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The Role of Chemical Interactions in Ion-Solid Processes

Brian W. Dodson

Sandia National Laboratories

Albuquerque, NM 87185-5800

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Abstract

Computer simulation of low-energy ion-solid processes has greatly broadened in scope in recent years. In particular, realistic descriptions of the ion-solid and solid-solid interactions can now be utilized. The molecular dynamics technique, in which the equations of motion of the interacting atoms are numerically integrated, can now be used to characterize ion-solid interactions in a range of model material systems. Despite practical limitations of this procedure, a number of substantial results have appeared. The available results are examined to investigate the qualitative influence that chemical interactions have on low-energy ion-solid processes.

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WHEN IS CHEMISTRY IMPORTANT?

The overall interaction of an energetic ion with a solid results from a complex combination of electronic and nuclear (collisional) interactions. Fully accurate treatment of all these interactions poses an extremely difficult problem. Fortunately, in any given energy region approximations can be chosen which substantially reduce the complexity of the problem. In the high-energy regime, for example, the usual approximation is that the ion-solid interaction potential is a sum of purely repulsive pairwise screened Coulomb potentials between the cores of the interacting particles, combined with exchange and correlation energies based on a simple density-functional model and superposition of static charge densities.

As smaller beam energies are utilized, the approximations used to describe high-energy ion-solid interactions break down. A low-energy regime may be defined using a set of physically based criteria. The kinetic energy of the incoming ions must be at least on the order of chemisorption energies, typically several eV. An ion with this energy will perturb the local environment at least as much as occurs during chemisorption. A reasonable lower limit for the "low-energy" beam regime in most cases is thus 5-10 eV.

Establishing an upper limit for the "low-energy" regime is not as straightforward. One should require that the beam velocity is less than the Fermi velocity of the valence electrons of the target material. This limit generally corresponds to beam energies of several hundred keV, and thus appears much larger than appropriate for our current purposes. A more appropriate limit can be set by determining when the approximations used to describe high-energy (>>10 keV) ion beam interactions break down. In the absence of reactions, only repulsive interactions are considered in the high-energy regime. Rapidly moving atoms do not have time to form chemical bonds (i.e., the sudden approximation holds.) In addition, pairwise interactions are appropriate because the dominant interactions take place at small interatomic radii. Both of these approximations begin to break down near beam energies of a few hundred eV. In addition, the 'breakeven' energy for substrate sputtering (where the beam flux equals the sputtering rate) is on the order of 1000 eV for many systems. The low-energy regime thus encompasses beam energies of roughly 10-1000 eV.

ENERGETICS OF LOW-ENERGY ION-BEAM PROCESSES

In order to model low-energy ion-solid interactions with atomic-scale simulation techniques, tractable approximations for the dominant interactions are again necessary. These include the effect of the ion-solid "nuclear" interaction and the collective vibrational excitations in the substrate. The collective vibrational excitations in the substrate can be described within a molecular dynamics simulation simply by including an accurate interatomic potential for the substrate material. The primary difficulty is the ion-solid potential, which must include chemical bonding interactions at low energies. In the limit of very slow motion, the ion-solid interaction is treated adiabatically using the Born-Oppenheimer approximation, which states that the electrons are always in stationary eigenstates of the current nuclear configuration. At high energies, the sudden approximation is appropriate, and pairwise repulsive interactions can be used. In both high-energy (>> 1 keV) and extremely low-energy (< 10 eV) processes, the energetics of ion-solid interactions depend only on the instantaneous positions of the interacting atoms. This is not true in intermediate energy regimes.

In the intermediate energy regime, the collision may not be fully adiabatic. Some degree of electronic redistribution, which may perhaps be described as formation of nascent chemical bonds, occurs during the collision, but the conventional chemical bonds do not have time to form. In this situation, the nature and strength of the ion-atom nuclear interaction will depend not only on the present positions of the particles, but also on the relative velocity and past trajectories of the ion-atom pair. In this intermediate energy range, then, the ion-atom interaction should be treated using a <u>velocity and history-dependent description</u>.[1] Simulations reported therein suggest that such nonadiabatic effects are most prominant in the 10-100 eV regime, where they can produce major changes in the size and nature of collision cascades. Unfortunately, explicit treatment of nonadiabatic effects is not practical at this time.

