Simulating growth of Mo/Si multilayers

W. Lowell Morgan
Kinema Research, 18720 Autumn Way, Monument, Colorado 80132

David B. Boercker
Lawrence Livermore National Laboratory, P. O. Box 808 L-299, Livermore, California 94550

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Multilayer structures of alternating thin layers of molybdenum and silicon are of great interest as x-ray optics components and a considerable amount of effort has been expended in their development. The efficiencies of these structures depend upon both the accurate control of the layer thicknesses and the sharpness in the interface between layers. High-resolution electron microscopy reveals that the interface created by deposition of Mo on Si is much more diffuse than that produced by depositing Si on Mo. We have used molecular dynamics to simulate the deposition processes and observe significant penetration of the Si substrates by the incident Mo atoms, while incident Si atoms remain on the surface of the Mo substrate.

The microstructure of x-ray mirrors constructed of alternating layers of molybdenum and silicon has been studied extensively in the laboratory.[1–3] These Mo/Si multilayers are fabricated by conventional sputter deposition techniques. In these structures the Mo layers are mostly crystalline while the Si layers are amorphous. In addition there is an asymmetry in the sharpness of the interfaces between the layers. The interfaces formed by Mo atoms deposited on Si substrates are much more diffuse than those formed by Si atoms incident upon Mo substrates.[2,3] The ratios of the interlayer thicknesses can vary from about 1.5 to 4, depending upon the details of the deposition process.[3] Since the sharpness of the interlayers can significantly affect the performance of the multilayer mirror, the mechanisms which determine interlayer thickness are an important area of research.

In this letter we discuss simulations that we have performed, using the molecular dynamics (MD) technique, of the deposition of Mo–on–Si and Si–on–Mo. These are atomistic simulations in which the dynamics of an atom incident on a surface and the dynamics of the atoms comprising the surface are computed by solving the classical equations of motion of all the particles in the system. The atoms in the system interact via pairwise and many body forces.

The interatomic potential functions are a critical component of an MD simulation. The silicon interactions are modeled using a combination pair and angle dependent three body potential developed by Stillinger and Weber.[4] This is one of the most commonly used potential functions for silicon modeling. Molybdenum interactions are modeled by a pair potential devised by Miller[5] specifically to yield the BCC lattice as the lowest energy crystal structure. We have used in our calculations this potential as rescaled by Ding and Andersen.[6]

The potential that we have used to describe the interatomic forces between molybdenum and silicon is an adaptation of the one constructed by Ding and Andersen[6] to describe Mo and Ge alloys. This interatomic potential consists of a Mo–Ge pair interaction and a Mo–Ge–Ge three body interaction. Possible terms involving a Mo–Mo–Ge triplet have been ignored. The forms of the functions are identical to those devised by Stillinger and Weber[4] for silicon. We have adapted the Ding and Andersen Mo–Ge potential for Mo–Si by slightly reducing the scale energy (ε) and the scale length (σ). The other parameters in the two and three body potential functions have remained unaltered.

In simulating particle deposition on a substrate using molecular dynamics we first arrange several layers of atoms (either Si or Mo) in an appropriate *structure and* project adatoms, one at a time, toward the substrate with energies selected from a specified distribution. The atoms in the upper layers are allowed to move according to Newtonian mechanics while the bottom layers are constrained through a generalized Langevin equation[7] to maintain a given average kinetic energy. In the calculations presented here the atoms in the bottom layer were maintained at 300 K. This constraint mimics the heat flow from the substrate into the bulk. The trajectories of all of the atoms in the substrate, as well as those projected toward it are calculated in full detail. After many atoms have hit the surface their distributions can be compared to experimental results. Typically one uses several hundred to a few thousand atoms and a time step of several femtoseconds for the numerical integration of the equations of motion. Simulation of processes over length scales of a few hundred Angstroms for tens of picoseconds are quite feasible. Despite the limitations it is possible to gain valuable insight into the physics and chemistry of the deposition process by modeling small systems over a short time.

We have performed prototype calculations of both the deposition of Mo–on–Si and of Si–on–Mo. We used both amorphous and crystalline substrates for silicon and a BCC crystalline substrate for molybdenum. The crystalline substrates were constructed of six layers of 16 (4×4) atoms each. In order to construct an amorphous silicon slab we performed an MD relaxation calculation using the Stillinger and Weber silicon potentials on the 216 atom amorphous structure generated by Wooten, *et al.*[8,9] Empirically, the incident energy of the adatoms is sensitive to a wide variety of experimental parameters.[10,11] In our simulations,

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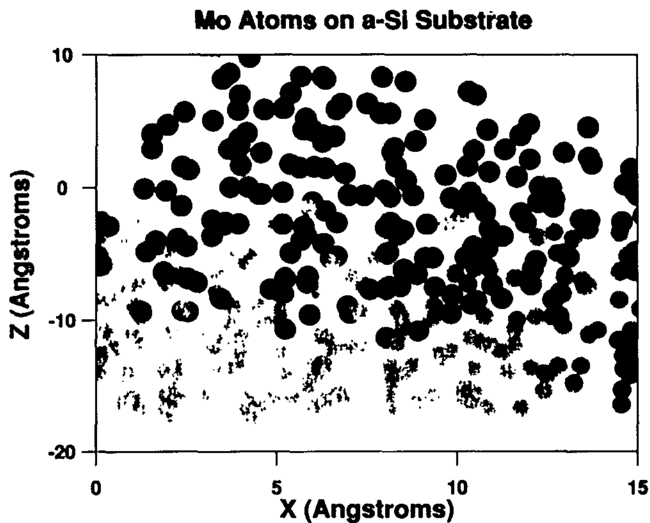

FIG. 1. Side view at an instant in time of 216 atom *a*-Si slab (gray circles) after deposition of 192 Mo adatoms (dark circles).

