peak at high energies for near grazing incidence. For intermediate angles the distribution is rather broad.

In the following, we address the effect of surface roughness on the angular and energetic distribution as the atoms will normally not experience a perfectly flat surface. For im-

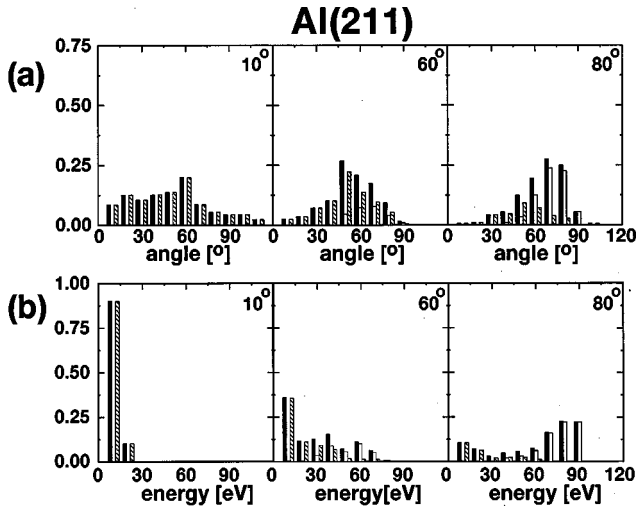


FIG. 2. Panel (a) angular distribution of Al atoms leaving the Al(211) surface after the impact of an Al atom with an initial kinetic energy of 100 eV for three different off-normal incident angles, namely 10°, 60°, and 80°. Panel (b) energetic distribution for the case of incidence as in panel (a). The black columns depict the total probabilities, the striped columns the contribution due to etch events and the light grey columns the contribution due to specular reflection events.

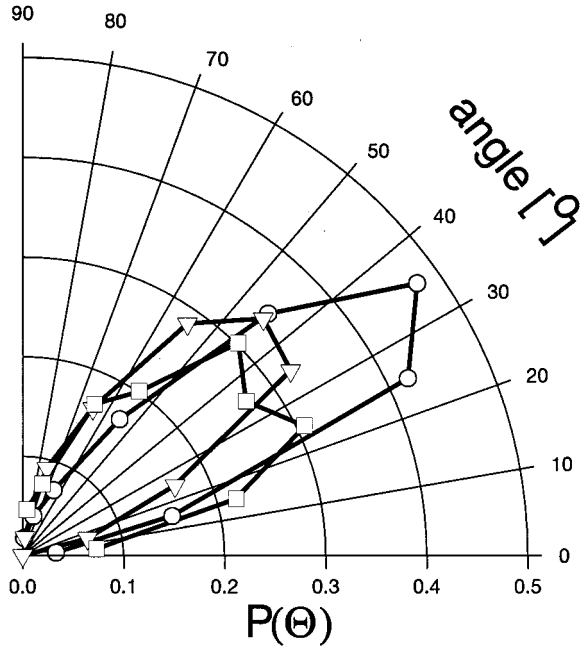


FIG. 3. Polar plot of the angular probability distribution $P(\Theta)$ of Al atoms leaving the Al(111) (solid line, open circles), the Al(211) (solid line, open squares) and the Ti(100) (solid line open triangles) after the impact of an 100 eV Al/Ti atom with an initial off normal angle of 0°. The distributions are normalized such that $\int P(\Theta) sin(\Theta) d\Theta = 1$.

pact on the highly stepped Al(211) surface panel (a) of Fig. 2 shows the angular distribution for the same deposition conditions and impact angles as in Fig. 1. As above the total probability for atoms having a certain angle after the impact is marked with black bars, the contribution of the etch processes as striped bars, and the specular reflection events are shown as light gray bars. Comparing the angular distribution from Al(211) to Al(111) for near normal incidence we do not have the cosine like distribution as on the flat surface. On the flat surface the maximum of the angular distribution is due to a preferential ejection direction, which is of course still present on the stepped surface but strongly disturbed by the presence of the steps. This disturbance of the direction of preferential ejection becomes especially evident by looking at a polar plot of the probability for atoms leaving the surface. Figure 3 shows this probability as a function of the off normal angle. The solid line with open circles corresponds to the flat Al(111) surface where the preferential ejection around 35° is clearly visible. The line with the squares depicts the ejection probability for the stepped surface where evidently the distribution is broadened and the direction of preferred ejection is less pronounced. For comparison we also added the same quantity for Ti atoms leaving the Ti(100) surface, which is shown as a solid line with open triangles. Due to the different crystal orientation and lattice types (bcc for Ti and fcc for Al) the direction of preferred ejection is now located around 45°. We propose the following model for the preferential angle of emission. For an adatom sitting on the flat Al(111) or Ti(100) surface respectively, its nearest-neighbor bond and the surface normal form an angle of 35° and 55°, respectively. The adatom adsorption sites are minima in the potential energy surface such that an atom that is etched away from the surface will be attracted by the surface adsorption well. This attractive potential will influence the particles trajectory during emission and hence there will be a preferred direction of emission. It seems plausible that the orientation of the adatom surface bond appears as a peak in the spectrum. This explanation is nicely confirmed in our calculations for Al and holds also within some error for Ti.