INTERATOMIC POTENTIALS

In the past, very simple pairwise potentials have been used to describe the interactions between ions and atoms. In these, the total cohesive energy is a sum of energy of interaction between all pairs of atoms in the structure. The most common pairwise potential is the Lennard-Jones potential, which is the sum of a hard-core repulsive potential and a van der Walls attractive interaction. Adjustable parameters are fit to properties of the material under study. Another common pairwise potential is the Morse potential, which is a sum of attractive and repulsive exponential interaction terms. Such potentials have been used extensively for study of various issues in statistical mechanics.

For most materials, however, pairwise potentials do not provide an adequate description of the structural energetics. Even in condensed rare gases as much as 10% of the lattice energy is the result of nonadditive many-body interactions[2]; this proportion increases in systems having strong chemical bonds. During ion-solid processes, a wide range of non-bulk-like atomic configurations are encountered. As a result, the common practice of embedding many-body interactions into an 'effective' pairwise potential, which is sometimes quite useful in problems with a simple and well-defined atomic environment, should not be used. Instead, a description of the many-body interactions which is suitable for use over a wide range of bonding configurations must be obtained.

Several empirical many-body potentials have been developed to describe arbitrary configurations of silicon atoms.[3-7] The most commonly used potential is that of Stillinger and Weber.[3] They describe the potential energy of the system as sums of two and three-body interactions. This potential has a number of adjustable parameters, which were fit to the elastic properties and melting point of bulk silicon and to the structure of liquid silicon. This potential has been tested on a wide range of trial geometries, ranging from the high-pressure bulk phases to various surface structures. The generally satisfactory performance on these test structures has made the Stillinger-Weber potential the workhorse for simulations of tetrahedral semiconductors. Other potentials take on a range of different forms, but also have a number of free parameters which are fit to the properties of silicon.

Considerable success in the description of atomic interactions in metals has been acheived based on the idea that, to first order, the energy of an atom in the presense of other atoms is equal to the energy of the same atom 'embedded' in a homogeneous electron gas whose density is defined by the surrounding atomic configuration. Such a description is loosely based on density functional theory, but in practice the potential is fit to known properties of the metal under consideration. Examples of such techniques include the embedded atom method[8,9] and the effective medium theory.[10] When applied to close-packed metals and metal alloys having relatively simple electronic interactions, the embedded-atom method has proven transferable to a wide range of structural problems. Owing to the lack of explicit description of orbital hybridization, however, such techniques are currently limited to treatment of simple metals or metals having a nearly filled d-band.

ATOMIC-SCALE SIMULATION OF LOW-ENERGY ION-SOLID PROCESSES

There are three general classes of simulation techniques for study of atomic-scale structure generated by low-energy ion-solid events. The simplest, and most widely used for high-energy ion processes, are the Monte Carlo methods, with the TRIM-based codes[11] providing the best-known examples. Using the binary collision approximation, the ion-atom interaction is treated as a simple binary scattering event. The solid is assumed to be amorphous, and the distance to and impact parameter for the next collision are randomly chosen based on the average properties of the lattice. This procedure is iterated until the kinetic energy is dissipated. Evaluation of the extent of permanent damage is accomplished by identifying an average 'displacement energy' for formation of lattice defects. Such simulations are essentially pragmatically defined stochastic descriptions with limited basis in the actual dynamics of the system. They provide reasonable accuracy for the collisional regime of high-energy ions primarily because a highly refined empirical fitting process has been developed over several decades. In the low-energy regime, however, essentially all of the approximations used in development of Monte Carlo techniques break down.