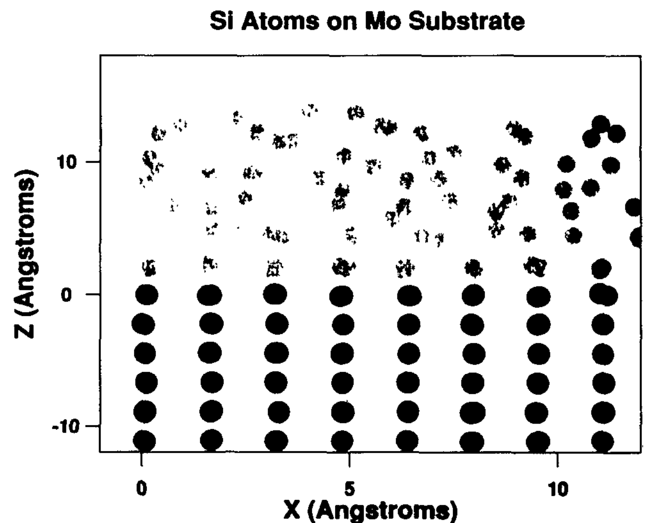

FIG. 3. Side view of 96 atom Mo BCC crystalline slab (dark circles) with 80 Si adatoms (gray circles) deposited on the (110) face.

we selected the incident energy for both Mo and Si to be 1 eV as a good compromise between completely thermalized energies and high energies in excess of about 10 eV. There was an interval of about a picosecond (600 time steps) between the arrival of individual adatoms. This is a long enough period for the system to become thermalized between impacts of successive adatoms.

Figure 1 shows a side view of the 216 *a*-Si slab upon which 192 Mo atoms have been deposited. We see that most of the Mo atoms initially deposited have mixed into the silicon and that the later arriving adatoms have begun to form a purely molybdenum layer. This enhanced mixing of the Mo adatoms into the silicon surface appears to be due to the agitation of the surface atoms by the incoming 1 eV Mo atoms. Figure 2 shows the average atomic mass as a function of z (sampled in increments of $\Delta z = 1$ Å). The shaded area indicates the original 216 atom *a*-Si slab. We see clearly the extent of the transition region where the Mo

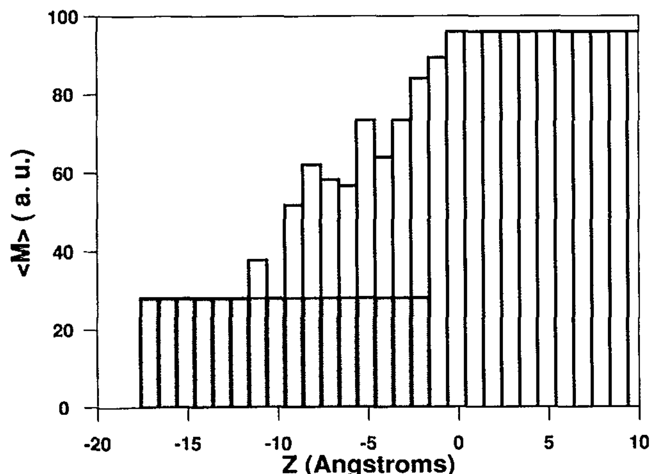

FIG. 2. Average atomic mass as a function of z (in Å) for the slab shown in Fig. 1. The shaded area indicates the original 216 atom *a*-Si slab.

and Si have mingled. In reality this region may be composed of $MoSi_2$ but it is unlikely that the somewhat crude Mo–Si potential used in these simulations is appropriate for molybdenum disilicide. We have computed Mo–Mo radial distribution functions in the purely molybdenum layer and have found that the average first coordination number is about 8, which is appropriate for a BCC material. It is feasible that for a larger slab and deposition of a much greater number of Mo atoms that layered growth of the molybdenum layer would occur in the simulation. It is found experimentally that eventually the Mo does grow in (110) layers after a transition region.

Figure 3 shows a side view of a Mo crystalline slab upon which Si atoms have been deposited. We see a sharp transition from the crystalline Mo to the amorphous Si. Sputtered silicon forms an amorphous structure experimentally. There have been several studies made[12–14] of the simulated growth properties of silicon using the Stillinger and Weber model for the Si interatomic potential. It has been found[13] that simulated growth does not produce ordered overlayers at temperatures below about 480 K. Consequently, the sputtered Si overlayer in these simulations is, as expected, amorphous. Experimentally some mixing at this interface is observed, but that may occur on much longer time scales than we can investigate in our simulations.

Our results reproduce many of the qualitative features seen in high resolution electron micrographs[2,3] taken of actual multilayers. Most significantly we reproduce the asymmetry in the interlayer thicknesses that are observed depending upon which of the components is the substrate. When Mo atoms are incident upon Si our simulations show that they penetrate several layers deep. In contrast, incident Si atoms make barely any penetration at all into the Mo substrates. The principal weakness of these simulations is the crudeness of the interatomic potential models, which make any quantitative comparisons doubtful. We are presently trying to improve the Mo–Si potentials through com-

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parisons with linearized muffin tin orbital (LMTO) calculations of the energy and structure of $MoSi_2$[15] and by utilizing available data on Mo_3Si and Mo_5Si_2. We also have available more accurate many body potentials for pure molybdenum.[16,17] We believe that the results presented here are encouraging enough to justify further research along these lines.

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