Increasing the angle of incidence to 60° (see Fig. 2) there are less specular reflection events on the stepped surface than on the flat surface due to the additional adsorption sites at the step edges. Furthermore the peak of the angular distribution is shifted from 60° on the flat surface towards 50° on the stepped surface. This is due to the fact that on Al(211) the surface normal would be tilted by $\simeq 20°$ with respect to Al(111). Hence, atoms impinging with 60° correspond to impact angles of 40° and 80° depending on the direction of incidence. Finally, for incident angles in the regime of 80° there is a broader angular distribution on the stepped surface compared to the flat Al(111) surface. For this angle we also get atoms stemming from etch processes due to the presence of step-edge atoms that contribute to the angular distribution for smaller angles.

Panel (b) in Fig. 2 shows the energetic distribution for the same impact angles as in panel (a). For normal incidence there is nearly no difference between the flat and stepped surface as specular reflections are completely absent here. The small difference in surface binding energy (0.1 eV) on Al(111) and Al(211) can be neglected compared to the energy of the impinging atom (100 eV). For an impact angle of 60° there are more etch events on the stepped surface and hence the energetic distribution of the stepped surface has a larger peak at low energies than the flat surface. Finally, for near grazing incidence the energy distribution for Al(211) is

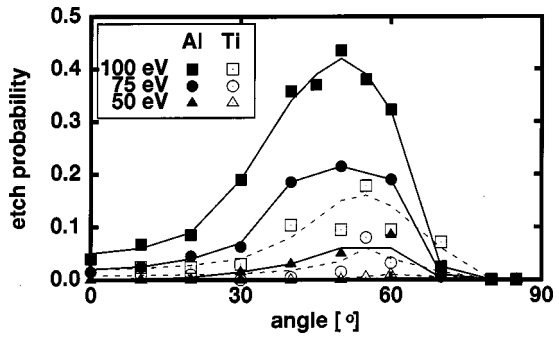


FIG. 4. Sputter probabilities for Al and Ti atoms impinging on Al(111) and Ti(100), as a function of incident angle and energy (50, 75, and 100 eV). The filled symbols correspond to data points for Al and are connected by a solid lines, the open symbols to data points from Ti which are connected by dashed lines.

completely different in comparison to Al(111). The stepped surface exhibits a broad energetic distribution and only for higher energies specular reflections contribute. The atoms in the low-energy regime stem from etch processes.

It is interesting to note that for off-normal angles up to 50° the total reaction rates for the Al(111) and the Al(211) surface are not very different. Approaching the situation of grazing incidence, on the flat surface nearly all the impinging atoms become specular reflected whereas on the stepped Al(211) surface atoms hitting the step edges cause atoms to be etched away. On Al(111) the etch probability for an incident kinetic energy of 100 eV and 70° is 0.05 and decreases to zero for larger angles. In contrast on Al(211) this probability amounts to 0.25 for 70° and drops to 0.05 for 85°.

Thus, we find that the surface roughness that sensitively depends on the deposition conditions can have a large effect on the energetic and angular distribution of atoms etched away or being reflected upon impact. This has drastic implications for the filling of vias and trenches during the metalization. In such a process most atoms will either interact with the sidewall or the top and bottom walls of the structure. The first case belongs to near grazing incidence the second one to normal incidence. For deposition with highly energized atoms especially the less-peaked energetic distribution for large angles towards the surface normal will have an ample impact on the resulting film structure. For rough surfaces the atoms will undergo less multiple reflections and hence will not reach the bottom of the structure as easily as for perfectly flat surfaces.

Thus, our calculations help to resolve the still puzzling question how the surface morphology influences the resulting topography not only by qualitative but also by quantitative arguments. Future work is going on to develop a feature scale simulator including the effect of surface roughness and orientation.