A significant refinement of the Monte Carlo techniques is sometimes called the binary-collision lattice technique. The best-known code of this type is probably MARLOWE.[12] These techniques follow the Monte Carlo procedures, save for two factors. First, rather than assuming an amorphous lattice, the actual lattice of the solid determines the trajectories of the incoming ions. Second, the angle of deflection is calculated in each binary collision. The trajectory through the lattice is then followed from collision to collision throughout the lattice until the kinetic energy is dissipated. The result is a deterministic calculation of the ion trajectory and the corresponding cascade, fixed by the crystal lattice, interaction potential, and the initial beam trajectory. This procedure is more accurate for range calculations, because lattice effects, such as channeling, are included. However, the treatment of lattice damage is still probablistic in nature (based on an average displacement energy), the collisions are still assumed to be binary in nature, and the moving particle is assumed to travel on straight lines between these binary collisions. All of these assumptions are questionable in the low-energy regime.

Finally, the molecular dynamics techniques[13] provide a description of ion-solid processes as accurate as the description of interactions between the various parts of the system. In this approach, the Newtonian equations of motion of the individual atoms are integrated in time to obtain the actual trajectory of the entire system through phase space. (For beam energies above 10 eV, the deBroglie wavelength of an ion is several orders of magnitude less than interatomic spacings. The assumption of classical trajectories is therefore justified.) This is a wholly deterministic procedure, and naturally includes lattice damage, collective effects of the solid, and simultaneous interactions amongst several particles. In principle, then, the molecular dynamics techniques are the ideal approach toward low-energy ion-solid process simulation, including both the collisional and thermalization phases. The difficulty is that these techniques are orders of magnitude more difficult to carry out from a computational viewpoint. As a result, only a handful of such simulations have been performed at this time.

SIMULATIONS OF LOW-ENERGY ION-SOLID PROCESSES

Ion-Solid Interactions

Simulations of the interaction of low-energy (<50 eV) neutral Si beams with a (111) silicon substrate have been carried out.[14] All atom-atom and ion-atom interaction were treated using an empirical many-body potential[6] which captures the essence of the covalent solid-state bonding. (The tacit assumption of fully adiabatic bonding was made here. This is probably reasonable in this very-low energy regime.) In the case of near-normal incidence, both the range of the ions and the extent of lattice damage were found to be greater than expected from the conventional Monte Carlo or binary-collision lattice models. (See Figure 1.) The extended range is caused by interactions which steer the ions into lattice channeling directions, allowing deeper penetration than expected. The overall picture resulting from this study is very different from that suggested by the stochastic simulation techniques.

Grazing incidence trajectories have also been studied.[15] In these, incoming neutral Si ions were directed along glancing (3-30°) trajectories intersecting the (110) rows of atoms on a Si(111) surface. At larger angles of incidence, the ions were found either to scatter off the surface or stick near the impact site. As the incidence angle is reduced, however, the vertical momentum is absorbed by phonon-mediated inelastic interaction with the substrate, and the ion is steered into a trajectory parallel to and above the substrate, where it is trapped by the chemical bonding between the ion and the substrate atoms (Fig. 2). Ions following these 'surface channeling' trajectories experience very little energy loss, and can travel large distances (hundreds of Å) from the point of impact. A closely related effect was recently observed experimentally for low-energy K ions incident on a Si substrate.[16]

Ion Beam Deposition

Molecular dynamics studies have been made of low-energy ion-beam deposition, in which the relevant non-thermal physics takes place primarily on a subnanosecond timescale. The ion-beam deposition of Lennard-Jones atoms on a two-dimensional substrate over a range of incident kinetic energies has been simulated by Muller.[17] Thermal deposition processes carried out at very low substrate temperatures were found to yield a spongy, porous microstructure. In contrast, direct deposition with incident beam energies equivalent to only a few eV were sufficient to drive formation of a nearly perfect epilayer (Figure 3). Muller has also studied ion-assisted deposition (ion bombardment simultaneous with thermal deposition)[18], where small beam energies greatly improve the microstructure of homoepitaxial metallic growth. The qualitative effect of the incident kinetic energy of the impinging atoms in overcoming deposition conditions resulting in very low surface mobility is probably valid in general.

Cluster Beam Deposition

A recent addition to the collection of experimental techniques used in vapor-phase growth of thin films is ion cluster beam deposition (ICBD).[19] Clusters having roughly 1000 atoms are formed by adiabatic expansion of a hot source vapor through a nozzle. A fraction of the resulting clusters are then ionized by electron bombardment, and are subjected to an accelerating voltage typically of a few keV (hence, a few eV/atom). ICBD techniques allow growth of difficult combinations of materials, and also allow high-quality epitaxial growth at substrate temperatures well below those required for conventional MBE growth.

Muller[20] has examined two-dimensional ICBD growth of Lennard-Jones clusters on a matching substrate for a range of accelerating voltages. (Energies will be normalized to aluminum.) Cluster energies were varied roughly from 1 to 30 eV/atom. The growth process was simulated by depositing a number of clusters, allowing the system to cool between subsequent cluster impacts (Figure 4). For energies below about 10 eV/atom, the impacting clusters do not deform greatly, and the result is a porous polycrystalline growth whose crystallite size is the cluster size. At higher energies, however, the clusters melt on impact and conform nicely to the substrate and to each other, giving a dense epitaxial overlayer. This work suggests that kinetic energy only a bit larger than the chemical bonding energy will optimize the ICBD process, in rough agreement with the experimental studies.

Three-dimensional simulations of the impact of small (8-50 atom) clusters of silicon on a silicon substrate have been performed by Biswas, Grest, and Soukoulis.[21] These clusters were provided with initial energies of 0.23-1.05 eV/atom. They find that the cluster melts upon impact if the kinetic energy is high enough. The resulting epitaxial orientation is due to a regrowth process which requires tens of picoseconds. This regrowth velocity is consistent with that observed in laser annealing of silicon.

Sputtering

An interesting dependence on chemical interactions also appears in molecular dynamics studies of sputtering.[22-25] Garrison and coworkers[22,23] studied the use of the embedded atom method in calculating sputtering from metal surfaces, in particular examining Rh and Cu sputtering driven by 5 keV Ar ion bombardment. (Although the beam energy is considerably above the low-energy regime, the atomic interactions within the substrate which lead to sputtering predominantly occur within the cascade, and therefore have much lower energies.) The primary result of including the many-body interactions is to approximately double the energy of the peak of the energy distribution, and to greatly increase the extent of the high-energy tail. They find that the energy and angular distributions predicted by molecular dynamics simulations are in reasonable agreement with the relevant experimental data, although the form of the EAM interactions had to be adjusted to obtain this result. This provides a clear example of the need to include many-body interactions to accurately model low-energy ion-solid processes.

Summary

There is a physically defined low-energy regime for ion-solid processes. This regime is distinguished from chemisorption by having incident kinetic energy greater than typical chemisorption energies, and from the high-energy ion-solid regime by the breakdown of the purely repulsive and binary collision approximations. These considerations establish a low-energy regime from about 10-1000 eV, in which collective excitations of the crystal lattice, many-body effects, and ion-solid bonding interactions cannot be safely ignored. There remain fundamental problems concerning appropriate potentials for this non-adiabatic regime. The many-body and non-adiabatic effects are not yet well understood, but the studies described indicate that they can produce qualitative global changes in ion-solid processes. As a result, such atomic-scale simulations should not yet be regarded as routine tools in the study of ion-solid processes, but rather as active objects of research in themselves.