*Comparison of different materials.* We have chosen Ti as the second material system. For three representative incident kinetic energies, namely 50, 75, and 100 eV the etch rate as a function of off-normal angle is summarized in Fig. 4. The calculated points for Al are shown as filled symbols and those for Ti as open symbols. It is interesting to note that for all incident energies the etching probability reaches a maximum at about 50° and decreases for angles exceeding 50° as near-grazing angles are approached. For small deviations from normal incidence, the etch rate initially raises, since the probability of a surface atom to gain momentum directed away from the surface increases when the incoming atom arrives at an oblique angle at the surface. At large angles of incidence the etch rate drops because of the competing specular reflection events. At low energies (50 eV) and 50° there is already a non-negligible etching probability of about 10% for Al, whereas for Ti the latter quantity is well below 2%. Increasing the incident kinetic energy to up to 100 eV we find for Al a distinct maximum in the etching probability for an angle of 50° with respect to the surface normal. The peak for Ti appears for the same angle although its absolute value is less than half the etching probability of Al. Experimental observations[19] confirm the existence of a maximum in the etch rate as well as the lower etching probability for Ti. Furthermore, we thus find a lower threshold energy for Al than for Ti that is mainly due to the 50% larger cohesive energy of Ti ($E_c = 3.36$ eV for Al and $E_c = 4.90$ eV for Ti) which is again in accordance with experiment. Thus, it costs more energy to remove a surface atom from the Ti surface in comparison to the Al surface. Another interesting feature of the total etch rates is that with increasing impact energy the maximum in the etch rate tends to smaller angles. We assign this effect to the larger penetration depth with increasing impact energy, which facilitates the surface atoms getting momentum directed away from the surface. It is also interesting to investigate the nature of the sputtering processes. We term these processes to be of $n$th order if upon the impact of a single-particle $n$ particles are etched away from the surface. In the following, we discuss the angular dependent order of the sputter processes for Al atoms with an initial kinetic energy of 100 eV. For incident angles up to $30^o$ first order sputter processes are dominant but also a sizable fraction of second-order processes is present. Increasing the angle further to 40° the probability for first-order and second-order sputter processes approach similar size and a small number of higher order etch processes can be found. In the range of $50-60°$, close to the maximum in the yield curve, second order processes are dominant. In most cases for a sputter process of $n$th order $n$-independent particles leave the surface. The formation of small cluster, i.e., dimers, trimer, etc. is rarely observed. As the surface binding energy does not vary significantly compared to the incident kinetic energy we do not expect the above observations to change with surface orientation.

In conclusion, we performed detailed theoretical calculations of the probabilities for surface reactions taking place during ionized physical vapor deposition conditions and analyzed the angular and energetic distribution of the atoms involved in the surface reactions. Our molecular-dynamics calculations revealed for high-incident energies a strong dependence of the angular and energetic distribution on the roughness of the surface. These results allow a quantitatively prediction of the influence of the surface roughness on the filling characteristics and shows the importance not to restrict molecular-dynamic studies to perfectly flat surfaces. Investigating the total etch probabilities for Al and Ti on Al(111) and Ti(100), respectively we find for both materials a distinct maximum in the etch rates for angles of 50°. The existence of the maximum in the etch rate and the larger etch

probability for Al compared to Ti are both in accordance with experimental observations. Furthermore, we were able to predict a preferred direction of emission and could shine light on the influence of crystal structure and orientation of this effect. Our results represent a major step ahead over earlier calculations using only flat surfaces and allow us to predict the influence of surface roughness and different materials on the filling process using ionized sputter deposition techniques.

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[1] H. J. Barth, Mater. Res. Soc. Symp. Proc. **472**, 253 (1996).
[2] S. M. Rossnagel and J. Hopwood, Appl. Phys. Lett. **63**, 3285 (1994).
[3] S. S. Winterton, T. Smy, S. K. Dew, and M. J. Brett, J. Appl. Phys. **78**, 3572 (1995).
[4] S. M. Rossnagel, D. Michalsen, H. Kinoshita, and J. J. Cuomo, J. Vac. Sci. Technol. B **11**, 2796 (1993).
[5] S. M. Rossnagel and J. Hopwood, J. Vac. Sci. Technol. B **12**, 449 (1994).
[6] J. Dabrowski, H.-J. Müssig, M. Duane, S. T. Dunham, R. Goossens, and H.-H. Vuong, Adv. Solid State Phys. **38**, 595 (1998).
[7] D. E. Hanson, A. F. Voter, and J. D. Kress, J. Appl. Phys. **82**, 3552 (1997).
[8] D. G. Coronell, D. E. Hanson, A. F. Voter, C. L. Liu, and J. D. Kress, Appl. Phys. Lett. **73**, 3860 (1998).
[9] J. D. Kress, D. E. Hanson, A. F. Voter, C. L. Liu, X. Y. Liu, and D. G. Coronell, J. Vac. Sci. Technol. A **17**, 2819 (1999).
[10] U. Hansen, P. Vogl, and V. Fiorentini, Phys. Rev. B **59**, 7856 (1999).
[11] D. Frenkel and B. Smit, *Understanding Molecular Simulations: From Algorithms to Applications* (Academic Press, Boston, 1996).
[12] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1996).
[13] A. F. Voter, Mater. Res. Bull. **21**, 17 (1996).
[14] U. Hansen, P. Vogl, and V. Fiorentini, Phys. Rev. B **60**, 5055 (1999).
[15] G. J. Ackland, Philos. Mag. A **66**, 917 (1992).
[16] A. A. Abrahamson, Phys. Rev. **178**, 178 (1969).
[17] S. Hamaguchi and S. M. Rossnagel, J. Vac. Sci. Technol. B **13**, 183 (1995).
[18] W. D. Westwood, in *Microelctronic Materials and Processes*, edited by R. A. Levy (Kluwer, Dordrecht, 1989), p.133.
[19] R. E. Lee, J. Vac. Sci. Technol. **16**, 164 (1979).