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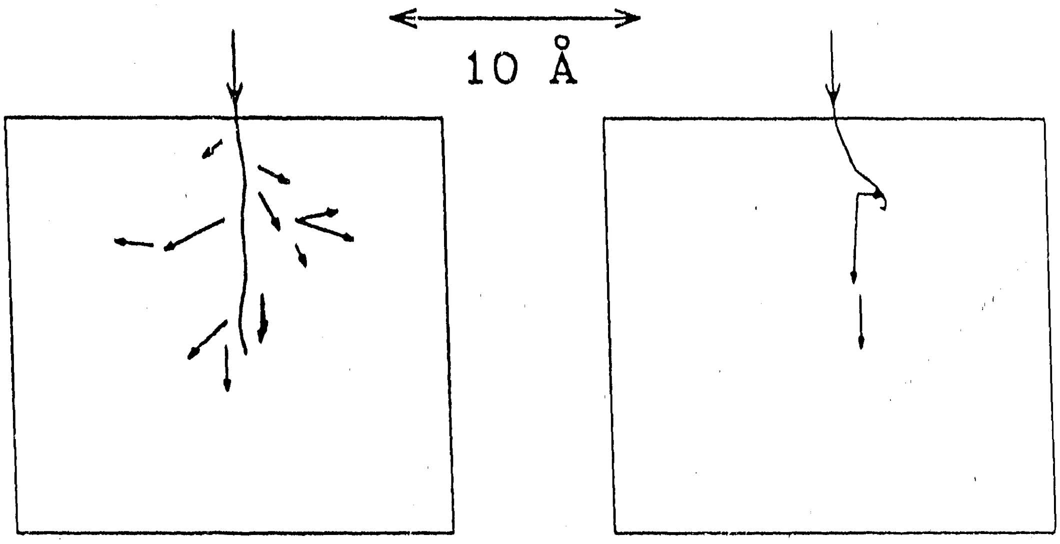
Figure Captions

Figure 1. Collision cascades produced in a Si(100) substrate by a very-low energy neutral Si ion at normal incidence. The impact location is the same for all examples shown. The beam energy is 12.5 eV in (a), and 50 eV in (b). The cascades marked "non-bonding" result from use of the universal nuclear potential of Ref. 26. to describe ion-atom interactions, whereas those marked "adiabatic bonding" use an empirical many-body potential (Ref. 6). In all cases, the substrate atoms interact via this many-body potential to accurately include the effect of lattice vibrations. The distinction between the non-bonding and adiabatic bonding ion-atom interactions is clearly seen.

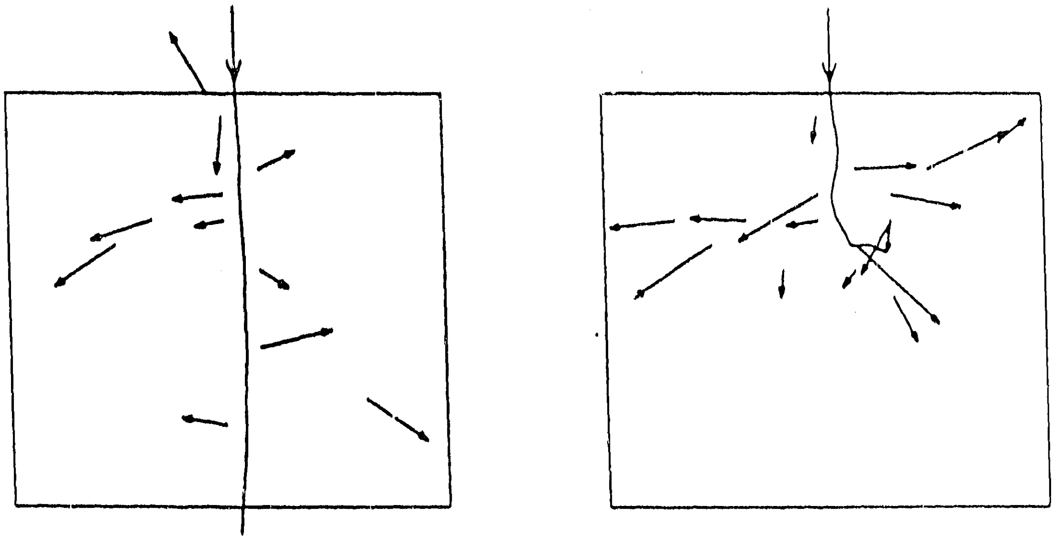
Figure 2. The surface channeling trajectory of a 40 eV silicon atom incident at an angle of 10° on the Si(111) surface (Ref. 15). The perpendicular momentum of the beam atom is lost by inelastic generation of collective substrate excitations, causing the beam atom to be trapped at the surface. The resulting trajectory is nearly parallel to, and about 2 Å above, the surface of the substrate.

Figure 3. Molecular dynamics simulation of growth of two-dimensional Lennard-Jones crystals (Ref. 17). The kinetic energy of the beam atoms is approximately 0.5 eV in the top, 3 eV for the middle, and 15 eV in the bottom figure. The influence of nonthermal kinetic energy appears clearly, with beam deposition resulting in growth of material having nearly the ideal crystal density.

Figure 4. Cluster beam growth simulations as a function of initial cluster energy (Ref. 20). The top figure represents clusters arriving with a kinetic energy of 1 eV/atom, which is on the order of thermal energies. Very little cluster deformation occurs, and the resulting growth is misoriented and filled with voids. The middle growth occured at an energy of 5 ev/atom, resulting in roughly the same type of overlayer. In contrast, when a cluster energy of 15 eV/atom is used (bottom figure), the clusters deform to form a dense and well-ordered growth.



(a) NON-BONDING ADIABATIC BONDING



(b) NON-BONDING ADIABATIC BONDING

FIG 1

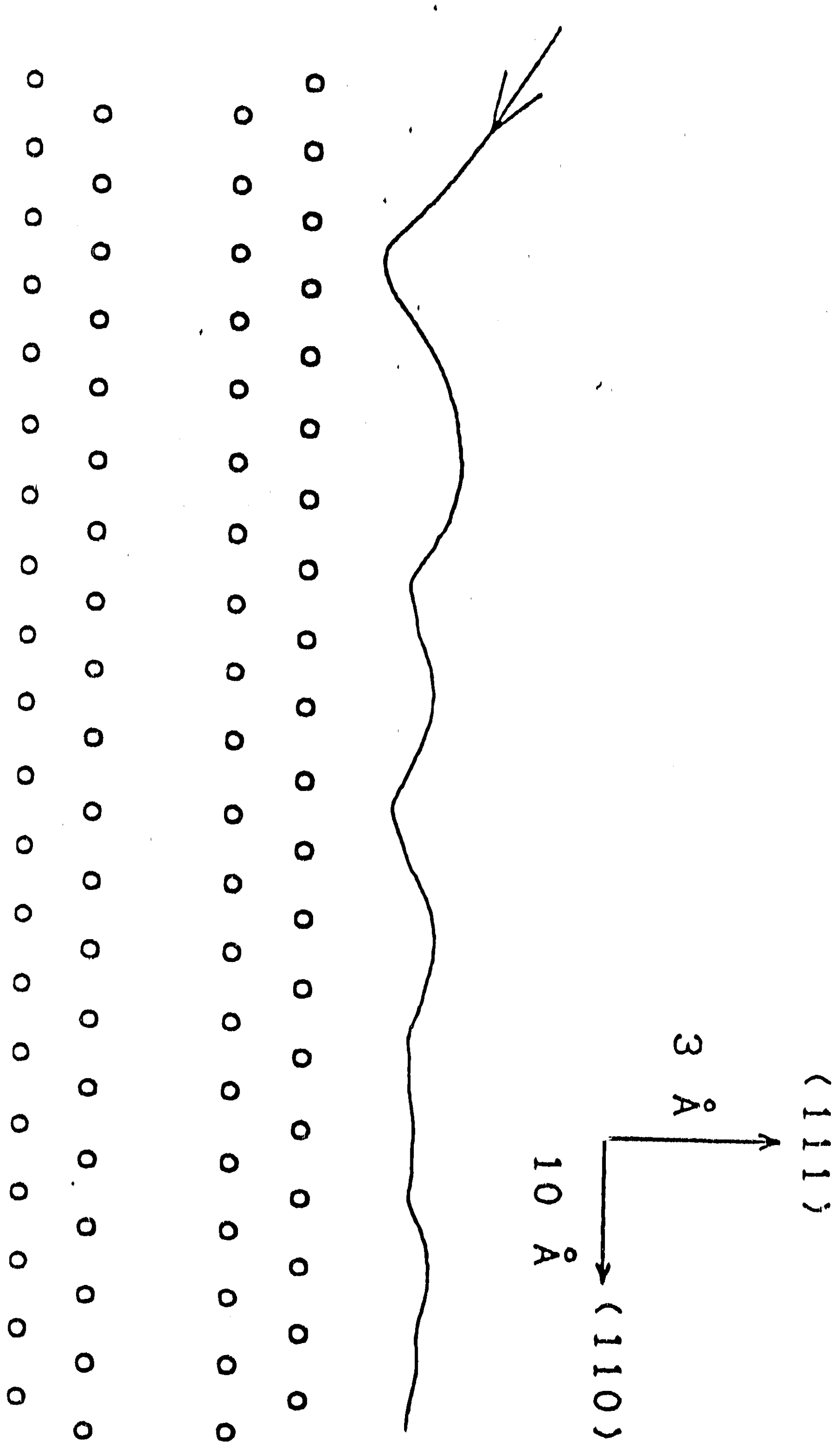


FIG 2

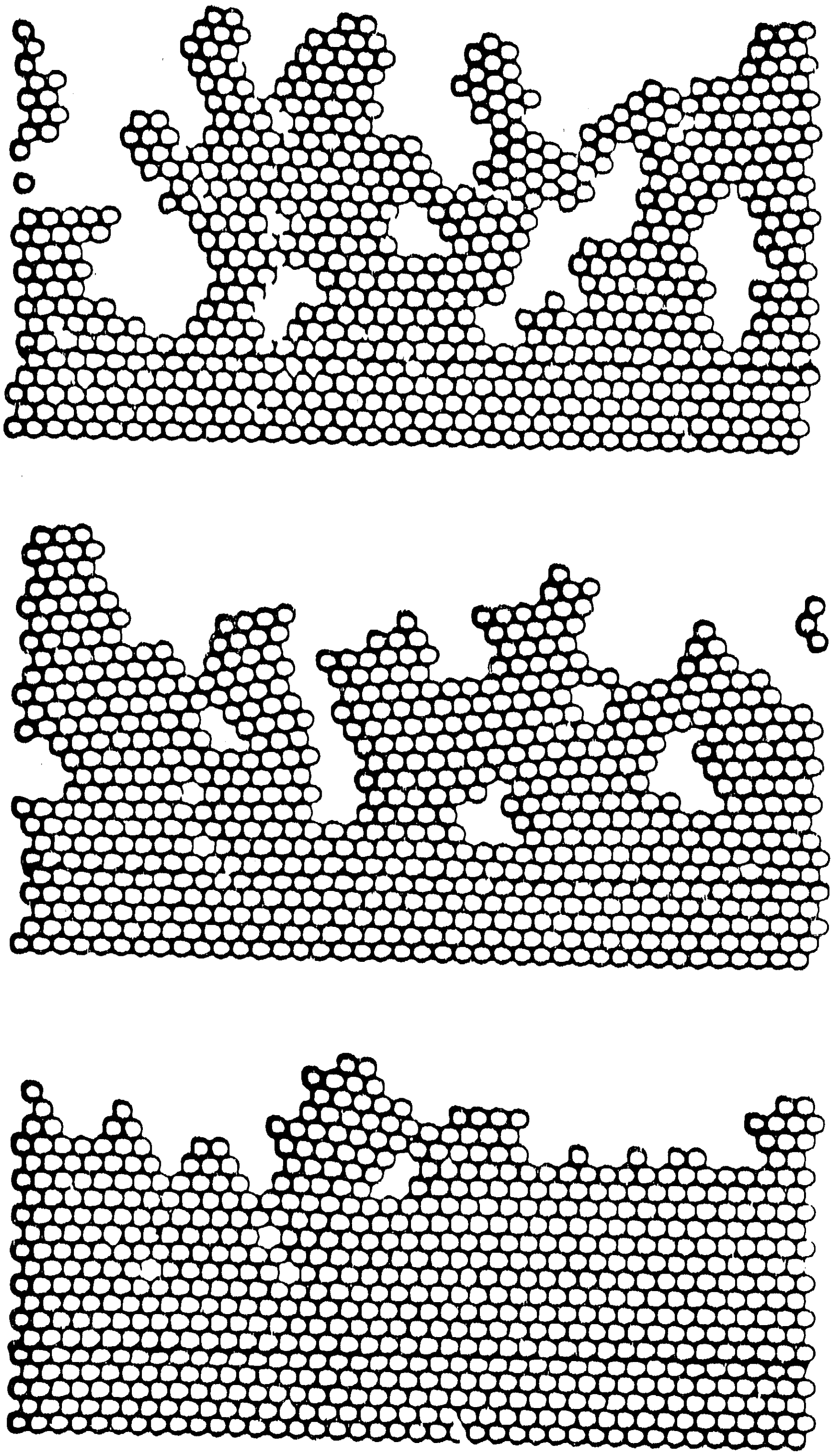


FIG 3

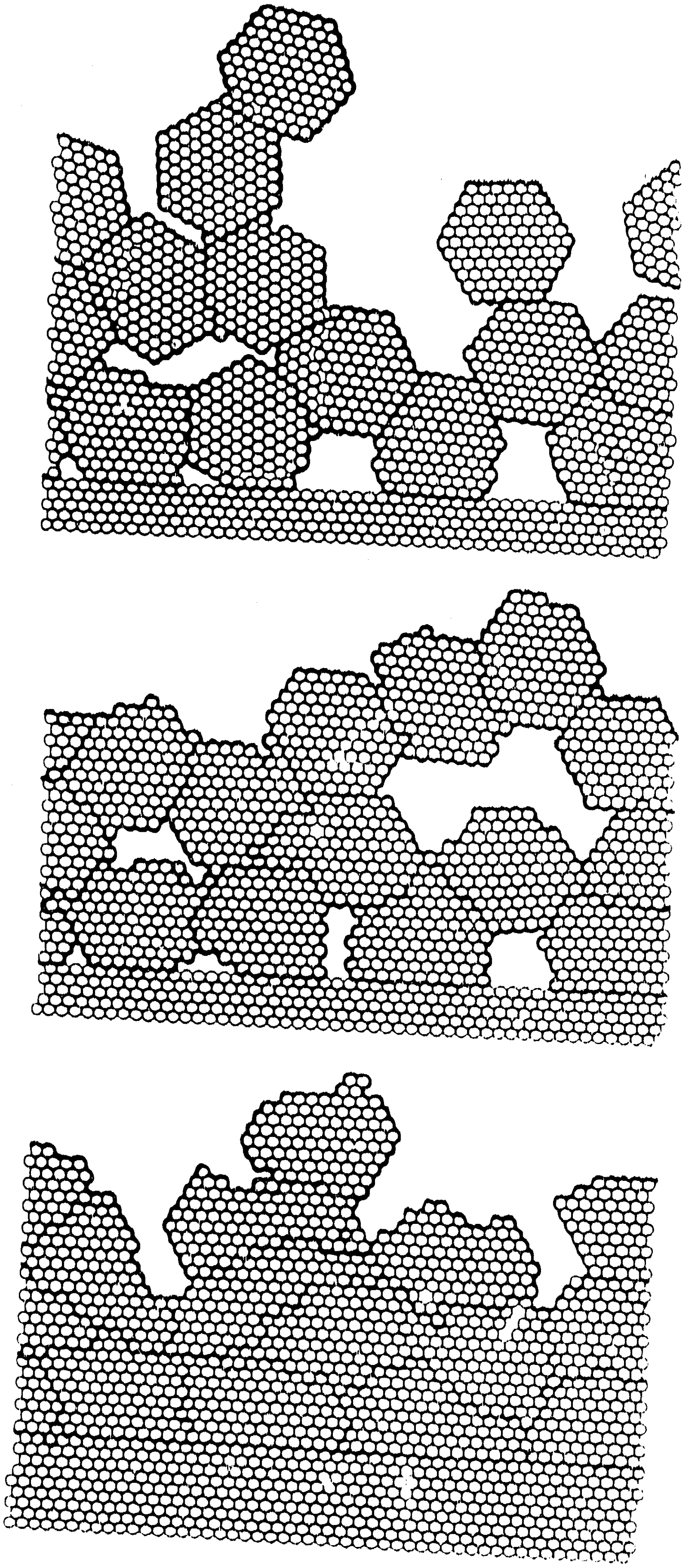


FIG 4

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